STEEL SLAG, A SUBSTITUTE OF LIMING MATERIALS IN AGRICULTURE

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Keywords: steel slag, amendment, agriculture.

ABSTRACT

Regular application of amendments and fertilizers in required doses causes significant and lasting chemical changes in the soil, in relation with the degree of success of crop production. Steel slag is a highly alkaline material considered a by-product of the steelmaking process. This material is used in many different applications including the amendment for acid soils. Amendment is a practice commonly used for rapid elimination of problems of soil acidification. As a product applied in agriculture, the steel slag has been studied in many parts of the world somewhat with satisfactory results. In some European countries, researches have shown an improvement in acid soil properties. The ability of the steel slag to improve the acidity of the soil can be explained by the high content of CaO and MgO and Al_2O_3 low. When a liming material such as limestone or steel slag is evaluated, it is compare to calcium carbonate, and its neutralizing value is called the Calcium Carbonate Equivalent (CCE) value. Application of amendments, including by-products such as steel slag can restore soil quality by balancing the pH value, organic matter intake, increasing water retention capacity, reducing compaction, etc. For reasons of environmental protection, steel slag properties should always be tested given the wide variety in terms of their physical and chemical indicators.

INTRODUCTION

Soil acidity is among the most important environmental factors that can influence plant growth and can seriously limit crop production. Therefore, acid soil amendment is the very important for good management of soil and production.

In recent years, the direct effort increased regarding the application of industrial residues for remediation of degraded soils taking into account the reduction of costs associated with waste disposal.

Steel slag is a highly alkaline material considered a by-product of the steelmaking process.

This material has been used in many different applications including the amendment for acid soils (Mack and Gutta, 2009).

MATERIAL AND METHOD. RESULTS.

1. SOIL ACIDITY

Soil acidity is caused by H^+ ions (H_3O^+) resulting by ion exchange, ionic dissociation or after hydrolysis process. In mineral soils, Al^{3+} and hidroxialuminium polymers, after hydrolysis, H^+ are together with carboxyl groups derived from organic matter, the most important source of acidity in the soil (Metodologie, 1981).

Acid soils cause problems in production by limiting the accessibility of nutrients essential for plants increasing the levels of toxic elements in the soil solution, such as aluminum and manganese, the major cause of poor production in acid soils (Ball, 1999).

Below pH 5.5 in soil, aluminum can be concentrated so as to limit or stop rooting.

As a result, plants can not absorb water and nutrients, stop growing and appear symptoms of nutrient deficiency (especially those for phosphorus). Toxic levels of manganese interfere with the normal growth processes of the aerial part of the plant, stagnant growth and development and cause poor yields (Ball, 1999).

There are four major reasons for becoming acidic soils - rainfall and leaching, acid parent material, reducing the amount of organic matter and high-yielding crop harvesting. Wet climate has a greater potential for acid soils. In time, excessive precipitations cause leaching in the soil profile of the basic elements (calcium, magnesium, sodium and potassium), these elements prevent the acidity of the soil.

The decrease of organic matter content influences hydrogen ions (H^+) amount that are responsible for acidity. As at the precipitation phenomenon, the development of the acidity by lowering the soil organic matter content is insignificant in the short term (Ball, 1999).

Harvesting crops with high yield has the most significant role in increasing soil acidity. During growth, crops absorb basic elements such as calcium, magnesium and potassium for their nutritional needs.

Nitrogen fertilizers can be held liable on issues of increasing soil acidity. When ammonia fertilizers are applied to the soil it produce hydrogen ions, but the form of nitrogen removed from the culture is similar to that found in the fertilizer. In fact, nitrogen fertilizers increase the acidity of the soil by increasing the crop yield, thus increasing the amount of basic elements which are removed from the soil.

Soil acidity can be easily corrected by amending or adding liming materials to neutralize the present acidity. Acidified soil is neutralized with the addition of limestone. The most common material is aglime (agrolime) amendment. Limestone is not very soluble in water which makes it easier to handle. The reaction of limestone or calcium carbonate with an acid soil is described in Figure 1 and shows acidity on the surface of soil particles (Ball, 1999).

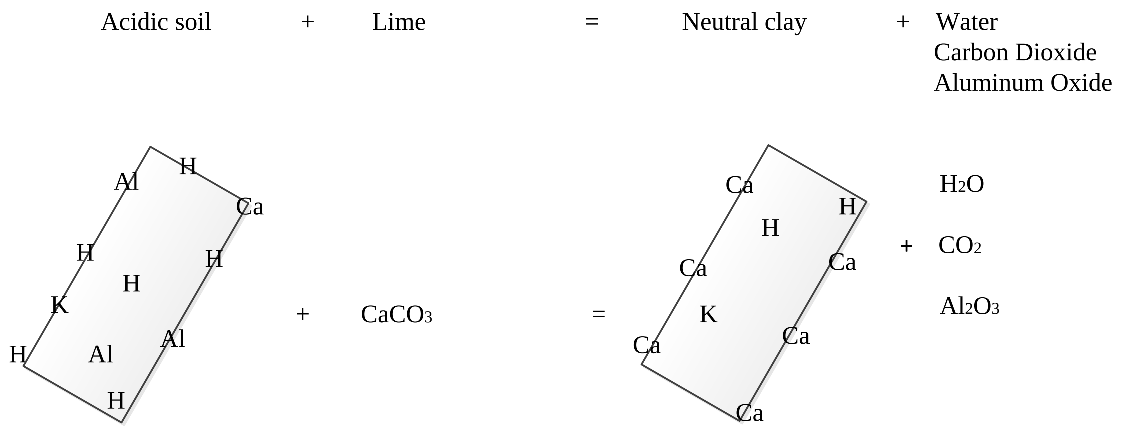

Figure 1. How lime neutralizes acidic soil (Ball, 1999)

Soil acidity is composed of two components: active acidity and exchangeable acidity. (Douglas et al., 1995)

The active acidity is the H^+ ions concentration in the soil solution expressed as pH but it is not a measure of the total acidity of the soil. pH of the soil is a general indicator showing whether limestone amendment is necessary to reduce the acidity.

Exchangeable acidity refers to the amount of H^+ ions in exchangeable cations sites of negatively charged clay and in soil organic matter fractions.

Exchangeable acidity of the soil determines the amount of necessary amendment to increase the soil pH. Therefore, soil testing reports shows both pH and exchangeable acidity of the soil and recommendations for the implementation of the amendment based on the total acidity, as well as on other factors. Initially, each soil type has a certain level of acidity depending on the composition, on the natural vegetation, the amount of rainfall and other various factors which, over time, cause changes in the pH of the soil (Douglas et al., 1995).

Leaching, erosion, and absorption by the plant of basic cations (Ca^{2+}, Mg^{2+}, K^{+}), deposition and decomposition of plants residues and exudates through the roots of the plants are means by which the acidity of the soil may increase. However, a common source of acidity stands for H^{+} ions which are released when high contents of aluminum (Al^{3+}) in the soil reacted with the water molecules. Acid residues occur also from certain fertilizers.

2. EFFECTS ON PLANT SOIL ACIDITY

For most crops, soil pH between 6.0 and 7.0 is ideal, however, the tolerance range of pH can vary for different crops. (Figure 2) (Douglas et al., 1995)

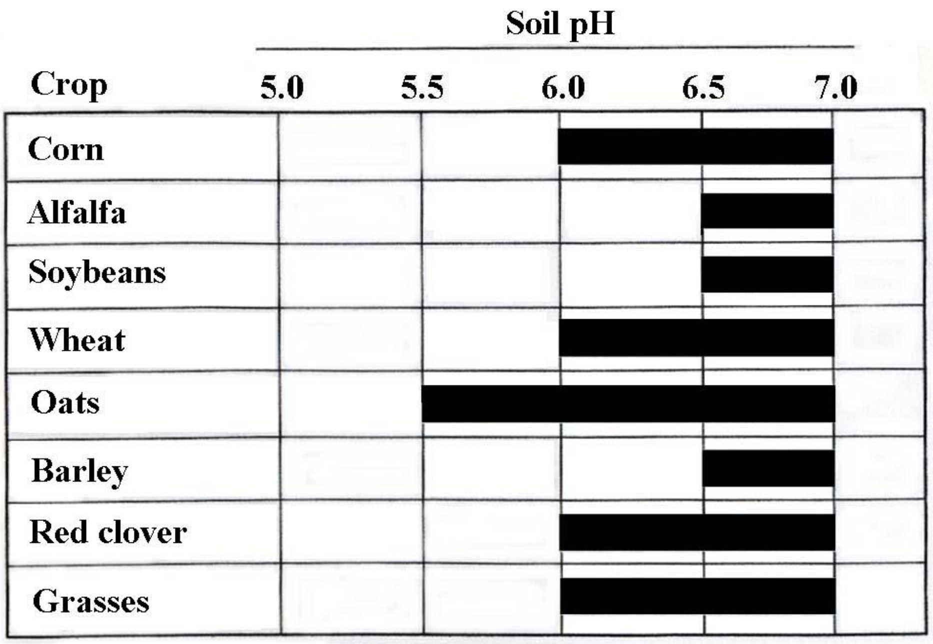

Figure 2. Favorable pH ranges for common crops (Douglas et al., 1995)

If the pH drops below 5.5 the availability of aluminum and manganese increases and can touch point of toxicity for plants. The excess of aluminum (Al^{3+}) in the soil solution affects root growth and function and also restrict absorption of nutrients in plants such as Ca^{2+} and Mg^{2+}. Acid soils amendment reduces the activity of Al and Mn.

Availability of micronutrients increases as the pH of the soil decreases, except the molybdenum. While the micronutrients are required to plants in small amounts, the toxicity for plants, among other effects, are manifested at excessive amounts. This is shown in Fig. 3 explaining the relationship between pH and nutrients availability.

In acid soils, phosphorus forms insoluble compounds with aluminum and iron. Amendment of soils with low pH allows phosphorus to be more accessible. However, amendment of soils beyond the pH 7.0 makes the phosphorus to form complexes with Ca and Mg, therefore, it is best to maintain the soil pH between 6.5 and 6.8 to avoid these problems. (See Figure 3)

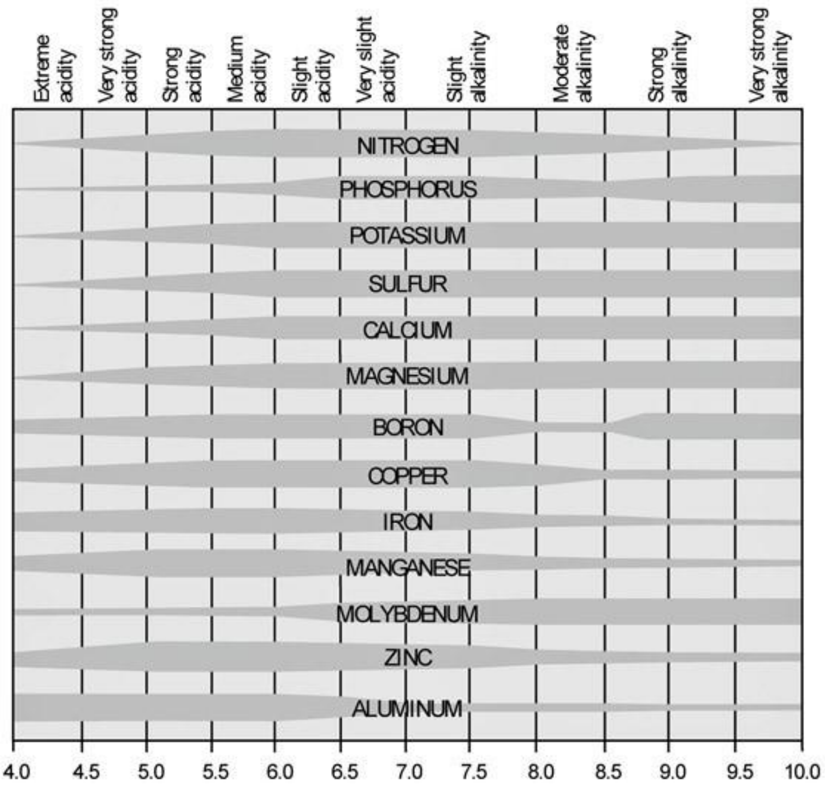

Figure 3. How soil pH affects availability of plant nutrients and aluminum (Douglas et al., 1995)

3. AMENDMENTS. STEEL SLAG

Application of amendments restores soil quality by balancing pH, contribution of organic matter, increase water retention capacity, restore the microbial community and reduce compaction. (www.epa.gov)

There are several types of problems addressed to amendments for soils such as low soil health and slow ecosystem functioning problems.

Aglime (agricultural liming material) is composed of calcium carbonate, magnesium carbonate, and other minerals which neutralize the soil acidity and provides calcium and magnesium for the growth of plants. Limestone is composed primarily of calcium carbonate. Dolomitic limestone is composed primarily of magnesium carbonate. Dolomitic limestone is preferable of calcitic limestone because it works more slowly and contains magnesium, an essential element for plant growth. Dolomitic limestone and calcitic limestone are available in powder form. The rates of application for aglime are shown in Table 1. (Ducklow and Peterson, 2006)

Table 1

Quantity of calcitic or dolomitic lime needed to raise soil pH to 6.5 (Ducklow and Peterson, 2006)

Soil pH	…………………………Soil Type………………………………………		
	Sand t/ha	Loam t/ha	Clay t/ha
6,0	0,9	1,6	2,3
5,5	2,0	3,4	4,5
5,0	2,9	4,5	6,8
4,5	3,6	6,8	9,1
4,0	4,5	7,9	10,4

A good amendment program is based on a soil test that determines the degree of acidity of the soil and the right amount of material necessary to neutralize this acidity. Once this quantity determined, a material amendment has to be selected and it will have to satisfy economically speaking the recommendations and results of the soil test to the maximum, with efficient production. However, before taking into account the necessary amount of the amendment it is helpful a correct knowledge of the material amendment, its quality and knowledge of legislation.

STEEL SLAG

There are different types of steel slag produced in the steelmaking process. These include oven slag or exhaust (Furnace Slag or Tap), scraping slag (Slag Raker) and synthetic slag (Ladle Slag).

The most important physical characteristic of the steel slag is the particle size distribution. The finer the particle, the material will be more reactive neutralizing soil acidity. (www.nationalslag.org)

The steel slags have high specific weight (3.2 - 3.6 g/cm^3) and bulk density also large (1.6 - 1.9 g/cm^3) compare to agriculture lime material (2, 7 to 2.9 and, respectively 1.4 to 1.5 g/cm^3). This is a consequence of the residual metals from slag. (www.nationalslag.org)

The steel slag contains from 35% to 45% calcium oxide which makes it a conditioned product of soil in terms of restoring the natural balance of acid soils. [13]

Steel slags contain many chemicals; they contain calcium silicate, CaO and MgO free. Part of the slag chemical composition (Portland, USA) is given in Table 2.

(knowing the fact that the slags contain different chemical compounds, in different amounts and from the various steel mills). (www.nationalslag.org)

Table 2

Chemical characteristics of steel slag (www.nationalslag.org)

Constituent	% by wt.
CaO	40 – 52
SiO_2	10 – 19
Al_2O_3	1 – 3
MgO	5 – 10
Fe (FeO or Fe_2O_3)	10 – 40
MnO	5 – 8
TiO_2	0,5
P_2O_5	0,5 – 1
CaO free	2,1
Fe metallic	0,5 – 1,0

The amendment value of an alkaline material as limestone or steel slag is the total amount of neutralizing material. This is determined by reaction of material with a strong acid followed by titration of the excess acid remaining. (Agricultural liming materials) **The total amount of neutralization** is expressed in terms of equivalent to pure limestone ($CaCO_3$) and is defined **Calcium Carbonate Equivalent** (CCE). When a liming material such as limestone or steel slag is evaluated, it is compare to calcium carbonate, and its neutralizing value is called the Calcium Carbonate Equivalent (CCE) value.

Materials for amendment, in most states, must have a value of amendment guaranteed, and some states require a minimum CCE to be classified as a material amendment. Other states also require that this material to have some grit to ensure effective reaction with acidic soils. Virginia State, USA, requires that 30% of the material passes through 100 mesh sieve, 50% passing through 60 mesh sieve and 20% pass through a sieve with a mesh of 20. (www.nationalslag.org)

The buffering capacity of the soil can be determined by titrating a sample of the soil to a desired pH but there are more rapid tests used in the laboratory. The necessary amendment of a calcareous soil amendment in tons of agricultural lime per acre (0.405 ha = 1acre) is based on pH-buffering and pH of the soil desired. To convert the lime requirement based on limestone to that of steel slag, the CCE of the slag would be divided into 95. For example, if necessary of a ground limestone was 2 tons / acre and the CCE of the steel slag was 25%, the application rate of steel slag will be 2×95: 25 = 7.6 tons / acre (18, 76 tons / ha). (www.nationalslag.org)

CCE limestone value is obtained directly by dissolving the material in acid sample. However, the analysis of agricultural limestone material is often reported in various ways, such as calcium oxide (CaO) and magnesium oxide (MgO) or in the form of calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$). CCE can be easily calculated using the conversion factors listed in Table 3 (Douglas et al., 1995).

Table 3

Conversion factors for liming materials (Douglas et al., 1995)

Ca ×	2,50 = $CaCO_3$
Mg ×	4,17 = $CaCO_3$
CaO ×	1,79 = $CaCO_3$
MgO ×	2,50 = $CaCO_3$
$MgCO_3$ ×	1,19 = $CaCO_3$
$Ca(OH)_2$ ×	1,36 = $CaCO_3$
Example:	
Ca 35% × 2,50	= 87,50%
Mg 2% × 4,17	= 8,34%
CCE	**= 95,84%**

The **Neutralization Potential** (NP) of steel slags can vary between 45 and 78%. Most of the residues are in the form of iron oxides and aluminosilicates. (Ziemkiewiecz and Skousen, 1998) The leaching studies were carried out (removal of the alkalinity content of the slag) with columns of different thicknesses and different types of slags. Alkalinity is given as mg / L $CaCO_3$ equivalent; pH of the solution can reach values over 11.7. (Ziemkiewiecz and Skousen, 1998)

Since most steel slags contain heavy metals, many tests were conducted to study about heavy metals in slag. It is important to remember that not all steel slags are the same, they vary in composition, quality and fineness. (Table 4), (Ziemkiewiecz and Skousen, 1998)

The leaching studies were carried out on a column with different thicknesses of slag. Leachate samples were analyzed for pH, electrical conductivity, content of alkalinity and metals. The concentration of metals in the leachate was compared with standards for the U.S. Environmental Protection Agency's Toxicity Characteristics Leaching Procedures (TCLP) and EPA standards for drinking water. The results indicated that slag has not released any element in larger quantities than TCLP limits. (Ziemkiewiecz and Skousen, 1998)

The possibility that metals become mobile in the environment when used steel slag has been carefully and extensively researched. Another problem is that the steel slag has a higher soluble salts content than limestone; soluble salts should be tested.

Table 4

The concentrations of metal of the percolate when steel slag Mingo Junction was percolated with deionized water, compared with the standards USEPA TCLP (US Environmental Protection Agency's Toxicity Characteristics leaching procedures) and EPA standards for drinking water (Environmental Protection Agency). (Ziemkiewiecz and Skousen, 1998)

Mingo Junction Slag		TCLP Limit	EPA drinking water Limit
pH	11,7		
Cond.	4780 μS/m		
Alcalinity	1450 mg/L		
As	<0,05 mg/L	5 mg/L	50 μg/L
Se	0,05 mg/L	1 mg/L	50 μg/L
Ba	0,02 mg/L	100 mg/L	2000 μg/L
Cd	<0,001 mg/L	1 mg/L	5 μg/L
Cr	0,03 mg/L	5 mg/L	100 μg/L
Cu	0,058 mg/L		
Pb	0,1 mg/L	5 mg/L	15 μg/L
Ni	0,041 mg/L	70 mg/L	10 μg/L
Zn	<0,002 mg/L	1 mg/L	6 μg/L
V	<0,05 mg/L		
Tl	<0,05 mg/L	7 mg/L	2 μg/L
Be	0,0013 mg/L	0,007 mg/L	4 μg/L
Ti	<0,05 mg/L		
Sb	0,08 mg/L		
Mc	0,008 mg/L		
Ag	<0,005 mg/L	5 mg/L	
Hg	<0,0003 mg/L	0,2 mg/L	
SO_4	1,6 mg/L		2 μg/L

CONCLUSIONS

Although recycling byproduct has been made already as a commitment by the steel industry, increased production of steel in recent years has pressed the industry to increase its use in a more efficient manner in order to achieve a steel production sustainable. Even if the slag obtained in the production of steel are continuously studied in order to improve their recycling, there are some limiting factors for their use.

In particular, a small quantity of slag is used as fertilizer in agriculture and the use depends on the market conditions. Because of the low market value of fertilizers, long distance transportation is a limiting factor. In addition, natural calcareous fertilizers are competing with the use of the slag. Therefore, development of new markets of slag in order to ensure its future use is required. With this in mind, the steel industry has undertaken to reduce the amount of slag which must be deposited and to improve its use by increasing its ability to amend. (Drissen, P. et all, 2009)

Steel slag can be used as a substitute for lime to neutralize the acidity of the soil; for many years research has shown that using slag is comparable or superior limestone in some cases. In addition to its benefits to amend, the slag contains the necessary nutrients which can increase plant yields. Slag also contains silica which has been shown that increases production of crops such as rice and sugarcane and also helps as a treatment against diseases in crops. (www.nationalslag.org)

While steel slags contain different concentrations of trace elements, such as Cr (III) and Zn, the bioavailability of these metals is very low.

As a byproduct of industrial products, steel slag provides significant advantages such as costs compared to limestone commercial.

Steel slag can be a cheap source alkaline causing a rapid increase of pH value in comparison with limestone but the question remains: what can happen over time? Larger or smaller quantities of metals will be released over a period of time? (Mack and Gutta, 2009)

All the above conclusions, transferred to the situation in which steel slag is used as an amendment in agriculture can put a series of questions about the transformations occurring in acidic soils treated with steel slag.

ACKNOWLEDGMENT

The financial support provided by ANCSI – project no. PN 16 07 03 03 – Corectarea rectiei solurilor acide prin amendarea cu zgura de otelarie si impactul folosirii acesteia asupra solului.

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