

A Guide for the use of Steel Slag in Agriculture and for Reclamation of Acidic Lands



**National Slag Association** 



# Guide for the Use of Steel Slag in Agriculture and for Reclamation of Acidic Lands

#### Introduction

This guide discusses the use of steel slag, a co-product of the steel making process, as a substitute for limestone for agricultural applications, and its use in reclamation of acidic lands. As early as the 1930s, steel slag was being used as an agricultural amendment in Alabama, Illinois, Indiana, Kentucky, Maryland, New York, Ohio, Pennsylvania and West Virginia. White et al. (1937) reported on field trials in Pennsylvania that crop yields of corn, wheat, oats, buckwheat and soybeans with steel slag applications were as good or better than an equivalent amount of limestone. In addition to the liming materials, steel slag contains various concentrations of plant nutrients, such P, S, Mn, Fe, and Mo. Steel slag contains significant amounts of calcium silicate, and several crops, including wheat, rice and sugar cane have shown positive growth responses to silicate applications. Anderson (1991) reported yield increases of sugar cane with calcium silicate slag, and attributed the increase to higher plant tissue Si concentrations. Silicon has also been shown to resist fungal infections in grass species (Datnoff et al., 1990).

# **Steel Slag Production Process**

#### **Basics of steel production**

Virtually all steel is made in plants using the basic oxygen process, or in electric arc furnaces (EAF). In the basic oxygen and EAF processes, molten metal, and/or scrap, and fluxes (lime (CaO) or dolomitic lime (Cao.MgO)) are placed in the furnace. High-pressure oxygen is injected into the furnace with a lance. The oxygen reacts with carbon and non-iron impurities to form a number of oxidized compounds. These, in turn react with the lime or dolomitic lime to form slag. The liquid steel is poured from the furnace while the slag remains and is then poured into a separate vessel.



#### Types of steel slag

There are different types of slag produced in the steel-making process. These include furnace or tap slag, raker slag, synthetic or ladle slags. Figure 1 presents a diagram of the general flow and production of different slags in a modern steel plant. Following processing and metal recovery, the nonmetallic products from the furnace, raker and ladle slags are used for various applications including as construction aggregate, in agriculture, or for reclamation of acidic lands.



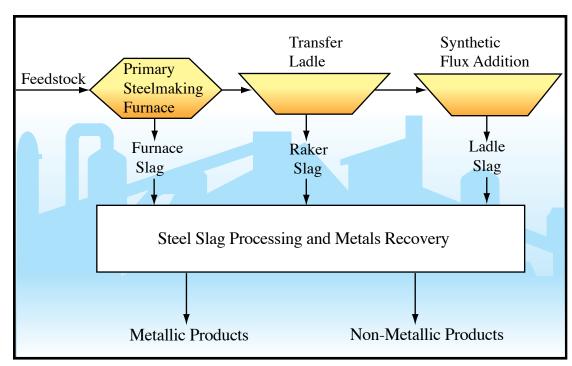


Figure 1. Slag production in a modern steel plant

The nonmetallic steel slag is used for various beneficial applications, while the raker, ladle and pit slags are recycled.

# **Characteristics of Steel Slag**

#### Physical characteristics

The most important physical characteristic of steel slag for use as an agricultural liming material is its particle size distribution. The finer the particle, the more reactive the material will be in neutralizing soil acidity.

Particle size distributions for slags from a number of studies are given in Table 1. The high percentage of the material passing 20 mesh or finer in the



White et al. (1937) study suggests that these slags were either pre-screened, as in the case of the 20 mesh slag or ground, as in the case of the slag meal.

Steel slags have high specific gravities (3.2-3.6 g/cm³) and high bulk densities (1.6-1.9 g/cm³) relative to agricultural limestone (2.7-2.9 and 1.4-1.5 g/cm³, respectively). This is a consequence of residual metal in the slag.



Table 1. Particle size distribution (% by weight) of steel slags from various studies.

Reference	Slag Type		Mesh Size	
	3 71	20	60	100
Munn (1997)	Blast furnace	23	5.9	4.0
	Steel furnace	18	6.7	6.5
	Metallic steel	11.7	4.9	11.9
Kerins (2008)	AgSlag	66.6	29.8	22.8
Beauchamp and Evans (1999)	Erie slag	42*	4	4
	Hilton slag	29	9	13
White et al. (1937)	20 mesh slag	98.6	89.9	77.5
	Slag meal	100	97.3	87.1
National Slag Association	Fine aggregate		32-70	5-15

# **Chemical composition**

Steel slags contain many of the same chemical compounds found in Portland cement. They contain calcium silicate and some free CaO and MgO. Chemical composition of steel slag from open hearth and the basic oxygen process is given in Table 2 (http://www.tfhrc.gov/hnr20/recycle/waste/ssa1.htm).



Table 2. Chemical characteristics of steel slag.

Constituent	(% by wt.)
CaO	40-52
SiO <sub>2</sub>	10-19
$Al_2O_3$	1-3
MgO	5-10
Fe (FeO or Fe <sub>2</sub> O <sub>3</sub> )	10-40
MnO	5-8
TiO <sub>2</sub>	0.5
$P_2O_5$	0.5-1
Free CaO	2.1
Metallic Fe	0.5-1.0

# **Liming Characteristics of Steel Slag**

#### Content of lime in steel slag and lime composition

As shown in Table 2, steel slag contains significant concentrations of Ca and Mg. These elements occur in the form of silicates, ferrites, aluminates, oxides and some free CaO and MgO. Steel slag is alkaline, with pH in the range of 8-10, but values of 12 or higher are possible if the free CaO content is high enough (CaO reacts with water to form Ca(OH)<sub>2</sub> which has a maximum pH of 12.5). While Ca silicate is alkaline and will act as a long-term liming agent in soil, the immediate liming effect comes from the free CaO and MgO.

#### Reactivity of lime in steel slag

The liming materials in steel slag comprise water-soluble and less water-soluble Ca and Mg compounds. Free Ca in slag reacts rapidly with water to form Ca(OH)<sub>2</sub>. The Ca(OH)<sub>2</sub> will react rapidly with soil acidity. The less soluble silicate compounds will react more slowly with soil acidity and will provide more long-term buffering of soil pH.



#### Analytical tests for lime in steel slag

The liming value of an alkaline material such as limestone or steel slag is its total neutralizing value. This is determined by reacting the material with excess strong acid and back titrating the residual acid (AOAC, 1965). The total neutralizing value is expressed in terms of its equivalency to pure limestone (CaCO<sub>3</sub>), and is termed the calcium carbonate equivalency (CCE). Liming materials in most states must have a guaranteed liming value, and some states require a minimum CCE to be classified as a liming material. Some states also require that the material have a specific fineness to guarantee effective reactions with acid soils. For example, Virginia requires that 30 % of the material pass a 100 mesh sieve, 50 % pass 60 mesh, and 90 % pass 20 mesh.

# **Application of Steel Slag to Agricultural Land**

#### Determining lime requirements for agricultural soils

The amount of lime to be added to an agricultural soil is a function of the crop to be grown and the acid buffering capacity of the soil. Organic soils have special liming needs. The ideal pH of a crop can vary over a wide range. Some crops, such as cranberries, require a low pH. Others, such as corn, can be grown over a wide range of soil pH, providing that nutrient levels are adequate. Others, such as alfalfa, prefer neutral to slightly alkaline pHs.

Organic soils are a special condition, in that liming much above pH 6 can result in tie up of micronutrients such as Cu and Zn.

The acid buffering capacity of a soil is a function of its mineral composition and organic matter content. Soils buffer pH in the acid range by releasing exchangeable  $H^+$  or  $Al^{3+}$  into solution. The cation exchange capacity of a soil is related to its texture and finer textured soils have higher acid buffering capacity than coarser textured soils.

Acid buffering capacity of soil can be determined by titrating a sample of the soil to the desired pH, but more rapid tests have been developed and are widely used by testing labs. These buffer tests involve reacting a sample of soil with a weak alkaline buffer and determining the equilibrium pH. A low equilibrium buffer pH means that the soil is strongly acid buffered and will require more lime to raise the pH to the desired value. The most commonly used buffer test is the Shoemaker McLean Pratt (SMP) test (SSSAP, 1961). The lime requirement of the soil in tons of agricultural limestone per acre is based on the buffer pH and the desired soil pH. Testing labs will typically only report the lime requirement. Agricultural limestone is assumed to be 95 % pure (e.g., it has a CCE of 95 %).

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 the lime requirement of a soil was 2 tons/acre, and the CCE of the steel slag was 25 %, the application rate of steel slag would be 2 x 95/25 = 7.6 tons/acre.

#### **CCE of Steel Slag**

Beauchamp and Evans (1999) determined the CCEs of two steel slags and reported values of 22 and 29 %. A steel slag from Maryland was reported to have a CCE of 55 % (Kerins, 2008). Munn (1998) studied steel slag, metallic steel slag, and blast furnace slag and reported CCEs of 80, 65, and 81 %, respectively. Beck and Daniels (2008) reported CCEs of 49 and 18 % for fine and coarse steel slags.



#### Frequency of application of steel slag to agricultural soils

Agricultural limestone is typically applied every 3-5 years. The slow release properties of limestone allow the desired pH to be maintained for that period. It is expected that Ca(OH)<sub>2</sub>, formed when the CaO in the slag reacts with soil moisture, will cause an immediate increase in soil pH, but not to the desired pH. The desired pH will be achieved over time as the less soluble liming constituents in the slag react with the soil. It is recommended that a lime reaction test be conducted for a specific slag. The lime reaction test involves mixing one or more representative acid soils with the rate of steel slag determined from the buffer lime test and observing changes in soil pH over time. The frequency of application would be based on the time that the slag was able to maintain the desired pH.

#### Methods of application and incorporation into the soil

Application of limestone to agricultural soil provides best results if the material can be incorporated into the top 15 cm of soil. This depth represents most of the rooting environment where the plant gets its water and nutrients. Incorporation is also important for coarser slag materials so as to provide maximum mixing with the soil.

In some cases, such as no-till cropping, hay crops, or orchards, incorporation may not be feasible. In this case, the more soluble Ca(OH)<sub>2</sub> may be able to leach into the soil from the

surface application but most of the pH rise will be in the surface 5 cm.

# **Use of Steel Slag for Reclamation of Acidic Lands**

#### Mine land reclamation

Use of steel slag for reclamation of acidic mine land is an excellent use for this material. Application rates to neutralize total potential acidity of mine land are high and reapplication of lime may not be technically or economically feasible. Munn (1998) showed that three steel slags were as effective as limestone in neutralizing an eastern Ohio coal mine spoil. These spoils are extremely acidic (pH <4) and

with toxic levels of available Al. There was no seed germination on the unlimed control plots in his study. Germination was successful in all treatments with limestone and slag.

#### Application to acidic landfill cover

A unique application for materials like steel slag is remediation of acidic landfill final cover. Along the east coast of the U.S., soils used for final vegetative cover on landfills have failed to maintain plant cover because of rapidly falling pH values. The drop in pH is due to the oxidation of sulfides in these coastal soils with the production of sulfuric acid. The rates of liming required are high and the use of limestone may not be economically feasible.

#### Tests for total neutralizing capacity of acidic lands

Unlike acidity in agricultural soils, which is attributable to exchangeable H<sup>+</sup> and Al<sup>3+</sup>, total acidity in acidic mine lands or acidic landfill cover may be due to the total oxidizable S in the material. Although there are no standard tests for oxidizable S, soil chemists at state



Land Grant universities would have the knowledge and skill to perform such tests. Failure to lime for the total acidity in the mine land or landfill cover could lead to brown outs, areas where pH has dropped to levels unable to support vegetative growth. Reapplication of lime to these spots is time consuming and expensive.

#### Methods of application and incorporation

Mine lands, in addition to having low pH, also suffer from a lack of organic matter, available nutrients, and poor structure. A common failure in reclamation of such lands is drought, caused by shallow application of lime, organic matter, and fertilizer. Whereas, slag is typically incorporated into agricultural land to a depth of up to 15 cm, it should be the goal to incorporate slag to the greatest depth possible, in order to encourage root development to greater depths. Since slag application rates will be much higher on mine lands than on agricultural soils, incorporation to greater depth prevents excessive liming of the surface and pH higher than desired.

# **Environmental Questions Regarding Use of Steel Slag in Agriculture and for Reclamation**

#### **Soluble salts**

Agricultural limestone (CaCO<sub>3</sub> or CaMg(CO<sub>3</sub>)<sub>2</sub>) has low water solubility and only dissolves by acid attack. Therefore, build up of soluble salts with these materials is not a concern. Steel slag will have a higher soluble salt content than limestone because of the content of CaO and MgO, which react with water to form Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub>. These hydroxides have water solubilities of 1.20 g/L and 0.009 g/L, respectively, compared to 0.014 g/L



for CaCO<sub>3</sub> and 0.013 g/L for MgCO<sub>3</sub> (National Lime Association, 1990). At typical agronomic lime application rates, this increase in soluble salts should be negligible, particularly in humid regions and with well-drained soils. Beck and Daniels (2008) reported soluble salt contents of fine and coarse steel slag of 3.68 and 2.55 decisiemens per meter (dS/m), respectively. Plants can tolerate up to 4 dS/m, so soluble salts should not be an issue with agricultural applications. On reclamation sites, with higher application rates and more concentrated near the surface, soluble salts should be tested.

#### Over liming

Each crop has an optimum soil pH range in which nutrient availability is maximized. Over liming can result in lowered plant availability of macronutrients, such as P, and of micronutrients, such as Fe, Cu and Zn. Because of the high reactivity of CaO and MgO in steel slag, and the high equilibrium pH of Ca(OH)<sub>2</sub> (pH 12.5), there is a greater risk of over liming with slag than with limestone, which has an equilibrium pH of 8.25 and is much less reactive than Ca(OH)<sub>2</sub>. It is important that slag application rates be based on the soil acid buffer test.



#### **Trace elements**

Steel slag will contain various concentrations of trace elements, depending on the type of steel produced and on the steel process used. Munn (1998) reported trace element concentrations for three steel slags (Table 3). At near neutral soil pHs, as would be expected from liming with steel slag, solubilities and bioavailabilities of the cationic metals (Al, Cr (III), Pb, Cd, Ni, Co, Be, Ba, and Sr) will be low. Beck and Daniels (2008) studied fine and coarse steel slags with 5169 and 4519 mg/kg, respectively, of total Cr (III). TCLP leachate concentrations for Cr (III) were 0.004 and < 0.003 for the fine and coarse slags, respectively, indicating very low solubility of this metal. There were small but non-environmentally important increases in extractable Cr (III) in soils amended with up to 10 tons/acre of slag.

Table 3. Trace element composition (mg/kg) of steel slags (Munn, 1998).

Element	Steel Slag	Metallic steel slag	Blast furnace slag
Al	1.6	1.5	3.3
Cr (III)	760	1707	244
Мо	26	189	53
Pb	24	44	< 3.3
Cd	< 0.3	< 0.3	< 0.3
Ni	83	941	399
Co	14	26	9
V	634	299	19.5
Be	2.6	3.4	11.9
Ba	30	82	364
Sr	147	163	312
Sn	< 3.3	< 3.3	< 3.3
Sb	144	168	123

The oxyanions trace elements (Mo, V, Sn, and Sb) would be expected to be slightly more soluble and bioavailable at near neutral pHs than the cationic metals.

#### **Conclusions**

Steel slag has been successfully used as a substitute for limestone to neutralize soil acidity in agricultural soils for many years, and research has shown slag use to be comparable to or superior to limestone in some cases. In addition, to its liming benefits, slag contains plant nutrients that can enhance plant growth. Slag also contains Si, which has been shown to increase yields of grass crops, such as rice and sugar cane, and Si also helps crops defend against crop diseases.

Although steel slags contain varying concentrations of trace elements, such as trivalent Cr (III) and Zn, the bioavailability of these metals is very low (Beck and Daniels, 2008).

As a co-product of an industrial process, steel slag offers considerable cost advantages over commercial limestone. There has been significant volatility in the cost of agricultural limestone in recent years, attributable in part to energy costs of production. Growers have deferred use of limestone to cover the rising costs of fertilizer, even at the risk of lower yields. Growers are increasingly looking to co-product liming materials like steel slag.



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