



**SLAGS AS AGRICULTURAL LIMES: REACTIVITY AND HEAVY
METAL AND PHOSPHORUS BIO-AVAILABILITY**

By

Johan Hilgard van der Waals

Submitted in partial fulfilment of the requirements of

MAGISTER SCIENTIAE: SOIL SCIENCE

In the

FACULTY OF NATURAL AND AGRICULTURAL SCIENCES

UNIVERSITY OF PRETORIA

PRETORIA

May 2001



DECLARATION

These studies have not been submitted in any form to another university and, except where acknowledged in the text, are the results of my own work.

A handwritten signature in black ink, consisting of several vertical strokes on the left and a large, sweeping loop on the right.

Johan Hilgard van der Waals



ACKNOWLEDGEMENTS

H Pistorius and Group (specifically Leo Pistorius and “Oom” Hendrik) for financial and moral support – as well as initiating the project,

THRIP for funding,

Personnel from the Registrar of Fertilizers with aiding in the collection of the liming materials,

Professor Andries Claassens for guidance, support and a lot of patience,

Personnel (Willem Kirsten and Charl Steyn) from the ISCW for advice on heavy metal testing,

Personnel from the department’s soil testing laboratory for help in conducting numerous tests,

Colleagues in the department for lending their ears and giving advice,

My parents for supporting me through major career changes that led to this study,

My wife Jacquie for believing in me and a lot of support through the tough times,

My Lord and Saviour Jesus Christ for life, the ability and the opportunity to discover His creation.



TABLE OF CONTENTS

SUMMARY (ENGLISH)	viii
OPSOMMING (AFRIKAANS)	x
LIST OF TABLES	xii
LIST OF FIGURES	xvi

CHAPTER 1: GENERAL INTRODUCTION

INTRODUCTION	1
Agricultural Soil Acidification	1
Lime Reactivity and Lime Requirement	3
Slags as Liming Materials	3
Testing of Slags	4
AIM OF THE STUDY	5

CHAPTER 2: HEAVY METAL AVAILABILITY FROM SLAGS

INTRODUCTION	6
The Use of Slags as Liming Materials	6
Heavy Metals in Soils	8
Soil pH	10
Speciation and Valency	11
Adsorption on Different Soil Surfaces and Soil Structural Aspects	12
Natural Occurrence	13
Extraction and Metal Interaction	14
Crop used and Total Soil Metal Content	15
Sampling and Testing	16
Essentiality, Toxicity and Plant Uptake	16
Acceptable Levels – Legislation and Suggested Levels	18



MATERIALS AND METHODS	19
Introduction	19
Liming Materials	19
Soil	19
Heavy Metal Content of Limes	20
Crops	21
Treatments	21
Fertilizers	21
Harvest, Sample Preparation and Plant Analysis	21
Statistical Analysis	22
Soil Sampling and Sample Preparation	22
EDTA Extractions	22
RESULTS AND DISCUSSION	23
Chromium	23
Nickel	27
Cobalt	31
Manganese	34
Other Heavy Metals	38
CONCLUSIONS	38
CHAPTER 3: REACTIVITY OF LIMING MATERIALS	
IINTRODUCTION	40
Reserve Acidity	40
Lime Requirement	41
Lime Reactivity	42
Study Aims	44



MATERIAL AND METHODS	44
Soil	44
Lime Requirement	45
Liming Materials	45
Lime Application	46
Measurement of pH, Statistical Analysis	47
RESULTS AND DISCUSSION	47
Lime Requirement Determination	47
Characteristics of the Liming Materials	49
Lime Application	50
Results of pH Determination	53
Trial 1	53
Trial 2	57
CONCLUSIONS AND RECOMMENDATIONS	58
CHAPTER 4: MODELING OF pH RESULTS	
INTRODUCTION	60
MATERIALS AND METHODS	60
RESULTS AND DISCUSSION	61
CONCLUSIONS	67
CHAPTER 5: PHOSPHORUS AVAILABILITY FROM SLAGS	
INTRODUCTION	69
MATERIALS AND METHODS	71
RESULTS AND DISCUSSION	72
CONCLUSION	77



REFERENCES	79
Appendix 1	89
Appendix 2	90
Appendix 3	97
Appendix 4	102
Appendix 5	109
Appendix 6	122



SUMMARY (ENGLISH)

Steel industry by-products (slags) are regularly used as agricultural limes on the South African Highveld where the soils are prone to natural and anthropogenic acidification. These materials are the products of a purification process aimed at extracting phosphorus and silica from iron (or related) ores. In the process several impurities such as heavy metals are incorporated into the slag. In certain quarters concern is being voiced about the environmental impact of these heavy metals.

Two pot experiments were conducted to test the heavy metal and phosphorus bioavailability from several commercial slags. Pot experiments differ from field experiments and heavy metal uptake is usually exaggerated in plants grown in pots. Furthermore, soil pH influences the mobility of heavy metals in soils. The limes were therefore applied to similar pH levels and the limes with high and low metal concentrations were compared.

The Resin Suspension Method (RH-value) was used as a reactivity parameter of the limes and a $\text{Ca}(\text{OH})_2$ equilibration method was used to determine the lime requirement of the soils. Twelve limes were collected with the aid of the Registrar of Fertilisers and applied in the heavy metal experiment to obtain pH values of 5.8, 6.8, and 7.8. A further experiment to determine phosphorus availability was conducted using four slags to obtain pH values of 5.5, 6.0, and 6.5.

The heavy metal uptake was tested using spinach as test crop. The concentrations in the plants were high. There were no significant differences between the high and low metal containing limes. Spinach accumulates high concentrations of trace elements and therefore aggravates metal uptake compared to most other crops. The conclusion is that the use of slags poses little threat in the short term. Due to the nature of the experiments trial it is not possible to comment on the desirability of long-term slag use. Further research is required to determine the impact if soil heavy metal concentrations are increased and management practices lead to acidification.



The RH-value proved to be the most accurate reactivity indicator when compared to the Calcium Carbonate Equivalent (CCE) in HCl. Two different soil to solution ratios (1:1 and 1:2.5) in the $\text{Ca}(\text{OH})_2$ determinations were used and compared with the pH at the end of the pot experiment. The 1:2.5 ratio combined with the RH-value gave pH predictions closest to the actual pH values. Although all the methods were relatively close to the actual values, the CCE HCl parameter led to wider variation in results. In limes with a small difference between the CCE HCl and RH values the predicted pH values also had a small difference. In the limes where the CCE HCl and RH values differed widely there was a corresponding large difference in predicted pH values.

In determining the P-availability from the slags it appeared as though the Si in the slags influenced the P-concentrations in the plants (spinach). In a soil with a low P-concentration the P-uptake was very low leading to the conclusion that the P was not available from the slags. This could also be because the P-levels in the slags were lower than reported by the producers and that the P desorption rate of the soil is very low. Due to the difficulty in differentiating between P reserves in the soil and P applied through the slags a different approach should be considered when testing P-availability from slags.



OPSOMMING (AFRIKAANS)

Staalverwerkingsniewe-produkte word gereëld gebruik as landboukalke op die Suid Afrikaanse Hoëveld waar gronde onderhewig is aan natuurlike en antropogeniese versuring. Hierdie materiale is die produkte van 'n suiweringsproses wat ten doel het om fosfor en silika van yster (of verwante) erts te ontrek. In die proses word verskeie onsuiverhede soos swaar metale in die slak geïnkorporeer en het hierdie situasie gelei tot vrae oor die impak van dié metale op die omgewing en gesondheid.

Twee pot eksperimente is gedoen om die swaar metale en fosfor se bio-beskikbaarheid vanaf die slakke te toets. Pot eksperimente verskil van veld eksperimente deurdat verhoogde opname van metale vanuit grond in potte gewoonlik plaasvind. Grond pH beïnvloed die mobiliteit van die swaar metale. Die slakke is dus tot soortgelyke pH teikens toegedien om die kalke met hoë en lae swaar metal konsentrasies te vergelyk.

Die Harssuspensiemetode (RH-waarde) is gebruik as 'n aanduiding van die kalke se reaktiwiteit en 'n $\text{Ca}(\text{OH})_2$ ekwilibrasie metode is gebruik om die grond se kalkbehoefte te bepaal. Twaalf kalke is versamel met die hulp van personeel van die Registrateur van Misstowwe en is in die swaar metaal eksperiment toegedien om drie teiken pH waardes van 5.8, 6.8, en 7.8 te verkry. 'n Verdere eksperiment om fosfaat beskikbaarheid te bepaal is gedoen deurdat vier slakke toegedien is aan 'n verskillende grond tot pH teiken waardes van 5.5, 6.0, en 6.5.

Die swaarmetaal opname is bepaal deur die gebruik van spinasie as toetsgewas. Die vlakke was baie hoog in die plante. Daar was egter geen noemenswaardige verskil tussen die hoë metaal inhoud kalke en dié met laer vlakke nie. Spinasie akkumuleer hoë vlakke spoor elemente en vererger dus swaar metaal opname in vergeleke met ander gewasse. Die gevolgtrekking is dat die slakke min gevaar inhou in die korttermyn. Na aanleiding van die aard van die eksperimente is dit nie moontlik om kommentaar te lewer op die wenslikheid van die langtermyn gebruik van slakke nie. Verdere navorsing is nodig om



die impak te bepaal wanneer swaar metaal konsentrasies verhoog word en bestuurspraktyke lei tot versuring van die grond.

Die RH-waarde is bewys as die mees akkurate aanduiding van reaktiwiteit indien vergelyk met die Kalsium Karbonaat Ekwivalent (KKE) in HCl. Twee verskillende grond-tot-oplossing verhoudings (1:1 and 1:2.5) in die Ca(OH)_2 bepaling was gebruik en is vergeyk met die pH waardes aan die einde van die eksperiment. Die 1:2.5 verhouding gekombineer met die RH-waarde het pH voorspelling gelewer wat die naaste aan die teiken waardes was. Alhoewel al die metodes waardes gelewer het wat redelik naby aan die werklike waardes was het die KKE in HCl parameter tot wyer variasie gelei. In kalke waar daar 'n klein verskil was tussen die KKE in HCl en RH waardes was daar 'n klein verskil in die pH waardes verkry. In kalke met 'n groot verskil tussen die KKE in HCl en die RH waardes was daar 'n ooreenstemmende groot verskil tussen die voorspelde pH waardes verkry.

In die bepaling van die P-beskikbaarheid van die slakke wil dit voorkom asof die Si in die slakke die P-konsentrasies in die plante (spinassie) beïnvloed het. In 'n grond met 'n lae P-konsentrasie was die P-opname laag wat lei tot die gevolgtrekking dat die P nie beskikbaar was vanuit die slakke nie. Dit kan toegeskryf word daaraan dat die P-vlakke in die slakke laer is as wat weergegee is deur die produseerders van die slakke en dat die P desorpsie tempo van die grond baie laag is. Na aanleiding van die onvermoë om te onderskei tussen P reserwes in die grond en die P toegedien deur die slakke sal 'n ander benadering oorweeg moet word wanneer P-beskikbaarheid van slakke bepaal word.



LIST OF TABLES

TABLE 2.1. Average composition of slags before refining into agricultural lime (Source: Columbus Steel and Highveld Steel).	8
TABLE 2.2. Heavy metal content, essentiality and toxicity in plants, animals, and man (After Pais and Benton Jones, 1997).	17
TABLE 2.3. Maximum permissible contaminant concentration (mg/kg, dry basis) in ameliorants (Department of National Health and Population Development, 1991) and suggested preliminary threshold value for NH ₄ -EDTA (pH 4.5) extractable heavy metals for the soils of South Africa. (Brummer and van der Merwe, 1989)	18
TABLE 2.4. Selected chemical and physical properties of the soils used in the study.	20
TABLE 2.5. Chromium content of limes and amounts of lime and Cr added per pot.	24
TABLE 2.6. Chromium content (mg.kg ⁻¹) of spinach leaves and pH of the growth medium.	25
TABLE 2.7. NH ₄ -EDTA extraction (Cr) on soils ameliorated with Limes 2, 3, and 6, seven months after lime application.	27
TABLE 2.8. Nickel content of limes and amounts of lime and Ni added per pot.	28
TABLE 2.9. Nickel content (mg.kg ⁻¹) of spinach leaves and pH of the growth medium.	29



TABLE 2.10. Cobalt content of limes and amounts of lime and Co added per pot.	31
TABLE 2.11. Cobalt content (mg.kg^{-1}) of spinach leaves and pH of the growth medium.	32
TABLE 2.12. NH_4 -EDTA extraction (Co) on soil ameliorated with Limes 3 and 6, seven months after lime application.	34
TABLE 2.13. Manganese content of limes and amounts of lime and Mn added per pot.	35
TABLE 2.14. Manganese content (mg.kg^{-1}) of spinach leaves and pH of the growth medium.	36
TABLE 3.1. Selected chemical and physical properties of the soils used in the study.	45
TABLE 3.2. Resultant pH values after incubation with Ca(OH)_2 (Trial 1 and 2).	48
TABLE 3.3. Amount of CaCO_3 required per pot to attain the target pH.	49
TABLE 3.4. Results of laboratory analysis of twelve liming materials.	50
TABLE 3.5. Analysis results of twelve liming materials and amounts added per pot (Trial 1)	51
TABLE 3.6. Corrected amounts of lime needed per pot expressed in the equivalent of ton.ha^{-1} (Trial 1).	51



TABLE 3.7. Analysis results of four liming materials (and CaCO ₃ Lab Reagent) and amounts added per pot (Trial 2).	52
TABLE 3.8. Corrected amounts of lime needed per pot expressed in the equivalent of ton.ha ⁻¹ (Trial 2).	52
TABLE 3.9. The deviation of the pH _(Water) values from target pH for three rates at three and seven months after lime application for Trial 1*.	55
TABLE 3.10. Trial 1 pH _(KCl) results after 3 months.	56
TABLE 3.11. Trial 1 pH _(KCl) results after 7 months.	56
TABLE 3.12. Trial 2 pH _(Water) value deviation from target pH for three rates.	58
TABLE 4.1. Resultant pH values after incubation with Ca(OH) ₂ at different stages of Trial 1.	62
TABLE 4.2. Deviation of mean values from targets for 12 liming materials as predicted by three different lime requirement determinations and two different reactivity determinations (RH = Resin Suspension Method, HCl = CCE HCl method, A = After trial, B = Before trial).	65
TABLE 5.1. Average P and Si content of two slags before refining into agricultural lime (Source: Columbus Steel and Highveld Steel).	70
TABLE 5.2. Total and citric acid soluble P in four slags.	72
TABLE 5.3. P-content of spinach leaves for twelve liming materials (Trial 1).	73



TABLE 5.4. Wheat yield and P content for four slags and a control treatment at three different application rates. 75

TABLE 5.5. Amounts of P applied to the soil in the different limes and application rates. 77



LIST OF FIGURES

Figure 2.1. Cr content of spinach leaves for each lime at the average pH value.	26
Figure 2.2. Trend in Cr uptake across nine limes at the average pH value.	26
Figure 2.3. Ni content of spinach leaves for each lime at the average pH value.	30
Figure 2.4. Trend in Ni uptake across nine limes at the average pH value.	30
Figure 2.5. Co content of spinach leaves for each lime at the average pH value.	33
Figure 2.6. Trend in Co uptake across nine limes at the average pH value.	33
Figure 2.7. Mn content of spinach leaves for each lime at the average pH value.	37
Figure 2.8. Trend in Mn uptake across nine limes at the average pH value.	37
Figure 3.1. $\text{Ca}(\text{OH})_2$ incubation curve for Trial 1 and 2.	48
Figure 3.2: pH(Water) results for three target applications after three months (Trial 1).	54
Figure 3.3: pH(Water) results for three target applications after seven months (Trial 1).	54
Figure 4.1. $\text{Ca}(\text{OH})_2$ buffer curves for three determinations.	63
Figure 4.2. Average pH(Water) values for six methods used compared with the target values.	64



Figure 4.3. Average pH(KCl) values for the six methods used.	64
Figure 4.4. Predicted pH values for Lime 7 from calculated lime recommendations.	66
Figure 4.5. Predicted pH values for Lime 2 from calculated lime recommendations.	66
Figure 5.1. P content of spinach grown on soil ameliorated with Limes 1 to 6.	74
Figure 5.2. P content of spinach grown on soil ameliorated with Limes 7 to 12.	75
Figure 5.3. P content of wheat plants grown on soil ameliorated with four slags and a lime laboratory reagent at three application rates.	76
Figure 5.4. Average yield of wheat plants grown on soil ameliorated with five different liming materials at three application rates.	76