Long-Term Heavy Metal Pollution Risk Due to the Use of Slags as Agricultural Limes on the South African Highveld

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Abstract

The agricultural soils on South Africa's Eastern Highveld are acidified to some extent due to the relatively high rainfall, management practices and to a lesser extent acid rain. These soils are very sensitive to acidification due to sandstone dominated parent materials, leading to sandy soils with low buffer capacities. Several thousand tons of slags are used annually as liming materials in this area due to the close proximity of two slag producing steel plants. No clear guidelines presently exist in South Africa concerning the use of heavy metal-containing slags as agricultural limes. Three slag products from these two sources were tested for their Cr, V, Ni, Co, Cu, Zn and Mo levels. A soil that had received approximately 20 tons of one of the slags over the past 10 years was subjected to acidification in pots with HNO_3 and H_2SO_4 separately. EPA 3050, EDTA and NH_4NO_3 extractions were done on the treated soil and wheat grown in the pots was dry-ashed and Cr, V, and Ni levels determined. In all the cases except the EPA 3050 the metal levels were very low, indicating almost no risk of food-chain pollution with the use of this slag. Long-term projections of current application rates indicate a very slight risk of heavy metal build-up over 100 years for all three slags. There is however a pronounced need for proper guidelines and research to be conducted on the long-term impact of slag use – especially for conditions that differ from those mentioned here.

Introduction

Soils on the South African Eastern Highveld are acidified to some extent (Beukes, 1995) mainly due to a relatively high rainfall (>800 mm y^{-1}) and the use of N-fertilizers. These soils, used mainly for commercial maize production, are also very sensitive to acidification (Fey & Dodds, 1998) due to a low buffer capacity derived from predominantly sandstone parent materials. Acid rain also plays a small role in the acidification of the soils of the region (Fey & Guy, 1993) although some workers indicate that dry deposition of particulates is more important (Michael, personal communication).

Slags and metal industry by-products have regularly been used as liming materials in the region since the early '80s due to the close proximity of two producers (Highveld Steel and Vanadium close to Witbank and Columbus Steel close to Middelburg). Exact volumes of the slags sold and used on the Highveld are not known because two rival companies market them. Furthermore, statistics kept by the Fertilizer Society of South Africa (FSSA) on lime usage do not include a distinction between slags and regular limes. Nevertheless, estimates of sales range from 60 000 – 100 000 tons for the Highveld Steel and Vanadium and 60 000 – 80 000 tons for the Columbus Steel slag.

These slags contain large quantities of silicates and carbonates as well as some oxides of Ca and therefore have a relatively high acid neutralizing capacity. The slags also contain heavy metals, the type depending on the ore, and these can reach levels of several parts per thousand (Table 1 – Note: No mention is made by the two producers concerning Ni in the slags). During the refining process of the slags many of the larger metallic particles are removed through sieving and the use of a magnetic roller (Pistorius, personal communication), thereby decreasing the metal content considerably.

TABLE 1. Average composition of slags before refining into agricultural lime (Source: Columbus Steel and Highveld Steel)

Chemical Compound	Columbus Steel %	Highveld Steel and Vanadium %
Al_2O_3	2.3	1.3
CaO	49.5	55.4
Cr_2O_3	3.0	-
FeO	0.6	16.7
MgO	11.4	6.5
MnO	0.9	1.1
P	-	0.4
S	-	0.4
SiO_2	30.6	17.9
TiO_2	0.7	-
V_2O_5	-	1.6

Recently, the use of slags has also increased in the sugar industry in the KwaZulu-Natal province due to their high Si content. Sugarcane has a high Si requirement and the element also promotes resistance to certain insect pests (Meyer, 2003). The soils in this region are highly weathered and lime recommendations are made using acid saturation values rather than absolute pH (as used on the Highveld). Due to the larger buffer capacities of the soils, high rainfall, and use of acidifying N-fertilizers, the quantity of slag applied to specific soils is therefore also larger than on the Highveld. No research has been conducted concerning the use of slags and its heavy metal content in this industry.

There are no clear guidelines in South Africa governing heavy metal additions to soils through the application of slags as agricultural ameliorants. Maximum levels of metals in soils are stipulated in guidelines but these levels have recently been questioned due to the fact that many soils in South Africa contain higher natural background levels than those proposed (Herselman & Steyn, 2001). Vanadium is also presently not included in guidelines.

Most studies on heavy metal bioavailability in the environment have focused on sewage sludge and very few on slags (Amaral Sobrinho et al., 1992; Amaral Sobrinho et al., 1993). This could possibly be ascribed to the fact that the application of slags containing heavy metals increases the pH of acid soil and that liming is considered to be one of the remedies for heavy metal pollution in soil (Logan, 1992; Hooda et al., 1997; and Chaney *et al*., 2001). In South Africa some studies have been conducted on the use of slags in agriculture by different institutions but those focusing on metals remain confidential.

The risk posed by slag use in agriculture is a function of its metal concentration, the amount added (as influenced by the soil's lime requirement or prevailing management practice), as well as the number of years that the slags are used. An aspect of concern is the possible change in land-use after a long period of continuous use of the slags. If the soil is allowed to acidify again it could result in the mobilization of accrued metals.

In order to investigate the impact of long-term slag applications the ideal would be to use different long-term application sites. The availability of such sites for research is hampered, though, by the fact that farmers do not use lime (or slags) continually from the same source over an extended time period. Neither is it feasible to add large quantities of a slag to soil due to the over-liming effect and the time it would take for such a site to reach a condition similar to a long-term application site.

Recently several users of the slags (farmers, institutions involved in the amelioration of Acid Mine Drainage, and competing lime producers) have voiced their concern about the types and levels of heavy metals present in the slags. As there are no clear guidelines available for the use of heavy metal-containing slags in agriculture in South Africa, it was decided to investigate the reactivity and heavy metal levels of three slags as well as the possible long-term impact of the most widely used slag.

Studies on Slags Used on the Highveld

Reactivity

Van der Waals and Claassens (2002) investigated the reactivity of twelve liming materials including

several slags. From the study it was clear that the slags used on the Highveld compared very favourably to regular liming materials available in the same area (Table 2). This implies that the amounts of slag added will not differ significantly from those of regular limes. Liming materials 2, 3, and 6 (Table 2) are the slags most widely used on the Highveld. (Note: slags 2 and 3 are from the same source).

Heavy Metal Pollution Risk

Sampling of the slags under the supervision of The Registrar of Fertilizers yielded the values listed in Table 3. It is expected that these values could vary within certain ranges but there is presently no data available to quantify this variation. The metals Cr, V and Ni were present in the highest concentrations with most of the other metals present in very low concentrations.

Table 3. Concentration of heavy metals in the slag products from the two sources

Metal	Concentration in the slags (mg kg^{-1})		
	Lime (Slag)		
	2	3	6
Cr[1]	825	886	1053
V[1]	1526	1455	337
Ni[2]	64	71	566
Co[2]	19	20	7
Cu[3]	40	36	14
Zn[3]	49	54	31
Mo[2]	1	2	29

[1] EPA 3050 digestion, determined by ICP-MS
[2] $HClO_4/HNO_3$ digestion, determined by ICP-MS
[3] $HClO_4/HNO_3$ digestion, determined by AAS

It is generally accepted that the amount of lime required to maintain a realistic pH in the sandy soils of the Highveld is 1.5 tons ha^{-1} $year^{-1}$. Assuming that: 1) the values in Table 3 are representative; 2) 1.5 tons ha^{-1} were to be applied yearly over the next 100 years and; 3) the slag was incorporated to a depth of 30 cm in a soil with a bulk density of 1.5 Mg m^3; the concentration increase will not exceed 50 mg kg^{-1} for most of the metals (Table 4). Only Cr, V, and Ni will have accumulated to relatively high levels but these are still below the maximum metal content in soil (80 mg kg^{-1} for Cr and 50 mg kg^{-1} for Ni, with no reference to V) as stipulated by the Water Research Commission (WRC, 1997).

Table 4. Total concentration increase in the soil if the three slags were to be applied at 1.5 tons ha^{-1} $year^{-1}$ for 100 years

Metal	Concentration increase (mg kg^{-1})		
	Lime (Slag)		
	2	3	6
Cr	27.50	29.53	35.12
V	50.87	48.50	11.23
Ni	2.13	2.37	18.87
Co	0.63	0.67	0.23
Cu	1.33	1.20	0.47
Zn	1.63	1.80	1.03
Mo	0.03	0.07	0.97

Due to the influence of several factors this risk is highly overstated. It is highly unlikely that the slag will be available for such a long time and it is even less likely that the agricultural practices in the area will remain the same or that farmers will use limes from the same source continuously for such a period of time. The risk is therefore considered to be very small under regular crop production practices.

Long-term Slag Application Site

A field (loamy-sand soil) that had continuously received applications of Lime 2 (slag) over a period of more than 10 years to an accumulated total of approximately 20 tons was identified. The field was used solely for the production of maize. It is evident that the slag influenced the soil's condition (Table 5) leading to a very high pH and base saturation. These conditions are not found in natural Highveld soils when similar positions in the landscape and parent materials are considered. Table 6 presents the EPA3050 (U.S. Environmental Protection Agency, 1986), NH_4-EDTA (The Non-affiliated Soil Analysis Work Committee, 1990), and NH_4NO_3 extractable metals from this soil. The NH_4NO_3 method was adapted from the $BaCl_2$ method of Hendershot and Duquette (1986) in that 5g of soil was shaken with 50cm^3 0.2 M NH_4NO_3 in a stoppered bottle on a horizontal shaker for 1 hour and filtered afterwards. This extractant is regularly used as a

neutral salt extractant to determine extractable metals (Becket, 1989; McLaughlin *et al*., 2000).

TABLE 5: Selected physical and chemical properties of the slag amended soil

Parameter	
Texture	Loamy Sand
Clay (%)	7
pH (Water)	7.1
pH ($CaCl_2$)	6.5
pH (KCl)	6.3
CEC ($cmol_c kg^{-1}$ soil)	2.9*
Base Saturation (%)	97
Organic C (%)	0.44

*Based on the summation of $BaCl_2$ extractable cations (less the water soluble cations) and extractable acidity (adapted from Hendershot and Duquette, 1986).

The natural heavy metal background levels in the area are unknown due to atmospheric deposition in the vicinity of the Highveld Steel and Vanadium plant as well as agricultural practices such as the use of slags as agricultural limes during the past 10 to 20 years. The results (Table 6) indicate that even though metal levels in the region of 50 mg kg^{-1} were found in the soil (Cr and V with EPA3050), the levels extracted with weaker extractants were significantly lower. In the case of both Cr and Ni the levels extracted with NH_4-EDTA and NH_4NO_3 were close to or below those that are considered the minimum sensitivity for the procedure. This indicates a very low risk in terms of leaching and/or plant uptake of these metals.

Table 6. Extractable V, Cr, and Ni from the long-term slag-amended soil

Extractant	Metal (mg kg^{-1})*		
	V	Cr	Ni
EPA 3050	53.2	45.7	8.1
EDTA	4.8	0.03	< 0.005†
NH_4NO_3	0.31	0.02	< 0.005†

† Values are below what is considered the minimum sensitivity for the extraction method

Acidification Trial - Soil

To determine the influence of acidification on the extractability and plant-availability of the metals, 700 kg of topsoil was collected from the long-term application site. The soil was acidified separately with H_2SO_4 and HNO_3 in pots at four increasing rates. Cr, Ni, and V were determined by ICP-MS in NH_4-EDTA (The Non-affiliated Soil Analysis Work Committee, 1990) and NH_4NO_3 (method described earlier) extracts of the soil after the trial. The results for two of the acid rates are presented in Table 7.

Metal levels in both extractants were very low. The V levels were higher in the higher pH treatments, indicating its presence in the soil in the anionic form. The Cr and especially Ni levels were very close to what is considered the critical sensitivity of the procedure. The low extractability of the metals is probably due to the near neutral pH of the soil and the fact that the metals were applied in relatively small quantities over an extended period of time, therefore leaving adequate time for precipitation and stabilization. This could also be the reason for the low mobility of the metals, even after the extreme acidification.

Acidification Trial – Plant Content

During the trial an Al-tolerant wheat variety was grown in the pots, harvested after 3 months, dried, and the dry-matter yield determined. The plant material was dry ashed according to the method by Soon (1998) and V, Cr, and Ni levels were determined by ICP-MS. Potassium and P-fertiliser was applied to all the pots and N only to the pots that did not receive HNO_3. No leaching was allowed.

The low metal mobility was also reflected in the plant analysis where no significant difference was found between any of the treatments in terms of metal uptake by the plants (Table 8). Again the plant analyses from only two of the acid treatment rates are presented.

Conclusions and Recommendations

From the data presented it is clear that the use of slags on the Eastern Highveld does not pose a threat at current levels of use and agricultural practices – even in the long-term. This is due to the fact that the slags are generally applied at low rates and that the same liming material is not often continuously used over long periods. Drastic fluctuations in the metal levels could change this

situation and it is therefore recommended that the levels be monitored on a regular basis.

The low risk scenario is likely to change in the event of higher application rates on different soils and crops in other areas of the country – such as in the sugar industry. This aspect should be further investigated before large-scale use is advocated. Even though the risk seems to be slight, proper guidelines concerning the use of heavy metal-containing slags should be drawn up through the use of data from long-term trials.

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TABLE 2. Selected chemical and physical properties of 12 limes investigated (from Van der Waals and Claassens, 2002)

Lime No	Ca (%)	Mg (%)	CCE HCl† (%)	RH-Value‡ (%)	% Passing sieve size (mm): < 1.7	< 1.0	< 0.25	< 0.106	Source of lime
1	17.20	11.23	83.00	75.83	98.52	96.89	91.66	84.13	Natural
2	30.02	7.37	95.48	49.67	95.53	87.93	67.45	39.90	Slag
3	31.06	5.57	84.98	64.57	99.36	92.01	64.98	42.48	Slag
4	37.76	0.95	98.04	91.72	99.90	99.80	98.90	98.13	Paper mill
5	16.27	14.63	85.75	59.60	97.70	88.35	66.20	59.80	Natural
6	27.02	9.32	95.88	59.60	99.59	91.21	59.58	37.25	Slag
7	37.30	1.18	98.54	87.75	99.96	99.86	98.48	94.88	Paper mill
8	16.64	14.68	88.38	54.97	87.04	72.46	50.73	43.75	Natural
9	18.20	11.99	87.98	77.48	99.71	89.46	57.13	29.00	Natural
10	19.95	12.11	91.40	54.64	99.68	99.30	73.58	67.56	Natural
11	40.43	4.95	104.28	76.16	99.53	99.13	89.73	61.53	Slag
12	26.02	5.55	74.90	46.59	97.67	80.77	43.57	22.87	Slag

† Calcium Carbonate Equivalent in HCl
‡ "Relatiewe Harswaarde" – Relative Resin Value (Bornman *et al*., 1988)

Table 7. Extractable V, Cr, and Ni from the acidified soil in the pot trial

Extractant	Treatment	pH (H_2O)	Metal (mg kg^{-1})* V	Cr	Ni
EDTA	Control	6.50	5.0^{a}	0.02^{a}	$< 0.005^{\dagger}$
	N2 (HNO_3)	5.37	3.1^{b}	0.02^{a}	0.05
	N4 (HNO_3)	4.48	2.1^{c}	0.03^{a}	0.09
	S2 (H_2SO_4)	5.59	3.8^{b}	0.02^{a}	$< 0.005^{\dagger}$
	S4 (H_2SO_4)	4.77	2.9^{bc}	0.03^{a}	$< 0.005^{\dagger}$
NH_4NO_3	Control	6.50	0.24^{de}	0.01^{d}	$< 0.005^{\dagger}$
	N2 (HNO_3)	5.37	0.10^{fg}	0.04^{d}	$< 0.005^{\dagger}$
	N4 (HNO_3)	4.48	0.06^{g}	0.03^{d}	$< 0.005^{\dagger}$
	S2 (H_2SO_4)	5.59	0.17^{ef}	0.02^{d}	$< 0.005^{\dagger}$
	S4 (H_2SO_4)	4.77	0.13^{fg}	0.04^{d}	$< 0.005^{\dagger}$

* Values in the same column (and extractant) with the same letter indicate no significant difference
† Values are below what is considered the minimum sensitivity for the extraction method

Table 8. Heavy metal concentration in wheat (mg kg^{-1} dry matter) for five different soil treatments

Treatment	Metal (mg kg^{-1} dry matter)* V	Cr	Ni
Control	0.19^{a}	0.65^{a}	0.39^{a}
N2 (HNO_3)	0.13^{a}	0.34^{a}	$<0.05^{\dagger}$
N4 (HNO_3)	0.10^{a}	0.27^{a}	$<0.05^{\dagger}$
S2 (H_2SO_4)	0.15^{a}	0.36^{a}	0.27^{a}
S4 (H_2SO_4)	0.17^{a}	0.58^{a}	0.62^{a}

* Values in the same column with the same letter indicate no significant difference
† Values are below what is considered the minimum sensitivity for the method of determination