

## Review

## Correcting soil acidity with the use of slags

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Soil acidity correction is mandatory for plants to reach their production potential. Lime is the most used product; however, it has hindrances for action in depth, especially when liming is broadcast on the soil surface. Silicates (or slags), originating from the industrialization of iron and steel, are byproducts that present corrective effect. These two types of corrective differ on specific area (contact area) and in neutralization ability. The corrective power of slags can be greater due to the particle characteristics, presenting greater specific surface, which confers greater reactivity. The application of Ca and Mg silicates as acidity corrective does not differ from lime use. Therefore, the soil acidity correction demand is determined initially, and the silicate dose used should follow the same recommendations established for lime application. In a consolidated no till system, where corrective application is broadcast on the soil surface, it should correct the 0-10 cm layer, and the silicate dose to be applied should be one half of that found for the conventional cultivation system.

**Key words:** Calcium and magnesium silicate, liming criteria, aluminum, bases saturation, reactivity.

### INTRODUCTION

Soil acidity is the main factor that contributes to chemical degradation. Nearly 70% of the agricultural soils in Brazil are considered acids, which decrease crop yields up to 40% (Quaggio, 2000; Nolla and Anghinoni, 2006, Bortoluzzi et al., 2008). Generally, these soils have low pH in water (<5.5), high levels of aluminum (> 1.0 cmol<sub>c</sub> kg<sup>-1</sup>) and high anions adsorption capacity, especially phosphate (Sousa and Lobato, 2004, Ramos et al., 2006), resulting in a lower absorption of water and nutrients, because the lower volume of soil exploited by roots. Nutrient availability is related to soil pH. In soils with low pH (<5.5), there is a low calcium, magnesium and phosphorus availability, that reduce plant growth and

productivity.

In Brazilian Cerrado soils, soil acidity includes the topsoil (0-20 cm) and subsurface (> 20 cm) (Sousa and Lobato, 2004; Aleoni et al., 2005; Ramos et al., 2006; Montezano, 2009). Thus, correcting soil profile is needed to the plant root system explore a larger volume of soil, and absorb nutrients for development (Amaral et al., 2004; Anghinoni, 2007). Usually limestone is used to neutralize soil acidity, which increases crop yields due to the improvement of chemical attributes in the soil. However, the action of lime is restricted to the topsoil (up to 0-20 cm) due to slow reaction in soil (Amaral et al., 2004; Nolla and Anghinoni, 2006). In no-tillage, the crops

root system exploits mainly the topsoil because liming is broadcast on the soil surface (Amaral et al., 2004; Ramos et al. 2006, Lasso, 2011). Surface roots can reduce crop yields because in Brazilian Cerrado soils is frequent the occurrence of dry spells, and result in a lower availability of water and nutrients in topsoil (0-20 cm).

Just as limestone, slags (or calcium and magnesium silicates) correct soil acidity and provide calcium, magnesium and anions in soil solution ( $\text{SiO}_3^{-2}$ ). Silicate anions ( $\text{SiO}_3^{-2}$ ) have the same valency as carbonate anions ( $\text{CO}_3^{-2}$ ) and can decrease iron, manganese and aluminum toxicity (Korndorfer et al., 2003; Souza et al., 2009; Lopes et al., 2011). According to Alcarde and Rodella (2003), the calcium silicate is 6.78 times more soluble than calcium carbonate ( $\text{CaCO}_3 = 0.014 \text{ g dm}^{-3}$  and  $\text{CaSiO}_3 = 0.095 \text{ g dm}^{-3}$ ), presenting a higher potential for the correction of soil acidity in the subsurface than lime.

The objective of this work is to study the mechanisms of soil acidity correction using slags (or silicates) and their interactions with the environment.

## SOIL ACIDITY

In general, cultivated tropical soils have a high degree of weathering and acidity. These soils have low pH in water (<5.5), toxic levels of aluminum (>1.0  $\text{cmol}_c \text{ dm}^{-3}$ ) and high adsorption capacity of anions, especially phosphate (Ernani et al., 1998; Anghinoni, 2007; Lasso, 2011). Aluminum toxic ( $\text{Al}^{+3}$ ) present in soil solution causes inhibition of root growth and subsequently decreasing and thickening of plant root system (Taylor, 1988), resulting in and lower absorption of water and nutrients, because there is a lower volume of soil explored by roots.

Nutrient availability is related to soil pH. In acid soils with low pH (<5.5), especially in sandy soils, which have a low availability of calcium, magnesium and phosphorus (Sousa and Lobato, 2004). These original characteristics of agricultural soils reduce plant growth causing reduction in yield.

There are many factors that soil acidification contribute, however, the more important are rainfall (dissociation of carbonic acid -  $\text{H}_2\text{CO}_3$ ), decomposition of soil organic matter (proton dissociation from phenolic radicals of organic matter and crop residues), nitrogen fertilizer (urea, ammonium sulfate), leaching of cations as calcium, potassium and magnesium (Comissão, 2004; Nolla and Anghinoni, 2006), and soil cultivation (nutrient uptake by plants root system) managed in no-tillage or conventional cultivation system (Anghinoni, 2007, Lasso, 2011).

In Brazilian Cerrado, nearly 70% of soils studied by Cochrane and Azevedo (1988) presented an aluminum saturation higher than 10%, level considered phytotoxic (Anghinoni and Salet, 2000; Nolla and Anghinoni, 2006; Rossato et al., 2009). Moreover, Cochrane and Azevedo (1988) observed that 86% of Brazilian Cerrado soils

presented low level of exchangeable calcium (>0.4  $\text{cmol}_c \text{ kg}^{-1}$ ), indicating that lime is needed to correction of soil acidity and increase the calcium and magnesium concentration.

Liming is a common practice, but it is necessary to use correct criterion for definition of a representative soil sample to be analyzed and an appropriate corrective dose. The term "liming requirement" indicates the corrective dosage required to neutralize soil acidity, starting from an initial condition (Ribeiro et al., 1999; Nolla and Anghinoni, 2006). Correcting criterion vary according to the analytical principles and objectives. The choice of a particular index is conditional on its behavior in soils evaluated, and liming does not depend only on the soil pH, but especially the soil buffering capacity, which is directly related to types and clay content and the soil organic matter content (Nolla and Anghinoni, 2006).

## CORRECTING SOIL ACIDITY

The soil acidity correction is done by applying of products that release anions ( $\text{OH}^-$ ) to neutralize acid protons ( $\text{H}^+$  and  $\text{Al}^{+3}$ ) that cause acidification of soil solution. Thus, it is necessary to use correctives that have basic components to release anions and neutralize soil acidity (Alcarde and Rodella, 2003; Rossato et al., 2009).

The materials used as correctives are basically oxides, hydroxides, calcium and magnesium silicates or carbonates (Alcarde and Rodella, 2003; Anghinoni, 2007). Limestone is the corrective more used, however it is necessary to dissolve in water to correcting soil acidity (Nolla and Anghinoni, 2006). Anions released by liming react with  $\text{Al}^{+3}$  and  $\text{H}^+$  in the soil, until there is neutralization of soil acidity or all lime was exhausted.

As limestone, slags has been applied for correction of soil acidity and calcium silicate ( $\text{CaSiO}_3$ ) and magnesium silicate ( $\text{MgSiO}_3$ ) are the main constituents (Ramos et al., 2006). However, not all the silicates can be used in agriculture, its use depend on the heavy metals levels present in these correctives. Slags are purified by a process where heavy metals are removed. In products with high levels of heavy metals the process becomes very expensive, that prevent agricultural use. However, there are materials derived from the steel industry with low heavy metal levels, and in some cases levels below that of limestone (Korndorfer et al. 2003).

Main difference between lime and slags is due to the presence of silicon in slags. The silicon was recently included in Brazilian legislation fertilizer as a beneficial micronutrient to plants (Brasil, 2004). Silicon (Si) benefits include the increased plant resistance because the higher tolerance to drought, higher photosynthetic capacity, decreasing of plant lodging, reduced transpiration and increased resistance to pests and diseases. Thus, plants grown in soil where the correction of soil acidity is done through applications of slags may have a higher yield,

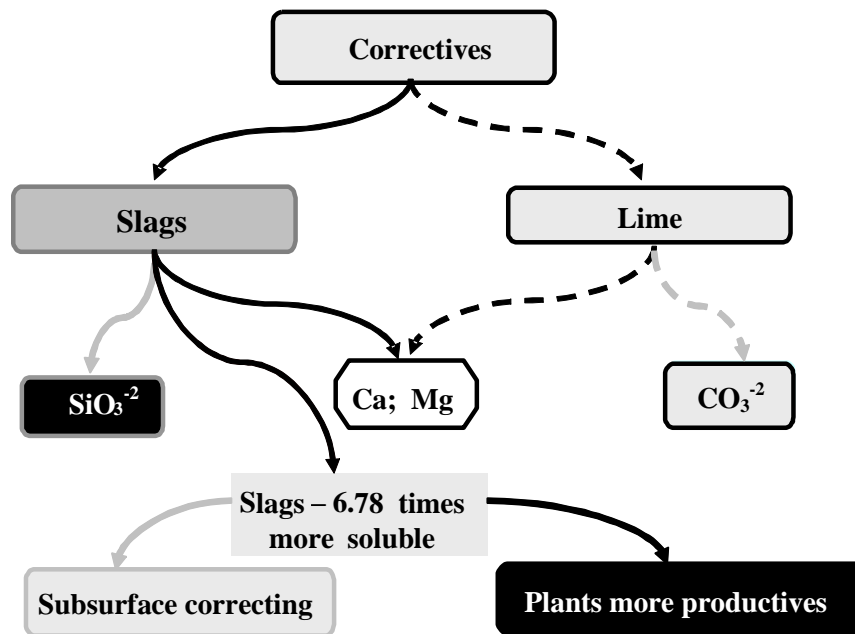
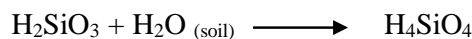
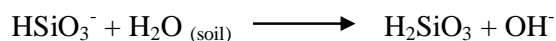
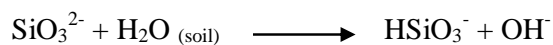
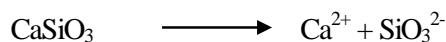


Figure 1. Reaction of slags (calcium and magnesium silicates) and lime in soils.

because slags provide a higher resistance to biotic and abiotic stresses (Korndorfer et al., 2003; Nolla et al., 2012).

The correcting soil acidity mechanism with the use of slags results in formation of monosilicic acid ( $\text{H}_4\text{SiO}_4$ ), which dissociates less than  $\text{H}^+$  adsorbed to the exchangeable cation capacity, and therefore soil pH increases, according to the equations described by Alcarde and Rodella (2003):



Slags (or calcium and magnesium silicates) used in agriculture release calcium, magnesium and silicate ( $\text{SiO}_3^{2-}$ ) ions in the soil solution (Figure 1), whereas silicate has the same valence as the carbonate ( $\text{CO}_3^{2-}$ ) from the limestone. Thus, slags have the same potential to correcting soil acidity than limestone. Moreover, slags have a high levels of silica and can be used as a nutrient source for plants, since consecutive crop reduce silicon concentration in soil (Korndorfer et al., 2003; Nolla et al., 2006).

Slags application has decreased the aluminum toxicity in several plants, including corn, cotton, rice and sorghum (Cocker et al., 1998; Korndorfer et al., 2003). This reduction in aluminum phytotoxicity is attributed to the formation of hydroxy aluminum silicates (Hodson and Evans, 1995). Some authors believe that

the reduction of aluminum phytotoxicity, induced by Si, may be due to the pH increase and it is not a direct effect of silicon in soil solution (Korndorfer et al., 2003). In an experiment with corn, silicic acid addition decreased the effect of inhibiting root growth caused by the presence of aluminum in soil solution (Ma and Matsumoto, 1997). Aluminum phytotoxicity reduction is usually observed when it is increased the silicon concentration in soil solution. These results suggest that the interaction between aluminum and silicon occur in solution, probably by the formation of a complex between aluminum and silicon that it is not toxic to plants. However, many authors believe that the interaction between aluminum and silicon can also occur inside the plant (Cocker et al., 1998).

Agronomic superiority of slags compared to limestone, in some cases, it is attributed to silicon and micronutrients (fertilizer effect) levels. In the slag are found macronutrients, micronutrients and heavy metals (Alcarde and Rodella, 2003). Except for the nitrogen and chloro, other nutrients may be contained in the basic steel slag, because such elements are part of the iron ore, coal, fluxes and refractory material, usually magnesite. However, slags have a neutralizing power of 86% compared to pure calcium carbonate, as shown in Table 1 (Alcarde and Rodella, 2003). Ribeiro et al. (1986), working with blast furnace slag incubated for 30 days, concluded that the slag application increased the sorghum yield, so that the application equivalent to  $3.7 \text{ t ha}^{-1}$  was able to neutralize  $\text{Al}^{+3}$  in soil solution. Wutke et al. (1962) observed that the blast furnace and steelmaking slag, presented the same efficiency than limestone to increase soil pH. In the field the slags were superior of lime in increase potato yield. Dalto (2003) observed that the application of slags and limestone increased soybean yield. However, the highest

**Table 1.** Equations used to determine slagging and liming requirement in the state of São Paulo and Minas Gerais - Brazil (Rajj et al., 1997; Ribeiro et al., 1999).

State	Formula to the slagging requirement
Minas Gerais	$SR = LR = \{Y \cdot (Al^{+3} - (m_t \cdot t/1000)) + [x - (Ca^{+2} + Mg^{+2})]\}$
São Paulo	$SR = LR = T(BS_2 - BS_1)/10 \cdot PRNT$ ;

SR = slagging requirement; LR = Liming requirement; Y = variable value depending on the soil buffering capacity;  $m_t$  = maximum aluminum saturation value tolerated (%) by a crop; t = effective cation exchange capacity (CEC effective) in  $cmol_c \text{ dm}^{-3}$ ; x = variable value – calcium and magnesium requirement by crop; T = cation exchange capacity at pH 7.0 (CEC potential), obtained by the sum of  $Ca^{+2} + Mg^{+2} + K^{+1} + Na^{+1} + (H^{+} + Al^{+3})$ , in  $mmol_c \text{ dm}^{-3}$ ;  $BS_1$  = base saturation in the soil e;  $BS_2$  = base saturation to be achieved; PRNT = relative neutralizing power (%).

**Table 2.** Neutralizing power of different products in comparison with calcium carbonate ( $CaCO_3$ ) Font (Alcarde and Rodella, 2003).

Product	Neutralizing power relative to calcium carbonate - $CaCO_3$ (Eq. $CaCO_3$ )
$CaCO_3$	1.00
$MgCO_3$	1.19
CaO	1.79
MgO	2.48
$Ca(OH)_2$	1.35
$Mg(OH)_2$	1.72
$CaSiO_3$	0.86
$MgSiO_3$	1.00

Eq. = equivalent to calcium carbonate.

yield was obtained when it was applied 4 tonnes of slag, and the increase compared with the control was  $537 \text{ kg ha}^{-1}$  (22%). Uitdewilligen (2004) studying corn with application of lime and slags dosages, concluded that slag application resulted in a higher corn yield (13% higher than lime).

Residual effect of slags, in the same way as limestone, depends on the particle size, management used, the contact time of the product with the soil and climate of the region (Alcarde and Rodella, 2003). In rice, slags provide a long residual effect, which can extend over several years (Lian, 1992), decreasing the reapplication cost of correcting soil acidity. In sugarcane, Prado et al. (2003) observed that slag showed residual effect 56 months after corrective application.

Slag capacity to correcting soil acidity is similar to limestone. However, it is important to observe that these two correctives differ in the specific surface area (contact area) and in the neutralization power (NP). Neutralization potential of these products can be higher, depending on the particles characteristic. Slags have a greater specific surface area, presenting a higher reactivity (Ramos et al., 2006). However, according to Louzada (1987) when limestone and slags are applied with similar grain sizes

(same reactivity), slags are somewhat less effective in increasing soil pH, that are attributed to lower NP (86%) of slags (Alcarde and Rodella, 2003).

Pereira (1978) studying the corrective power of a slag compared to limestones of different sources, applied in two ultisols, concluded that there is not difference between the correctives. However, Veloso et al. (1992) studying different correctives (calcined limestone and dolomite, gypsum and slag) to increasing soil pH, concluded that calcinated limestone application resulted in the greatest soil pH, followed by limestone and slag.

The application of slags in correcting soil acidity does not differ from limestone. Thus, according to Korndorfer et al. (2003), the slagging requirement (SR) should follow the liming requirement (LR). In the states of São Paulo and Minas Gerais – BRAZIL, it is recommended to use the formulas presented in Table 2. Thus, the season, the application form (broadcast or incorporated) and the reapplication criteria follow liming criteria. As limestone, slags have also high residual effect (3-5 years).

SMP index described by Shoemaker et al. (1961) are another method used to obtain the requirement to correcting soil acidity (Nolla and Anghinoni, 2006). This method is considered cheap, fast, accurate and it has a

**Table 3.** Liming requirement (lime with PRNT 100%) based on the SMP index to correcting soil acidity in soils of Rio Grande do Sul and Santa Catarina – Brazil (Comissão, 2004).

SMP index	pH in water to reach		
	5.5	6.0	6.5
	tonnes ha <sup>-1</sup>		
≤ 4.4	15.0	21.0	29.0
4.5	12.5	17.3	24.0
4.6	10.9	15.1	20.0
4.7	9.6	13.3	17.5
4.8	8.5	11.9	15.7
4.9	7.7	10.7	14.2
5.0	6.6	9.9	13.3
5.1	6.0	9.1	12.3
5.2	5.3	8.3	11.3
5.3	4.8	7.5	10.4
5.4	4.2	6.8	9.5
5.5	3.7	6.1	8.6
5.6	3.2	5.4	7.8
5.7	2.8	4.8	7.0
5.8	2.3	4.2	6.3
5.9	2.0	3.7	5.6
6.0	1.6	3.2	4.9
6.1	1.3	2.7	4.3
6.2	1.0	2.2	3.7
6.3	0.8	1.8	3.1
6.4	0.6	1.4	2.6
6.5	0.4	1.1	2.1
6.6	0.2	0.8	1.6
6.7	0.0	0.5	1.2
6.8	0.0	0.3	0.8
6.9	0.0	0.2	0.5
7.0	0.0	0.0	0.2

high correlation with the values of the soil incubation method - standard (Quaggio, 2000). For this, it has been used to liming requirement in the states of Rio Grande do Sul and Santa Catarina - Brazil, since 1.960 (Comissão, 2004; Nolla and Anghinoni, 2006). In this method, after soil incubation with calcium carbonate, to establish the relationship between stabilized pH and the dosage of calcium carbonate added (Shoemaker et al., 1961), soil samples are mixed with a buffer solution (SMP). Thus, it is done the measurement of soil solution pH (soil: buffer solution), whose value is called pH SMP. With pH SMP values and the correcting requirement, tables are elaborated for the liming requirement, as shown in Table 3 (Comissão, 2004). The SMP method is based in the soil buffering capacity, that increase corrective requirement when increase the organic matter level. Likewise, the slagging requirement (SR) based on the SMP index should follow the lime requirement, as shown in Table 3.

It is important to indicate that requirements to correcting soil acidity were calibrated to conventional cultivation system (Comissão, 2004). However, the soil cultivation under no-tillage system, used in large agricultural areas in Brazil, promotes different dynamics compared to the conventional system, due to increase in organic matter levels, surface accumulation of nutrients and lower levels of exchangeable aluminum. Thus, according to Anghinoni and Salet (2000) and Nolla and Anghinoni (2006) it has been observed high yields after 5 to 10 years without lime reapplication, in soils with low pH (5.5) and high exchangeable aluminum (> 1.0 cmol<sub>c</sub> kg<sup>-1</sup>). Thus, liming and slagging requirement in consolidated no-tillage system, where the correction soil acidity is done when lime or slag is broadcast on the soil surface, should aim to correct 0 to 10 cm layer, so that the slag or lime dosage should be half that calculated from Tables 2 and 3 (Comissão, 2004).

Recent papers suggest the slags application not only to the total area, but also for application in line with the seed. This application form allows the slags use in lower dosages promoting the rhizosphere, that can reduce the acidity released of the acidulated fertilizers, and increase yield (Ramos et al., 2006; Nolla et al., 2006; Faria et al., 2008). The slags are 6.78 times more soluble than calcium carbonate (CaCO<sub>3</sub> = 0.014 g dm<sup>-3</sup> and CaSiO<sub>3</sub> = 0.095 g dm<sup>-3</sup>), so that the lime neutralizing is smaller than slags because its base (CO<sub>3</sub><sup>-2</sup>) is weaker (KB1 = 2.2 × 10<sup>-4</sup>) that slags base (SiO<sub>3</sub><sup>-2</sup> - KB1 = 1.6 × 10<sup>-3</sup>). Thus, lime has a lower releasing of OH<sup>-1</sup> in soil solution (Alcarde and Rodella, 2003). Ramos et al. (2006) studied the slag and lime effect at depth under greenhouse conditions and observed that slag increased soil pH in a high values than lime in 0-25cm and 0-30 cm layer, when it was applied 500 and 1000 kg ha<sup>-1</sup>. Barbosa et al. (2003) observed a calcium increase of 68% to depth 40 cm when slag was applied, indicating the greatest potential of slags to correction of soil subsurface acidity (>20 cm layer). Nolla et al. (2006) also observed a progressive increase in soil pH by slag application of 6000 kg ha<sup>-1</sup>, where the pH increased, 0.6 units in a Quartzipsamment soil and 0.5 units in a typical Oxisol. Moreover, slags were more efficient to correcting soil acidity in the subsurface compared to lime, probably due to higher solubility (6.78 times higher than limestone; Alcarde and Rodella, 2003).

## Conclusions

Soil acidity correction is required in order present conditions for the expression of plant production potential. Lime is the most used corrective; however, there are alternative products, such as silicates, presenting the same soil acidity correction potential. The use of silicates should be based on indicators of the demand of acidity correction and on the recommendation of application dose. These parameters and formulas are

the same used for liming. Na advantage of the use of silicate is its origin as byproducts of iron and steel production, so their use in agriculture reduces an environmental liability from the industry. Silicates also present greater reactivity, which could indicate a thicker soil layer corrected, improving the possibility of plants deepening the root system and absorbing more nutrients. Silicates supply silicon to the soil solution, increasing plant resistance to biotic and abiotic stresses.

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