Chapter

The Comprehensive Utilization of Steel Slag in Agricultural Soils

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Abstract

The use of metallurgical solid wastes such as steel slag, in agricultural activity, has become very important to contribute to reducing the accumulation of such wastes in the environment and to increase crop production. So, this chapter aims to emphasize the main aspects of the application of slags to soil chemical attributes as elevation of pH and neutralization of Al^{3+} toxic in acid soils and increase nutrient content as phosphorus, calcium, magnesium, some micronutrients, and silicon. In addition, the advance in studies of the utilization of these residues in no-tillage systems in tropical soils will be discussed. Aspects related to monitoring the presence of heavy metals will be addressed.

Keywords: calcium and magnesium silicate, soil fertility, steel industry residue

1. Introduction

The metallurgical industries can produce various residues, and some of these residues can be utilized with success in the agricultural activity, as in the case of the steel slag, which has brought important contributions in agricultural production.

In agriculture, slags can be used as fertilizers and corrective of soil acidity [1]. Slags are calcium and magnesium silicates, which show neutralizing action due to SiO_3^{2-} base [2]. Additionally, steel slags have been used as a low-cost source to supply Si to rice plants [3]. In China, the first steel slag fertilizer program invested by Taiyuan Iron and Steel Group and Harsco Corporation of the USA started building in 2011 [4].

Steel slag is the result of industrial processes in which iron mineral is reduced, generating products as pig iron (iron with a high proportion of carbon) and steel. These processes can occur in different types of furnaces such as basic oxygen furnace or electric arc furnace [5]. Inside the furnaces, oxygen pressure is injected to remove impurities such as gaseous carbon monoxide, silicon, manganese, phosphorus, and some iron as liquid oxides; these impurities combine with lime and dolomitic lime to form the steel slag. Steel can also undergo a greater process of refinement, into a ladle and, at the end of the process, to generate ladle steel slag [5]. The steel slags from these two furnaces are very similar. However, ladle steel slag, resulting from further refining, is quite different from steel slag [5]. For production of every tone of steel, nearly 150 kg of slag is generated [6].

There are several types of steel slag, which present variation in chemical composition, physical composition, and solubility, and these variations occur mainly, due to the different processes and different raw materials used in the metallurgical industries. Examples of slags are steel slag, stainless steel slag, ladle furnace slag, and blast furnace slag; all of these residues have already been tested for agricultural use at some moment, as will be shown in the chapter.

2. Steel slag composition

The main chemical components, which slags contain in their composition and which are important for their use in agriculture, are CaO, MgO, SiO_2, P_2O_5, FeO, and MnO. The amount of these components in each slag varies widely depending on raw materials, type of steel made, furnace conditions, and other aspects [4, 5].

Table 1 shows the chemical composition of different steel slags compared to wollastonite which is a rock and is considered as the standard of silicates [7]. The chemical evaluation of soil acidity correctives for agricultural purposes consists of the following determinations: neutralization power (NP) and calcium and magnesium contents [8]. The different slags have different contents about the components that characterize a material as soil acidity corrective that can provide different effects in the neutralization of the soil acidity.

Considering the Brazilian legislation of soil acidity corrective materials [9], for example, all the slags evaluated in **Table 1** can be considered as an alternative source to limestone, because the values of NP and somatory (%) of CaO and MgO are according to the established values of 60% $ECaCO_3$ and 30%, respectively; this means that the application of such materials allows good performance in the neutralization of soil acidity.

We can also observe different concentrations of Si and P_2O_5 in the different slags. LS showed the highest content of Si, while SS has a great amount of P_2O_5 (**Table 1**). These variations may lead to possible increase in the content of these elements in the soil and increase in the availability to the plants.

Table 2 indicates the micronutrients and heavy metal contents in different slags [7]. It is noted that some materials have a higher amount of micronutrients, for example, the steel slag with a higher presence of iron than the other materials and

Materials	CaO	MgO	NP	RR	ECC	Si	P_2O_5	K_2O
	%		$\%ECaCO_3$		%		g kg^{-1}	
SSS	37.65	9.55	84	71	60	13.6	3.5	0.3
SS	28.13	6.10	70	71	50	14.2	11	0.3
LS	36.10	5.76	77	80	62	21.6	2.5	0.3
W	30.00	3.00	60	100	60	16.0	1.5	0.1

Adapted from [7].
SSS, stainless steel slag; SS, steel slag; LS, ladle slag; W, wollastonite; NP, neutralization power; RR, reactivity rate, expresses the percentage of corrective material that reacts in 3 months; ECC, effective calcium carbonate.

Table 1.
Chemical and physical characterization of different slags.

Materials	Cu	Fe	Mn	Zn	Cd	Ni	Pb	Cr	Hg
	mg kg^{-1}								
SSS	20	38.000	5.300	50	3.1	53.6	12.6	990	<0.1
SS	30	193.500	21.500	70	14.5	3.0	<0.5	941	<0.1
BFS	20	17.400	51.000	50	1.8	1.4	<0.5	104	<0.1
LS	20	28.600	3.700	50	1.6	1.1	<0.5	126	<0.1
W	10	600	100	40	<0.03	0.3	<0.5	0.5	<0.1

Adapted from [7].
SSS, stainless steel slag; SS, steel slag; LS, ladle slag; BFS, blast furnace slag; W, wollastonite.

Table 2.
Micronutrients and heavy metal contents in different slags.

the blast furnace slag with higher content of manganese; the presence of higher micronutrients could be interesting to provide this element for the plant.

The main restriction for the use of slags is the presence of heavy metals in its composition, which have to be evaluated before their soil application. Heavy metal contents in the slags shown in **Table 1** agree with the values which are considered tolerable for application to the soil [10].

3. Steel slag modifying soil chemical attributes

The results of the researchers with the use of steel slag in agriculture have demonstrated that the proper application of these residues brings benefits on the chemical attributes of the soil, such as increase of pH in acidic soils; increase in the nutrient content of phosphorus, calcium, and magnesium; and increase in the content of the beneficial element silicon [6, 11–14]; these aspects contribute to greater crop production.

For proper application, the initial chemical characterization of the soil to calculate the dose either for use as corrective of soil acidity or fertilizers is important. The homogeneous application of the residue in the area and the adequate incorporation in the soil are also important aspects to be considered.

The application of slag can neutralize part of the soil acidity; this occurs because these materials have in their composition the neutralizing base SiO_3^{2-} [15] that reacts in water and releases hydroxyl (OH^-) ions, according to the equations below [2]:

$$CaSiO_3 + H_2O \rightarrow Ca^{2+} + SiO_3^{2-} \quad (1)$$

$$MgSiO_3 + H_2O \rightarrow Mg^{2+} + SiO_3^{2-} \quad (2)$$

$$SiO_3^{2-} + H_2O\ (soil) \leftrightarrow HSiO_3^- + OH^-\ \left(Kb_1 = 1.6 \text{ x } 10^{-3}\right) \quad (3)$$

$$HSiO_3^- + H_2O\ (soil) \leftrightarrow H_2SiO_3 + OH^-\ \left(Kb_2 = 3.1 \text{ x } 10^{-5}\right) \quad (4)$$

$$OH^- + H^+\ (\text{Soil Solution}) \rightarrow H_2O \quad (5)$$

$$OH^- + Al^{3+}\ (\text{Soil Solution}) \rightarrow Al(OH)_3 \quad (6)$$

The value of the ionization constant (Kb_1) shows that SiO_3^{2-} is a weak base, that is, the OH^- forming reaction is relatively slow and partial. The hydroxyl (OH^-) produced neutralizes the H^+ of the soil solution and the phytotoxic Al^{3+}, and, consequently, there is an increase in pH and a decrease in the concentration of the potential acidity (H + Al) [16].

Correction of acidity with slag occurs similarly to the use of limestone. In addition to the decrease in acidity levels, Ca and Mg supply also occurs in soil [6, 11, 12], with positive effects for crops such as potatoes, rice, black oats, beans, soybeans, alfalfa, coffee, and sugarcane, among others, making steel slag a source capable of being used instead of limestone [11, 13, 17–21, 23].

The application of steel slag was also studied in acidic tropical soils cultivated under no-tillage system. Tropical soils are characterized by being acid with excess of Al^{3+} that is a toxic element to plants because it limits the root development.

The no-tillage system is growing in these areas; however, one of the requirements for the success of this system is that there is no soil revolving, so the acidity corrective material should be applied to the surface without incorporation. Due to the fact that the limes present low solubility in water and little movement in the soil profile [24], the study of the use of slags (silicates) in no-tillage system has increased due to the greater solubility of this residue [2]. Calcium silicate is 6.78 times more soluble than lime [2], so the use of steel slag in the no-tillage system can be an important alternative source for the process of soil acidity correction, because it may promote greater mobility of SiO_3^{2-} anions in soil profile, ensuring faster soil acidity correction in deeper layers in relation to the lime.

Studies conducted by [19, 22, 25–28] showed positive effects in soil acidity correction of surface application of steel slag compared to lime in no-tillage system, in tropical soil.

After 27 months of application of steel slag at doses 2, 4, and 8 t/ha, without incorporation, under no-tillage system, there was an increase in base saturation and

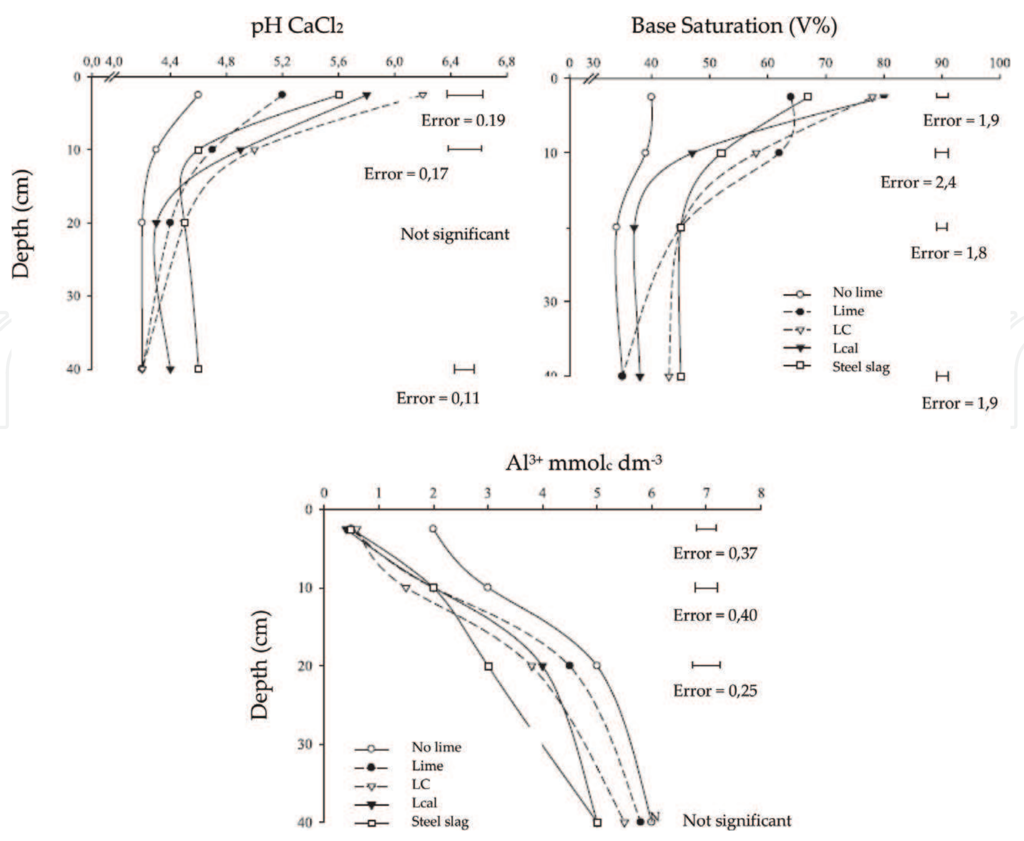

Figure 1.
pH, base saturation (V%), and Al^{3+} content at different depths of a dystrophic Red Latosol at 27 months after surface application of lime, centrifuged sewage sludge (LC), steel slag, and lama cal (Lcal) in the no-tillage system (source: [22]).

reduction of Al^{3+} up to 0.40 m with application of steel slag; in the same period, the effects of limestone on the soil were observed up to 0.20 m (**Figure 1**) [22].

In a long-term experiment under no-tillage system, [26] applied limestone and slag to increase base saturation to 70% and observed that the steel slag corrected acidity and increased the bases up to 0.10 m at 12 months. After 18 months of reaction, the steel slag corrected the soil acidity up to 0.60 m and increased the bases up to 0.40 m, while the effects of the lime were observed until 0.20 m [28].

On the other hand, the study conducted by [7] with surface application of steel slag, blast furnace slag, ladle furnace slag, and stainless steel slag at the installation of the no-tillage system presented that the ladle furnace slag, stainless steel slag, and steel slag had similar efficiency to the lime in the neutralization of soil acidity at 24 months after application. The divergence of the results reported above with the application of slag in no-tillage system can be explained by the chemical composition of these residues, because the industrial process promotes the production of several types of slag, with different recrystallization depending on the amount of Ca and Mg and of the cooling time, aspects that may reduce its solubility [29].

In addition to the corrective effect of the slag, several studies point to the efficiency of slag to increase phosphorus nutrient in the soil [7, 17, 19]. Some researchers attribute the P content increase with the use of slag due to the competition between Si and P that occurs through the same adsorption sites of soil colloids. This occurs due to the application of slag (silicates) to generate a concentration gradient of the anion silicate (SiO_3^{2-}), which removes the P adsorbed to the colloids of Fe and Al oxides from the soil, which under the conditions of the tropical soils are in great quantity [30]. Others relate the P content increase with the increase of the soil pH provided by these materials, as well as greater solubilization of the organic phosphorus and the labile fraction, increasing its content in the form available to the plants. In addition, steel slag has P in its composition, which may contribute to such results, as can be seen in **Table 1**.

The application of steel slag in soil can contribute to the chemical attributes of the soil, reflecting the benefits to the agricultural sector; however, this contribution is variable depending on the composition of the used residue making it always important to know the chemical and physical characterization of the residue before its application to the soil.

The presence of heavy metals in steel slag is one of the problems with its use that at high levels, it can become toxic and limit its use in agricultural activities. The steel residues have very variable chemical composition due to the different processes to obtain them, becoming the important quantification of these elements in the soil and the crops after long-term residue application.

After 18 months of steel slag incubation in an Argisol, it is observed [31] that the solubility of Zn, Mn, Pb, Ni, Cd, and Cu decreased due to the passage of the exchangeable form retained in oxides and residues, explained by the phenomenon of chemosorption influenced by the soil pH. In another study [33], it is found that the application of 8 and 4 Mg ha^{-1} of steel slag, respectively, did not increase the availability of heavy metals of the soil. The increase of heavy metals, such as cadmium (Cd), chromium (Cr), nickel (Ni), mercury (Hg), lead (Pb), and arsenic (As), was insignificant compared to the application of 8 t/ha [32]. The steel slag, ladle slag, and stainless steel slag (chemical characterization in **Tables 1** and **2**) applied as soil acidity correctives, at the dose necessary to raise the initial soil saturation to 70%, did not change the soil metals content evaluated at 12 and 23 months after the application of residues, and the Pb content decreased with the application of residues [7]. Also, the additions of heavy metals were not observed in the plant tissue of beans, soybean, and black oats cultivated in the area where the slags were applied [7, 32]. The presence of elements in the composition of residues in nontoxic amounts and the soil pH increase contributed to avoid toxicity by heavy metals [32].

In the soil, heavy metals can be adsorbed by specific reactions (chemosorption) influenced by soil pH or nonspecific [33]. The pH and CEC and the presence of cations affect the adsorption and ionic speciation of heavy metals in soils [34]. In weathered soils, such as those of the cited studies, the presence of colloids with pH-dependent charges represents more than 70% of the total cation binding sites. Thus, in this soil type, the acidity correction is of great importance in the adsorption of heavy metals [33].

Although the above studies did not observe an increase in the heavy metals' levels in soil and plants, monitoring of the availability of these toxic elements in the soil and in the plant, as well as the characterization of the residue to be used, is fundamental for the success in the residues used in agriculture.

4. Benefits of using steel slag for crops

Slag application favors the increase of pH and the availability of nutrients such as Ca, Mg, and Si in the soil, which leads to the increase in the absorption of these elements by the plant, favoring the growth and yield of the crops. Slags application may supply silicon which is considered a beneficial element to plants. Silicon may bring benefits to plants such as reduction of foliar diseases; improvement in pest control; increase in photosynthetic capacity due to the silicon benefit to the architectural activity of the plant, leaving the leaves more upright [32]; and improvement in the use of water by the plant [35]. Si may also influence the uptake and translocation of various macro- and micronutrients and increase plant tolerance to excess of Mn and Fe [37] and Zn, Al, and Cd [38].

Slag-based fertilizers applied in Si-deficient paddy soil improved rice growth, productivity, and brown spot resistance [39]. The application of steel slag in the soil increases the concentration of Si in the rice straw and promotes a higher yield of grains [40]. Also, studying the effect of slag in rice crop, [41] observed an increase of base saturation and availability of silicon and phosphorus in the soil, with a consequent increase in grain yield, Si content, and accumulation in rice straw, in 2 years of cultivation.

The supply of P and Si available in the soil for the potato crop, through the application of slag, increased the absorption of these nutrients by the plant, decreasing the lodging and increasing the height of plants and the production of tubers [17].

Nitrogen fertilization associated with steel slag also increases the dry mass production and the absorption of Si by the marandu grass [42].

Steel slag, used as soil acidity corrective material, increased the contents of Ca, Mg, P, and Si in the soybean leaves and Ca, Mg, and Si in maize and also provided increased shoot dry matter yield and grain yield of both cultures under no-tillage system; compared to limestone, steel slag was more effective in improving maize grain yield [27].

5. Conclusions

The steel industry generates large volumes of slag, which are considered as an environmental problem; it is necessary to increase the use of this waste in new processes to avoid disposal in landfills. Steel slags can be used in several activities, such as construction and paving, and also in the agricultural sector due to its ability to correct soil acidity, as it contains some nutrients for the plants and also as silicate fertilizer that is capable of providing silicon to the plants. Thus, steel slags can be considered as a sustainable alternative to agricultural practice.

Conflict of interest

There are no conflicts of interest to declare.

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