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STEEL SLAG - UNCONVENTIONAL AMENDMENT FOR ACID SOILS

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Abstract

Initially, each soil type has a certain level of acidity depending on the composition, the natural vegetation, the amount of rainfall and various other factors that cause changes in soil pH over time. Soil amendment in order to obtain an optimal pH improves also the yields for long-term. This paper refersto the selection of an agriculture lime material to be used in experiments on acidity correction of an acid soil. In Romania, according to official data are obtained annually approximately 75 000 t of steel slag. If the slag is not dangerous for the environment and public health, then the priority should be given to the use of recycled materials. Considered an unconventional amendment, steel slag was selected taking into account its quality and association with legislation. Steel slag presented an Amendment Neutralization Potential very high (ANP = 114%) reported to the content of calcium oxide and magnesium oxide. Steel slag can be considered a mineral amendment used to improve soil acidity, and also a source of calcium and magnesium. Using steel slag as amendment for acid soils can be considered a potential and significant environmental risk, which is why the whole process of amendment must be conducted in terms of environmental protection.

Key words*: amendment, steel slag, acid soil.*

INTRODUCTION

Soil acidification, or a decrease in soil pH, is a natural process that is accelerated by crop production practices, primarily the use of nitrogen (N) fertilizers such as urea, ammonium sulfate, or other fertilizers containing ammonium-N (Anderson et al., 2013).

Seco et al. (2011) studied the effect of adding different fertilisers (lime, natural gypsum, magnesium oxide) on the swelling and strength behaviour of highly expansive clay soil. The results showed that adding 2% of lime with 1% of magnesium oxides tremendously reduced the swelling percentage of the treated clay soil.

Onur (2009) investigated the effect of limestone and marble dust on the swelling behaviour of expansive soils. The results showed that around 21-28% reduction in the percentage swell was achieved when 5% of dust added to the treated soil. Some researchers have turned their attention to industrial byproducts for the purpose of ameliorating acid soils (Li et al., 2010). Biomass ash (BA) is the byproduct of combusting biofuels in biomass power plants. It is reported that some BA, such as wood and straw ashes, not only contain an amount of alkalis, but also contain significant amounts of K, Ca, Mg and other nutritional elements (Mozaffari et al., 2000). Therefore, BA could ameliorate soil acidity and improve soil nutrient levels (Park et al., 2005).

Bone meal (BM) is a byproduct of the bone rendering industry and has been authorized as a fertilizer for arable crops in regulation No. 181/2006 of the European Commission since 2006. It is regarded as an effective resource of P for crops due to the large amount of P in BM (Garcia and Rosentrater, 2008).

Alkaline slag (AS) is the waste of ammonia-alkali production of sodium carbonate, with sea salt and limestone as raw materials. Some studies suggested that application of AS can effectively alleviate acidity of topsoil and subsoil due to the high contents of alkaline substances and $CaCl_2$ (Li et al., 2015).

Most researches just focus on the effect of a single amelioration material on soil acidity. However, it is difficult to thoroughly deal with soil acidity and nutrient deficiencies with any one of BA, BM or AS. While, combined application of BA, BM and AS may ameliorate soil acidity and improve soil fertility simultaneously (Shia et al., 2016).

Broken carbonate rocks, generically defined as limestone or calcium carbonate, are widely

used materials in removing direct or indirect unwanted effects of acidity. With a high basicity, steel slag can be used in agriculture to improve soil acidity and their mineralization.

MATERIALS AND METHODS

In principle, the acidic reaction correction of soil is performed by adding substances into the soil containing Ca, Mg known aslime amendments (limestone, lime, dolomite etc.) to neutralize the soil acidity to the desired pH (or optimal saturation basesdegree, usually 80%).
Fine texture of lime amendments improves the structure and this involves several positive attributes including reduced formation of the crust, a better plant emergence, fewer requirements regarding the necessary operations in soil tillage (Beegle et Lingenfelter, 1995).
The required amount of amendment depends on: the size of acidity and soil texture; change of desired pH; amendment composition. Amendmentparticles fineness is important to ensure a quick amendment reaction.
A good amendment program is based on a soil test that determines the degree of soil acidity and the right amount of amendment material necessary to neutralize this acidity. Once this quantity determined, anagriculture lime material will be selected and will have to satisfy economically recommendations and soil test results to maximum, with efficient yield. However, before taking into account the necessary amount of amendment, is fair knowledge of the agriculture limematerial, its quality and association with legislation.
Limestone amendments qualityused in agriculture varies significantly and should be an important consideration in the management of these amendments.
Among the most important factors in determining the amendment quality are chemical purity, speedof reaction, magnesium content, etc.
The chemical purity of limestone amendments determines how much material can neutralize soil acidity. The chemical purity is indicated by Calcium Carbonate Equivalent (CCE) of material, amount that can neutralize soil acidity compared to pure calcium carbonate (calcite limestone, $CaCO_3$).
Calcium carbonate equivalent to some agriculture lime material is given in Table 1.

Table 1. Common agriculture lime materials (Beegle et Lingenfelter, 1995)

Material	Chemical formula	% ECC (Calcium Carbonate Equivalent)
Pure calcite limestone	$CaCO_3$	100
Dolomitic lime	$(Ca, Mg)CO_3$	109
Calcium oxide	CaO	179
Calcium hydroxide: hydrated, powder	$Ca(OH)_2$	136
Marl and shells	$CaCO_3$	70–90
Slag (various)	$CaSiO_3$	60–90
Primary product obtained from industrial residues (by-product)	varies	varies

The speed of reaction which an agriculture lime material reacts with soil to neutralize the acidity, and thereby increase the soil pH is determined by the material fineness.
The finer the material is, the faster it will react becauselimestone solubility increases with fineness. The agriculture lime material should react with the soil as soon as possible.
The agriculture lime material fineness is given by the material percentage passing through sieves of specified meshes (Beegle and Lingenfelter, 1995).
Number of the sieve mesh, the finer material will be. The effect of the agriculture lime material fineness (particle size) on the speed of reaction is shown in Figure 1 (Beegle and Lingenfelter, 1995).

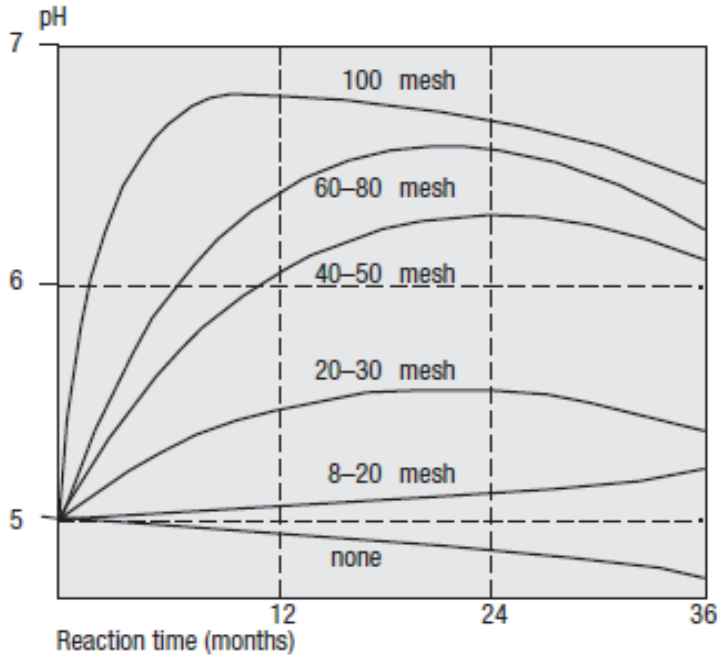

Figure 1. Effect of the agriculture lime material fineness on the speed of reaction

The material passed through 100 mesh sieve neutralized soil acidity with an increase in pH to value 7.0.

Choosing a material in terms of the percentage of particles sizes is a decision to be taken so that the material is fine as to satisfy the agronomic point of view, but also be economical in terms of shred cost.

A finer agriculture lime material is recommended in situations that require a very quick reaction.

In addition to the capability of neutralizing, the limestone it serves as a source of calcium and magnesium.

Steel slag is an accessible mineral amendment, used as the equivalent of calcium carbonate as adsorbent and fertilizer with manganese and silicon.

Steel slags are materials that combine the usually conditions for soil correction beside phosphate, magnesium and sulphur content, steel slag contains from 35% to 45% calcium oxide which makes it a soil treatment in restoring the natural balance of acid soils (www.cst.com.br).

Using slag has a great advantage over conventional amendments as long as calcium oxide present in the steel slag is chemically combined with silicon, iron and manganese. This allows for gradual release of calcium oxide in order to prevent "extinction" or carbonate transformation.

It is important to remember that not all steel slags are similar, they vary in composition, quality and fineness.

The legal status in terms of ferrous slag, such as classification as a residue and as a product or by-product has been discussed over the world for more than 25 years. EUROSLAG presented its point of view on this issue in 2006 a document entitled "The legal status of slags" (EUROSLAG & EUROFER, 2012)

This document refers only to furnace slag and steel slag, slag excluding other types such as nonferrous slag. EU Framework Directive 2008/98/EC on waste include steel slag in residue (waste) list. (Waste Framework Directive 2008/98/CE).

RESULTS AND DISCUSSIONS

Soil acidification is reversed by adding a liming material. Liming materials are oxides, hydroxides, carbonates, and silicates of Ca and/or Mg. The anion in liming materials (chemically speaking, a “base”) reacts with soil acidity (H) to neutralize it (Figure 2). The most common liming material, “aglime,” supplies carbonate as the base. Calcium alone does not increase soil pH. For example, gypsum (calcium sulfate) and other additives contain

Cabut do not contain a basic anion (carbonate, hydroxide, oxide, or silicate). Therefore, they do not neutralize soil acidity (Anderson et al., 2013).

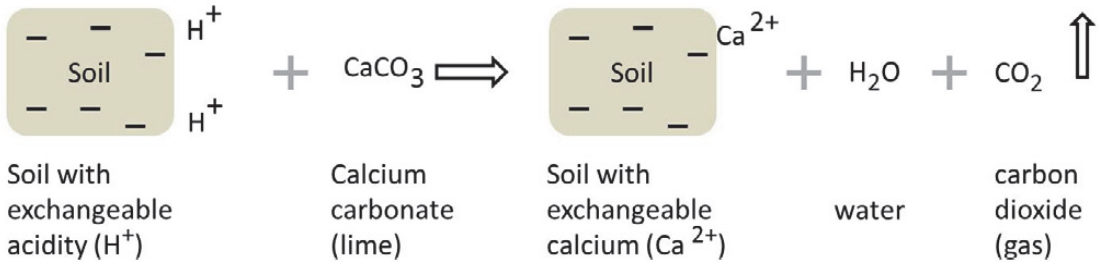

Figure 2. Soil acidity reacts with lime to form water and carbon dioxide. The carbon dioxide gas is lost to the atmosphere. This chemical reaction continues until all of the lime has reacted. Figure by Dan Sullivan

In Romania, according to official data are obtained annually approximately 75,000 t of steel slag. Have been identified as sources of steel slag (Popescu et al., 2016):

- ✓ manufacturer of steel equipment for energy industry;
- ✓ manufacturer ofalloy steel for the production of rolling stock;
- ✓ manufacturer of semi-finished long steel products.

The paper refers to the selection, collection and characterization of steel slag used for the purpose of amending an acid soil. Uniform lots of sample slag were established given the variety in composition, particle size and quality.

The granulometric composition of the slag is presented in Table 2 (Popescu et al., 2016).

Table 2. The granulometric composition of the slag (n = 3)

Granulometric fraction	**%**
> 0.09 mm	6.2
> 0.06 mm	3.0
< 0.06 mm	90.8

It is noted that the fine fraction predominate, meaning that 90.8% are particles smaller than 0.06 mm.

Steel slags have generally, higher specific weight (3.2-3.6 g/cm^3), which is a consequence of the residual metals existence in their chemical composition (www.nationalslag.org).

Table 3. The chemical composition of the steel slag (n=3)

Element	**Steel slag**
	%
Na	0.029
Ca	41.50
B	0.08
Fe	1.80
Mg	8.40
Al	3.10
Si	8.80
Zn	0.010
Cu	0.005
Ni	0.005
Cr	0.027
Pb	0.009
Sn	0.009
Sb	0.001
Mn	0.95
Cd	0.001
Ti	0.12

The chemical composition of the steel slag is presented in Table 3. It have been found a high content of calcium and magnesium as well as a rather high content of silicon.
Slag material has a very strongly alkaline reaction with a pH by 11.96.
The total content of soluble salts is very high (conductometric residue = 717 mg/100 g slag).
It have a very high amendment neutralization potential (ANP = 114%) reported to the calcium oxide and magnesium oxide contents and expressed as a percentage of calcium oxide (25%) (Treatwell and Zurcher, 1939). Some chemical characteristics of steel slag are presented in Table 4.

Table 4. Some chemical characteristics of steel slag (n=3)

Sample	pH_{H2O}	ANP* (%)	CaO** (%)	Conductometric residue (mg/100 g slag)
Steel slag	11.96	114	25	717

*ANP: Amendment Neutralization Potential, after Treadwell method, 1935
**CaO: content estimation of Ca and Mg oxides and hydroxides in limestone amendments, direct titration method

CONCLUSIONS

The steel slag have a very strongly alkaline reaction (pH = 11.96).
In terms of calcium carbonate equivalent, based on the contents of calcium oxide and magnesium oxide (expressed together as a percentage of calcium oxide) steel slag has anamendment neutralization potential very high.
Steel slag can be considered a mineral amendment used to improve soil acidity, and also a source of calcium and magnesium.
Due to the high content of metals and soluble salts, using steel slag as amendment for acid soils can be considered a potential and significant environmental risk, which is why the whole process of amendment must be conducted in terms of environmental protection.

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***www.cst.com.br. Arcelor Mittal Brazil - Product - Coproducts - Applications.

***www.nationalslag.org Ghide for the Use of Steel Slag in Agriculture and for Reclamation of Acidic Land. NSA - National Slag Association, P.O. Box 1197, Pleasant Grove, UT 84062.