Soil Amendment (1930's)

- Alabama
- Illinois
- Kentucky
- Maryland
- New York
- Ohio
- Pennsylvania
- West Virginia

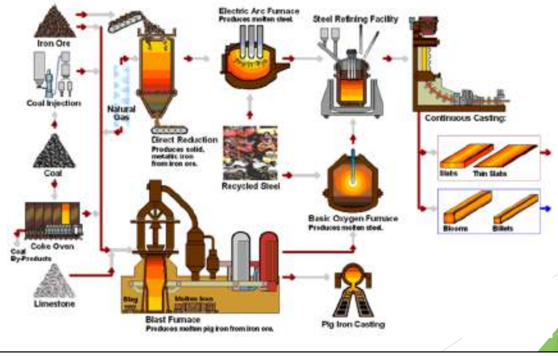
Why

- Liming
- Nutrients
  - Phosphorous
  - Sulfur
  - Manganese
  - Iron
- Beneficial Substances
  - Calcium Silicate
- Compost
- Feed Lots

Definition of Steel Slag

The **A**merican **S**ociety for **T**esting **M**aterials (ASTM) defines Steel Slag as a non-metallic by-product, consisting of essentially calcium silicates and ferrites combined with fused oxides of iron, aluminum, manganese, calcium and magnesium, that is developed simultaneously with steel in basic oxygen, electric arc, or open-hearth furnaces.

Production



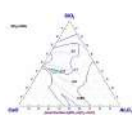
Types of Steel Furnace Slag

- Like Natural Aggregate there are many types:
  - Basic Oxygen Furnace (BOF / BOS)
  - Electric Arc Furnace (EAF)
  - Ladle Modification Furnace (LMF)
  - Argon Oxygen Decarburization (AOD)
- Characterize
- Segregate

Characterization

Typical Steel Slag Chemical Composition	
Constituent	**Composition (%)**
CaO	40 - 52
SiO_2	10 - 19
FeO	10 - 40
MnO	5 - 8
MgO	5 - 10
Al_2O_3	1 - 3
P_2O_5	0.5 - 1
S	< 0.1
Metallic Fe	0.5 - 10

Typical Physical Properties of Steel Slag	
Property	**Value**
Specific Gravity	3.2 – 3.6
Unit Weight (lbs./cu.ft.	100 - 125
Absorption	Up to 4%



Steel Furnace Slag

Major primary mineral constituents	Molecular and structural formula
larnite, beta-dicalcium-silicate	beta-Ca_2SiO_4
srebrodolskite, calcium-iron-oxide	$Ca_2Fe_2O_5$
brownmillerite, calcium-aluminium-ironoxide	$Ca_2AlFeO5$
spinel	$Me_{2+}Me_{3+2}O_4$
wuestite, solid solution of iron(II)-oxide with MgO and MnO	$(Fe_{1-x-y},Mg_x,Mn_y)O_z$
gehlenite, calcium-aluminium-silicate	$Ca_2Al_2SiO_7$
bredigite, calcium-magnesium-silicate	$Ca_{14}Mg_2Si_8O_{32}$

Liming Characteristics of Steel Slag

- Gradation
  - Gradation ranges for reactivity
- Calcium Carbonate Equivalent
  - Test Methods
- Neutralizing Value
  - CCE / Gradation
- Spreadability
  - Density

Physical Properties (Gradation)

Reference	Slag Type	Mesh Size 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

Analytical Tests for Lime in Steel Slag

- Determined by reacting the material with excess strong acid and back titrating the residual acid.
  - Expressed in terms of its equivalency to limestone.
  - Calcium Carbonate Equivalent (CCE
- ASTM C-25 (1965)
- AOAC 944.01 (1995)
- ASTM C-25
- Ferric Acid
  - Set Point
  - Colorimetric vs measured (sp)

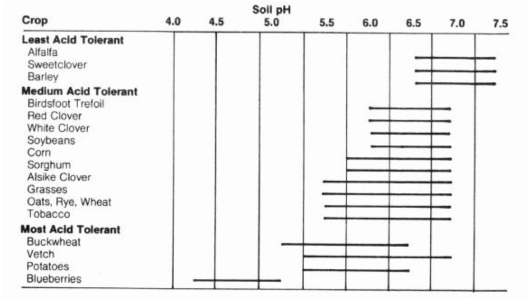
Calcium Carbonate Equivalent of Steel Slag Neutralizing Value

- Calcium Carbonate Equivalent (CCE)
  - Type of Slag
    - Chemistry (Differential)
    - Particle Size Distribution
  - Test Method
- Neutralizing Value (RNV)
  - Target = 60
    - -60 requires additional material
    - +60 requires less

North Carolina

- Agricultural liming materials must be crushed so that 90 percent passes through a U.S. standard 20-mesh screen (with a tolerance of ± 5 percent).*
- For dolomitic limestone, 35 percent must pass through a U.S. standard 100-mesh screen; for calcitic limestone, 25 percent must pass through a U.S. standard 100-mesh screen (with a tolerance of ± 5 percent).
- A product must contain a minimum of 6 percent magnesium to be classified as a dolomitic limestone.
- There is no minimum calcium carbonate equivalent requirement for limestone sold in North Carolina. However, the product must be labeled to show the amount necessary to equal that provided by a liming material having a 90 percent calcium carbonate equivalent. Lime recommendations in North Carolina are based on 90 percent calcium carbonate equivalency. For example, a product having a calcium carbonate equivalent of 80 percent would be labeled "2,250 pounds of this material equals 1 ton of standard agricultural liming material."

Liming Recommendations



Alabama Liming

Analysis	Basic Slag 1957	Basic Slag 1964	Basic Slag 1975	Basic Slag 1997	Basic Slag 2003	Ground Limestone (Minimum Quality)
Neut. Value (%CCE)	**78**	**68**	**55**	**60**	**85**	**90+ (**)**
Phosphorous (% P2O5)	**10.9**	**7.4**	**2.1**	**0.3**	**0.7**	--
Iron	--	17.9	--	24.4	26.2	--
Calcium		22.7			23.6	--
Magnesium	--	2.8	--	4.9	6.5	6+ in Dolomite
Manganese	--	1.8	--	2.6	1.2	--
Zinc	--	<0.1	--	0.1	0.1	--
Boron	--	<0.1	--	--	0.06	--
% Passing #60 Mesh	**--**	**--**	**--**	**--**	**35**	**50+**
% Passing #100 Mesh	**80**	**70**	**80**	**50**	**--**	**--**

Comparisons

- White et a. 1937
  - In field trials in Pennsylvania, crop yields of corn, wheat, oats, buckwheat and soy beans with steel slag applications were as good as or better than an equivalent amount of limestone
- Boyd Ellis, Michigan State University, 1965
  - When the same size fractions from each material were added to soil in quantities to give equal neutralizing values, steel slag reacted as fast as calcic limestone and faster than dolomitic limestone.
- Edw. C. Levy 2008
  - Two corn fields in Paw Paw, Michigan. One field was treated with 2 tpa processed steel slag while the other used Hi-Cal Lime. The neutralizing response was the same on both.

Agricultural Lime Definition

- **Liming Material is defined as** "all or any form of limestone, lime rock, marl, slag, by-product lime, industrial or factory refuse lime, water softener lime, and any other material manufactured, prepared, sold or distributed primarily to correct soil acidity."

Nutrients

- Increased nutrient uptake efficiency
  - Phosphorous
  - Nitrogen
- Iron (Wang Xian & Cai Qing-Sheng 2006)
- Increasing Ca and Mg (G. Besga et al. 1996)
  - Better solubility than that of magnesium carbonate in natural limestone and dolomite
- Trace Elements
  - Manganese
  - Copper
  - Zinc
  - Boron

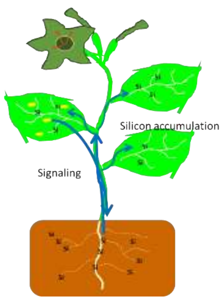
Nutrient Availability

Component	Guaranteed Level	Actual Level
Soluble Silicate	-	10 ~ 13%
Alkaline	≧40%	45 ~ 50%
Citric acid-Soluble Magnesium	≧ 1%	3 ~ 5%
Citric acid-Soluble Manganese	-	3 ~ 5%
Citric acid-Soluble Phosphate	-	1 ~ 2%
Iron	-	23 ~ 27%
Citric acid-Soluble Boron	-	0.1

AAPFCO - Plant Beneficial Substance

- Plant Beneficial Substance: is any substance or compound other than primary, secondary, and micro plant nutrients that can be demonstrated by scientific research to be beneficial to one or more species of plants, when applied exogenously.
- Calcium Silicate: is derived from naturally occurring minerals, such as Wollastonite, or synthetically derived having the principal formula $CaSiO_3$.

Stress Induced Si Accumulation (SISA)



Silicon in Agriculture

- Physical
- Biochemical

J. Plant Nutr. Soil Sci. 2005, 168, 269–274

Osmotic stress and silicon act additively in enhancing pathogen resistance in barley against barley powdery mildew

Effects of foliar- and root-applied silicon on the enhancement of induced resistance to powdery mildew in *Cucumis sativus*

Y. C. Liang, W. C. Sun, J. Si and V. Römheld

PMPP

PMPP

The Effects of Silicon Supplementation on Cucumber Fruit: Changes in Surface Characteristics

A. L. SAMUELS, A. D. M. GLASS, D. L. EHRET and J. G. MENZIES

Calcium Silicate Slag

Changes in pH and Mehlich-3 Extractable Nutrients of Selected Soils From the Midwest and South USA As Influenced by Different Rates of Iron Calcium Silicate Slag.

Brenda Tubana / Lawrence Datnoff: School of Plant, Environmental, and Soil Sciences, Louisiana State University AgCenter, Baton Rouge, LA. John Yzenas: Edw. C. Levy Co. Detroit, MI. 2012.

Multi-Year Response of Sugarcane to Calcium Silicate Slag on Everglades Histosols

D. L. Anderson[*] **and G. H. Synder :** Everglades Res. Ed. Ctr., P.O. Box 8003, Belle Glade, FL;
F. G. Martin : Statistics Department Univ. of Florida, 413 Rolfs Hall Gainesville, FL 3261

Effect of Different Silicon Sources On Acetic Acid-Extractable Silicon Content of Two Alluvial Soils of Louisiana.

Narayanaswamy Chowdappa[1]*,* ***Saoli Chanda***[2]*, Brenda Tubana*[2] *and Lawrence Datnoff*[3]*, (1)Indian Farmers Fertilizer Cooperative in Karnataka India / Louisiana State University AgCenter, Baton Rouge, LA. 2012*

Evaluating the Potential for Slag as a Source of Supplemental Silicon in Container Crop Production

Jonathan Frantz[1]**, John Yzenas**[2]**, and Russell Friedrich**[1]
[1]USDA-ARS, Greenhouse Production Research Group, Toledo, OH
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INTRODUCTION

Evidence of the potential beneficial effects of supplemental silicon in fertility programs for crop production is plentiful. Recent acceptance of silicon as a fertilizer in organic practices increased the profile of the nutrient, so the potential sources of silicon must be determined. Slag is a granular product produced during the manufacture of iron and steel, and depending on the process, can vary greatly in its composition. Within any given smelting process, the resulting slag is predictable and consistent. We sought to determine 1) if different slag types could be used as a supplemental silicon source in containerized crop production, and 2) if any heavy metals were also leached from the materials.

Figure 1. Zinnia leaves fed with or without Si and inoculated or not inoculated with powdery mildew. Si activates plant defense pathways that allow the plant to fight off this stress. Si application can be accomplished a number of different ways; slags provide a method that is easily adapted within existing plant production practices.

MATERIALS AND METHODS

Expt. 1: Different particle sizes of slag were extracted with water, filtered, and analyzed on ICP.
Expt. 2: Slag was mixed with a peat:perlite substrate, loaded into glass columns (Fig. 2), and extracted 10 times (1x per day) with the Saturated Media Extract procedure using water as the extractant (Fig. 3).
Expt. 3: Zinnia (*Zinnia elegans* 'Oklahoma White') were grown in containers with one of 3 rates of slag: adjusted to 2 tons per acre or field rate, 7x or 14x field rate. They were compared with no amendment (control) or a substrate drench containing 2 mM Si as potassium silicate. All containers were fertilized at each irrigation. Mature, fully expanded leaves were analyzed for total Si concentration and for heavy metals with ICP.

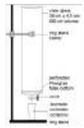


Figure 2. A diagram of a glass column setup that is used to perform series of SME on substrate mixtures. Little is known about how Si should be quantified for predictions of Si bioavailability. We filled the columns with peat:perlite mixtures and amended them with different slag types and rates of slag. Each day, we filled the columns with water, ...

Figure 3. ... containing peat:perlite ... and types of slag were ... placed on the tops of each ... Solution was filtered ...

RESULT

Expt. 1.

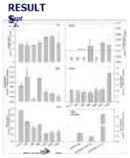


Figure 4. Amount of Si extracted with water from different slags of differing particle sizes ... materials are also shown. ... based on particle sizes. Based on this test, BF-, and EAF-types have the most potential for Si release.

Expt. 2.

Slag type	field	7 x field	14 x field	Trend in time
BF	2.1de	4.46a	1.9e	increase
BOF	3.35c	3.77bc	1.31f	increase
EAF	2.56d	4.11ab	3.75bc	NC
Caster	0.21ij	0.06j	0.01j	decrease
Debris	0.47hij	0.26ij	0.03j	decrease
Wollastonite	2.17de	3.98ab	3.88b	decrease
Control	0.28ij	-	-	decrease

Table 1. Average amount of Si released in the series of SME from the columns and the trend over time in amount released. Even though the amount increased or decreased, the magnitude of change was small over the 10 extraction. Based on this analysis, BF, BOF, EAF, and Wollastonite would be able to supply Si. NC indicates "no change" over the 10 sequential extractions.

Expt. 3.

Slag app rate	BF	BOF	EAF	Caster	Debris	Wollastonite	Control	Drench
field	2.9fg	5.4ef	5.2ef	1.0g	0.9g	8.5de	-	-
7 x field	8.2de	10.8b	14.9b	2.1fg	1.9fg	12.6bc	-	-
14 x field	9.8cd	13.3a	21.4a	2.2fg	2.3fg	12.8bc	-	-
other						-	1.3g	14.2h

Table 2. Total amounts of Si in zinnia leaf tissue grown with different amounts of slag. High rates of slag were used to establish a worst-case scenario for heavy metal leaching and to account for greater leaching from irrigation in containers. Growth in BOF, EAF, and Wollastonite resulted in the most Si in leaves, and had levels comparable to soluble potassium silicate (Drench treatment) at 2 mM Si. Not shown: pH increased to above 7.0 in BOF treatment. There was no significant concentration of heavy metals with most metals (except Mn and Al) being below detectable limits.

CONCLUSIONS

Using water as an extractant, the series of SME from the columns provided the best predictions of Si availability from different materials.
- At high rates, slag may raise pH above optimal ranges.
- Based on these experiments, there is no / low risk of heavy metal leaching from these slag types, even if applied at rates much higher than 2 tones / acre.

ACKNOWLEDGEMENTS

We thank Doug Sturtz, and Alycia Pittenger for assistance with plant analysis.

Compost

Processing livestock waste requires a system that provides high quality compost in a short period of time. [Solution] The system promotes composting by reusing steel slag, which is a by-product of the steel industry and has not been effectively utilized in the past, as a raw material mixed with livestock waste; and efficiently utilizes soluble silicic acid, lime, iron and the like included in the steel slag as a fertilizer resource. This system is capable of reducing the time to produce compost by: accelerating the temperature increase at the beginning of composting so that the temperature of a mixture of livestock waste and steel slag reaches at least 50°C within 48 hours after mixing; and reducing the moisture content of the mixture to 30 to 50%.

Composite Sample Results

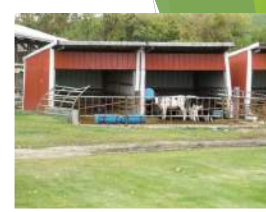
All are well within acceptable results

	USEPA Pollutant Ceiling Concentrations* mg/kg (dry basis)	IDEM Pollutant Ceiling Concentrations** mg/kg (dry basis)	SDI Composite Compost Cells 1-9 mg/kg (dry basis)
Arsenic	75	41	1
Cadmium	85	39	8
Copper	4,300	1,500	53
Lead	840	300	9
Mercury	57	17	<1
Molybdenum	75	75	9
Nickel	420	420	220
Selenium	100	100	BDL
Zinc	7,500	2,800	170

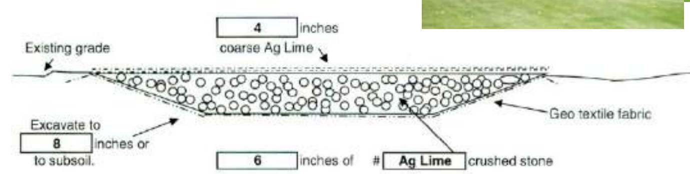
* 40 CFR 503.13, USEPA applicable limits
** 327 IAC 6.1-4-9(c) Table 3, Non site-specific or marketing and distribution permit levels

University of Maryland / USDA-ARS

Heavy Use Areas



- Feed Lots
  - Stability
  - Healthier animals



Environmental

- USDA / EPA / AAPFCO / State
- Although steel slags contain varying concentrations of trace elements, the bioavailability is very low (Beck and Daniels, 2008)
- Compare to local soils, utilizing appropriate test methods.

Element	Symbol	Common Range (ppm or mg/kg)	Average Concentration (ppm or mg/kg)
Aluminum	Al	10,000 - 300,000	71,000
Antimony	Sb	2 - 10	-
Arsenic	As	1 - 50	5
Barium	Ba	100 - 3,000	430
Beryllium	Be	0.1 - 40	6
Boron	B	2 - 100	10
Bromine	Br	1 - 10	5
Cadmium	Cd	0.01 - 0.7	0.06
Cesium	Cs	0.3 - 25	6
Chlorine	Cl	20 - 900	100
Chromium	Cr	1 - 1,000	100
Cobalt	Co	1 - 40	8
Copper	Cu	2 - 100	30
Fluorine	F	10 - 4,000	200
Gallium	Ga	0.4 - 300	30
Gold	Au	-	<1
Iodine	I	0.1 - 40	1
Lanthanum	La	1 - 5,000	30
Lead	Pb	2 - 200	10
Lithium	Li	5 - 200	20
Magnesium	Mg	600 - 6,000	5,000
Manganese	Mn	20 - 3,000	600
Mercury	Hg	0.01 - 0.3	0.03
Molybdenum	Mo	0.2 - 5	2
Nickel	Ni	5 - 500	40
Radium	Ra	8×10^{-5}	-
Rubidium	Rb	5 - 500	10
Selenium	Se	0.1 - 2	0.3
Silver	Ag	0.01 - 5	0.05
Strontium	Sr	50 - 1,000	200
Thallium	Tl	-	5
Tin	Sn	2 - 200	10
Tungsten	W	-	1
Uranium	U	0.9 - 9	1
Vanadium	V	20 - 500	100
Yttrium	Y	25 - 250	50
Zinc	Zn	10 - 300	50
Zirconium	Zr	60 - 2,000	300

Source: USEPA Office of Solid Waste and Emergency Response, Hazardous Waste Land Treatment, SW-874 (April 1983), page 273.

USDA / EPA Regulatory Limits

Table 1. Regulatory limits on heavy metals applied to soils (Adapted from U.S. EPA, 1993).

Heavy metal	Maximum concentration in sludge (mg/kg or ppm)	Annual pollutant loading rates		Cumulative pollutant loading rates	
		(kg/ha/yr)	(lb/A/yr)	(kg/ha)	(lb/A)
Arsenic	75	2	1.8	41	36.6
Cadmium	85	1.9	1.7	39	34.8
Chromium	3000	150	134	3000	2,679
Copper	4300	75	67	1500	1,340
Lead	420	21	14	420	375
Mercury	840	15	13.4	300	268
Molybdenum	57	0.85	0.80	17	15
Nickel	75	0.90	0.80	18	16
Selenium	100	5	4	100	89
Zinc	7500	140	125	2800	2500

American Association of Plant Food Control Officials (AAPFCO)

- **Statement of Uniform Interpretation and Policy (SUIP) #25 "The Heavy Metal Rule**

Metals	ppm per 1% P_2O_5	ppm per 1% Micronutrient[3]
Arsenic	13	112
Cadmium	10	83
Cobalt	136[6]	2,228[6]
Lead	61	463
Mercury	1	6
Molybdenum	42	300[4]
Nickel	250	1,900
Selenium	26	180
Zinc	420	2,900[4]

Conclusions

- Careful selection and processing of appropriate slag qualities ensures an effective activity in the soil.
- Verify both agricultural and environmental requirements for land application.
- Compare metals limits to both local soils and regulations
- Steel Slag can be an economical and efficient Liming Material for ph adjustment in agricultural applications.
- Follow typical liming recommendations.
- Steel Slag can provide nutrients when properly processed.
- Calcium Silicate slag can be a beneficial substance for plants.
- Steel Slag can be an excellent addition to Compost .


Thank You
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