THE USE OF MINE IMPACTED WATER AND ITS TREATMENT BYPRODUCTS IN AGRICULTURE

by

BONOKWAKHE HEZEKIEL SUKATI

Submitted in partial fulfilment of the requirements for the degree
PhD Soil Science
in the Department of Plant and Soil Sciences
University of Pretoria

Supervisor:	**Prof. J.G. Annandale**
Co-supervisors:	**Prof. J.M. Steyn**
	Dr. P.D. Tanner

August 2020

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA
Denkleiers • Leading Minds • Dikgopolo tša Dihlalefi

DECLARATION

I, Bonokwakhe Hezekiel Sukati, declare that the thesis, which I hereby submit for the degree Doctor of Philosophy (Soil Science) at the University of Pretoria, is my own work and has not been previously submitted by me for a degree at this or any other tertiary institution.

Signed: ____________________
(Bonokwakhe Hezekiel Sukati)

Date: 13 August 2020

DEDICATIONS

This PhD work is dedicated to my lovely parents, Mrs Hleziphi N. and the late Mr Richard M. Sukati. Also, to my dear wife, Gcinaphi N. Sukati who has been the pillar of support throughout my studies and keeping my family in shape, to my lovely children; Sakhiwo, Lindelwa, Mthobisi, Uyazi, Bayazi and Iyazi as well as to my siblings; Nombulelo N., Mbongeni W., Thobile F. and Hlengiwe P. Sukati.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA
Denkleiers • Leading Minds • Dikgopolo tša Dihlalefi

ACKNOWLEDGEMENTS

This degree could have not been possible without dedicated and full support from my supervisors and technical personnel. I would like therefore to acknowledge firstly my main supervisor, Professor JG Annandale who trusted my potential and decided to award this rare opportunity and full support to me. He fully supported financially all experiments conducted, including my upkeep during my studies. Together with my co-supervisors, Professor JM Steyn and Dr PD Tanner, who through their guidance and constructive criticisms ensured a high quality and scientifically acceptable thesis. I would like to acknowledge and extend my sincere gratitude to Mr PC de Jager, who ensured through constructive comments and criticism that the whole-body work remains scientifically sound and true to the soil science discipline as the degree demands. This was the greatest challenge because most of the work dealt with High Density Sludge, a gypseous inorganic solid waste, instead of soil.

My acknowledgments are also extended to Mr C. Hertzog, who guided and helped with all analyses that were required from the laboratory. This included the use of laboratory equipment and ensuring the availability of chemicals. I would also like to acknowledge Mrs Vanessa Doman from the Department of Civil Engineering who helped with physical analysis of the sludges and to Mrs Jeanette Dykstra Strydom (X-Ray Fluorescence Analyst) and Mrs Wiebke Grote (X-Ray Diffraction Analysist) from the Department of Geology, Stoneman Facility, who helped with the analysis of total elemental content and mineralogy of the sludges. Acknowledgment is also extended to the staff of the University of Pretoria Experimental Farm, who provided space and supported the greenhouse trial.

My sincere gratitude is also extended to the funders of the project, the Water Research Commission (WRC) and to Anglo American (Khwezela North Colliery and eMalahleni Mine Water Reclamation Plant), who provided the four sludges and data from the analysis of Acid Mine Drainage (AMD) and Circum-Neutral Mine Water.

ACRONYMS

AMD:	Acid Mine Drainage
EHC	Exchangeable Hydrolysable Cations
EMWRP	eMalahleni Mine Water Reclamation Plant
EPA	Environmental Protection Agency
EDS	Electron Diffraction Spectroscopy
EDTA	Ethylene Diamine Tetra Acetic acid
FFU	Fitness-For-Use
Gyp	Gypseous material from HDSP that uses limestone plus hydrated lime to treat AMD
GypB	Gypseous material with Brucite from HDSP (limestone plus hydrated lime treatment)
GypFeMnNi	Ferriferous gypseous material with Mn and Ni from HDSP using only limestone to treat AMD
GypFeMn	Ferriferous gypseous material with Mn from HDSP (limestone plus hydrated lime treatment)
HDS	High Density Sludge
HDSP	High Density Sludge Process
HI	Harvest Index
IWQDSS	Irrigation Water Quality Decision Support System
LAI	Leaf Area Index (m^2 m^{-2})
LC	Leachable Concentrations (mg L^{-1})
LCT	Leachable Concentration Thresholds (mg L^{-1})
MDL	Method Detection Limit (mg kg^{-1})
ML	Maximum Levels (mg kg^{-1})
MED	Manganese Electron Demand (mg e^- kg^{-1})
NH_4OAc	Ammonium Acetate
NSW	New South Wales
SAWQG	South African Water Quality Guidelines
SCC	Specific Contaminant Concentrations (mg kg^{-1})
SEM	Scanning Electron Microscopy
SSA	Specific Surface Area (m^2 g^{-1})

RSA	Republic of South Africa
TC	Total Concentrations (mg kg^{-1})
TCLP	Toxicity Characteristic Leaching Procedure (mg L^{-1})
TCT	Total Concentration Thresholds (mg kg^{-1})
TED	Total Electron Demand (mg e^{-} kg^{-1})
USEPA	United States Environmental Protection Agency
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

The Coalfields of the Republic of South Africa (RSA) discharge approximately 360 Ml d^{-1} of mine impacted water, referred to as Acid Mine Drainage (AMD), requiring neutralization to reduce risk to the environment. High Density Sludge Process (HDSP) is commonly used

to treat AMD, and neutralization is typically with either limestone ($CaCO_3$) alone to save costs, or with limestone plus hydrated lime ($Ca(OH)_2$) to effectively reduce acidity and improve metal removal. This water either needs to be further treated to reduce metal content and salinity, or a potential option is to use it for irrigation. Since, it would be possible to lime a soil and irrigate directly with AMD as this would be potentially easy to manage than an HDS plant and save costs on the plant. The treatment process produces a circum-neutral mine water that requires further treatment with reverse osmosis to potable water. Suitability of these waters for irrigation can be evaluated with the Irrigation Water Quality Decision Support System (IWQDSS) for RSA. This study therefore evaluated the two specific mine impacted waters for irrigation. The treatment process also generates gypseous products, referred to as High Density Sludges (HDS), which may be classified as hazardous, based on metal (Mn, Ni, Pb) content, in which case expensive waste storage is required. However, these sludges may have some value for use in agriculture since they are gypseous. Four out of six sludges considered in this study were investigated for potential use in agriculture since their chemical characteristics depend on the quality of AMD and the treatment process. If hazardous, a potential approach was to add phosphate to them since this has been shown before to immobilize metals. The influence of phosphate on the availability of elements in sludges was therefore investigated. Hence, the objectives were to investigate; 1) the fitness for use of AMD and circum-neutral mine impacted waters for irrigation with IWQDSS, 2) chemical and physical properties of sludges, 3) hazardous status of sludges using the RSA waste classification system including those of the United States Environmental Protection Agency (USEPA), Australia, China and Canada, 4) phosphate potential in reducing the solubility of metals in sludges, 5) crop and soil response to sludges applied on their own as soil amendments and when co-applied with phosphate, 6) the influence of phosphate co-applied with sludges to the phyto-availability and uptake of Ni and Pb, including food safety. Assessment with IWQDSS showed that both waters were not fit for irrigation because of some quality issues. However, AMD can only be used if the soil can be limed and used as a reactor and further showed that there would be no leaf scorching. The circum-neutral mine water was found to be not effectively saline. Micro irrigation should not be considered for these waters due to suspended solids they contain.

Four of the six sludges assessed for agricultural use included; a Ferriferrous Gypseous sludge

(GypFeMnNi) with Fe, Mn and Ni from a limestone process, and three others generated from three stages of a limestone plus hydrated lime process; Ferriferrous Gypseous sludge with Mn (GypFeMn), Gypseous sludge with Brucite (GypB) and Gypseous sludge (Gyp) with Fe removed. Chemically, the sludges, GypFeMn, GypB and Gyp showed pH values of 8.2, 9.4 and 9.5, exhibiting $CaCO_3$ equivalents (CCE) of 510, 601, 617 mg kg^{-1}. The sludge, GypFeMnNi, had a pH of 5.5 and a CCE of 250 mg kg^{-1}. All four sludges showed to be largely gypsum (72 – 95 %) composed. Physically, all sludges had particle sizes falling between 0.4 to 906 µm. These four sludges were further considered for hazardous assessment, including two sludges; GypFeNi and GypFe from a different limestone process. USEPA rated all six sludges non-hazardous, while Canada and China found GypFeNi as hazardous based on Ni solubility, Australia found GypFeMn as hazardous. RSA considered GypFeMnNi and GypFeNi hazardous, based on Ni and Mn solubility. Limestone was therefore less effective in reducing the solubility of Ni and Mn in the sludges than limestone plus hydrated lime. The sludges found hazardous (GypFeMnNi and GypFeMn) were then phosphated to reduce Mn and Ni solubility. Their solubility was reduced in both sludges. GypFeMnNi and Gyp, were further considered for use as soil amendments and selection was based on differences in the treatments that generates them. A pot trial was conducted where both were applied at 10 and 20 t ha^{-1} each to a soil with pH 3.75 and co-applied with phosphate at application rates of 40 and 100 kg ha^{-1}. Maize (*Zea mays*) was planted and harvested at physiological maturity. Effect on soil showed that both sludges marginally increased pH, with Gyp at 20 t ha^{-1} and 100 kg ha^{-1} P increasing it the most by 0.46 units. This pH was still not suitable for plant growth. The sludge, Gyp increased soil salinity the most from 7.8 mS m^{-1} to 728 mS m^{-1}, suitable only for salt tolerant crops. The effect on the maize showed that both sludges on their own marginally increased plant height and biomass, but co-application with phosphate increased these parameters. Grain was present only in treatments where phosphate was co-applied with either sludge. The highest grain yield was obtained when Gyp was applied at 20 t ha^{-1} with 100 kg ha^{-1} P. With food safety, Ni and Pb concentrations in the grain were below thresholds regarded as toxic.

It is suggested that irrigation with AMD may be possible on condition that the soil is limed and used as treatment reactor to prevent the reduction of soil pH. Also, micro irrigation systems are to be avoided when irrigating with AMD and circum-neutral mine impacted waters because they contain suspended solids that can clog them. Irrigation should be with

an appropriate leaching fraction to reduce accumulation of salts in the soil profile. It can also be concluded that two of the sludges from a limestone only HDSP were found to be hazardous by the RSA waste classification system due to Mn and Ni solubility., whereas international systems felt these materials were non-hazardous. The RSA waste classification system was found to be overly cautious compared to international systems and should be revisited. Sludges from HDSP can rather be used as soil amendments instead of being classified hazardous and destined to expensive waste management sites. If certain trace elements are excessively available, the study demonstrated that phosphating reduces mobility and toxicity, ensuring the safety of produce from soils treated with HDS.

Keywords: AMD, HDS, Circum-neutral mine water, waste classification, amendment

CHAPTER 1

GENERAL INTRODUCTION

Large volumes (360 Ml/day) of mine impacted water, often referred to as Acid Mine Drainage (AMD), are discharged by both defunct and operational mines in the Coalfields of the Republic of South Africa (RSA), Mpumalanga Province (Annandale et al. 2006, Hutton et al. 2009). This acidic mine impacted water is generated by the exposure of sulphide minerals, especially pyrite (FeS_2), to water, oxygen, and *Thiobacillus ferrooxidans*, catalytic bacteria that survive in acidic (pH 1.0 – 3.5) solutions (de Almeida et al. 2015, Jamal 2015). During the dissolution of FeS_2, chemical reactions occur, resulting in ferric hydroxide ($Fe(OH)_3$) and sulphuric acid (H_2SO_4) forming in the solution (Ravengai et al. 2005, Akcil and Koldas 2006, Gaikwad et al. 2010, Vahedian 2014). The sulphuric acid increases the acidity of the water by reducing pH to between 2.0 and 4.0. This acidity also facilitates the solubility of environmentally toxic metals and metalloids (e.g. Pb, Ni, Cd, Cr, Hg, Co, As, Se) from FeS_2 and other minerals in contact with it, releasing them into solution, together with other pollutants of environmental concern (du Plessis 1983, Sheoran and Sheoran 2006, Mackie and Walsh 2015, Rakotonimaro et.al. 2017). According to Skousen et al. (2019) group II elements are present in AMD, with the transition metals Fe and Al dominating, with sulphate and carbonate the most common anions. The extreme acidity of AMD persists as long as either the FeS_2 is still exposed, or ferric iron (Fe^{3+}) is still highly concentrated in solution (Jamal 2015). The acidity, in combination with the high concentration of metals, is extremely toxic to the receiving environment. There is direct toxicity to organisms, modification of habitats by precipitated metals, visual changes of surface water and sediments to orange or yellow, and nutrient cycles are disrupted (Skousen et al. 2019). For this reason, treatment of this water with the intention to reduce its acidity and to remove toxic metals through precipitation into hydroxides, remains a priority (Mackie and Walsh 2015).

Most often limestone ($CaCO_3$), or a combination of limestone plus hydrated lime ($Ca(OH)_2$), are used to treat AMD (Kalin et al. 2006). However, there are other alkaline chemicals, such as caustic soda (NaOH), soda ash (Na_2CO_3), quicklime (CaO), ammonia (NH_3) and magnesium oxide (MgO) that are also used (Rakotonimaro et.al. 2017, Skousen et al. 2019). To achieve the desired pH of the water, a 2:1 ratio of the neutralising potential of the chemical to the maximum potential acidity of AMD, is recommended (Skousen et al. 2019). The advantage of using $CaCO_3$ plus hydrated $Ca(OH)_2$ over the use of just hydrated lime, is to save treatment costs, with some of the neutralization achieved with more affordable limestone, and the remainder with more costly lime. The $Ca(OH)_2$ is capable of increasing the pH of the solution to >10.5, precipitating most of the metals as hydroxides, whereas $CaCO_3$ can only increase the pH of the solution to circum-neutral levels (Balintova and

Petrilakova 2011). As such, a metal like Mn mostly remains in solution if only $CaCO_3$ is used, because it precipitates effectively at an alkaline pH of 9.5. Below this pH, Mn is removed possibly by mechanisms other than precipitation. During the treatment of AMD through a High Density Sludge (HDS) process, a slurry of $CaCO_3$ plus $Ca(OH)_2$, or $CaCO_3$ alone, is mixed with recycled sludge at a sludge/lime ratio of 15:1 to 35:1 to initiate the production of a solid gypseous material (largely gypsum), referred to as High Density Sludge (HDS), through heterogenous nucleation that catalyses precipitation (Aubé and Zinck 1999, McDonald and Web 2006, Rakotonimaro et al. 2017). The lime-sludge mixture is rapidly mixed with AMD and the pH of the solution is raised to > 10.5 if $Ca(OH)_2$ is used, oxidising most of the metals, including Mn, into hydroxides. At this point, circum-neutral mine water with suspended solids is generated. This treated water proceeds to a clarifier where flocculation of these solids and settlement of precipitates occurs, resulting in the production of HDS and clarified circum-neutral mine water that is sometimes further treated through reverse osmosis, or released to the environment. There has been work done on the successful use of such neutralised saline mine waters for irrigation (Annandale et al. 2006) but this is currently not permitted in South Africa.

The use of AMD and circum-neutral mine water in agriculture can relieve some pressure on scarce water resources. For agricultural purposes, Du Plessis (1983) theoretically (with modelling) demonstrated the feasibility of using circum-neutral mine water for irrigation as opposed to purification with expensive reverse osmosis technology. Du Plessis (1983) reported that this water is neutral and contains no Fe-bearing compounds and further pointed out that if used for irrigation it should be to field capacity (FC) to encourage mineral precipitation like gypsum, reduce leaching, reduce salinity and there would be no serious impact on the physical properties of the soil by Na. Irrigation with circum-neutral mine water has been viewed by some researchers (Annandale et al. 2006) as a cost effective alternative mine water utilization strategy. Recently, several studies have focussed on field irrigation with circum-neutral mine water. While the success of using untreated AMD as irrigation water has only been demonstrated under controlled conditions (green house pot trials) by Madiseng (2018). The cost of operating and managing the treatment plant could be cut if a limed soil can successfully be irrigated with AMD, where the soil could act as a reactor. What also requires investigation is the field and greenhouse irrigation with circum-neutral mine water with suspended solids has not yet been demonstrated.

Although irrigation has been successfully demonstrated with some mine impacted waters, their fitness for use for irrigation needs to be assessed to understand possible longer-term effects on crops, soils and irrigation equipment. The Department of Water Affairs and Forestry (DWAF) in 1993 developed the first South African Water Quality Guidelines (SAWQG) to assess the fitness of water for irrigation. To develop these guidelines, several global water assessment guidelines were consulted and these included; Australian Water Quality Guidelines for Irrigation Water Supplies, Canadian Irrigation Water Guidelines, Food and Agricultural Organization's (FAO) Guide for Evaluating the Suitability of Water for Irrigation, United States of America (USA) Quality Criteria for Irrigation Water, United States Department of Agriculture (USDA) Handbook on Diagnosis and Improvement of Saline and Alkali Soils and American Society of Civil Engineers (ASCE) Publication on Agricultural Salinity Assessment and Management. The limits for each constituent in SAWQG were then developed, including ranges that will affect the irrigation infrastructure delivering the water. The Department then updated the guidelines and developed a second edition (DWAF 1996).

Based on the second edition of the SAWQG, an Irrigation Water Quality Decision Support System (SAWQDSS) was then developed by Du Plessis et al. (2017), allowing the user to assess the fitness-for-use (FFU). The assessments for FFU was further split into two levels of sophistication, Tier 1 (generic and conservative) and Tier 2 (site specific). Generic guidelines tend to be very conservative, but there are large differences in crop sensitivities to constituents in irrigation water, and the climate and irrigation management are also cardinal in determining whether water of a specific quality can be used for irrigation. For these reasons, being able to take site specificity into account is very valuable when decisions are made on the conditions under which a particular water may be suitable for irrigation. The newly developed DSS Tier 2 simulations, enable the input of crop (name of crop, copping system, planting date) climate (weather data), soil (e.g. texture, soil depth, initial salt content) and irrigation management data (e.g. irrigation timing, refill option, irrigation system). For FFU, the output reports on four colour coded categories (from ideal to unacceptable) for each water quality suitability indicator (Du Plessis et al. 2017).

Gypseous products from the HDS treatment process contain more solids (15 – 70 %) with dry bulk densities of 1050 – 1370 kg m^{-3}, compared to products generated by conventional AMD neutralization plants, because the HDS process recycles, and therefore thickens, the sludge (Coulton et al. 2004, McDonald et al. 2006, Zinck et al. 1997). Currently, some of the physical properties of HDS from the Coalfields of RSA have not been investigated. The chemical composition of these materials depends on the chemistry of the AMD treated and the efficiency of the treatment process (Kalin 2006, Zinck 2006, Johnson and Hallberg 2005). The sludges have been reported to contain metals of environmental concern (e.g. Ni, Hg, Pb, Se, As, Mn, Zn, Al, Fe) (Zinck et al. 1997, O'Kelly 2005, Zinck 2006, Rakotonimaro et al. 2017), and due to the content and solubilities of these metals, are often classified as a hazardous and destined for expensive storage facilities (Zinck et al. 1997, O'Kelly 2005, Zinck 2006). Therefore, assessment of the risk these materials pose to the environment and human health is critical. A focus on the classification of these materials using local and international classification systems is an important part of risk assessment and is required.

However, metal solubility in HDS may be chemically reduced by phosphate (PO_4), hopefully making the product benign to the environment. Metal solubility reduction by PO_4 was demonstrated in bottom ash of municipal solid wastes (Crannell et al. 2000), in polymineralic mine wastes (Harris and Lottermoser 2006), and in soils (Kumpiene et al. 2006). Transition metals form phosphates of low solubility (Barthel and Edwards 2004), Kumpiene at al., 2008) such as lead hydroxypyromorphite ($Pb_5(PO_4)_3OH$) (Crannell et al. 2000). Phosphate is not redox active, and the redox immobilization of metals that phosphate can introduce may have not been investigated in previous studies.

The sludge products have also been reported in literature to be largely composed of gypsum ($CaSO_4.2H_2O$), a mineral known to be somewhat soluble in water, and therefore able to release Ca and S, which can benefit crops growing on acid soils that are often deficient in these elements (Aubé and Zinck 1999, Tsang et al. 2013, Rakotonimaro et.al. 2017). Also present are amorphous Fe oxides that can help sorb metals and release Fe (Aubé and Zinck 1999, Tsang et al. 2013, Rakotonimaro et.al. 2017). This can substantially reduce phyto-availability of metals and reduce environmental contamination. Tsang et al. (2013), and

Tsang and Yip (2014), provide evidence of metal immobilization in soils treated with HDS containing Fe oxides. There was nearly complete sequestration of As, Cu and Cr after 9 months of incubation due to the material's surface area (163 – 212 m^2 g^{-1}) and reactive hydroxyl groups. According to Maree et al. (2004) and Zinck (2006), HDS may contain substantial alkalinity that can reduce the acidity of a soil. However, because of the Fe oxide content, HDS has often been used to remove metals from wastewater (Keefer and Sack 1983, Wei et al. 2008, Sibrell et al. 2009, Fernando et al. 2018), rather than being used as a soil amendment.

Amongst metals of environmental concern in HDS, if used as soil amendment, it would be the solubility and phyto-availability of Ni and Pb to consider due to their toxicity, bioaccumulation and persistence in the environment (Shahid et al. 2017). These elements are also a threat to animal and human health once in the food chain. Root uptake of these metals by plants is controlled by several factors, with soil pH the major variable. Martinez and Motto (2000) reported that the solubility of metals, including Ni and Pb, increased with a decrease in soil pH in a study that involved amending several soils contaminated with metals. During uptake and translocation, there exists elemental interaction mechanisms (Malvi 2011), synergism (where the excess of one element improves the uptake of another) and antagonism (where the excess of one element suppresses the uptake of another). According to Shahid et al. (2017), after uptake, the translocation of metals within the plant is basically through chelation assistance and their transportation is generally controlled by transpiration. Uptake by plants and translocation of metals when HDS (generated by AMD treatment in the RSA coalfields) has been applied as a soil amendment, has not yet been investigated.

The uptake of Pb and Ni by plants is a food safety concern due to their accumulation in edible parts. These metals are non-biodegradable, have extended biological half-lives and are a health risk to humans and animals, even at low concentrations (Sharma et al. 2018). However, with food safety, toxic metals are amongst other contaminants of concern (Thielecke and Nugent 2018). Food safety of edible plant parts grown in HDS-Soil mixtures has also not been investigated before. To asses this, food safety standards by Codex Alimentarius (2006) are often used, as are a collection of internationally adopted standards (developed by different countries) and related texts aimed at protecting consumers' health and ensuring fair practices in the food trade (Codex Alimentarius Commission, 2010). However, some of the adopted standards include those from the European Food Safety Authority and National Food and Drug Administrations (US FDA) (Thielecke and Nugent 2018) and those of China, National Standard of the People's Republic of China (2012).

1.1 Rationale of the study

There are large costs incurred in the treatment of AMD by the HDS process and also during further treatment of the circum-neutral mine water with reverse osmosis. Irrigation can be viewed as a long-term and cost-effective alternative utilization strategy for AMD. Large cost savings could be possible if limed soil can be used as AMD treatment plant, eliminating the need for the disposal of the gypseous product or if this product generated in the HDS process can be applied directly to the field as a soil ameliorant. Irrigating with circum-neutral mine water could eliminate the need for further treatment with reverse osmosis. However, both mine impacted waters (AMD and circum-neutral mine water from RSA coalfields in Mpumalanga) would need to be assessed with the Irrigation Water Quality Decision Support System (IWQDSS) for RSA to ascertain their fitness for irrigation.

Cost savings could also be possible if the large quantities (20 t day^{-1}) of the gypseous product generated by the treatment of 360 Ml of AMD from Mpumalanga coalfields and stored could be used to benefit agriculture as a soil amendment. Currently the product may be classified as hazardous due to content and solubility of metals. However, the product has also been reported to be largely gypsum in literature, has a substantial amount of Fe oxides and alkalinity making it potentially valuable as a soil amendment. Therefore, a thorough physical and chemical characterization of the product followed by determination of its hazardous status (using local and international classification guidelines) needed to be carried out to ascertain its usefulness as a soil amendment. Further, classifying the product with both local and international systems could help in improving the RSA system, the efficiency of AMD treatment plants (by providing information on the hazardous status of the products generated by the different treatment processes) and utilization of the gypseous product in agriculture. The solubility of metals in the product (making it hazardous) needed to be reduced by adding phosphate to improve its potential use in agriculture and further reduce its environmental risk. Phosphate is known to form sparingly soluble precipitates with metals, especially Pb.

An acid soil which was low in bases, was treated with this product to assess its potential to improve soil acidity, to supply bases and further enhance the growth of a plant to maturity. This enabled the assessment of the potential of the product to 1) improve the fertility status of the soil through the addition of Ca and S from the dissolution of gypsum, 2) to increase the pH of the soil since the product contains alkaline solid phases, such as, $CaCO_3$ and $Mg(OH)_2$ that can contribute to alkalinity and 3) to reduce the phyto-availability of metals through sorption by the Fe and Mn oxides contained. Both soil and crop response needed to be assessed to determine the potential of the product to improve soil fertility. Further, the uptake of metals, Pb and Ni by the plant and their translocation within the plant were assessed. Food safety assessment of the edible plant parts was also done with e.g. Codex Alimentarius (2006) food safety standards, which are a collection of internationally adopted standards by different countries. It was envisaged that the success of the product to improve soil fertility will lead to reduction in the storage volumes and management costs.

1.2 Hypotheses

With this background, the study therefore hypothesized that:

1) based on chemical composition, both AMD and circum-neutral mine impacted waters are not fit for irrigation;

2) subjecting gypseous sludges from HDS treatment to different extractants will provide information related to solubility of metals and transformation of these products;

3) gypseous products have physical properties that give them value for use as soil amendments;

4) the use of international classification systems will indicate how the material would be classified by other countries and help improve the local system by pointing out its strengths and weaknesses;

5) phosphate can chemically stabilise the solubility of metals through the formation of insoluble phosphate minerals, thus minimising environmental pollution and reducing the hazardous status classification of sludge products;

6) gypseous sludges on their own, or when co-applied with phosphate, can improve soil fertility and crop biomass if used as a soil amendment through their contribution of Ca and S and through increasing soil pH;

7) oxides, especially those of Fe, contained in the sludges can sorb metals of concern and reduce their phyto-availability and therefore improve food safety.

1.3 Objectives of the study;

1) To assess the fitness of two mine impacted waters; AMD and circum-neutral treated mine water, for irrigating selected summer and winter crops in a rotational cropping system using IWQDSS – Beta Version 1.1 of 2018;
2) To determine chemical status, solubility and transformation of HDS when subjected to different extraction solutions;
3) To investigate physical properties (particle size and distribution, densities) of HDS;
4) To assess the P-sorption capacity of HDS;
5) To investigate the classification of HDS using the local South African waste classification system, and those of Australia, Canada (Ontario and Manitoba, British Columbia and Alberta), China, and the United States of America (USEPA). This is to ascertain if the South African guidelines are perhaps too conservative, or indeed, too lenient;
6) To investigate the effectiveness of phosphate (PO_4) as a form of environmental stabilisation of metals in HDS;
7) To assess the response of an acid soil when amended with HDS;
8) To assess the response of a grain crop grown in HDS amended acid soil; and
9) To assess the uptake of Ni and Pb by a crop, their translocation within the plant, and the food safety status of the edible plant parts when growing on an acid soil amended with HDS

1.4 Thesis layout

The objectives of the study are addressed in eleven chapters. Chapter 2 reviews literature, giving background to the subsequent chapters. Chapter 3 focusses on assessing the fitness of AMD and circum-neutral mine impacted waters for irrigation purposes. Chapter 4 provides insight into the chemical composition and mineralogy of selected gypseous products that were further considered in chapters 8, 9 and 10 for agricultural use. It further provides an understanding of the transformation of these products when subjected to different extractants that may possibly be in contact with in the environment. Chapter 5 focusses on investigating the physical properties of all the gypseous products considered in chapter 4. Chapter 6 attempts to classify six gypseous products (including those considered in chapters 4 and 5), using local and international waste classification systems. It also displays how these products would have been classified by other countries and if the local system is in fact too strict, or perhaps too lenient. An article was published out of this chapter in the journal *'Sustainability'*, of the Molecular Diversity Preservation International and Multidisciplinary Digital Publishing Institute (MDPI). Chapter 7 discusses chemical immobilization of metals in the sludges found hazardous in chapter 6 using phosphate and discusses the merits of this method in reducing their hazardous status. This chapter was published in the *'IMWA|ICARD September 2018 International Conference Proceedings'*. Chapter 8 focusses on the response of a soil when amended with a sludge derived from a limestone only HDS process, and another from a limestone plus hydrated lime process. Chapter 9 focusses on the response of a grain crop (maize) grown in a soil amended with the sludges used in chapter 8 as soil amendments. Chapter 10 discusses the uptake of Ni and Pb of this crop. This chapter also deals with translocation of these metals between plant organs and further assesses food safety of grain in maize. This Chapter is currently under review by the *Journal of Archives of Agronomy and Soil Science*. Chapter 11 covers conclusions, recommendations and highlights important opportunities.

CHAPTER 2

LITERATURE REVIEW

2.1 Understanding the generation and chemical composition of Acid Mine Drainage (AMD)

Large volumes (360 Ml d^{-1}) of acid mine drainage (AMD) are discharged from both operational and defunct coal mines in Mpumalanga, South Africa (MWCB 2009). Basically, AMD is generated through the oxidation of sulphide minerals, especially pyrite (FeS_2) when exposed to water (H_2O) and oxygen (O_2) in the presence of catalytic bacteria *Theobacillus ferrooxidans* (Lottermoser 2007, McCarthy 2011, De Almeida et al. 2015, Jamal 2015). This process begins with the oxidation of sulphur in the sulphide minerals into sulphate, ferrous ions and protons (Equation 2.1). The ferrous ions produced is then converted into ferric ion (Equation 2.2) a process mediated by bacteria *(Theobacillus ferrooxidans)*. Ferric ions are then hydrolysed into ferric hydroxide (Equation 2.3) further producing acidifying protons. The acidity is regenerated and to achieve this, sulphide is oxidised by ferric ions (Equation 2.4) and this reaction proceeds until either the ferric ion or the exposed sulphide mineral is depleted. An overall reaction (Equation 2.5) shows the production of ferric hydroxide and sulphuric acid that reduces the pH of the solution to between 2.0 and 4.0 which then induces the solubility of toxic metals and other pollutants from minerals into solution (du Plessis 1983, Sheoran and Sheoran 2006, Vahedian et al. 2014, Gaikwad et al. 2010, Ravengai et al. 2005).

$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$ Eq. 2.1

$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$ Eq. 2.2

$4Fe^{3+} + 12H_2O \rightarrow 4Fe(OH)_3 + 12H^+$ Eq. 2.3

$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$ Eq. 2.4

$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8H_2SO_4$ Eq. 2.5

Chemically, AMD is composed of high concentrations of; SO_4^{2-}, Al, Fe, Ca, Mg, Na, K, Mn, Cu, Cd, Pb, Ni, As and Zn (Bigham and Schwertmann 1996, Shim et al. 2015). The acidity combined with the high concentration of toxic metals is the major cause of concern with AMD, as this pollutes the environment. To avoid environmental contamination, AMD is treated with alkaline minerals to neutralize the acidity and remove toxic metals through precipitation into hydroxides by increasing the pH to alkaline levels (Mackie and Walsh 2015, Jamal 2015).

2.2 Acid Mine Drainage (AMD) treatment process and generation of by-products

The treatment of AMD is often initiated naturally through exposure to basic minerals such as calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), ankerite ($Ca(Fe,Mg,Mn)(CO_3)_2$) and siderite

($FeCO_3$) resulting in an increase in pH to circum-neutral or even alkaline levels. However, this process is often insufficient due to the large volumes of AMD discharged and the scarcity of these basic minerals (Akcil and Koldas 2006, Cravotta III and Trahan 1999). Deliberate AMD treatment, therefore, becomes unavoidable and follows two main strategies. Active processes involve chemical treatment at a centralized plant, and passive processes route AMD through natural or constructed wetlands (Kalin et al. 2006). For the purpose of this study, the focus will be on the active process, as it is widely used, is very efficient for AMD treatment and provides an opportunity to assess the by-products of the neutralisation process (Aube and Zinck 2003, Johnson and Hallberg 2005). Chemicals used in this technology include either limestone or a combination of limestone plus hydrated lime (Jamal 2015, Johnson and Hallberg 2005).

AMD is treated either through a conventional or a High Density Sludge (HDS) process (Figure 2.1). The conventional process involves direct mixing of the liming material with AMD to increase the pH of the solution to precipitate metals into hydroxides and a flocculant is added to the solution before it proceeds to a clarifier for the separation of solids from the solution. This process is more effective in raising the pH compared to natural/passive processes, but it is not as efficient as the High Density Sludge Process (HDSP). Sludge generated by the conventional process contains < 5 % solids, whilst sludges emanating from HDS process contain > 5 % solids (Aubé and Zinck 2003, Gan et al. 2005, Johnson and Hallberg 2005).

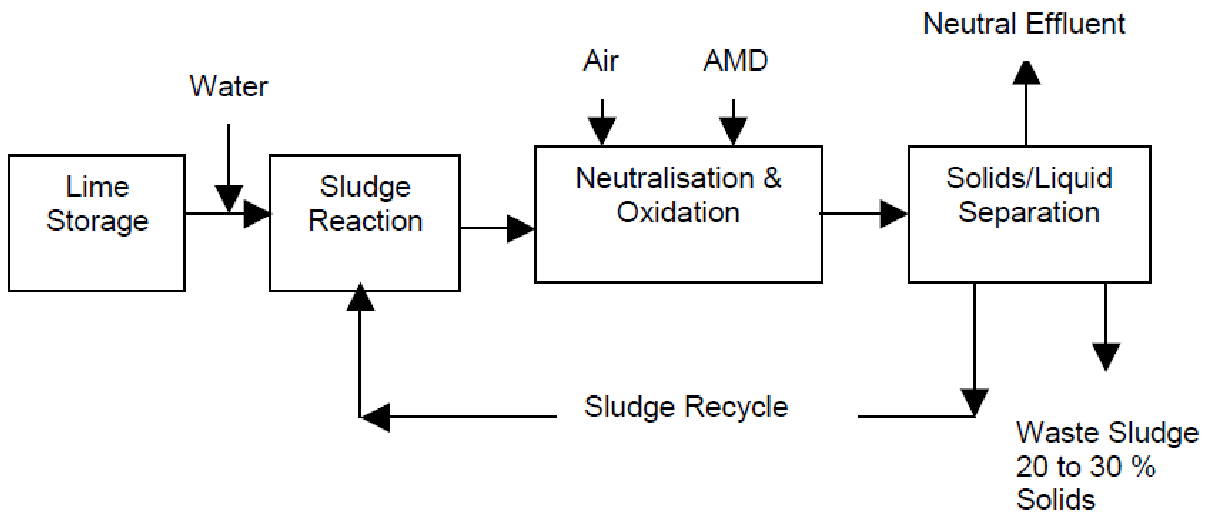


Figure 2.1: High Density Sludge Process (Günther et al. 2003)

The HDS process begins with the addition of hydrated lime (slurry lime) mixed with recycled sludge in a separate compartment prior to the introduction of AMD (Figure 2.1). The sludge/lime mixture then proceeds to an aerator where AMD is rapidly mixed with it to facilitate oxidation. The recycled sludge serves as a seeding agent that increases density in order to produce HDS. It also facilitates dissolution of undissolved lime particles in the sludge. The pH of the solution is raised to alkaline levels in the aerator and through rapid oxidation, most of the metals form hydroxides. For example, (Figure 2.2), hydroxides of Fe^{3+} and Al^{3+} start precipitating at pH 3 and pH 3.7-4.5, and maximum at pH 6.5-7.5 and at 7.5-8.5. While those of Fe^{2+}, Zn^{2+} including Ni^{2+} (not in Figure 2.2) precipitate completely at pH 11-12, pH 9-10 and pH 8 respectively (Kalin et al. 2006). Mn^{2+} is oxidized to Mn^{4+} with subsequent precipitation into sparingly soluble Mn(IV) oxides under high pH (9-9.5) conditions (Aubé and Zinck 2003, Skousen 2014).

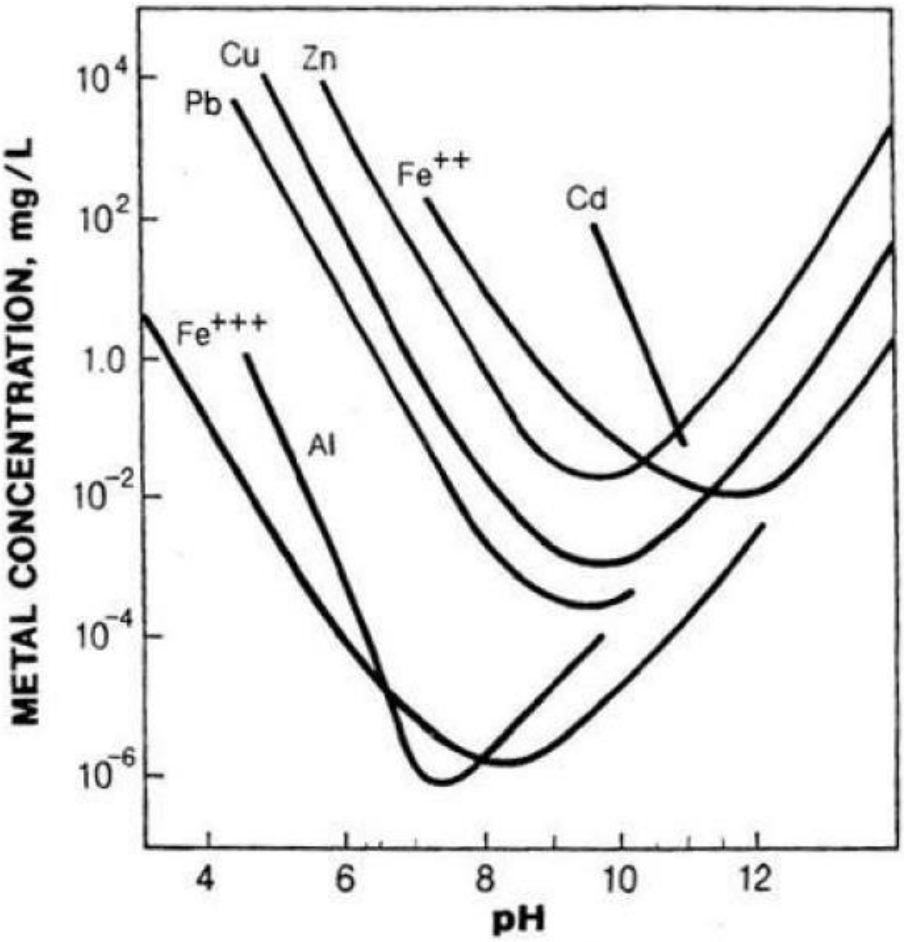


Figure 2.2: Hydrolysis solubility curves of some metals (Aubé and Zinck 2003)

The circum-neutral solution that overflows from the aerator has a high concentration of suspended solids. A flocculant is added to the solution which then proceeds to a clarifier where the solids, including precipitates (hydroxides and carbonates), are separated from the solution and settle at the bottom as gypseous material. Part of the sludge is recycled, and the rest is pumped to storage facilities. The circum-neutral mine water then overflows from the clarifier (Jovanovic et al. 1998, Annandale et al. 2001, Johnson and Hallberg 2005, Zinck 2005). This circum-neutral mine water contains no ferrugenous (Fe bearing) compounds, but has a high content of dissolved solids, sulphates (mainly Mg sulphate and gypsum) that limit its usefulness in agriculture (du Plessis 1983, Kalin et al. 2006, Gaikwad et al. 2010). The salinity of this water typically ranges between 130 and 290 mSm^{-1}, resulting mainly from Ca^{2+} and SO_4^{2-} ions (Jovanovic et al. 1998). Discharge of this treated water to the environment is undesirable, and additional treatment or utilisation strategies are needed (Annandale et al. 2001, Kalin et al. 2006, Mackie and Walsh 2015).

2.3 Fitness for use of mine impacted water for irrigation

2.3.1 Possible use of mine impacted water in irrigation

The AMD treatment products, circum-neutral mine water, with or without suspended solids and the sludge need cost-effective, environmentally responsible, management strategies. As for the circum-neutral mine water, du Plessis (1983) theoretically (through modelling) showed the feasibility of using it for irrigation as opposed to further purification to potable water using expensive reverse osmosis technology. Du Plessis (1983) mentioned that circum-neutral mine water contains no ferrugenous compounds, and pointed out that if this water is used for irrigation, this should be to field capacity to encourage gypsum precipitation and reduce salinity. He also expected no serious impact on soil physical properties through Na. Subsequently, irrigation with circum-neutral mine water has been demonstrated as a cost effective, alternative utilisation method (Annandale et al. 2007). Although some elements are precipitated out as hydroxides and sulphates from the circum-neutral water, but still this water contains appreciable concentrations of essential plant nutrients (Fe, S, Ca, Mg, K, Mn and Zn) suggesting that it may have some value in agriculture.

Jovanovic et al. (1998) carried out a crop screening trial in the field with lime treated AMD to monitor crop response and changes in soil chemical properties. This was very successful, as no symptoms of foliar injury were evident, however, shallow rooting of most crops, which was associated with soil acidity, soil compaction and P deficiency in deeper layers, was recorded. Soil salinity introduced by this water fluctuated following rainfall patterns and soil pH increased after 3 years of irrigation. After this trial, Annandale et al. (2001) carried out a commercial scale field trial and irrigated crops with circum-neutral mine water aiming to determine crop response, impact on virgin and rehabilitated land and validation of the Soil Water Balance (SWB) computer model. This trial was also a success, since results showed satisfactory yields of all crops, and although salinity increased, this was within acceptable limits, provided drainage and salt leaching was not limited by soil conditions. Idowu et al. (2007) modelled the effect on crops of accumulated salts in soils when irrigated with neutral mine water using an agrohydrological model, ACRU2000. Results indicated that the increase in salinity was not expected to affect crops planted on both virgin and rehabilitated soils. Simulated saturated soil extract electrical conductivity values from the model indicated that several crops can be successfully irrigated at 100% yield potential.

Annandale et al. (2007) used circum-neutral mine water rich in Ca and SO_4^{2-} for crop production with appropriate irrigation management. Similar to findings of Jovanovic et al. (1998), no symptoms of foliar injury were observed in all crops considered. However, in this study by Annandale et al. (2007), the presence of high levels of Ca and Mg in the water suppressed the uptake of K by crops. However, such deficiencies can be addressed by supplementation through fertilisation. According to Dama-Fakir et al. (2017), salt-tolerant crops (e.g. ryegrass, wheat and soybean) can be irrigated with circum-neutral water, for instance, wheat and soybean grown in rotation showed yields of 9 and 5 t ha^{-1}. These yields were not different from those obtained by irrigating with surface water.

2.3.2 Fitness for use assessment of mine impacted water for irrigation

A risk-based, site-specific decision support system (DSS), that relies on information contained in the published RSA water quality guidelines for irrigation (DWAF, 1996), has recently been developed with the objective of facilitating the assessment of the fitness-for-use (FFU) for irrigation water (Annandale 2018, Du Plessis et al. 2017) (Figure 2.3). Fitness for use refers to the judgement of how suitable the quality of water is for its intended use or for protecting the environment while water quality requirement determines the physical, chemical and biological composition in relation to intended use (Annandale 2018, Du Plessis et al. 2017). The assessments for FFU is further split into two levels of sophistication; Tier 1 which is generic and conservative, and Tier 2, which is site specific. Tier 2 assessments allow the input of cropping systems (i.e. name of crop, planting date) climate (weather data), soil (e.g. texture, soil depth, initial salt content) and irrigation management data (e.g. irrigation timing, refill option, irrigation system).

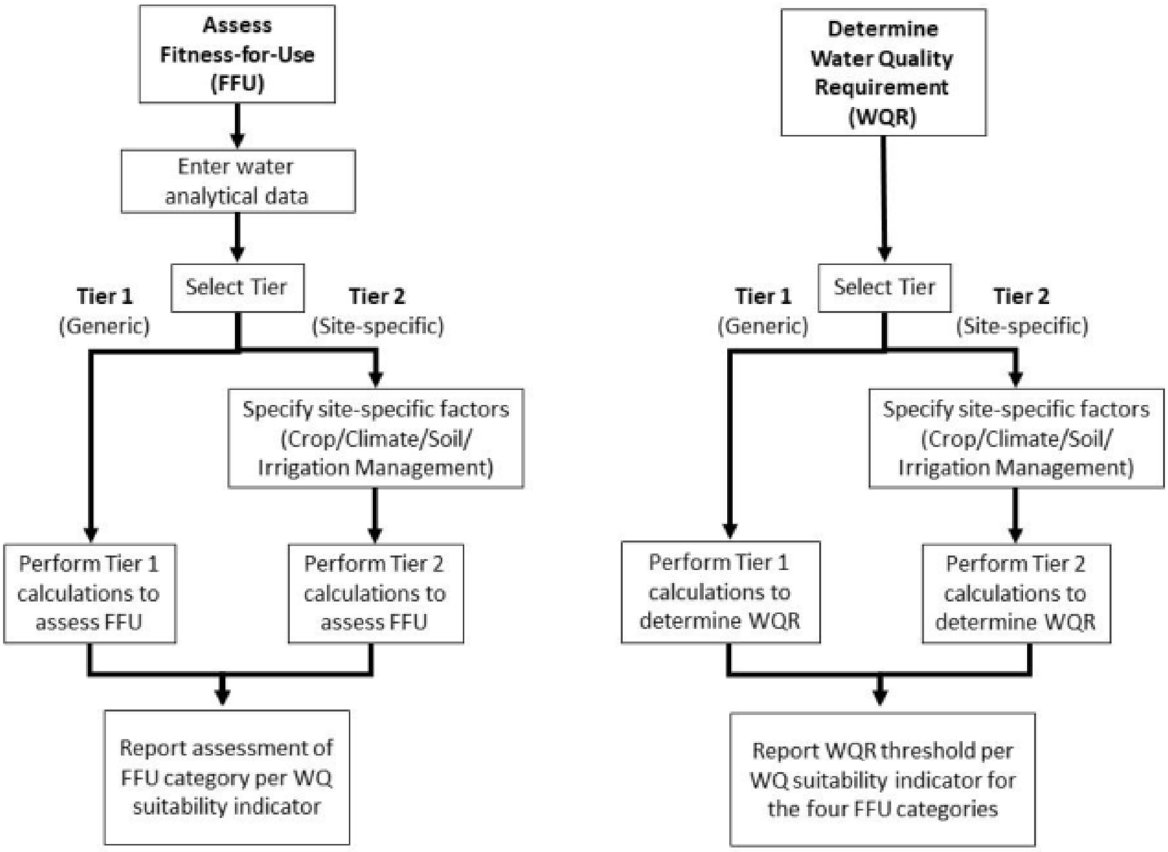
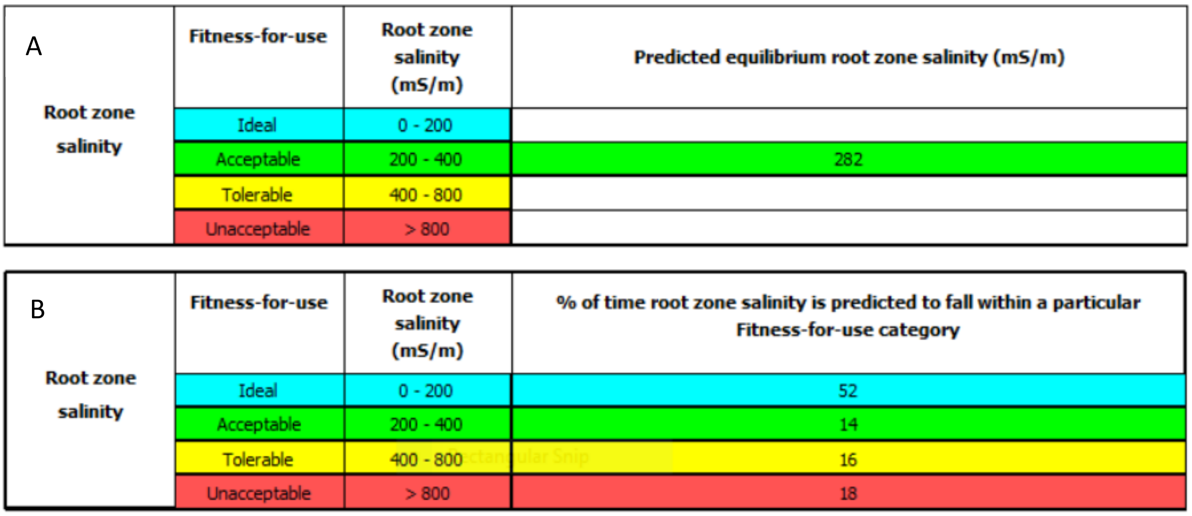


Figure 2.3: Schematic layout for the Irrigation Water Quality Decision Support System (DSS) (Du Plessis et al. 2017)

Suitability indicators reported by the IWQDSS

The DSS provides colour coded suitability indicators to evaluate effects on soil quality, irrigation equipment, and crop yield and quality (Du Plessis et al. 2017). With soil quality, indicators are root zone salinity, soil permeability as affected by Na and salinity (further divided into hydraulic conductivity and infiltrability), oxidizable carbon loading, and trace element accumulation. With respect to crop yield and quality, the following suitability indicators describe the effects irrigation water constituents have on these parameters; relative yield as affected by root zone salinity, B, Cl and Na; leaf scorching when wetted; contribution to N, P and K removal by crop; microbial contamination, and qualitative crop damage by atrazine. For irrigation equipment the DSS reports scaling/corrosion and clogging of drippers. For example, Figures 2.4 A-D have been provided to show the output for root zone salinity indicators, highlighted in different colour codes for ease of identification and interpretation, for FFU assessments at both tiers.



A Root zone salinity	Fitness-for-use	Root zone salinity (mS/m)	Predicted equilibrium root zone salinity (mS/m)
	Ideal	0 - 200	
	Acceptable	200 - 400	282
	Tolerable	400 - 800	
	Unacceptable	> 800	

B Root zone salinity	Fitness-for-use	Root zone salinity (mS/m)	% of time root zone salinity is predicted to fall within a particular Fitness-for-use category
	Ideal	0 - 200	52
	Acceptable	200 - 400	14
	Tolerable	400 - 800	16
	Unacceptable	> 800	18

Figure 2.4: Output for A & B) Tier 1: fitness-for-use (FFU) (Du Plessis et al. 2017 and Du Plessis et al. 2017)

2.4 High Density Sludge (HDS) chemical properties and disposal

High Density Sludge is a gypseous product of the HDS process and according to Chen et al. (2015) large volumes of brownish black sediment material are produced. This material is dewatered and contains ferric oxides. All of the sludges produced either through the conventional or HDS processes are composed of crystalline goethite, amorphous oxy and hydroxyl iron and aluminium oxides, and calcite, but HDS sludge is dominated by gypsum (Kalin et al. 2006). Chemically, sludges can either be alkaline or acidic, depending on the chemicals used to treat AMD. Sludges produced through AMD treatment using a combination of limestone and hydrated lime are usually alkaline. Limestone can only increase the pH of AMD to close to neutral (precipitating mostly Fe and Al as hydroxides) and hydrated lime increases it to pH > 9.5, precipitating most of the transition metals (e.g. Mn, Ni, Pb), also as hydroxides. The combination of both hydrated lime and limestone or even hydrated lime alone substantially reduces metal concentration in the final solution produced (neutral mine water). Therefore, most of the metals end up in the sludge and its chemical composition depends on the chemical composition of the treated AMD (Johnson and Hallberg 2005) and the efficiency of the treatment process. HDS sludges tend to be high in metal content due to efficient treatment with $CaCO_3$ plus $CaOH_2$. There is also increased crystallization and therefore reduced leaching potential of metals compared to HDS sludges generated by limestone treatment alone (Kalin et al. 2006). Disposal of these sludges either from $CaCO_3$ plus $CaOH_2$ treatment or limestone process are of environmental concern due to possible solubility of the precipitated hydroxides, toxic metals and $CaSO_4.2H_2O$ (Chen et al. 2015).

The characteristics of the sludges are often linked to the AMD treatment process and have a great influence on its management (Zinck 2006). Some of these characteristics and other parameters that need to be considered during sludge management include amount of sludge, dewatering ability, density, volume, chemical and physical characteristics, composition, disposal location availability and economics (Zinck 2006). Most sludges are disposed in ponds, pit lakes, landfills, specially designed facilities and sometimes co-disposed with tailings (Zinck 2006). Some see sludge as an opportunity to extract Fe and produce red iron oxide pigment (Chen et al. 2015), for recovery of metals (Wei et al. 2005), production of building materials (e.g. aluminous cement) or metal adsorbents for industrial wastewater treatment, for carbon dioxide sequestration, land reclamation and for agricultural land application as it contains $CaSO_4.2H_2O$ (Zinck 2006).

2.5 Possible uses of HDS in agriculture as a soil amendment

Although it is often classified as hazardous due to metal content and solubility, its mineralogy mainly makes it a potential agricultural resource. These materials are largely composed of gypsum (Zinck 2006), a widely used soil amendment for saline soils, and one that can release Ca and S upon dissolution. According to Maree (2004), HDS contains solid phases of $CaCO_3$ and $Mg(OH)_2$ that can contribute to alkalinity (Zinck 2006) and increase the pH of an acid soil. However, this is a highly transient property which is dependent on the management of the material. The highly effective adsorbent, ferric hydroxide (($Fe(OH)_3$) in HDS, has the potential to sequestrate transition metals in soils. Shultz and Xie (2002) demonstrated the recovery of metals in mine wastewater using HDS due to its ferric hydroxide component. These researchers pointed out that effective recovery of metals was at pH 7.8 and increasing the sludge dosage increased metal removal. Some of the metals recovered in wastewater included Cu, Cd and Zn. The solution ionic strength, E_h and concentration of complexing agents, such as, humic substances, as well as interactions of precipitated solids, contributed to metal removal (Kalin et al. 2006). Hamon et al. (2007) reported a reduction in Zn toxicity to grasses where mixtures of industrial wastes, such as, biosolids (sewage sludge) and inorganic industrial wastes (coal fly ash) were used as soil amendments. The reduction in Zn toxicity to grass remained for more than 6 years of grass production. Combinations of industrial biosolids with wood ash or industrial biosolids with agricultural lime also decreased the uptake of Pb, Zn and Cd.

2.6 HDS waste classification using local and international guidelines

Waste classification may prevent HDS use as an agricultural resource. It should be noted that the classification outcome/status of any waste depends on the system used. Waste classification systems differ globally, but for the purpose of this study, only systems from RSA, Australia (New South Wales-NSW), China, Canada (Alberta, British Columbia, Ontario and Manitoba) and the United States of America (USEPA) will be discussed.

2.6.1 Republic of South Africa (RSA) Waste Classification System

This system considers a total of 20 constituents, with six (Mn, Sb, V, Cl, SO_4^{2-}, NO_3) appearing only in this system (National Environmental Management 2008 and DWAF 1998) (Table 2.1). This system compares Leachable Concentrations (LC) of the waste, against Leachable Concentration Thresholds (LCT). These thresholds are divided into LCT0 (minimum threshold), LCT1, LCT2 (intermediate thresholds), and the maximum threshold, LCT3 (Table 2.1). According to the National Environmental Management Act (2008) and Costley (2013), LCT1 values were derived from the minimum values (LCT0) of the Standards for Human Health Effects for Drinking Water in RSA, by multiplying by 50 (a generic Dilution Attenuation Factor (DAF)). This factor was suggested by the “Industrial Waste Resource Guidelines: Solid Industrial Waste Hazard Categorisation and Management" of June 2009. The LCT2 values were derived by doubling the LCT1 values, while the maximum threshold (LCT3) values were derived by multiplying the LCT2 values by a factor of 4, to further still raise the thresholds. This factor is also used by the Environment Protection Authority (EPA) Australia, Victoria State, to calculate some thresholds from drinking water values.

The regulation further compares Total Concentration (TC) of the material against Total Concentration Thresholds (TCT). These thresholds are only divided into TCT0 (minimum threshold), TCT1 and TCT2 (maximum threshold). The TCT0 values were obtained from RSA Soil Screening Values that are protective of water resources, while TCT1 values were derived from the Land Remediation Values for Commercial/Industrial Land determined by the Department of Environmental Affairs' "Framework for the Management of Contaminated Land", of March 2010. The TCT2 values were derived by multiplying TCT1 with a factor of 4 (National Environmental Management Act 2008). To complete the assessment, the system categorises the waste as either Type 0 (high environmental risk, a material that needs to be treated first and reassessed before disposal in a structure with lining to prevent leaching), Type 1 (high risk waste, does not require prior treatment, but still needs a structure with lining to prevent leaching), Type 2 (moderate risk waste that still needs a structure with lining to prevent leaching), Type 3 (low risk waste, does not need a structure with lining to prevent leaching) or Type 4 (inert waste, similar to Type 3, a structure with lining is not a priority), and the worst category for each constituent determines the overall classification of the waste (National Environmental Management 2008) (Table 2.2). The Type is then used to decide on the disposal regulations applicable for the waste. The difference between Types 0 and 4 may have large cost/environmental implications. The fact that leaching is not regarded as a concern with Types 3 and 4 Wastes, opens an opportunity to explore these materials for use in construction or agriculture.

Table 2.1: Environmental risk assessment using the RSA guidelines (National Environmental Management Act 2008, Costley, 2013, DWAF 1998)

Element	TCT0	TCT1	TCT2	LCT0	LCT1	LCT2	LCT3

	mg kg^{-1}			mg l^{-1}			
As	5.8	500	2000	0.01	0.5	1	4
B	150	15000	60000	0.5	25	50	200
Ba	62.5	6250	25000	0.7	35	70	280
Cd	7.5	260	1040	0.003	0.15	0.3	1.2
Co	50	5000	20000	0.5	25	50	200
Cr	46000	800000	N/A	0.1	5	10	40
Cr(VI)	6.5	500	2000	0.05	2.5	5	20
Cu	16	19500	78000	2.0	100	200	800
Hg	0.93	160	640	0.006	0.3	0.6	2.4
Mn	1000	25000	100000	0.5	25	50	200
Mo	40	1000	4000	0.07	3.5	7	28
Ni	91	10600	42400	0.07	3.5	7	28
Pb	20	1900	7600	0.01	0.5	1	4
Sb	10	75	300	0.02	1.0	2	8
Se	10	50	200	0.01	0.5	1	4
V	150	2680	10720	0.2	10	20	80
Zn	240	160000	640000	5.0	250	500	2000
Cl				300	15 000	30 000	120 000
SO_4				250	12 500	25 000	100 000
NO_3				11	550	1100	4400
F				1.5	75	150	600

Note: TCT – Total Concentration Threshold values and LCT – Leachable Concentration Threshold values

Table 2.2: Criteria for assessing wastes (National Environmental Management: Waste Act No. 59, 2008, DWAF (1998) and Costley, 2013)

Type of waste	Element or chemical substance concentration	Risk	Management

Type 0	LC > LCT3 or TC > TCT2	Very high risk	Direct landfilling not allowed, needs to be treated first, reassessed/classified, needs structure with lining (H:H facility) for disposal to prevent leaching
Type 1	LCT2 < LC ≤ LCT3 or TCT1 < TC ≤ TCT2	High risk	Treatment not a pre-requisite, needs a structure with lining (H:H facility) for disposal to prevent leaching
Type 2	LCT1 < LC ≤ LCT2 and TC ≤ TCT1	Moderate risk	Needs a structure with lining (H:H facility) for disposal to prevent leaching
Type 3	LCT0 < LC ≤ LCT1 and TC ≤ TCT1	Low risk	Leaching is not a major concern, as such a structure without lining (H:h facility) is used for disposal (can be explored for use in construction industry and agriculture)
Type 4	LC ≤ LCT0 and TC ≤ TCT0	Inert	A structure without lining (H:h facility) is used for disposal as leaching is not a major concern (can be explored for use in construction industry and agriculture)

Note: H:H = Hazardous Waste Landfill with lining to prevent leaching, can receive from 1 up to 4 rated wastes; but H:h = Hazardous Waste Landfill without lining to prevent leaching, can only receive 3 and 4 rated wastes

2.6.2 Australian (New South Wales) Waste Classification System

The New South Wales (NSW) guidelines are covered because they are partially aligned to the National Waste Classification system that forms part of the Australian Waste Database (AWD). These guidelines consider a total of 9 elements (New South Wales Environment Protection Authority (EPA) 2014). Some of these elements (F, Mo and Ni) were derived from the Australian Drinking Water Guidelines (NRMMC 2011), but As, Cd, Cr(VI), Pb, and Ag were adapted from United States of America Environment Protection Authority (USEPA) 2012b. The threshold for Be was calculated based on Be in The Health Risk Assessment and Management of Contaminated Sites (NSWEPA 2014). Similar to the RSA regulations, Australia considers TC of the material, referred to as Specific Contaminant Concentrations (SCC) (Environment Act 2000) and LC data. Waste is screened by considering the SCC thresholds (Table 2.3), where a waste can be labelled as either General Solid Waste or Restricted Solid Waste.

Minimum Specific Contaminant Concentrations (SCC1) i.e. putrescible (liable to decay) or non-putrescible (equivalent to Types 3 and 4 of the South African system), or if also this requirement is not met, can be labelled as Restricted Solid Waste (TC ≤ Maximum Specific Contaminant Concentrations (SCC2) referring to wastes that have the potential to pollute the environment (equivalent to Types 1 and 2 of the RSA system). If a TC of a constituent in a waste exceeds SCC1 values, further assessment with the Toxicity Characteristic Leaching Procedure (TCLP) may be carried out (Table 2.4), but if TC exceeds SCC2 thresholds, then a TCLP assessment must be done. Australia divides SCC into SCC1 and SCC2 thresholds, TCLP into TCLP1 (minimum threshold) and TCLP2 (maximum threshold). A material can therefore be classified as General, Restricted or Hazardous Solid Waste (equivalent to Type 0 of the RSA system) (New South Wales Environment Protection Authority (EPA) 2014).

Table 2.3: Waste classification without TCLP data (NSW Environment Protection Authority (EPA), 2014)

Element	General Solid Waste	Restricted Solid Waste
	SCC1 (mg kg^{-1})	SCC2 (mg kg^{-1})
Ag	100	400
As	100	400
Be	20	80
Cd	20	80
Cr	100	400
F	3000	12000
Pb	100	400
Hg	4	16
Mo	100	400
Ni	40	160
Se	20	80
Overall		

Note: SCC = Specific Contaminant Concentrations, N.A. = Not analysed, RSW = Restricted Solid Waste and GSW = General Solid Waste.

Table 2.4: Assessment of sludge hazardous status based on both TCLP and SCC thresholds (New South Wales Environment Protection Authority (EPA) 2014)

Element	General Solid Waste		Restricted Solid Waste	
	TCLP1 (mg l^{-1})	SCC1 (mg kg^{-1})	TCLP2 (mg l^{-1})	SCC2 (mg kg^{-1})
Ag	5.0	180	20	270

As	5.0	200	20	500
Be	1.0	100	4	400
Cd	1.0	100	4	400
Cr	5.0	1900	20	7600
F	2.0	75	8	300
Pb	5.0	1500	20	6000
Hg	0.2	50	0.8	200
Mo	5.0	1000	20	4000
Ni	2.0	1050	8	4200
Se	1.0	50	4	200

2.6.3 The United States of America (USEPA) waste classification Guidelines

The USEPA regulation is managed by the Resource Conservation and Recovery Act (RCRA) of 1976, and classifies wastes based on hazardous properties (Wen 2014). They consider eight elements of concern (United States Environmental Protection Agency (EPA) 1990 (Table 2.5). These elements are considered to cause acute or chronic health effects via the groundwater route and were sourced from the National Interim Primary Drinking Water Standards (NIPDWS) (United States Environmental Protection Agency (EPA) 1990). The consideration of these inorganic constituents was further facilitated by available and appropriate chronic toxicity reference levels (CTRL) on which to base the calculation of thresholds. These elements also had adequate data for the fate and transport model used to establish element specific dilution attenuation factors used to convert CTRL to threshold values. Furthermore, these constituents have been shown to have toxic, carcinogenic, mutagenic or teratogenic effects (United States Environmental Protection Agency (EPA) 1990). The main concern is solubility of these constituents, and as such, the approach adopted considers TCLP data that are evaluated against thresholds.

The critical difference between the USEPA guidelines and the others considered is that essential trace elements for plants/crops do not form part of their hazardous waste classification. These are B, Mn, Fe, Zn, Ni and Cu. The USEPA regulation, therefore, opens the possibility for waste materials/by-products from industry and mining that have low contents and solubilities of non-essential elements for plants and environmentally harmful constituents, to be considered for use in agriculture.

2.6.4 Chinese, USEPA and Canadian (Alberta, British Columbia, Ontario and Manitoba) waste classification systems

The Canadian and Chinese regulations evaluate TCLP data for the material against established thresholds. China adopted the USEPA guidelines (Liu et al. 2015), except that they consider Cu, Ni, Be and Zn in addition, but not Se. Thresholds for all other elements, except for Hg, in both guidelines (China and USEPA) are identical. The Canadian guidelines are also similar to those of the USEPA, except that in addition, Alberta considers B, Co, Cu, Ni, Fe, U, Zn; British Columbia considers B, Cu, U, Zn, while Ontario and Manitoba consider B and U (Table 2.5). The USEPA guidelines consider As that the guidelines in Canada exclude.

Table 2.5: Assessment of HDS based on leachable concentrations (LC) using regulatory guidelines for Canada, the USEPA and China (Liu 2015, Zinck et al. 1997)

Country	Province	Ba	B	Cd	Cr	Co	Cu	Fe	Pb	Hg	Ni	Se	Ag	U	Zn	As	Be
		mg l^{-1}															
Canada	Ontario & Manitoba	100	500	5	5				5	0.1		1	5	2			
	British Columbia	100	500	5	5		100		5	0.1		1	5	10	500		
	Alberta	100	500	1	5	100	100	1000	5	0.2	5	1	5	2	500		
USEPA	-	100		1	5				5	0.2		1	5			5	
China	-	100		1	5		100		5	0.1	5		5		100	5	0.02

To summarize, the USEPA and RSA systems represents the two ends of the spectrum of constituents considered. The USEPA guidelines only consider eight universally accepted elements of major environmental concern and omit essential elements for plants. The RSA guidelines consider 20 constituents, with the other countries falling in between these limits, considering between nine and 14 elements. The USEPA, Canadian and Chinese regulations consider TCLP data to evaluate wastes, whereas Australia and RSA consider both leachable and total concentrations.

2.7 Immobilization of metals in HDS using phosphate

The use of phosphate to chemically stabilize waste by decreasing the solubility of metals of environmental concern, is a well-established practice that can reduce the hazardous rating of a material. The immobilization of metals by PO_4 was demonstrated; in bottom ash of municipal solid wastes by Crannell et al. (2000), in polymineralic mine wastes by Harris and Lottermoser (2006), and in soils by Kumpiene et al. (2006). All these studies showed that metals form phosphates of low solubility (Barthel and Edwards 2004, Kumpiene at al. 2008). For instance, Pb was reported to form lead hydroxypyromorphite ($Pb_5(PO_4)_3OH$) by Crannell et al. (2000). Phosphate minerals, such as $Ca_5(PO_4)_3OH$ can also reduce the solubility of metals (e.g. Zn, Cu, Cd etc.) through either sorption or by isomorphous substitution for Ca in the $Ca_5(PO_4)_3OH$ structure (Eighmy et al. 1997, Crannell et al. 2000). HDS contains amorphous ferric hydroxides and ferric iron is a strong electron acceptor and susceptible to reductive dissolution.

2.8 Food safety concerns when crops are irrigated with poor quality mine impacted water or when HDS is used as a soil amendment

Food and feed safety standards for humans and animals, as discussed by Codex Alimentarius Commission (CAC) (2006), began in the early 1800s, by coding food and establishing the first general food laws. The first harmonized standards were established in the 1900s, with standards for milk and milk products developed in 1903. In 1945, the Food and Agricultural Organization (FAO) was established and part of its mandates was to develop food standards. Soon after the establishment of FAO in 1948, the World Health Organization (WHO) was established, and also had to set food standards as part of its responsibilities. Joint WHO/FAO meetings began in 1950, FAO established the Codex Alimentarius Commission, with the responsibility to develop a food standards programme. In 1962, the joint WHO/FAO requested CAC to implement the joint WHO/FAO food standards. The World Health Assembly approved the establishment of this joint WHO/FAO food standards programme and adopted the statutes of the CAC.

Codex Alimentarius is a collection of internationally adopted food standards of different countries and related texts aimed at protecting consumers' health and ensuring fair practices in the food trade (CAC 2010). Individual countries develop their own food regulations to submit to the Codex Alimentarius Commission, but these regulations are often conflicting and contradictory. The CAC therefore developed criteria to follow when developing Maximum Levels (MLs) for contaminants. The criteria involve acquiring integrated toxicological expert advice regarding a safe/tolerable intake level of a specific contaminant. The advice involves toxicological information on the identification of the contaminant, metabolism by humans and animals, toxicokinetics and toxicodynamics, data on acute and long-term toxicity, and advice regarding the acceptability and safety of intake levels of contaminants. The criteria also involve acquiring analytical data (supply of validated qualitative and quantitative data). They also consider intake data (e.g. presence in food that is widely consumed, presence in feed and food components, data on intake by susceptible groups and data on intake by food producing animals). Technology is also considered (e.g. information on contamination processes, technological possibilities, production and manufacturing practices and economic aspects related to contaminant level management and control). Risk assessment and risk management is conducted in accordance with the Working Principles for Risk Analysis for Food Safety Application (CAC 2010).

Following these criteria, CAC then established maximum and guideline levels for contaminants and toxins in foods. The guidelines include mycotoxins (aflatoxins, ochratoxin, patulin), radionuclides, acrylonitrile, chloropropanols, dioxins and vinylchloride monomer, and transition metals (As, Cd, Pb, Hg, methylmecury, Sn). However, there has been no indication of high levels of As and Hg in cereals, pulses or legumes, therefore, CAC (1995) decided to discontinue the establishment of standards for these elements and moreover, they did not appear to present a problem in international trade. The MLs are set when a contaminant is found in concentrations that are significant for the exposure of the consumer and are set to ensure that the consumer is adequately protected. The main concern in this study is concentration of transition metals and their effect in cereals, pulses and grain crops. In cereal grains, CAC considers Pd to be contaminants of concern (Table 2.6).

Table 2.6: Maximum levels of contaminants in cereal grains (CAC 2010 and National Standard of the People's Republic of China, 2012)

	Element	Product name	Maximum level (mg kg^{-1})
Codex Alimentarius Commission	Pb	Cereal grains	0.2

Chinese food standards	Ni	Vegetable oils and oil-based products	1.0

However, the main concern in this study is the concentration of Pb and Ni in the grain of maize. Therefore, a different food safety standard needs to be sourced to assess Ni toxicity in grain. Several food standards; European, Canadian, USA, Australian and South African were scrutinized to ascertain if Ni is included, but none of them consider it a toxic contaminant in food except for Guojia Biaozhun/National Standard of the People's Republic of China (GB). Other than Ni, the Chinese food safety standards also consider Pb, Cd, Hg, As, Tin, Cr, NO_3 and NO_2 (GB, 2012). The thresholds in dried food are calculated according to the corresponding dehydration rate or concentration rate of the food raw material. These may be determined through food analysis, information provided by producers or data and information obtained by other means. The Chinese food standards assess the toxicity of Ni only in fats and its products and according to this standard this refers to products produced by hydrogenated vegetable oil and hydrogenated vegetable oil. This standard set the threshold of Ni at 1.0 mg kg^{-1} (National Standard of the People's Republic of China, 2012).

2.9 Summary

Due to its chemical composition and acidity, AMD is toxic to the environment. Thus, AMD requires treatment with alkaline chemicals such as limestone or a combination of limestone and hydrated lime before it can be considered for discharge to the environment. A combination of limestone/ hydrated lime and recycling of sludge ensures precipitation of most transition metals and produces a gypseous sludge and circum-neutral treated mine water. The management of the sludge and neutral mine water is a costly operation since the sludge is composed of high concentrations of metals and the neutral mine water has elevated salinity. Therefore, both the water and sludge require alternative cost-effective disposal or utilisation strategies. Researchers have demonstrated the possibility of irrigating several different crops with neutral mine waters, and results indicate no foliar damage, with crops attaining their potential yields. However, there have been no demonstrations whereby AMD is used to irrigate crops directly, and if such a practice is successful it would eliminate both sludge generation and the need for expensive HDS water treatment facilities. It is expected that this will be possible if AMD is used only on a limed soil which becomes our neutralization reactor. In addition, micro irrigation systems should be avoided when irrigating with AMD as it contains suspended solids.

Unlike neutral mine water, the effect on different summer and winter crops irrigated with AMD in field trials has not yet been assessed.

The sludge from AMD treatment plants is often classified as hazardous due to its chemical composition and leachability of metals. However, the hazardous status attached to it depends on the classification system considered. Classification systems differ based on the constituents considered. The RSA and USEPA represent both ends of the spectrum, since RSA considers 20 constituents, while USEPA considers only 8. All other countries considered in the study have the total number of constituencies falling between these extremes. The RSA waste classification system has not yet been compared to international systems in classifying wastes. This will also provide an opportunity to determine the hazardous status of local sludges emanating from treatment plants that use limestone plus hydrated lime and treatment plants that use only limestone to treat AMD. This will indicate if the local system is overly cautious or not.

The use of local sludges from AMD treatment plants have not yet been used as soil amendment to produce a crop. This can eliminate the storage and management of the sludges in expensive facilities. HDS has the potential to be used as a soil amendment since it is largely gypsum that can increase the concentration of Ca and S in deficient soils, and has high alkalinity that can increase soil pH. It is also dominated by Fe oxides that can potentially sequestrate metals in soils. A major concern is food safety of crops grown in soils amended with HDS. Food and animal feed safety standards internationally are the responsibility of the Codex Alimentarius Commission, which is a collection of internationally adopted food standards and related texts aimed at protecting consumers’ health and ensuring fair practices in food trade. However, Codex food safety standards exclude Ni, but this is included in the National Standard of the People’s Republic of China (2012). The use of phosphate to chemically immobilize metals in these sludges has not yet been used. Phosphate has the potential to reduce their hazardous condition and enhance food safety of edible plant parts.

CHAPTER 3

IS MINE IMPACTED WATER FIT FOR IRRIGATION?

ABSTRACT

Fitness assessment of any water intended for irrigation provides an insight to potential effects on soil quality, irrigation equipment, and crop yield and quality. The objectives were to assess the fitness of mine impacted water intended for the irrigation of selected summer and winter crops in a rotational cropping system. Acid mine drainage (AMD) and its treatment product, circum-neutral mine water, from a treatment plant that uses limestone in the Republic of South Africa (RSA) coalfields in Mpumalanga, were considered. Samples collected were analysed for both chemical and physical characteristics. To assess the fitness for use, the Irrigation Water Quality Decision Support System (IWQDSS) – Beta Version 1.1 of 2018, developed based on the South African Irrigation Water Quality Guidelines (SAWQG) of 1996, was used. Results showed that both sources of water were not fit for irrigation due mainly to total dissolved solids (TDS), total suspended solids (TSS) and concentrations of Al, Fe and Mn that exceeded thresholds in these mine impacted waters. Suspended solids have the potential to clog drip irrigation systems, while Al, Fe, Mn in AMD will reach soil accumulation thresholds in less than 3 years, and less than 15 years for the circum-neutral mine water. Salinity of both waters was predicted to reduce yields for maize, rye, sorghum, soybean, barley and wheat. Acid Mine Drainage contributed > 50% to the removal of N, P, K by a crop, but circum-neutral mine water will contribute > 50% to the removal of only N and K by most crops. Acid Mine Drainage would corrode irrigation infrastructure as it had a Langelier Index of < -2. All other parameters for both sources of water were tolerable, acceptable or ideal. However, to facilitate usage of both waters, the soil to irrigate should be limed to reduce acidity as both waters had pH values of < 5.7. The elements Al, Fe and Mn are abundant in the soil and are not of concern if the soils are limed before irrigation. Sprinklers or cannons can be used instead of drippers to avoid clogging of drippers. Salt accumulation can be reduced through irrigation with an appropriate leaching fraction and through sequestration by precipitated gypsum and amorphous ferric hydroxides.

Keywords: AMD, circum-neutral mine water, IWQDSS

3.1 INTRODUCTION

Increasing human population in the Republic of South Africa (RSA) exerts pressure on scarce water resources, as the country is reportedly amongst the 40 driest globally, with an average rainfall of approximately 500 mm year^{-1} compared to 860 mm year^{-1} global average rainfall (Meissner et al. 2018, Mhlongo et al. 2018, Mettetal 2019). Only a small portion (14%) of arable land receives adequate rainfall in RSA (Mettetal 2019). Clearly, to sustain and improve agricultural production, alternative water resources need to be explored. The coalfields in the Mpumalanga Province of the country generate approximately 360 Ml d^{-1} of mine impacted water, often referred to as Acid Mine Drainage (AMD). Upon mine closure, much of this water will need costly treatment before discharge to the environment will be permitted (Annandale et al. 2006, Kalin et al. 2006, Sheoran and Sheoran 2006, Chandra and Gerson 2010). Both operational and defunct coal mines contribute to this AMD discharge. Treatment of AMD with advanced technologies is currently essential, since this water is characterized by low pH (2 – 4), high acidity (approximately 2000 mg l^{-1}) and contains metals (e.g. Pd, Fe, Ni, Mn, Cd, Al, Cr, As) of environmental concern (Du Plessis 1983, Sheoran and Sheoran 2006 and Mackie and Walsh 2015). Acid Mine Drainage also contains total dissolved solids (TDS), with some ranging from 4000 to 5000 mg l^{-1} (Petrik et al. 2003).

Acid Mine Drainage is inevitable, because it is generated by natural processes, that result from the exposure of pyrite (FeS_2), to water, oxygen and *Thiobacillus ferrooxidans* (De Almeida et al. 2015, Jamal 2015). Products of the reactions involved include ferric hydroxide ($Fe(OH)_3$) and sulphuric acid (H_2SO_4) (Ravengai et al. 2005, Akcil and Koldas 2006, Gaikwad et al. 2010, Vahedian 2014). The acid produced reduces the pH of the solution and further enhances the dissolution of minerals and solubility of metals (Du Plessis 1983, Sheoran and Sheoran 2006 and Mackie and Walsh 2015). Acid Mine Drainage regenerates itself as long as either FeS_2 or ferric iron (Fe^{3+}) or ferrous iron (Fe^{2+}) are still in high concentrations (Jamal 2015). Its treatment through the HDS process produces circum-neutral mine water. The neutralised mine water can either be further treated using reverse osmosis to potable drinking water, released to the environment or used for irrigation if permitted by authorities (Jovanovic et al. 1998, Annandale et al. 2001, Johnson and Hallberg 2005 and Zinck 2005). However, disposal or use for irrigation of mine impacted waters remains of concern for the environment, due to salinity, hardness and the presence of transition metals (Du Plessis 1983, Annandale et al. 2001, Kalin et al. 2006, Gaikwad et al. 2010).

For agricultural purposes, Du Plessis (1983), theoretically through modelling, showed the feasibility of using gypsiferous mine waters for irrigation as opposed to further purification with expensive reverse osmosis technology. Du Plessis (1983) reported that the irrigation should be to field capacity (FC) to facilitate gypsum precipitation by reducing leaching, which will reduce salinity, and he also predicted no serious impacts on soil physical properties through Na. Since the initial work of Du Plessis (1983), irrigation with gypsiferous mine waters has been demonstrated and viewed by some researchers (Annandale et al. 2006) as a cost effective mine water utilization strategy. According to Dama-Fakir et al. (2017) salt-tolerant crops (e.g. ryegrass, wheat and soybean) can be irrigated with circum-neutral water, for instance, wheat and soybean grown in rotation showed yields of 9 and 5 t ha^{-1}. These yields were not different from those obtained by irrigating with surface water. Most studies to date have focussed on field irrigation with circum-neutral mine water, whereas the use of untreated AMD for irrigation has only been demonstrated under a controlled glass house environment in pots (Madiseng 2018).

Although irrigation has been successfully demonstrated with some mine impacted waters, their fitness for irrigation needs to be assessed to understand possible impacts on crops, soils and irrigation equipment. The Department of Water Affairs and Forestry (DWAF) in 1993 developed the first version of the South African Water Quality Guidelines (SAWQG) to assess the fitness of water for irrigation. To develop these guidelines, several global water assessment guidelines were consulted and amongst these were included; Australian Water Quality Guidelines for Irrigation Water Supplies, Canadian Irrigation Water Guidelines, Food and Agricultural Organization's (FAO) Guide for Evaluating the Suitability of Water for Irrigation and United States of America (USA) Quality Criteria for Irrigation Water. The limits for each constituent in SAWQG were then developed, including ranges that will affect the irrigation system. The Department (DWAF 1996) updated the guidelines and developed a second edition.

Based on the 1996 second version of SAWQG by DWAF, an Irrigation Water Quality Decision Support System (SAWQDSS) was developed, allowing the user to assess the fitness-for-use (FFU) of irrigation water (Du Plessis and WRC Report 2018). Fitness-for-use was further split into two levels, Tier 1 (generic and conservative) and Tier 2 (site specific). Site specific Tier 2 assessments are intended to allow the input of crop (name of crop, copping system, planting date), climate (weather data), soil (e.g. texture, soil depth, initial salt content) and irrigation management data (e.g. irrigation timing, refill option, irrigation system). The colour coded output reports suitability categories (ideal to unacceptable), for each water quality suitability indicator.

The objectives of this study, therefore, were to assess the fitness of mine impacted waters (AMD and Circum-neutral treated Mine Water) for irrigation of selected summer and winter crops in a rotational cropping system using the 2018 Beta Version 1.1 of the DSS. Both mine impacted waters were from the coalfields of the RSA in the Mpumalanga Province. The circum-neutral mine water was generated by treating AMD with limestone.

3.2 MATERIALS AND METHODS

3.2.1 Selected mine impacted water sources

In this study, two mine impacted waters were considered; a specific source of AMD generated by a mine in the coalfields of the Mpumalanga Province of the RSA, and a treated circum-neutral water, which was the final product of an HDS process using limestone (described by Günther et al. 2003), to treat this specific AMD. The process of treating AMD is discussed in detail in Chapters 2 and 6. The selection of AMD was necessitated by the fact that approximately 360 Ml d^{-1} is generated by RSA coalfields, requiring expensive neutralization to reduce risk to the environment, as this mine impacted water is extremely acidic and contains metals of environmental concern. The treatment process produces a circum-neutral mine water that requires further treatment with expensive reverse osmosis Technique to potable water because high metal content and salinity.

3.2.2 Determination of chemical composition of the mine impacted water

For safety and security reasons, the coal mine responsible for the treatment of the AMD opted to sample the waters and have them analysed for chemical composition and physical status. Standard USEPA methods were used to analyse both mine impacted waters; pH was measured following method 1501, concentration of metals was determined with Inductively Coupled Plasma (ICP) method 2007, total suspended solids (TSS) and total dissolved solids (TDS) were determined following gravimetric methods 160.2 and 160.1. While, total alkalinity was determined with titrimetric method 3101 and N following Kjeldahl method 1688. The results were then provided for this irrigation fitness assessment.

3.2.3 Irrigation Water Quality Decision Support System (IWQDSS – Beta Version 1.1 of 2018)

The system requires several inputs from water analysis; major constituents (Ca, Mg, Na, pH, EC, HCO_3, Cl, SO_4^{2-}, SS), biological constituents (*Escherichia coli*, COD), pesticides, trace elements (Al, As, Be, B, Cd, Cr, Co, Cu, F, Fe, Pb, Li, Mn, Hg, Ni, Mo, Se, U, V, Zn) including inorganic N, P and K. Only major constituents are required in the system, others are optional and no assessment is given if no data is provided. In its operation it also considers the specific site where the crop is produced (description/type of water, cropping system, the crop, planting date); weather station and location including years of simulation; soil parameters (soil depth, soil profile, initial water content, initial salt content, profile available water, plant available water, field capacity, wilting point and bulk density); irrigation management (irrigation timing, refill option and irrigation system) (Du Plessis et al. 2017 and Du Plessis et al. 2017. This model calculates its outputs using a steady state calculation procedure for Tier 1 assessments and for site specific Tier 2 assessments use the model with the help of the Soil Water Balance (SWB) Model running in the background. SWB is run successively for each of the selectable 10 – 50 years to generate a risk-based output.

As discussed in chapter 2, after including all the inputs, the support system (IWQDSS) enables the user to assess FFU of irrigation water (Du Plessis et al. 2017 and Du Plessis et al. 2017 a and b) and is further split into two levels; Tier 1 which is generic and conservative, and Tier 2, which is site specific (as described in Figure 2.3 in Chapter 2 and Figure 3.1). Tier 1 simulations are steady-state simulations, whereas Tier 2 runs simulations for many years (up to 45 years), so output is risk-based, specifying the fraction of time a particular suitability indicator will fall in a specific colour coded fitness for use class.

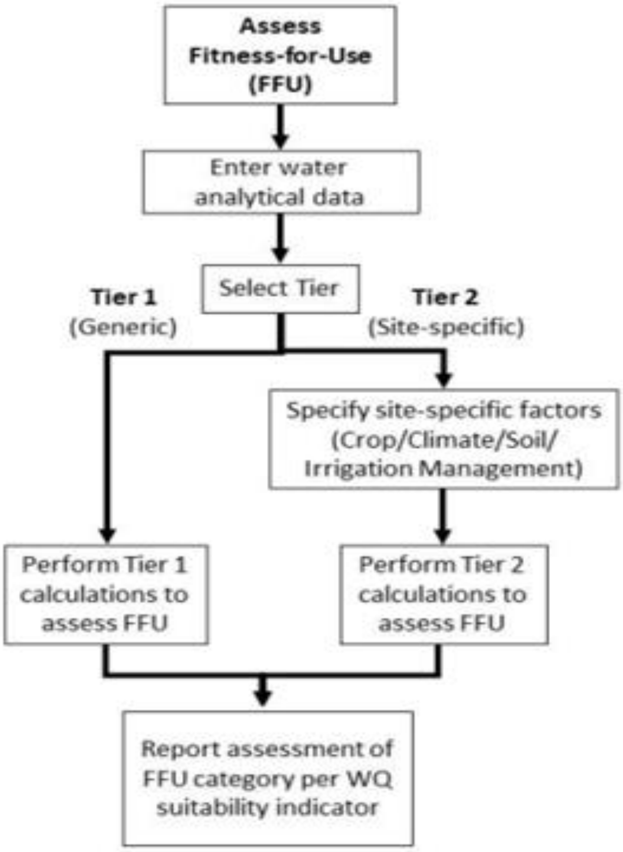
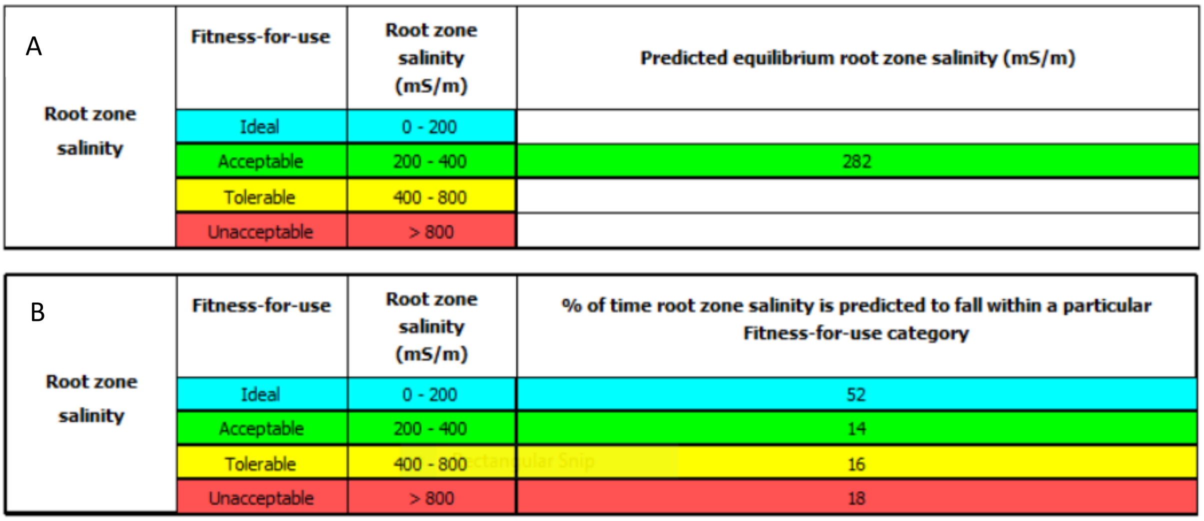


Figure 3.1: Schematic layout of the Irrigation Water Quality Decision Support System (DSS) (Du Plessis et al. 2017 and Du Plessis et al. 2017 a & b)

3.2.4 Suitability indicators reported by Irrigation Water Quality Decision Support System

In its output/report, IWQDSS provides colour coded indicators to evaluate; effects on soil quality, irrigation equipment, and crop yield and quality (Du Plessis et al. 2017 and Du Plessis et al. 2017 a & b). With soil quality, the indicators are for root zone salinity, soil permeability as affected by Na and salinity (further divided into hydraulic conductivity and infiltrability), oxidizable carbon loading, and trace element accumulation. With respect to crop yield and quality, the following suitability indicators describe the effects irrigation water constituents have on these parameters; relative yield as affected by root zone salinity, B, Cl and Na; leaf scorching when wetted; contribution to N, P and K removal by crop; microbial contamination, and qualitative crop damage by atrazine. On irrigation equipment, IWQDSS reports on scaling/corrosion and clogging of drippers. For example, Figure 3.2 A & B has been provided to show the output for root zone salinity indicators highlighted in different colour codes for ease of identification and interpretation. These indicators have also been discussed in Chapter 2, Figure 2.4; A – D.



A	Fitness-for-use	Root zone salinity (mS/m)	Predicted equilibrium root zone salinity (mS/m)
Root zone salinity	Ideal	0 - 200	
	Acceptable	200 - 400	282
	Tolerable	400 - 800	
	Unacceptable	> 800	

B	Fitness-for-use	Root zone salinity (mS/m)	% of time root zone salinity is predicted to fall within a particular Fitness-for-use category
Root zone salinity	Ideal	0 - 200	52
	Acceptable	200 - 400	14
	Tolerable	400 - 800	16
	Unacceptable	> 800	18

Figure 3.2: Output for A & B) Tier 1: fitness-for-use (FFU) (Du Plessis et al. 2017 and Du Plessis et al. 2017)

3.3 RESULTS AND DISCUSSION

3.3.1 Basic chemical characterisation of the mine impacted water

Chemical characterisation of AMD and circum-neutral lime treated mine water was carried out to help understand potential risks to the soil used to grow crops and effect on the crops planted if used for irrigation. It was found that neither of the two waters was neutral, AMD showed an extremely low pH of 3, while the circum-neutral lime treated mine water had a slightly acidic pH of 5.7 (Table 3.1). The low pH in AMD was due to the acidity induced by sulphuric acid (H_2SO_4) produced by the oxidation of pyrite (FeS_2) (De Almeida et al. 2015, Jamal 2015). Such acidity in AMD can drastically increase the acidity of a soil and reduce its pH if used for irrigation. The slightly acidic pH of the circum-neutral water was a result of the treatment process of AMD with $CaCO_3$ during oxidation (Skousen 2014). This pH (5.7) could have been close to neutral (pH 7) if a combination of limestone and hydrated lime ($Ca(OH)_2$) were used and in equilibrium in the solution. Hydrated lime is capable of increasing solution pH to >10, whereas the limestone reaction is often limited by armouring, resulting in slightly acidic pH levels of the solution (Skousen 2014). If used for irrigation this water (AMD) can possibly increase soil acidity as well and reduce soil pH. Treating AMD with limestone did not substantially reduce salinity. Both waters, therefore, in addition, had the potential to increase soil salinity if continuously used for irrigation. Total Dissolved Solids (TDS) and Total Soluble Solids (TSS) were not substantially reduced by the treatment process which could lead to clogging of irrigation systems, especially drippers. Therefore, micro irrigation systems should be avoided when these mine impacted waters are used for irrigation.

Acid mine drainage had high concentrations of Ca, SO_4, Mg and Fe, while circum-neutral treated mine water was dominated by Ca, SO_4, and Mg. The SO_4 and Fe could be traced back to the AMD, whereas the increase in Ca and Mg in the circum-neutral water likely came from the treatment process attributed to the material used for liming. The abundant Fe in AMD is a product of pyrite dissolution. Other constituents (B, F, NO_3, PO_4) were low in both waters. The treatment mainly aims on removing metals of environmental concern, such as, Pb, Cd, Ni including Mn, Al, Fe, Cu and Zn. Large differences in metal concentration between the two mine waters were observed with pH, Ca, Al and Zn. If used for irrigation both waters can supply major plant nutrients, such as, Ca, S and Mg.

Table 3.1: Chemical composition of Acid Mine Drainage and circum-neutral lime treated mine water

Parameter	Acid Mine Drainage	Circum-Neutral Mine Water
pH	3.0	5.7
EC (mS m^{-1})	367	377
Total alkalinity (mg l^{-1})	-	41
TDS (mg l^{-1})	4668	4562
TSS (mg l^{-1})	106	114
SAR	1.0	0.5
	Elemental concentration (mg l^{-1})	
Al	154	47
B	0.2	0.1
Ca	222	608
Cl	15	5
F	0.1	0.1
Fe	266	34
K	7	12
Mg	119	208
Mn	57	82
Na	13	10
NH_4-N	19	19
NO_3-N	0.4	0.3
PO_4	0.5	0.4
SO_4	3009	2995

3.3.2 Assessment of AMD and circum-neutral lime treated mine water using IWQDSS, FFU output (Tier 1)

This model calculates its outputs using a steady state calculation procedure for Tier 1 assessments and for site specific Tier 2 assessments use the model with the help of the Soil Water Balance (SWB) Model running in the background. SWB is run successively for each of the selectable 10 – 50 years to generate a risk-based output. IWQDSS, revealed that there will be no surface infiltrability and hydraulic conductivity problems with both waters (Table 3.2). It can take > 200 years of irrigation to reach soil accumulation thresholds for most metals except for Al, Fe and Mn in AMD, which is predicted to take 3, 2 and 0 years respectively; and this increases to 11, 15 and 0 years for circum-neutral mine water. However, addition of these elements may not be of concern as they are already abundant in soils and their toxicity is generally reduced by liming. To reach soil accumulation thresholds for F when irrigating with circum-neutral mine water, it is estimated this will take > 1000 years. Although, the model showed tolerable salinity problems for both qualities of water, root zone salinity is expected to reduce crop yields. However, the concentrations of B, Cl and Na in both waters were found to be ideal and not expected to affect crop yields. Irrigating with AMD could contribute > 50% to the removal of N, P and K by the generic crop; the same applies to the circum-neutral mine water for N and K, but not for P.

With respect to the irrigation system, the model predicted that only AMD would corrode the system, exhibiting a Langelier Index of < -2, while circum-neutral mine water was predicted to corrode the system to a tolerable level. The Langelier Index also showed that neither water is expected to cause any scaling. In terms of suspended solids, the model predicted that both qualities of water will clog drippers, and the concentrations of Mn and Fe are > 1.5 mg l^{-1} and therefore unacceptable for use with drip irrigation. The pH levels in both waters were predicted to be ideal for drip irrigation.

Based on the discussion above, both waters could be used for irrigation if the soil to be irrigated can be limed to reduce the acidity introduced by both waters and the toxicity of Al, Fe and Mn. Sprinklers or cannons can be used instead of micro irrigation to avoid clogging of drippers by suspended solids. It can also be envisaged that most of the salts will be sequestrated during mineral precipitation in the soil, especially as gypsum and amorphous ferric hydroxides reducing salinity development in the process. Salt accumulation can also be reduced through irrigation with an appropriate leaching fraction.

Table 3.2: Fitness of AMD and circum-neutral mine water for irrigation, summary for IWQDSS – FFU output (Tier 1)

Parameter		**Acid Mine Drainage**		**Circum-neutral Mine Water**	
		Comparison	**Fitness**	**Comparison**	**Fitness**
Predicted equilibrium root zone Salinity		689 mS m^{-1}	Tolerable	708 mS m^{-1}	tolerable
Soil permeability	Surface Infilt.	Slight	Acceptable	Slight	acceptable
	Soil Hydr. Conductivity	None	Ideal	None	ideal
Number of years to reach soil accumulation threshold	All other trace elements	> 200 years	Ideal	>200 years	ideal
	Al	3 years	unacceptable	11 years	unacceptable
	Fe	2 years	unacceptable	15 years	unacceptable
	Mn	0 years	unacceptable	0 years	unacceptable
	F	-	-	> 1000	ideal
Root zone effects (Rel. Crop yield)	Salinity	< 70% yield	unacceptable	<70%	unacceptable
	B, Cl, Na	97 – 100%	Ideal	100%	ideal
Leaf scorching	Cl, Na	None	No scorching	None	No scorching
Contribution to NPK removal	N	> 50%	unacceptable	>50%	unacceptable
	P	≥ 50%	unacceptable	40%	tolerable
	K	> 50%	unacceptable	>50%	unacceptable
Corrosion	Langelier Index	< -2.0	unacceptable	-1.0 to -2.0	tolerable
Scaling	Langelier Index	None	No scaling	None	No scaling
Clogging Drippers	Susp. Solids	>100%	unacceptable	>100%	unacceptable
	pH	3.0 (<7)	Ideal	5.7 (<7)	ideal
	Mn	>1.5 mg l^{-1}	unacceptable	>1.5 mg l^{-1}	unacceptable
	Fe	>1.5 mg l^{-1}	unacceptable	>1.5 mg l^{-1}	unacceptable

3.3.3 Site specific AMD and circum-neutral mine water fitness for irrigation

Crops to consider for the modelling were selected based on their salinity tolerance (Table 3.3). A rotational cropping system was adopted to enable summer and winter planting as follows; maize/ryegrass, sorghum/stooling rye, teff/barley, soybean/wheat. However, the model only had parameters for maize, rye, sorghum, soybean, barley and wheat in its database. Other assumptions made were; a sandy loam texture of rehabilitated land, 0.50 m soil depth, irrigation with a 10% leaching fraction, overhead irrigation and also used data for a nearby weather station. The model calculated using a steady state calculation procedure using the inputs described under materials and methods.

Table 3.3: Some of the crops considered for the model and their limiting salinity levels

Summer crops				Winter crops			
Crop	Specie	Growth	Salinity Threshold (mS m^{-1})	Crop	Specie	Growth	Salinity (mS m^{-1})
Maize	*Zea mays*	Ann.	180	Wheat	*Triticum spp.*	Ann.	600
Soybeans	*Glycine max*	Ann.	500	Annual Ryegrass	*Lolium multiflorum*	Ann. Temp.	760
Sorghum	*Sorgum bicolor*	Ann.	680	Stooling rye	*Secale cereale* L.	Ann. Temp.	1140

Note: Ann. = Annual, Temp. = Temperate

With respect to irrigation with AMD, it was only salinity that was predicted to affect the following crop rotations; maize/rye, sorghum/stooling rye, soybean/wheat including barley as a single crop. Irrigation with circum-neutral mine water showed maize in a rotation with rye to be affected by salinity. All other crops were predicted not to be affected by salinity. Allowing precipitation of minerals, especially gypsum and amorphous ferric hydroxides will help sequestrate salts and reduce salinity that could affect these crops. Liming the soil can also reduce the predicted toxicities of Al, Fe and Mn introduced by the waters.

3.4 CONCLUSIONS

The study showed that assessing water intended for irrigation provides insight to potential effects on soil quality, crops and irrigation system. Assessment with IWQDSS showed that both AMD and circum-neutral mine water were not fit for irrigation due to high levels of TDS, TSS, and high concentration of Al, Fe and Mn. It should be noted that these results were specific to AMD (discharged by the RSA coalfields in the Mpumalanga Province) and circum-neutral mine water generated by treating this AMD with limestone. The circum-neutral mine water had a slightly acidic pH of 5.7, and was therefore not really circum-neutral. If this pH had been increased with limestone plus hydrated lime treatment, the problems of Fe, Mn and Al may have been eliminated. Both waters were not fit for irrigation due to high levels of salinity, high concentration of Al, Fe and Mn and suspended solids. However, liming the soil can reduce the toxicity of Al, Fe and Mn. Sprinklers or cannons can be used instead of drippers to avoid clogging of drippers. Salt accumulation can be reduced through irrigation with appropriate leaching fraction and through sequestration by precipitated gypsum and amorphous ferric hydroxides. If all these can be taken into consideration both waters can be used for irrigation. As such it can be recommended for future research work that both mine impacted waters should be used to irrigate different crops on a field scale and focus mainly on the impact on the irrigation system and response of soil and different crops. Long term research trials, irrigating with these waters including different cropping systems are recommended to enable the assessment of long-term effects.

CHAPTER 4

SOLUBILITY OF HIGH DENSITY SLUDGE FROM ACID MINE DRAINAGE TREATMENT AND POSSIBLE ENVIRONMENTAL RISK

ABSTRACT

High Density Sludge (HDS) is a gypseous material, that maybe reported as hazardous due to metal composition and solubility. However, solubility of metals in HDS depends on the treatment process that generates it and the environment the sludge experiences on disposal. The aim of this chapter, therefore, was to investigate the impact the different treatment processes (limestone or limestone plus hydrated lime) have on the partitioning of the elements in the sludges and their solubility. Four HDS sludges were considered: A ferriferous gypseous which was largely gypsum, with Fe oxides, Mn and Ni (GypFeMnNi) from limestone AMD treatment, and three others from different stages of limestone plus hydrated lime treatment; a ferriferous gypseous product with high levels of Mn (GypFeMn); a gypseous product with brucite (GypB), and a gypseous product with Fe removed (Gyp). The sludges differed in their chemical composition due to the different AMD streams that were treated. X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) techniques were used to determine total elemental content and mineralogy. Solubility was assessed with deionized H_2O, as well as with diluted HCl (at pH = 4). In addition, the Toxicity Characteristic Leaching Procedure (TCLP) Method 1311 of the United States Environmental Protection Agency (USEPA), and ethylenediaminetetraacetic acid (EDTA) and ammonium acetate (NH_4OAc) were also used. Phosphate sorption capacity of sludges was also assessed. Results showed that GypFeMn, GypB and Gyp were basic, exhibiting $CaCO_3$ equivalent of 510, 601, 617 mg kg^{-1} and pH values of 8.2, 9.4 and 9.5. GypFeMnNi had an alkalinity of 250 mg kg^{-1} and a pH of 5.5. Therefore, all showed a potential to increase pH if used as a soil amendment. All materials were gypseous, largely composed of gypsum. GypFeMnNi and GypFeMn were substantially composed of iron oxides (22 – 28%) that can potentially sorb metals. In total, S was dominant in all sludges followed by Ca, while, Fe was the most dominant amongst transition metals except in GypB, where it was Mn. All other transition metals were extremely low, including Pb and Ni making all the materials safe to the environment. Most elements seemed to be water soluble in all the sludges. Sulphur was the most extracted in all the sludges. Reduction in Ca extractability could be due to armouring of gypsum by iron oxides. Manganese was the most released compared to the other metals (Pb, Cd, Fe, Ni and Zn) from all the sludges. All the materials have the potential to sorb phosphate, with GypFeMnNi, GypFeMn, GypB and Gyp showing maximum phosphate sorption capacities of 1810, 887, 887 and 236 mmol kg^{-1}.

Keywords**:** HDS, AMD, Mineralogy, Solubility, Phosphate Sorption

4.1 INTRODUCTION

High Density Sludge is continuously generated during AMD treatment described in Chapters 2 and 6 (Kalin et al. 2006 and Chen et al. 2015). According to Maree et al. (2004) an estimated 20 t of HDS is generated from 1 Ml of AMD treated with either limestone or a combination of limestone plus hydrated lime. The alkaline treatment of AMD not only neutralises acidity but also enhances the oxidation of Fe^{2+} to Fe^{3+} and Mn^{+2} to Mn^{4+} resulting in the precipitation of transition metals into hydroxides in the sludges (Aubé and Zinck 1999, Johnson and Hallberg, 2005, Jamal 2015). As a result, the sludge produced is mainly composed of gypsum with goethite and calcite forming minor components, with a substantial amount of amorphous Fe, Mn and Al hydroxides and oxides (Kalin et al. 2006). For the sludge to attain high density status, the HDSP mixes are recycled with either $CaCO_3$ or a combination of $CaCO_3$ and $Ca(OH)_2$ added prior to AMD introduction and oxidation (discussed in Chapters 2 and 6). The densification of the sludge is the result of surface precipitation on existing recycled sludge particles and co-precipitation forming new particles (Aubé and Zinck 1999).

Nickel, Cr, Cd, Pb and Hg have the tendency to precipitate as carbonates, oxides and hydroxides that end up accumulating in the HDS. The accumulation of metals and their solubility is often the reason why HDS may be classified as hazardous. The alkalinity introduced during the HDS process plays a determining role in the fate of these elements, and in turn, their solubility (Johnson and Hallberg, 2005, Kalin et al. 2006 and Zinck 2006). The HDS process also improves crystallization of the Fe(III) oxide fraction, which reduces its solubility (Johnson and Hallberg, 2005, Kalin et al. 2006 and Zinck 2006).

Although mineralogy of similar materials has been studied by several researchers globally, a comprehensive understanding of the solubility of metals and phosphate sorption potential of

HDS from the Mpumalanga Coalfields has not been studied yet. In this study therefore, three sludges generated by a combination of $CaCO_3$ and $Ca(OH)_2$ and another from a $CaCO_3$ treatment plant were subjected to various chemical extractions aiming to better understand their transformation, solubility of elements and their potential to sorb phosphate when in the environment. It was hypothesised that the use of limestone will facilitate solubility of some of the elements in HDS since it can only increase the pH of the solution to circum-neutral levels during AMD treatment, therefore some metals such as Mn that precipitate at pH > 9.5 remain in solution. It was also hypothesised that including lime in the treatment process will reduce elemental solubility in HDS, since lime increases the pH to > 9.5, thereby precipitating most of the elements during AMD treatment. The aim of the study, therefore, was to investigate the impact the different treatment processes (limestone and limestone plus hydrated lime) have, on the partitioning of the elements in HDS (or forms in which they exist in) and their solubility

4.2 MATERIALS AND METHODS

4.2.1 HDS sample preparation

Four gypseous materials from the Coalfields of Mpumalanga were considered. Three of the sludges designated as GypFeMn (gypsum with Fe oxides and Mn), GypB (gypsum with brucite), and Gyp (a refined gypsum product with Fe removed) generated at different stages of an AMD treatment plant that uses $CaCO_3$ plus $Ca(OH)_2$ were collected. These designated names of the materials were derived based on the fact that the sludges were generated by further adding $Ca(OH)_2$ in the treatment process, followed by centrifuging through hydro-cyclones and filtration that separate solids from liquid into fine and coarse particles. The other sludge was sourced from an AMD treatment plant that uses only $CaCO_3$ and was designated as GypFeMnNi (with gypsum, Fe oxides, Mn and Ni). Basically, all the sludges were gypseous but from different AMD treatment processes and AMD sources. These treatment processes have been described in Chapters 2 and 6.

4.2.2 Mineralogical analysis

Total elemental analysis using X-ray Fluorescence (XRF) and mineral determination using X-ray Diffraction (XRD)

Mineralogy analysis with XRD was carried out on samples before and after treatment with the different solutions. Crystalline phases in HDS were determined using PANalytical X'Pert Pro Powder Diffractometer and total elemental content using an ARL 9400XP+ Wavelength dispersive XRF Spectrometer. The XRF Spectrometer relied on software (UniQuant) to analyse raw spectral data qualitatively and quantitatively, as described by Loubser and Verryn (2008).

Mineral morphology analysis using Scanning Electron Microscopy (SEM) and Electron Diffraction Spectroscopy (EDS) to help understand solubility

The interest here was to determine the morphology of the minerals identified by XRD that can help in understanding their solubility. For instance, SEM and EDS can show if there is any armouring on the morphology of the mineral that can possibly reduce its solubility. Each dried sample was spread on a piece of double-sided tape and excess particles were removed using compressed air. The tape with the sample was pressed on a rectangular metal block in preparation for carbon coating. The block was then mounted on a tilting stand inside EMITECH K950X carbon coating equipment. The block was initially tilted to one side and coated with carbon three times. After coating, the samples were mounted to a Zeiss Gemini Ultra Plus for SEM analysis. During analysis, each sample was scanned, and representative morphological pictures were taken. For elemental composition of HDS, a thin layer of sample was spread at the base of a polyethylene container of approximately 1 ml in volume and then filled with Embed 812 Epoxy resin. The sample was then oven dried at 60 ^{o}C overnight and then polished mechanically using a LECO® GP20 Grinder/Polisher and coated with carbon before analysis. The sample was mounted to the Zeiss Gemini Ultra Plus for EDS analysis. All structures of interest in each sample were scanned for elemental concentrations. The elemental data provided by EDS was used to ascertain the identity of the structures/minerals scanned. The identified minerals were then compared to the data provided by XRD.

4.2.3 Dissolution of sludges

The determination of solubility as influenced by different solutions, was aimed at understanding expected behaviour of the materials if they were to come in contact with organic chelators, or be exposed to reductive, acidic or circum-neutral conditions in the environment.

Aqueous solubility

A similar dialysis tubing set-up to that described by Hsu (1966) was followed, but with transferring HDS to the tube instead of a solution (Appendix E). A 30 g HDS sample was transferred into a SnakeSkin® Dialysis tube (from Thermo Fisher Scientific, Rockford, USA). This membrane had 10 kDa molecular weight cut off (MWCO). It was tied at both ends and placed in a 500 ml Schott bottle. A volume of 500 ml of deionized water was added to achieve a solid to water ratio of 1:16.7. Initial pH and EC were measured immediately after setting-up the experiment. After equilibration, the solution was decanted; with 15 ml of the solution reserved for elemental analysis using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), and 50 ml for anion analysis using ion chromatography, a method described by Tabatabai and Frankenberger (1996). The decanted solution was replaced with fresh deionized water. The experiment was stopped when there was no change in pH and EC of the current solution when compared to the previous solution. At this point the experiment was stopped, the dialysis tubes containing the HDS were removed, air dried and analysed for total elemental content (using XRF) and mineralogy (using XRD).

Solubility with diluted HCl acid at pH 4

A 50 g sample of HDS sludge was transferred into a 250 ml Schott bottle and reacted with 200 ml of 0.1 mmol HCl at constant room temperature (25 ^{o}C) until attainment of equilibrium at a constant pH and EC. At this point the suspension was decanted, filtered through a 0.45 µm membrane filter into 15 ml centrifuge tubes and kept for elemental analysis using ICP-OES. The acidity of the remaining solution was then determined. The decanted acid was replaced (by weighing) with a fresh acid solution of the same concentration. The experiment was terminated when there was no change in pH and EC of the current solution when compared to the previous solution. A total of five successive extractions were carried out by the end of the experiment. Leachate was analysed after each extraction. After the last extraction, the acid leached HDS was analysed for total elemental content and mineralogy.

Leachability assessment using the USA Toxicity Characteristic Leaching Procedure (TCLP-1311)

The standard method used to assess leachability of solid wastes for disposal purposes, SW-846 Test method 1311: Toxicity Characteristic Leaching Procedure (TCLP) from United States Environmental Protection Agency (USEPA) (1992), was followed.

Organic chelation solubility

Extractable macro and micro-elements were determined using standard methods, namely with ammonium acetate (1 mol l^{-1}, pH 7) and di-ammonium EDTA, respectively, as discussed by the Soil Science Society of South Africa (1990).

4.2.4 Sorption capacity

Phosphate sorption capacity of sludges

Most of the sludges were reported to be gypsum/iron oxide mixtures, therefore the focus was to assess the potential of the iron oxide component in sorbing phosphate. This section therefore, focussed on phosphate sorption of HDS as this property could be a disadvantage if the material is used as a soil amendment, it can sequester applied phosphate. One-gram samples of air dried HDS were transferred into 50 ml centrifuge tubes and suspended in 30 ml of 2 mmol $CaCl_2$, 1 mmol $MgCl_2$ and 0.5 mmol NaCl of supporting electrolyte containing 0, 50, 100, 250, 500, 1000, and 2000 mg P l^{-1} prepared from KH_2PO_4. The tubes were then stoppered and shaken end to end at 180 oscillations per minute for 2 hours per day for 2 days and stored in the dark at constant temperature (25 ^{o}C). After 48 hours, the samples were centrifuged at 300 revolutions per minute for 10 minutes and filtered through Whatman No. 42 filter paper. Standard P solutions; 0, 5, 10, 50, 100 and 250 mg l^{-1} were prepared and read through ICP-OES. The filtered solutions were then analysed for P using the calibrated ICP-OES. The amount of P sorbed was calculated as the difference between the amount of P added and that remaining in solution. The sorption data were then fitted to a linearized form of the Langmuir equation (Essington 2004).

4.2.5 Determination of Method Detection Limits for elements

To ensure the quality of the data generated, method detection limits (MDL) for the different chemical methods (digestion, EDTA, NH4OAc, solubility through dialysis) used in this study were determined following a standard Procedure of the USEPA [40 CFR Appendix B to Part 136 (2011)]. Method detection limit data for each of the methods is presented in appendix A.

For instance, to assess the MDL for acid digestion, an ICP multi-element standard for 21 elements in diluted nitric acid (HNO_3) with a concentration of 1000 mg l^{-1} was considered. The elements included Ni and Pb (Appendix A). The lowest concentration used from this standard was 50 µg l^{-1}. 15 ml of 65% Suprapur HNO_3 was transferred to a 50 ml volumetric flask, spiked with 50 µg l^{-1} of the standard, and filled with deionized water to the 50 ml mark. This solution was then replicated 7 times and analysed. MDL was then calculated using the following equation:

MDL = Standard deviation of replicates x Student's t value $_{(n\text{-}1,\ 1\text{-}\alpha\ =\ 0.99)}$
Where: n = number of replicates, and α = level of significance

Method detection limits (MDL) for the different chemical methods ensure the quality of the data generated. Otherwise low-quality data or wrong data can be presented if the limits of the methods in determining specific elements are not known. That means even data falling outside of the method limits of detection can be recorded and presented as true data. Therefore, MDL need to be determined in the laboratory and used as reference for all analysis performed. For example, RSA waste classification in Chapter 6 of this thesis has some of the thresholds for constituents falling below method detection limits, therefore they cannot be determined.

4.3 RESULTS AND DISCUSSION

4.3.1 Mineralogy of sludges

With respect to GypFeMnNi, XRD showed that the crystalline phase ranged from 72 to 77% $CaSO_4.2H_2O$ (Appendix B). In addition to this gypsum, XRD further identified 4% of a carbonate mineral – ankerite ($Ca(Fe,Mg,Mn)(CO_3)_2$) (Appendix B). The precipitation of ankerite was not unexpected, since it is one of the minerals abundant in mine wastes (Lollar et al. 2005). Ankerite formation was facilitated by the lower pH (5.5) of GypFeMnNi, that reduced the kinetics of oxidation and increased the concentration of Fe and Mn (Hendry et al. 2000). In addition, solid phases of Fe(II) and Mn(II), decrease their propensity to be oxidised. The Mg and Ca in this mineral could be traced back to the liming material used to treat AMD. Diffractogram peaks developed and used to identify some of the minerals in GypFeMnNi (Appendix C; Fig. 1; i & ii), also showed prominent peaks of the Fe oxides hematite (Fe_2O_3), and goethite (FeOOH). This is in agreement with minerals such as goethite, hematite and magnetite, reported to exist in HDS by Rakotonimaro et al. (2017). Coprecipitated Fe at pH 3 – 6, promoted transformation of ferrihydrite into Fe_2O_3 (Zinck et al. 1997, Cornell and Schwertmann 2003). Other minerals identified through XRD peaks for GypFeMnNi were calcite ($CaCO_3$) and quartz (SiO_2) shown in Appendix C; (Fig. 1; i & ii), and through scanning electron microscope (SEM), jarosite-Na ($NaFe^{III}_3(OH)_6(SO_4)_2$), presented in appendix D; (Figure 1; d).

There was evidence of an amorphous structure in the GypFeMnNi, evident through the SEM imaging technique that was dominated by Mg, but also contained Ca, Mn and Fe (Appendix D; Fig. 1; b & d). Some of the amorphous structures were dominated by Fe and O (suggesting the existence of ferrihydrite), while some were dominated by Al, K, and O with traces of Na, S and Fe, resembling Jarosite-Na ($NaFe^{III}_3(SO_4)_2(OH)_6$). This can be seen in Appendix D; (Fig. 1; d). Zinck et al. (1997) also found that the amorphous phases of fresh HDS from a coal mine water incorporated Al, O, Ca, SO_4^{2-} Fe, Cu, Si, Mg, Mn and Na. The other sludges, GypFeMn (Appendix C; Figure 2, i & ii), GypB (Appendix C; Figure 3, i & ii) and Gyp (Appendix C; Figure 4, i & ii), in addition to their major fractions composed of $CaSO_4.2H_2O$, showed minor components of $CaCO_3$, SiO_2 and brucite ($Mg(OH)_2$). This is also presented in Appendix B. No other additional minerals were identified through the use of diffractogram peaks (Appendix C; Figures 1-4; i & ii).

Before and after the aqueous solubility test, all the sludges were dominated by gypsum (Appendix B), and according to Aubé and Lee (2015) the only actual crystals often identified in fresh HDS are calcite and gypsum. Deionized water could not completely solubilize $CaSO_4.2H_2O$ in all the products (Appendix C; Figures 1-4; iii & iv), possibly because of protection / armouring by iron oxides (Appendix D; Figure 1; e & f show some evidence of armouring). Also water could not completely facilitate the dissolution of $Ca(Fe,Mg,Mn)(CO_3)_2$ and SiO_2 (as latter, SiO_2 is not water soluble) in the sludge GypFeMnNi, but all other minerals were below detection limits (Appendix B). Diluting HCl to pH 4 facilitated complete dissolution of $Ca(Fe,Mg,Mn)(CO_3)_2$ in GypFeMnNi, and only $CaSO_4.2H_2O$ and SiO_2 were retained. The SiO_2 in GypFeMnNi, as determined by SEM-EDS (Appendix D; Fig. 1; d), is detrital in origin (Zinck et al. 1997), suggesting that it was formed from rock fragments. Similarly, for the sludges, GypFeMn, GypB and Gyp, gypsum was also not completely dissolved even with diluted HCl at pH 4 (Appendix B, Appendix C; Fig. 1-4; v & vi). $CaCO_3$ also remained intact after extraction with deionized water and diluted HCl at pH 4, possibly protected by iron oxides through armouring (Appendix D; Fig. 1; e & f).

4.3.2 Acid-base chemistry of sludges

GypFeMn, GypB and Gyp exhibited alkaline pH values of 8.2, 9.4 and 9.5 and total alkalinity exhibiting $CaCO_3$ equivalents (CCE) of 510, 601 and 617 mg kg^{-1}. This was expected, because the $Ca(OH)_2$ used in the process was capable of increasing the AMD solution pH to > 9 (Skousen 2014). The sludge GypFeMnNi showed an acidic pH of 5.5 and total alkalinity with CCE of 250 mg kg^{-1}. All the materials have the potential to reduce soil acidity if used as soil amendments due to the alkalinity possessed. The pH value for GypFeMnNi (5.5) was substantially lower than 8.2 reported by Zinck et al. (1997) for a fresh HDS sourced from a coal mine in Canada, while those of GypB and Gyp were substantially higher. There is a possibility that these authors reported a pH value of a sample collected from a process that uses $Ca(OH)_2$, since this pH value is similar to that of GypFeMn of 8.2. The pH 5.5 for the GypFeMnNi can be expected to increase with time if the material could be stored to allow chemical reactions to reach equilibrium. This can only occur in the absence of Fe(II) which is prone to oxidation in the material.

4.3.3 Total elemental content of GypFeMnNi, GypFeMn, GypB and Gyp Using X-Ray Fluorescence (XRF)

As expected, total elemental content showed that Ca and S were major components in all four sludges, but GypFeMn included Mg which was relatively abundant (Table 4.1). Each sludge had statistically different ($\alpha < 0.05$) concentrations for Ca, Mg and S (Table 4.1). All the materials can be potential sources of these elements if used as soil amendments. These are considered essential macronutrients, required in large quantities for plant growth, but are often deficient in acidic soils. The Ca can be traced back to the liming material used in the treatment process and the sulphur from the AMD. The Mg was also likely from the liming material used to treat AMD. Amongst the trace elements, Fe was the most abundant in all the materials, followed by Mn, which were statistically different ($\alpha < 0.05$) for each of the sludges (Table 4.1). All sludges also contained Zn, but in low concentrations, and as such, these materials cannot be regarded as important sources of this element. It is therefore evident that all these sludges are potential sources of essential trace elements (Fe, Mn, Zn), required by plants in small quantities. The availability of these elements for plant uptake is covered in chapters 8 and 9. The materials, GypFeMnNi, GypFeMn and GypB also had traces of Ni. The materials GypFeMn, GypB and Gyp from a single source of AMD and generated from different stages of the treatment process contained traces of Pb and Ni (metals of environmental concern). However, the solubility of Pb could be low in these materials, since they were generated by the process that uses a combination of limestone and hydrated lime. Therefore, Pb could exist in insoluble forms and this is investigated in chapter 10. The Pb could be a signature of the treatment process, since this element was below method detection limit (MDL) in GypFeMnNi (Appendix A). Cadmium was below MDL of 0.18 mg kg^{-1} in all the sludges irrespective of the treatment process.

When compared to similar materials, these sludges seem to have more value as soil amendments than sludges sourced from a coal mine in Canada, as reported by Zinck et al. (1997). Calcium content ranged from 18 to 23.7% in all the sludges investigated in this study, which is slightly higher than the Ca content (14%) reported by Zinck et al. (1997). The sludges in this study also appear to be better sources of Fe than those reported by Zinck et al. (1997). Iron content was more concentrated in GypFeMnNi (12.5% Fe) and GypFeMn (4.2% Fe), compared to only 1.5% Fe reported by these authors in a similar HDS material. Manganese and Mg concentration in all the materials was below 3.6% and 6%, and similar results were reported by Zinck et al. (1997) in HDS sludges. The Fe and Mn can be traced back to the chemical composition of AMD.

Table 4.1: Total concentration of selected major and trace elements in HDS

Constituents	GypFeMnNi	GypFeMn	GypB	Gyp	CV (%)	α
Major elements (mmol kg^{-1})						
Ca	4565^{c}	4499^{d}	5913^{a}	5602^{b}	2	< 0.05
K	2^{b}	3^{a}	1.7^{b}	1.6^{b}	4	< 0.05
Mg	268^{c}	1946^{a}	1448^{b}	113^{d}	3	< 0.05
S	1726^{d}	1914^{c}	2666^{a}	2329^{b}	2	< 0.05
Trace elements (mmol kg^{-1})						
Cd	< 0.18	< 0.18	< 0.18	< 0.18	-	-
Fe	2229^{a}	753^{b}	12^{c}	2.7^{d}	4	< 0.05
Mn	138^{a}	118^{b}	17^{c}	1.7^{d}	3	< 0.05
Ni	2^{a}	2^{b}	0.04^{c}	< 0.01	5	< 0.05
Pb	< 0.2	1^{a}	0.8^{a}	0.2^{b}	6	< 0.05
Zn	4^{b}	5^{a}	0.1^{c}	0.08^{c}	4	< 0.05

Note: GypFeMnNi = Ferriferous Gypseous with Mn and Ni; GypFeMn = Ferriferous Gypseous with Mn; GypB = Gypseous with brucite; Gyp = Gypseous. Any value with < sign in front represents the method detection limit (MDL) for that element. Means of the same letter across HDS products are not significantly different from each other.

4.3.4 Aqueous solubility of sludges using deionized H_2O

Successive extraction with water for a total of 5 weeks (once a week) showed that amongst major elements, S was the most soluble followed by Ca, Mg and K in descending order in all the sludges (Table 4.2). Statistically, the solubility of Mg was significantly different ($\alpha < 0.05$) across the sludges (Table 4.2). Relative to total concentrations, water in GypFeMnNi, GypFeMn, GypB and Gyp extracted 99.8, 77, 62 and 66% of S. With Ca, water extracted 22, 31, 28, 29% of this element from GypFeMnNi, GypFeMn, GypB and Gyp. The abundance of especially S extracted, was an indication that it resided mostly in gypsum which is water soluble. This showed that both materials could supply S in abundance if used as soil amendments and when in contact with water. However, the reduction in the extraction of Ca was not expected, and this was possibly influenced by armouring of gypsum by iron oxides (Appendix D). Relative to total concentration, water extracted 14, 38.4, 11 and 53% of the Mg from GypFeMnNi, GypFeMn, GypB and Gyp. When considering solubility of trace elements, Mn was the most extracted by water, followed by Zn in GypFeMnNi. Manganese release from this material was extremely low, suggesting that this element already existed as Mn(II). This showed that both Mn and Zn existed in soluble forms in this material which is expected, because it was generated by the limestone treatment process. All other trace elements were BDL in all four sludges. The supply of Mn and Zn could be beneficial if this material is used as a soil amendment. Iron in GypFeMnNi and GypFeMn existed in forms that were less soluble, yet both sludges had high concentrations of this element. XRD evidence showed that Fe occurred as Fe oxides and these oxides are sparingly soluble under circum-neutral conditions (Maree et al. 2004). Anions were released as follows; SO_4^{2-} > Cl^- > NO_3^- > F^- from all the sludges by successive solubility with water using dialysis tubes. Sulphate release was statistically different ($\alpha < 0.05$) across the sludges (Table 4.2).

Table 4.2: Selected water-soluble elements in the sludges (cumulative of 5 water extractions)

Constituents	GypFeMnNi	GypFeMn	GypB	Gyp	CV (%)	α
Major elements released (mmol kg^{-1})						
Ca	984^c	1378^b	1681^a	1643^{ba}	10	< 0.05
K	0.6^c	2.3^a	1.6^b	0.8^c	13	< 0.05
Mg	103^c	268^a	154^b	60^d	9	< 0.05
S	1723^a	1474^a	1650^a	1539^a	8	< 0.05
Minor elements released (mmol kg^{-1})						
Cd	< 0.04	< 0.04	< 0.04	< 0.04	-	-
Fe	< 0.2	< 0.2	< 0.2	< 0.2	-	-
Mn	7^a	< 0.01	< 0.01	< 0.01	10	< 0.05
Ni	< 0.3	< 0.3	< 0.3	< 0.3	-	-
Pb	< 0.04	< 0.04	< 0.04	< 0.04	-	-
Zn	0.09^a	< 0.03	< 0.03	< 0.03	6	< 0.05
Anions released (mmol kg^{-1}) by first extraction						
Cl^-	1.6^a	1.4^a	1.3^a	1.4^a	16	< 0.05
F^-	< 0.1	0.1^a	< 0.1	< 0.1	-	< 0.05
NO_3^-	0.2^b	1.1^a	0.2^b	0.2^b	22	< 0.05
SO_4^{2-}	296^c	31^d	303^b	314^a	25	< 0.05

Note: GypFeMnNi = Ferriferous Gypseous with Mn and Ni; GypFeMn = Ferriferous Gypseous with Mn; GypB = Gypseous with brucite; Gyp = Gypseous. Any value with < sign in front represents method detection limit (MDL) for that element. Means of the same letter across HDS products are not significantly different from each other.

4.3.5 Solubility of sludges with diluted acid at pH4

Proton promoted dissolution on successive extractions of the sludges on a mmol basis released S the most, followed by Ca, Mg and K in descending order (Table 4.3). Statistically, solubilities for K and Mg were significantly different ($\alpha < 0.05$) across the sludges (Table 4.3). Relative to total concentration, S was released mostly from GypFeMnNi than from any other sludge, where 36% of this element was extracted. The pH of the GypFeMn sludge (8.2), was reduced by 1.6 units, facilitating the release of elements from this material. However, at this pH (6.6) the dissolution of Fe oxides was negligible, since it was still above pH 4, known to facilitate the dissolution of these minerals. Relative to total concentration, Ca (6.7%) was also extracted mostly from GypFeMnNi than in any other sludge; Mg and K were released mostly from GypFeMn. The reason why there were minimal differences in Ca content across the materials was that the solutions were saturated with gypsum. Generally, the diluted acid (pH 4) extracted less Ca and S compared to extraction by deionised water. The pH values of extracts from diluted acid extraction ranged from 6.6 to 10.4 while those from deionised water extraction ranged from 5.7 to 10.7 due to the alkalinity in the sludges. For both extractants, all materials were extracted with a total of 2.5 L. Solubility of trace elements showed that Mn was the most released element from GypFeMnNi and GpFeMn. With GypFeMnNi, relative to total concentration, 6.5% of the Mn was extracted, followed by Fe and Zn. All other elements were BDL. The low pH (5.5) in GypFeMnNi and that of the extracting solution (pH 4) facilitated dissolution and extraction of these elements. It could be expected therefore that most of the trace elements in sludge are likely to be soluble once in contact with more acidic conditions in the environment. It is possible that there was pH buffering due to the solid phases of $CaCO_3$ and $Mg(OH)_2$ contained in the sludges that contributed to alkalinity reducing the dissolution rate of the materials. Generally, metal solubility in HDS increases with decreasing pH below 9.5 (Zinck et al. 1997), and this is in agreement with results obtained by Maree et al. (2004) who reported that metals in HDS were more soluble at pH < 6. However, this is partly true since the oxides in which metals reside in are amphoteric. A gradual increase in the solubility of trace elements is therefore expected once the sludges come in contact with acidic solutions.

Table 4.3: Selected soluble elements extracted with diluted HCl at pH 4 (5 cumulative extractions)

Constituents	GypFeMnNi	GypFeMn	GypB	Gyp	CV (%)	α
	Major elements released (mmol kg^{-1})					
Ca	305^{a}	275^{b}	324^{a}	314^{a}	5	< 0.05
K	0.9^{c}	3^{a}	1.9^{b}	0.5^{d}	3	< 0.05
Mg	82^{c}	245^{a}	119^{b}	45^{d}	6	< 0.05
S	515^{a}	501^{a}	409^{b}	349^{c}	5	< 0.05
	Trace elements released (mmol kg^{-1})					
Cd	< 0.04	< 0.04	< 0.04	< 0.04	-	-
Fe	0.34^{a}	< 0.2	< 0.2	< 0.2	7	< 0.05
Mn	9^{a}	0.02^{b}	< 0.01	< 0.01	2	< 0.05
Ni	< 0.3	< 0.3	< 0.3	< 0.3	-	-
Pb	< 0.04	< 0.04	< 0.04	< 0.04	-	-
Zn	0.1^{a}	< 0.03	< 0.03	< 0.03	14	< 0.05

Note: GypFeMnNi = Ferriferous Gypseous with Mn and Ni; GypFeMn = Ferriferous Gypseous with Mn; GypB = Gypseous with brucite; Gyp = Gypseous. Any value with < sign in front represents method detection limit (MDL) for that element. Means of the same letter across HDS products are not significantly different from each other.

4.3.6 Leaching GypFeMnNi, GypFeMn, GypB and Gyp with the Toxicity Characteristic Leaching Procedure (TCLP)

With respect to major elements, TCLP extracted mostly S followed by Ca, from all the sludges (Table 4.4). Once again, the substantially small differences in Ca content across the materials was because the solutions were saturated with gypsum. Statistically, the release of Mg and S was significantly different ($\alpha < 0.05$) across the sludges (Table 4.4). Relative to total elemental content, TCLP extracted more S (4.1%) from GypFeMnNi than from any other sludge. Amongst the major elements, Mg was the next most extracted after Ca, followed by K for all sludges. The concentrations of these major elements extracted by TCLP were below those extracted by water and diluted acid. All sludges had all trace elements BDL except for Mn and Zn in GypFeMnNi. Relative to total elemental content, only Mn (4%) and Zn (0.2%) were extracted from this material. Again, the extraction of these metals (Mn and Zn) from GypFeMnNi was facilitated by a reduction in pH (proton promoted dissolution) and also complexation with acetate. The general decrease in the extraction of trace elements by TCLP relative to HCl at pH 4 in the sludges, was because this procedure extracts the elements at a slightly higher pH of 4.9. Unlike with successive extraction with water, the release of anions by TCLP in descending order were as follows; SO_4^{2-} > Cl^- > F^- > NO_3^- from all the sludges. It was only the release of Cl^- which was significantly different ($\alpha < 0.05$) across the sludges (Table 4.4).

Table 4.4: Selected TCLP extractable elements

Constituents	GypFeMnNi	GypFeMn	GypB	Gyp	CV (%)	α
Major elements released (mmol kg^{-1})						
Ca	16^{a}	14^{b}	14^{b}	16^{a}	6	< 0.05
K	0.25^{a}	0.12^{b}	0.3^{a}	<0.1	17	< 0.05
Mg	3^{c}	4^{b}	5^{a}	0.5^{d}	16	< 0.05
S	71^{a}	55^{c}	61^{b}	45^{d}	2	< 0.05
Trace elements extracted (mmol kg^{-1})						
Cd	< 0.04	< 0.04	< 0.04	< 0.04	-	-
Fe	< 0.02	< 0.02	< 0.02	< 0.02	-	-
Mn	5^{a}	< 0.01	< 0.01	< 0.01	4	< 0.05
Ni	< 0.3	< 0.3	< 0.3	< 0.3		
Pb	< 0.04	< 0.04	< 0.04	< 0.04		
Zn	0.06^{a}	< 0.03	< 0.03	< 0.03		< 0.05
Anions extracted (mmol kg^{-1})						
Cl^-	4^{b}	5.8^{a}	1.1^{d}	2.3^{c}	15	< 0.05
F^-	0.8^{b}	1.3^{a}	<0.2	0.8^{b}	8	< 0.05
NO_3^-	0.1^{a}	<0.1	0.03^{b}	<0.1	18	< 0.05
SO_4^{2-}	473^{ab}	367^{b}	316^{c}	595^{a}	7	< 0.05

Note: GypFeMnNi = Ferriferous Gypseous with Mn and Ni; GypFeMn = Ferriferous Gypseous with Mn; , GypB = Gypseous with brucite; Gyp = Gypseous. Any value with < sign in front represents method detection limit (MDL) for that element. Means of the same letter across HDS products are not significantly different from each other.

4.3.7 Organic chelation dissolution of sludges

Calcium and S were the major elements mostly extracted from GypFeMnNi, GypFeMn and Gyp (Table 4.5), while in GypB, Mg was the most extracted followed by S and Ca. Relative to total elemental content, NH_4OAc extracted 15, 17, 12 and 14% of the Ca from GypFeMnNi, GypFeMnNi, GypB and Gyp. The extractant, EDTA extracted 8, 17, 28 and 32% of the S from GypFeMnNi, GypFeMn, GypB and Gyp. This indicated that both Ca and S existed in soluble forms and were susceptible to organic chelation in all the materials, but the concentrations extracted were lower than those of water. Amongst the major elements, K was the least exacted from all the sludges. The sludge, GypB, proved to be an important source of Mg if used as a soil amendment, especially for acid soils where this element is often deficient. With respect to trace elements, organic chelation extracted Fe, Mn, and Zn the most in all the sludges. All other trace elements were BDL in all the sludges and this showed that these materials may be of low risk to the environment.

Table 4.5: Selected elements extractable with EDTA and NH_4OAc

Constituents	GypFeMnNi	GypFeMn	GypB	Gyp	CV (%)	α
Major elements extracted with NH_4OAc (mmol kg^{-1})						
Ca	702^{d}	771^{b}	716^{c}	812^{a}	0.8	< 0.05
K	1^{c}	2^{a}	1.7^{b}	0.4^{d}	0.7	< 0.05
Mg	31^{d}	324^{b}	1370^{a}	89^{c}	10	< 0.05
S	137^{d}	776^{a}	739^{c}	751^{b}	0.9	< 0.05
Trace elements extracted with EDTA (mmol kg^{-1})						
Cd	< 0.01	< 0.01	< 0.01	< 0.01	-	-
Fe	7^{a}	0.5^{b}	0.0004^{c}	0.7^{b}	11	< 0.05
Mn	5^{a}	3^{b}	0.05^{d}	0.4^{c}	8	< 0.05
Ni	< 0.08	< 0.08	< 0.08	< 0.08		-
Pb	< 0.01	< 0.01	< 0.01	< 0.01		-
Zn	0.4^{a}	0.3^{a}	0.0006^{d}	0.02^{c}	8	< 0.05

Note: GypFeMnNi = Ferriferous Gypseous with Mn and Ni; GypFeMn = Ferriferous Gypseous with Mn; GypB = Gypseous with brucite; Gyp = Gypseous. Any value with < sign in front represents method detection limit (MDL) for that element. Means of the same letter across HDS products are not significantly different from each other.

Considering the solubility of elements in general (Table 4.6), both major and trace elements were extracted mostly by deionised water from all the sludges. This is an indication that deionized water has the greatest potential of any extractant considered in this study, to solubilise all of the elements present in all of the sludges studied. Generally, S was the most extracted from the sludges, compared to Ca, and this could be due to armouring of gypsum in the materials by iron oxides.

Amongst trace elements, Mn was the most released from all the sludges except from Gyp which showed all trace elements BDL. The extractant, EDTA, solubilized Fe more than Mn from GypFeMnNi. This indicates that all the materials are more likely to pollute the environment with these elements if in contact with water, acidic solutions and organic chelators, as Mn and Fe are of the constituents of environmental concern in the RSA Waste Classification Guidelines (discussed in Chapter 6). Other metals of environmental concern, Cd and Pd, were below detection limits in all extractants from all four sludges.

Table 4.6: Elements most released by the different extractants in sludges

Sludge	Extractants				
	Deionized H_2O	Diluted HCl at pH 4	EDTA	NH_4OAc	TCLP
	Most extracted major elements				
GypFeMnNi	S	S	-	Ca	S
GypFeMn	S	S	S	-	S
GypB	Ca	S	S		S
Gyp	Ca	S	-	Ca	S
	Most extracted trace elements				
GypFeMnNi	Mn	Mn	Fe	-	Mn
GypFeMn	Mn	Mn	Mn	-	-
GypB	Mn	-	-	-	-
Gyp	-	-	-	-	-
	Most extracted anions				
GypFeMnNi	SO_4	-	-	-	SO_4
GypFeMn	SO_4	-	-	-	SO_4
GypB	SO_4				SO_4
Gyp	SO_4				SO_4

Note: GypFeMnNi = Ferriferous Gypseous with Mn and Ni; GypFeMn = Ferriferous Gypseous with Mn; GypB = Gypseous with brucite; Gyp = Gypseous

4.3.8 Phosphate sorption capacity of sludges

The extraction of all trace elements, including metals of environmental concern (Pb, Ni, Cd), was extremely low from all of the sludges using the different extractants. This indicates that these materials, especially GypFeMnNi and GypFeMn, contain large amounts of poorly crystalline Fe oxides. Therefore, it is logical to expect these materials to have high P sorption capacities, which may minimise environmental contamination by these metals. This was investigated by determining phosphate sorption capacity of the materials. All of the sludges indicated steep initial slopes resembling H-curve adsorption isotherms, suggesting a high affinity for phosphate (Figure 4.2). This high sorption capacity could be a result of inner-sphere surface complexation of the phosphate, or a contribution from strong van der Waals forces (Sposito 2008). GypFeMnNi, GypFeMn, GypB and Gyp showed maximum sorption capacities of 1810, 887, 887 and 236 mmol kg^{-1}. It should be noted, however, that the sludge GypFeMnNi could still had the potential sorb additional phosphate. The substantial amount of ferric and Al hydroxides, especially in GypFeMn, created specific adsorption sites for phosphate (Sposito 2008, Zinck 2006), more so than in GypFeMnNi. These results showed that all sludges have strong sorption capacities that will resist the release of phosphate even when HDS is in contact with organic chelators, acidic solutions and water in the environment. This could be a disadvantage if used as a soil amendment for the production of crops since applied P would be adsorbed.

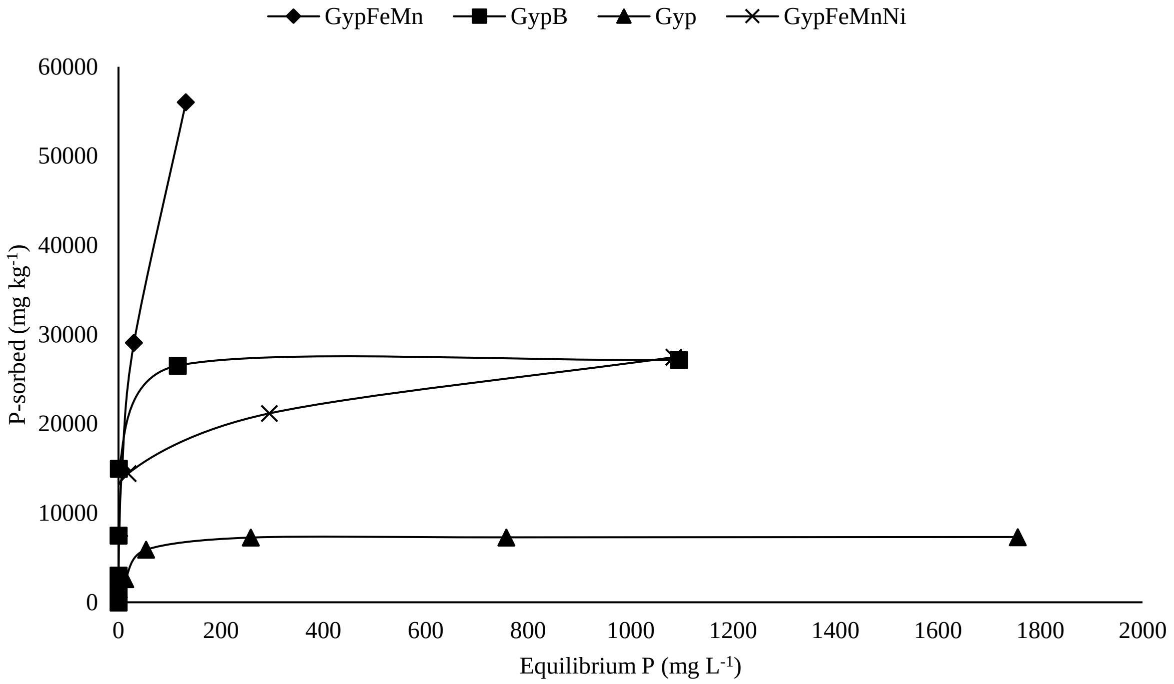


Figure 4.1: HDS phosphate sorption curves. Note: GypFeMnNi = Ferriferous Gypseous with Mn and Ni; GypFeMn = Ferriferous Gypseous with Mn, GypB = Gypseous with brucite; Gyp = Gypseous

4.4 CONCLUSIONS

The GypFeMnNi sludge was found to be slightly acidic (pH 5.5), with total alkalinity of 250 mg kg^{-1}, while the sludges GypFeMn, GypB and Gyp were alkaline with pH values of 8.2, 9.4 and 9.5 and total alkalinity values of 510, 601 and 617 mg kg^{-1}. All the materials have the potential to increase the pH of acid soils and to reduce soil acidity if used as soil amendments due to the alkalinity they possess contributed by $CaCO_3$ and $Mg(OH)_2$. Mineral status showed that all the materials were mainly composed of gypsum. They, therefore, also have the potential to be used to reclaim saline-sodic or sodic soils due to the high gypsum content. They therefore, have the potential to be used to reclaim saline-sodic or sodic soils due to the gypsum contained. In addition, GypFeMnNi and GypFeMn had substantial amounts of iron oxides that can potentially supply Fe and sorb metals of environmental concern. With total elemental content, generally S was dominant in all the sludges, followed by Ca, Mg and K in descending order. Iron was the most dominant amongst trace elements, followed by Mn in GypFeMnNi, GypFeMn and Gyp. In the other sludge, GypB, Mn was the most dominant followed by Fe. The concentration of other trace elements was extremely low. Cadmium was below detection limit in all the sludges, making them of low risk to the environment for this element.

Extractability showed that in general, both major and trace elements were extracted mostly by deionised water from all sludges. This is an indication that deionized water has the greatest potential to facilitate the solubility of all the elements in all of the gypseous materials than any extractant considered in this study. Generally, S was the most extracted from the sludges and the reduction in Ca extraction compared to S on percentage bases could be due to armouring of gypsum in the materials by iron oxides. Amongst trace elements, Mn was the most released from all the sludges, except with Gyp, for which all trace elements were extremely low. The extractant, EDTA, solubilized Fe more than Mn from GypFeMnNi. Both Mn and Fe are more likely to pollute the environment if these materials come in contact with water, acidic solutions and organic chelators. Manganese is part of the constituents of environmental concern in the RSA Waste Classification Guidelines. Other metals of environmental concern, Cd and Pb, were below detection limits with all extractants for all the sludges considered. All of the materials have the potential to sorb phosphate, with GypFeMnNi, GypFeMn, GypB and Gyp showing maximum phosphate sorption capacities of 1810, 887, 887 and 236 mmol kg^{-1}. Therefore, these results portrayed all sludges considered in this study as potentially safe materials to the environment, and in addition, have the potential to be used as soil amendments. The sorption of other essential plant nutrients (e.g. K, Mg, Ca) by these materials need to be assessed in future to predict impact on plant growth if used as soil amendments.

CHAPTER 5

PHYSICAL PROPERTIES OF HIGH-DENSITY SLUDGE GENERATED BY ACID MINE DRAINAGE TREATMENT

ABSTRACT

High density sludge is a gypseous product as it is largely composed of gypsum, but its suitability for use in agriculture as a soil amendment based on physical properties has not yet been thoroughly investigated. Physical properties, such as, particle size in gypsum is important in facilitating its solubility as it is a soil amendment. The aim of this chapter therefore, was to gain a better understanding of particle size distribution of four sludges from two different treatment processes and how they compare to gypsum (a soil amendment) as these sludges are gypseous. One sludge, designated as GypFeMnNi (from limestone treatment process), and three others GypFeMn, GypB and Gyp (generated at different stages of a treatment plant that uses limestone plus hydrated lime) were considered. Particle size distribution was investigated using the Laser Diffraction and Hydrometer methods, while specific surface area (SSA) and uniformity were investigated using Sieve ASTM E11:61. Particle density was assessed using a Pycometer. Results showed GypFeMnNi to have the largest SSA (1.7 m^{2} g^{-1}) due to the high content of iron oxides which are known to have a large surface area and small particle sizes. This was followed by GypB (1.2 m^{2} g^{-1}), GypFeMn (1.1 m^{2} g^{-1}) and Gyp (0.2 m^{2} g^{-1}). GypFeMnNi and Gyp showed a wider range of particle sizes (0.4 to 906 µm) compared to those of GypB (0.5 to 250 µm) and GypFeMn (0.4 to 168 µm). Generally, particle sizes for all the HDS materials were lower than those of normal agricultural gypsum. Gyp exhibited the lowest particle density (2312 kg m^{-3}), whereas, GypFeMnNi and GypFeMn had slightly higher densities of 2354 and 2386 kg m^{-3} due to increased contents of iron oxides, which are known to have densities above 5000 kg m^{-3}.

Keywords: HDS, AMD, Particle size

5.1 INTRODUCTION

HDS materials are known to possess substantially large particle sizes attained during treatment of AMD. Mixing promotes close contact between solids and facilitates coagulation of lime particles onto the precipitates of recycled sludge (Aubé 2004). The solids from recycled sludge act as seed particles for further development of precipitates (Gan et al. 2004). According to Aubé (2004), precipitation occurs mostly on the surface of the particles of the recycled sludge, promoting densification of the particles. The material contains 15 – 70 % solids, typically with dry bulk densities of 1.05 – 1.37 g cm^{-3} (Coulton et al. 2004, McDonald et al. 2006). There is also removal of free water molecules by the HDS process, achieved by altering the structure of the existing sludge particles and by forming precipitates with fewer water molecules per particle. This results in a dewatered material with high stability (Gan et al. 2004). The resulting high stability of the material is also favoured by a high Fe to total metal ratio. During storage, particle sizes further increase due to continuous evaporation of weakly bonded water molecules and crystallization (Gan et al. 2004, Zinck and Griffith, 2006).

As such, HDS is denser than sludge generated by the conventional AMD treatment process, it is stable, and can consist of up to 70% solids content (Gan et al. 2004, Johnson and Hallberg, 2005, Zinck and Griffith 2006). In a sludge characterization study, Zinck et al. (1997) reported that HDS solid contents (for 9 different sludges) ranged from 2.4 to 32.8%, had dry bulk densities ranging from 1.9 to 3.3 g cm^{-3}, and had median particle size that ranged from 5-10 µm. The density of the material increased with an increase in solid content. However, sludges produced by conventional AMD treatment (a process that excludes recycling of sludge), tended to have extremely low solid content (1 – 4%) with a wider particle size distribution compared to HDS (Zinck et al. 1997). This could be expected because the conventional process excludes recycling of sludge. In terms of appearance, the colour of HDS depends mainly on the treatment process, metal composition and particle size.

Currently, the assessment of HDS materials from the Coal Fields of RSA in Mpumalanga as soil amendments based on physical properties, has not yet been investigated. For instance, the size of particles of a soil amendment (e.g. gypsum) is important in facilitating its solubility. High density sludge is a gypseous product which can possibly be used as a soil amendment. The aim of the study, therefore, was to investigate if gypseous material from a treatment plant that uses limestone and three others generated from three different stages of a plant that uses $CaCO_3$ plus $Ca(OH)_2$, can be used as agricultural soil amendments. This investigation was based on physical properties, mainly particle size and distribution.

5.2 MATERIALS AND METHODS

5.2.1 Sources of sludges

The same HDS products (GypFeMnNi, GypFeMn, GypB and Gyp) considered in chapter 4 were investigated for physical properties in this chapter.

5.2.2 Particle size distribution determination of sludges using the Mastersizer 2000 Laser Diffractometer and Hydrometer Sedimentation Method

Since the materials contained more than 72% gypsum (which is water soluble), for comparison purposes, particle size distribution was assessed using both a Mastersizer 2000 Laser Diffractometer and the sedimentation method (Hydrometer) (Beuselinck at al. 1998). The Hydrometer method assumes that particles are not water soluble and that silt and clay-sized particles can be dispersed. Particles disperse if they possess appreciable surface charge and non-dispersal shows inadequate surface charge. Sieves were used to separate sand sized fractions.

With the Mastersizer 2000 Laser Diffractometer (Malvern Instrument), a slurry was prepared by mixing a small quantity of each of the sludges with deionized water as a dispersant and transferred into its dispersing unit for analysis. At this point, a beam of monochromatic light with a wavelength (λ) of 750 nm was passed through the sample and particles diffracted light through a given angle. To calculate the particle size distribution, the Mie scattering principle/theory model was used (Beuselinck et al. 1998). The instrument was capable of measuring materials with particle sizes from 0.045 µm to 2000 µm (Eshel et al. 2004). In addition to the dispersants, Ultrasound/Ultrasonics was applied to the slurry to enhance dispersion of particles. The data collected was used to draw particle size distribution curves for each of the samples. The uniformity coefficient of particle sizes was calculated as follows;
Uniformity = $D_{0.6}/D_{0.1}$

Where; $D_{0.6}$ is particle diameter for which 60% of the HDS is "smaller than", and $D_{0.1}$ is particle diameter for which 10% of the material is "smaller than" (Lal and Shukla 2004). Particle density was assessed using a Pycometer (AccuPyc II 1340). A material with uniform particle sizes will have a uniformity coefficient of 1 and any coefficient exceeding or falling below 1 indicates non uniform of particle sizes.

Particle size separates were further determined using the hydrometer method as described by Kroetsch and Wang (2008), but with slight modifications. A 20 g sample was transferred into a pre-weighed 400 ml beaker (to be used later for oven drying of the sand component) and further transferred into a stainless steel mixing flask. A total of 10 ml Calgon® solution (50 g l^{-1}) that contains hexametaphosphate as a dispersing agent was added, in addition to sufficient water (to enable stirring), and mixed for 5 minutes using a stirrer Model 1G9850. This process on average dissolved approximately 4.1 g of the gypsum from the 20 g sample. After dispersion, the suspensions were transferred into a clear 2 L measuring cylinder through a 0.054 mm sieve. The cylinder had a 1000 ml mark which was at 36 ± 2 cm from the bottom. The sieve was rinsed with water to fill the cylinder to the 1000 ml mark. The particles left on the sieve were transferred back into the pre-weighed beakers and oven dried at 110 ^{o}C to determine the sand component. The cylinders were placed and left to stand in a constant temperature (25 ^{o}C) room for 6 hours 35 minutes, after which a first hydrometer reading was taken. A plunger was then used to mix the sample in the cylinder after the first reading and further left to stand for 40 seconds, after which the last hydrometer reading was taken. The readings were taken using a Standard Hydrometer ASTM E100 No. 152H-TP with Bouyoucos scale in g l^{-1}. Clay and silt -sized particles were calculated from the hydrometer readings using the Stoke's Law (Lal and Shukla 2004). The Stokes' law assumes that particles are rigid and smooth spheres, so the results are expressed as equivalent spherical diameters (Beuselinck et al. 1998).

The oven-dried samples were removed after obtaining a constant mass, reweighed and transferred into a column of pre-weighed sieves. The sieves had the following apertures; 53, 100, 250, 500 and 100 µm, the column was arranged starting with the sieve that had the smallest aperture at the bottom fitted with a pan and the top sieve covered with a lid. The column was gentle tapped on a wooden bench approximately 30 times. Each sieve was then weighed with its contents. Each sample mass was expressed as a percentage of the initial sample mass. Texture for each sludge was then determined based on the percentages of sand, silt and clay as described by Lal and Shukla (2004). The particle separates were matched against several soil textures appearing in the textural triangle.

5.2.3 Determination of water retention by the sludges (GypFeMnNi, Gyp, GypFeMn and GypB)

A total of 36.6 g of each of the sludges (replicated 3 times) was packed at a density of 1.2 g cm^{-3} in a polyethylene tube with a volume of 30.5 cm^3. The samples were placed on ceramic plates set at specific pressures of -10, -100, -500 and -1000 kPa, saturated with water and then enclosed tightly in pressure plates that were to provide the specific different pressures. After excess water stopped exuding from the pressure plates, the pressure was released and the samples removed, weighed, and oven dried at 105 ^{0}C until attainment of constant mass to determine water content at different pressures (Lal and Shukla (2004).

5.3 RESULTS AND DISCUSSION

5.3.1 Particle size range, specific surface area and uniformity of sludges

The material, GypFeMnNi, had the largest (1.7 m^2 g^{-1}) specific surface area (SSA), followed by GypB (1.2 m^2 g^{-1}), GypFeMn (1.1 m^2 g^{-1}) and Gyp (0.2 m^2 g^{-1}) (Table 5.1). This property (SSA) of the material increased with an increase in the content of iron oxides. Iron oxides are known to have a high surface area due to small/fine particle sizes. For instance, ferrihydrite has a surface area of 600 m^2 g^{-1} (Schwertmann and Cornell 2000). The increase in surface area due to iron oxides can increase chemical reactivity in the soil if used as a soil amendment. Hence, increasing gypsum reduced SSA of the materials; GypB, GypFeMn and Gyp had more than 90% gypsum, whereas, GypFeMnNi had only 72 to 77%. The material, Gyp, had the smallest SSA due to its large particle sizes. This variation in SSA of the sludges was due to differences in particle size distribution (Figure 5.1), and possibly differences in the mineralogy of the materials (Ersahin et al. 2006). Surface area is an important property, as it is approximately proportional to; surface chemical reactions that could occur within the material and in the soil when added as a soil amendment, cation exchange capacity (CEC) and to the dissolution rates of minerals (Sposito 2004 and Ersahin et al. 2006). Basically, reactivity in the soil is a function of surface area and solubility. Based on uniformity coefficients, non of the sludges had uniform particle sizes. The uniformity coefficients for GypFeMnNi (3.9), GypB (1.5) and GypFeMn (2.2) exceeded 1 (for a material with uniform particle sizes) indicating polydisperse particle sizes (Table 5.1). While, the uniformity coefficient for Gyp (0.6) was below 1 indicating monodisperse particle sizes (Hillel 1998, Nimmo 2004, Lal and Shukla 2004).

Table 5.1: Particle size, surface area, particle density and uniformity of sludges

Sludge	Particle size range (µm)	SSA (m^2 g^{-1})	Uniformity	Particle Density (kg m^{-3})	$D_{0.1}$ (µm)	$D_{0.5}$ (µm)	$D_{0.9}$ (µm)
GypFeMnNi	0.4 – 906	1.7	3.9	2354	1.1	8.3	92
GypFeMn	0.4 – 168	1.1	1.5	2386	2.8	12.8	69
GypB	0.5 – 250	1.2	2.2	2313	1.8	11.5	84
Gyp	0.5 – 906	0.2	0.6	2312	46	109	234

Note: SSA = Specific Surface Area; $D_{0.1}$ = size of particle below which 10% of sample lies; $D_{0.5}$ = Median particle size, $D_{0.9}$ = size of particle below which 90% of sample lies. Note: GypFeMnNi = Ferriferous Gypseous with Mn and Ni; Gyp = Gypseous; GypFeMn = Ferriferous Gypseous with Mn; GypB = Gypseous with Brucite

The materials, GypFeMnNi and Gyp showed wider particle size distribution ranges of 0.40 – 906 and 0.54 - 906 µm, whereas GypB, and GypFeMn had narrower particle size distribution ranges of 0.49 – 250 and 0.40 – 168 µm respectively (Table 5.1). All of these particle sizes meet DAFF (2012) fertilizer regulations, which state that amendments containing mainly Ca, Mg and S, should have at least 90% of their particles pass through a 2 mm sieve. In addition, these materials are also soluble, as they are largely made up of gypsum. However, the upper limits of these ranges (for the studied materials) far exceed what is expected for typical AMD neutralization sludges. Beauchemin et al. (2010) reported that such sludges have extremely fine grains that rarely exceed 10 µm, but this value was comparable to what Rakotonimaro et al. (2017) reported for HDS. All the gypseous materials investigated here had finer particle size fractions compared to agricultural gypsum that has been reported by Bulletin 945 (2011) to have all particles (100%) exceeding 250 µm. Amongst the materials studied, Gyp had larger particle sizes compared to the other materials; at 10% ($D_{0.1}$) particles were < 46 µm; the median, at 50% ($D_{0.5}$), were < 109 µm, and at 90% ($D_{0.9}$) particles were < 234 µm (Table 5.1, Fig. 5.1 C). Compared to gypsum (crude crushed) reported by Wang et al. (2017) that had particles; at $D_{0.1}$ (11 µm), $D_{0.5}$ (296 µm) and $D_{0.9}$ (653 µm) all the sludges (GypFeMnNi, GypFeMn, GypB and Gyp) had smaller particle sizes (Table 5.1). But Gyp had its particle sizes at $D_{0.1}$ (46 µm) larger than that reported by Wang et al. (2017) at $D_{0.1}$ for the agricultural gypsum. The processing of gypsum for agricultural use manipulates its particle sizes. Further comparison to fine crushed agricultural gypsum; at $D_{0.1}$ (2.4 µm), $D_{0.5}$ (30 µm) and $D_{0.9}$ (112 µm) also reported by Wang et al. (2017), particle sizes for GypFeMnNi, GypFeMn and GypB at $D_{0.5}$ and $D_{0.9}$ were still lower. However, particle sizes for Gyp were slightly larger than those of fine crushed agricultural gypsum reported by Wang et al. (2017). In general, the sludges GypFeMnNi, GypFeMn and GypB have particle sizes that are comparable to particle sizes of the agricultural gypsum. According to Beauchemin et al. (2010), particle sizes of these materials are usually detrital material from calcite, quartz, pyrite, silicates and poorly-crystalline hydrated Fe phases. The shift in particle sizes towards larger sizes for Gyp was also shown by the cumulative particle size distribution curve (Fig. 5.2) and particle size distribution curves (Fig. 5.1 C & Fig. 5.3).

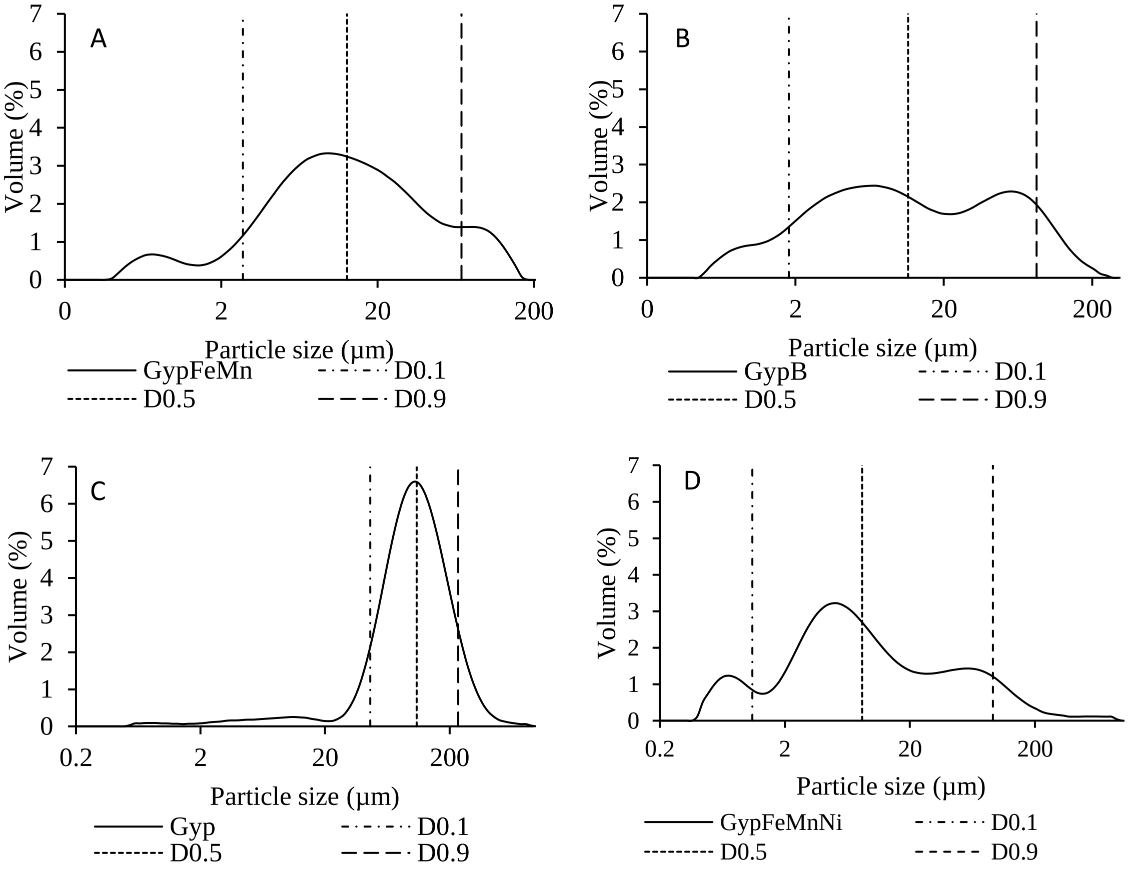


Figure 5.1: Particle size distribution with demarcations for $D_{0.1}$ (particles at 10%), $D_{0.5}$ (median particles at 50%) and $D_{0.9}$ (particles at 90%) for A) GypFeMn B) GypB, C) Gyp and C) GypFeMnNi sludge

Cumulative particle size distribution curves for all other materials indicated a shift towards smaller particle sizes (Fig. 5.2), due to higher iron oxide contents that have small/fine particles (Schwertmann and Cornell 2000). These curves were smooth and well-graded, similar to those of clay or loam soils (Hillel 1998). This indicates that if these materials are used as soil amendments, especially in sandy soils, they may be expected to increase microporosity and improve water retention (Mitrra et al. 2005). However, this may not be realised if the material dissolves, since it it largely composed of gypsum. GypFeMnNi was generally finer grained, and had the smallest particle sizes; at $D_{0.1}$ the particles were < 1.1 µm and at $D_{0.5}$ they were < 8.3 µm, but particle sizes at $D_{0.9}$ (< 92 µm; particle sizes of 10 – 19%) were greater than those of GypB (< 84 µm) and GypFeMn (< 69 µm) (Table 5.1, Fig. 5.1: A, B & D). Zinck et al. (1997) reported a $D_{0.5}$ of 42.5 µm for HDS, and this reported median is greater than those of GypFeMnNi sludge (8.3 µm), GypB (11.5 µm) and GypFeMn

(12.8 µm), but less than 109 µm for Gyp. When compared to inorganic soils, GypFeMnNi (with $D_{0.1}$ particle size < 1.1 µm) and GypB (with $D_{0.1}$ particle size < 1.8 µm) had their particle sizes falling below the clay/fine silt boundary (2 µm – clay region) (Fig. 5.3). There was a drastic shift in the $D_{0.1}$ particle size for the Gyp and GypFeMn sludges. The $D_{0.1}$ particle size for GypFeMn was < 2.8 µm, falling between 2 µm (clay/fine silt boundary) and 20 µm (fine silt/coarse silt boundary), and that of Gyp was < 46 µm, falling between the 20 µm fine silt/coarse silt boundary, and the 50 µm sand/coarse silt boundary (Fig. 5.3). The $D_{0.5}$ particle sizes for all sludges except Gyp fell between 20 and 50 µm, while that of Gyp fell above 50 µm (in the sand region). The $D_{0.9}$ particle sizes for all sludges fell in the sand region, that is, above the sand/coarse silt boundary (50 µm).

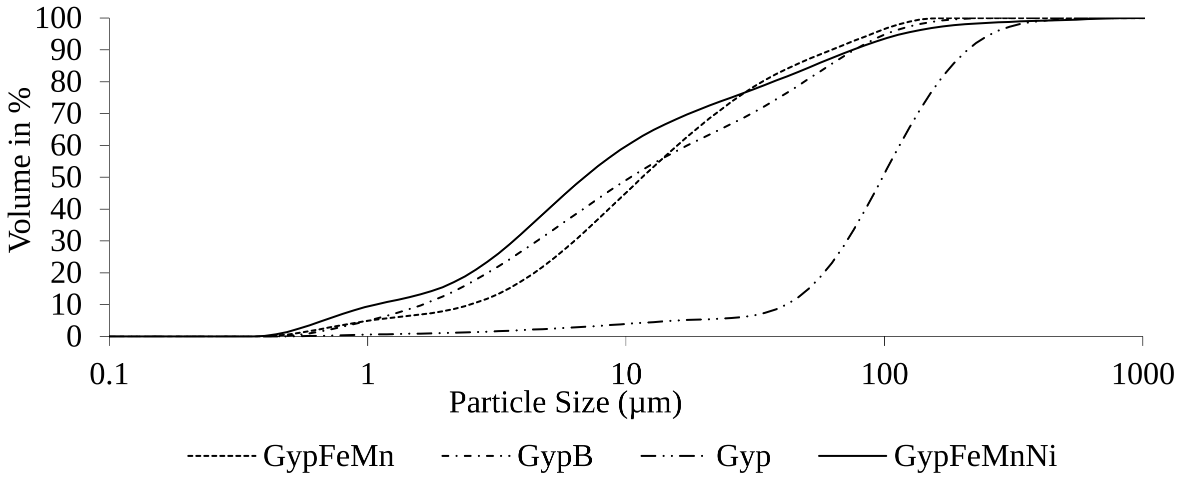


Figure 5.2: Cumulative particle size distribution curves for the sludges GypFeMn and GypFeMnNi including refined products GypB and Gyp

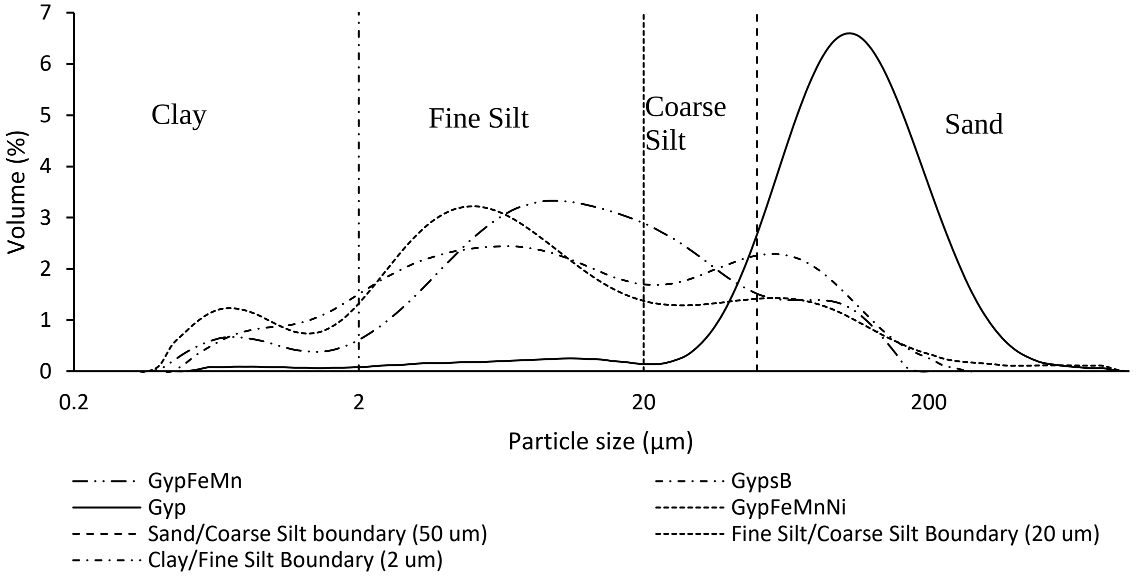


Figure 5.3: Particle size distribution and particle size boundaries for clay-, silt- and sand-sized particles

Based on the hydrometer method, statistically, the sand component in Gyp (75%) was the most dominant (as discussed) and significantly different ($\alpha < 0.05$) from any other (Fig 5.4).

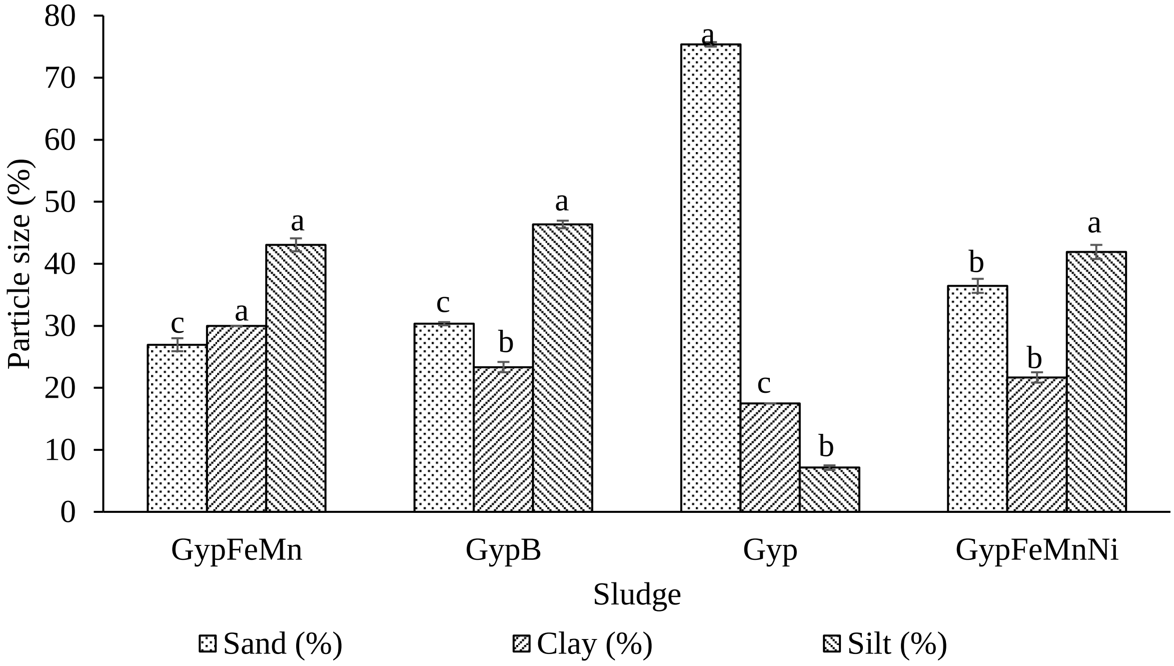


Figure 5.4: Proportions of sand-, silt- and clay sized particles for each sludge. Note: each particle component/separate was compared across the different sludges. Sand fraction: Coefficient of Variation (CV) = 3.8%, Least Significant Difference (LSD) = 4.5; Silt fraction: CV = 4.6%, LSD = 4.5; Clay (fraction): CV = 5.1%, LSD = 3.4

This indicates that applying this material as a soil amendment, especially to silty or clay soils, may increase macroporosity and improve water movement and aeration. However, this may only be possible if there is minimal solubility of this material, which is unlikely. The data generated by the hydrometer method was in line with that obtained by Laser Diffractometry, especially for Gyp in the sand fraction. This was also confirmed by a shift in the particle size distribution of this material (Gyp) towards slightly larger particle sizes (Fig. 5.1 C, 5.2 & Fig. 5.3). Sand size components of GypB and GypFeMn were not significantly different ($p > 0.05$) from each other. Silt was the least (7%) in Gyp and it was significantly different ($p < 0.05$) from any other. However, GypFeMnNi, GypB and GypFeMn had non-significantly different silt components. In Gyp, this component was the least (7%). GypFeMnNi and GypB sludges had clay components that were not significantly different ($p > 0.05$) from each other.

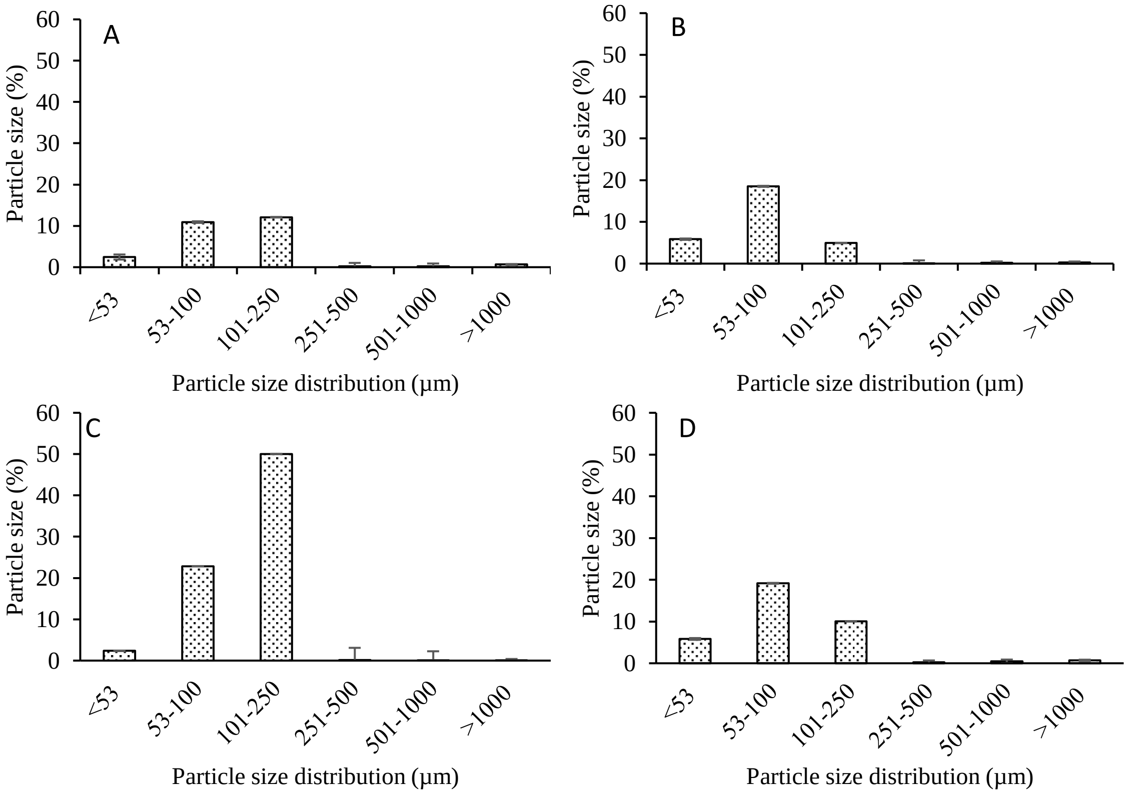


Figure 5.5: Particle size distribution for; A) GypFeMn, B) GypB, C) Gyp and D) GypFeMnNi sludges generated by the Hydrometer Method

As indicated by particle sizes at $D_{0.9}$ (Table 5.1), all sludges have substantial mass sizes falling in the sand region, with GypFeMnNi and GypB (Fig. 5.5: B & D) dominated by particles between 53 and100 µm, accounting for approximately 19%, based on mass, whereas Gyp and GypFeMn (Fig. 5.5: A & C) were dominated by particles between 101 and 250 µm. With Gyp, particle sizes on a mass basis between 101 and 250 µm accounted for 50%, and for GypFeMn this was 12%.

5.3.2 Particle density of sludges

With respect to particle densities, the sludges ranged from 2312 to 2386 kg m^{-3} and showed significant differences ($\alpha < 0.05$) (Table 5.1). These values were typical of those reported for minerals such as; Gypsum (2300 – 2470 kg m^{-3}) and Brucite (2380 – 3400 kg m^{-3}) (Eshel at al. 2004, Lal and Shukla 2004). The particle sizes of all the materials were close to the lower limit of the density range for gypsum. The overall particle densities for GypFeMnNi (2354 kg m^{-3}) and GypFeMn (2386 kg m^{-3}) were close to the 2400 kg m^{-3} reported by Zinck et al. (1997) for HDS, but densities for GypB (2313 kg m^{-3}) and Gyp (2312 kg m^{-3}) were slightly lower. GypFeMn was the only material with a significantly high particle density, with Gyp showing the lowest. The increase in particle densities of GypFeMnNi and GypFeMn was influenced by the increase in the content of iron oxides that generally have high densities, for instance Hematite has a density of 5260 kg m^{-3} (Schwertmann and Cornell 2000). The correlation (Fig. 5.6) between total concentration of Fe and particle density was weak (R^2 = 0.30).

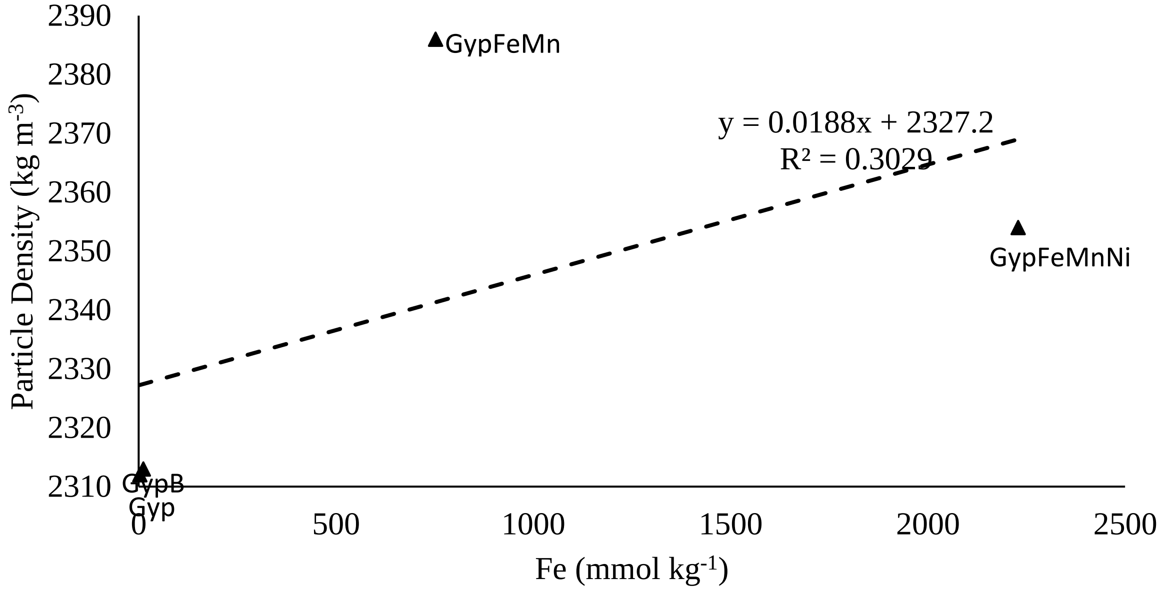


Figure 5.6: Relationship between total iron concentration in gypsum products (GypFeMnNi, GypFeMn, GypB, Gyp) and Particle Density.

5.3.3 Water retention of sludges

The relationship between water content and matric potential depends on the texture and structure of the material as it is determined by total porosity and pore size distribution (Lal and Shukla 2004). Subjecting the sludges to water potentials of -10 (close to saturation), -100, -500, and -1000 KPa drastically reduced the water content of each material (Fig. 5.7). The drastic reduction in water content was due to losses of water from pore spaces in the sludges. The water potentials from -100 to -500 KPa and from -500 to -1000 KPa could not further increase water removal from Gyp and GypFeMnNi and this water left at these potentials was hygroscopic and bonded tightly by electrostatic forces on precipitated minerals (Sposito 2008). The retention curve for Gyp indicated less water (5%) lost between -100 and -1000 KPa potentials on a mass bases, also had an extremely low water content (26%) at Field Capacity (FC), i.e., at -10 to -33 KPa (Lal and Shukla 2004).

Contrary to the retention curve of Gyp, the retention curve for GypFeMn resembled that of a clay loam/heavy textured soil, as indicated by the 22% water lost between -10 and -1000 KPa matric potential. It also had 50 % gravimetric water content at FC, and 28% water content at -1000 KPa. Water contents at FC were 39 and 42% for GypB and GypFeMnNi. At a water potential of -1000 KPa, these sludges had 21 and 22% mass water contents.

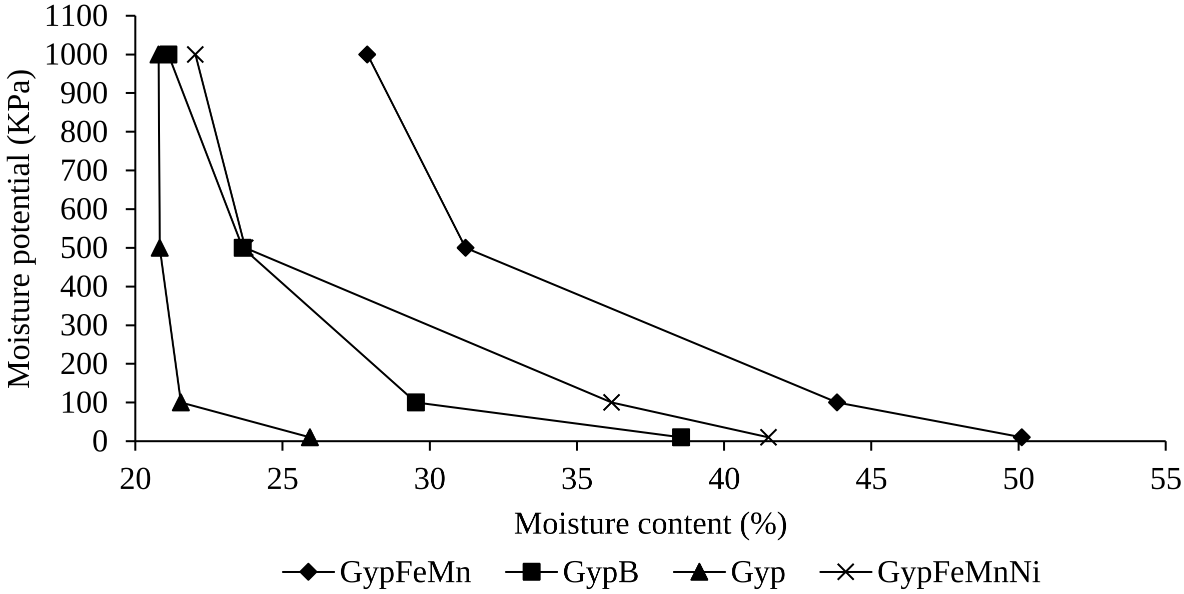


Figure 5.7: Water characteristic curves. Note: GypFeMnNi = Ferriferous Gypseous; Gyp = Gypseous; GypFeMn = Ferriferous Gypseous with Mn; GypB = Gypseous with Brucite

5.4 CONCLUSIONS

The focus was on evaluating GypFeMnNi, GypFeMn, GypB and Gyp as soil amendments based on physical properties. GypFeMn and GypB showed narrower ranges of particle sizes; 0.4 – 168 and 0.5 – 250 µm, whereas GypFeMnNi and Gyp showed a wider range of 0.4 – 906 µm. Generally, these particle sizes for all the materials were lower than those of agricultural gypsum. The material Gyp was dominated by sand sized particles (75 %), and if used as a soil amendment, it may be expected to increase macroporosity and improve water movement, especially in clay or silty soils. All the other materials may be expected to increase microporosity and water holding capacity of sandy soils. However, this may not be possible since the material is largely made up of gypsum, which is known to be water soluble. All the materials had particle densities close to the lower limit of the particle density range expected for gypsum of (2300 – 2470 kg m^{-3}). However, Gyp had the lowest particle density (2312 kg m^{-3}) whereas those of GypFeMnNi and GypFeMn were slightly higher, 2354 and 2386 kg m^{-3} due to high content of iron oxides known to have densities of > 5000 kg m^{-3}. Future research should focus on whether these materials can improve soil physical properties, e.g. soil structure if used as soil amendments.

CHAPTER 6

THE HAZARDOUS STATUS OF HIGH DENSITY SLUDGE FROM ACID MINE DRAINAGE NEUTRALIZATION

ABSTRACT

Classification of waste is an essential part of waste management to limit potential environmental pollution; however, global systems differ. The objective was to investigate selected international systems for waste classification of high density sludge (HDS) from acid mine drainage (AMD) treatment. Three sludges from two limestone treatment plants and three others from a limestone and hydrated lime treatment plant from the Mpumalanga Coalfields of the Republic of South Africa (RSA) were evaluated. Waste classification systems for the RSA, Australia, Canada, China, and the United States Environmental Protection Agency (USEPA) were considered. The USEPA system rated all six sludges non-hazardous, and the Canadian and Chinese systems allocated a hazardous status to a sludge from one of the limestone treatment plants based on Ni solubility. The RSA system considered two of the three sludges from limestone treatment plants to be higher risk materials than did the other countries. This was due mainly to the RSA system's inclusion of Mn and the use of appreciably lower minimum soluble levels for As, Cd, Pb, Hg and Se. None use of limestone plus hydrated lime during AMD treatment resulted in higher soluble Mn. Minimum leachable concentration thresholds for Cd, Hg, Pb, As and Se in the RSA system were below method detection limits for Toxicity Characteristic Leaching Procedure (TCLP) extracts, making the guidelines impractical, and revision is advised. It is apparent that HDS is more likely to be classified as hazardous waste if AMD is only subjected to limestone treatment because of increased solubility of trace elements.

Keywords: waste; classification; AMD; HDS; TCLP

6.1 INTRODUCTION

Neutralization of acid mine drainage (AMD) with hydrated lime ($Ca(OH)_2$) or limestone ($CaCO_3$) through conventional processes generates an inorganic solid, semi-solid or liquid waste referred to as sludge (Demers et al. 2017, Wang et al. 2009). If the sludge is recycled and mixed with hydrated lime or limestone prior to AMD addition, high density sludge (HDS) is generated (Zinck et al. 1997, Aubé and Zinck 1999, Kalin et al. 2006, Zinck 2006 and Chen et al. 2015). Acid mine drainage is a mine impacted solution generated by the exposure of sulphide minerals (e.g., pyrite–FeS_2) to water, oxygen, and catalytic bacteria (*Thiobacillus ferrooxidans)* (De Almeida et al. 2015, Yamal 2015, Li and Ji 2017). The solution can be extremely acidic (pH 2.0 to 4.0) and contains transition metals and metalloids which can be toxic to the receiving environment. The treatment of AMD is therefore needed to neutralize its acidity and remove/precipitate these metals and metalloids from solution, often as hydroxides, by raising the pH to >10.5. The by-product (HDS), consists of gypsum ($CaSO_4 \cdot 2H_2O$) and iron oxides (Demers et al. 2017 and Mackie and Walsh 2015). There are other processes focused on limiting pollution and environmental risk that also generate gypsum, for example, the flue gas desulfurization (FGD) process aimed at controlling sulphur dioxide (SO_2) emissions during the combustion of fuel fossils. Flue gas desulfurization facilitates dewatering of the sludge generated and encourages gypsum crystallization (Karatza et al. 2010 and Wang et al. 2012). However, what makes HDS different is the appreciable iron oxide content, and transition metals are often partitioned with the iron oxide fraction.

High density sludge solid content ranges from 15 to 70% (with dry bulk densities of 1050–1370 kg m^{-3}), compared to lower solids for sludges from conventional methods (Aubé and Zinck 1999 and Günther et al. 2003). The higher density is obtained through the recycling of sludge which promotes the precipitation of more solids by providing surfaces for heterogeneous nucleation (which catalyze precipitation) (Aubé and Zinck 1999 and McDonald and Webb 2006). This concentration of solids can unintentionally increase the risk of HDS being classified as hazardous waste, because of high content and/or solubility of some of its constituents (e.g., Ni, Mn, Hg, Pb, Se, As) (Zinck et al. 1997, Zinck 2006, O'Kelly 2005).

Large volumes of HDS are generated daily, and often stored in disposal facilities (Zinck 2006 and Maree et al. 2004). Maree et al. (2004) point out that an estimated 20 tons of HDS is produced from each megaliter of AMD neutralized. For the coalfields of Mpumalanga, a discharge of 360 ML day^{-1} AMD is predicted (Kalin et al. 2006, Anglo American thermal coal 2015, Department of Water Affairs 2013, Annandale et al. 2006, Sheoran and Sheoran 2006, Chandra and Garson 2010), translating to 7200 tons of HDS per day. If all this HDS is to be considered hazardous, this would have enormous logistical, cost, and environmental implications for operating mines and the government. An opportunity may be missed if the product is of some use to agriculture or industries.

Assessment of the risk HDS poses to the environment (soils, ground, and surface water) and to human health is critical. Risk assessment often includes various steps, for example, hazard identification, dose-response assessment, exposure assessment, and risk characterization (Bortonea et al. 2015 and Tepanosyan et al. 2017). However, this study focuses on waste classification, an important part of a risk assessment where the elemental make-up and solubility of the elements in the waste are determining. In general, waste classification systems are based on the solubility of specific constituents (Wen et al. 2014, Lucier and Gareau 2016). The chemical composition of the waste depends on the chemistry of the AMD neutralized and the efficiency of the neutralization process (Kalin 2006, Zinck 2006, Johnson and Hallberg 2005).

The aim of the study was to investigate the waste classification of selected high density sludges from neutralized AMD in the Mpumalanga Coal Fields of South Africa, using the local classification system and those of Australia, Canada (Ontario and Manitoba, British Columbia and Alberta), China, and the United States of America (USEPA). This was undertaken to ascertain if South African guidelines are perhaps too conservative, or indeed, too lenient.

6.2 MATERIALS AND METHODS

6.2.1 Generation of HDS by Limestone Sites 1 and 2

This discussion facilitates understanding of the source and characteristics of the sludges from Limestone Sites 1 and 2 (Table 6.1). The process generating HDS from two similar plants using $CaCO_3$ treatment alone, involves a single stage process. The process begins with mixing $CaCO_3$ (dissolved in water) in a separate mixing tank/compartment with a portion of the recycled sludge from the clarifier or solids/liquid separation compartment. The mixture is then transferred into the neutralization and oxidation reactor where AMD is introduced. The solution is rapidly mixed to encourage oxidation of metals, raising the pH to >5. This pH facilitates precipitation of $CaSO_4{\cdot}2H_2O$, iron oxides and various other metal oxides and hydroxides. From the reactor, the solution flows into the clarifier where solid/water separation is facilitated by addition of flocculants. Part of the sludge that is produced (designated GypFeMnNi to represent an Fe rich gypsum), is recycled back to the mixing tank/chamber and the remainder is transferred to a storage facility (Aubé and Zinck 1999, Günther et al. 2003 and Maree et al. 2004).

6.2.2 Generation of HDS by Limestone plus Hydrated Lime process

The generation of the different sludges from the plant/site using $CaCO_3$ plus $Ca(OH)_2$ begins with the introduction of acid water emanating from coal mines and the process consists of three stages. Stage 1 involves neutralization of AMD with $CaCO_3$ and $Ca(OH)_2$ in an aerated reactor, where the pH is increased to about 9.5. This high pH facilitates the precipitation of metals and including those of Fe and Mn as oxides. The solution overflows at the end of the reactors into clarifiers for solid/liquid separation; the circum-neutral mine water feeds to green sand filters for further removal of solids. Part of the sludge generated (designated as GypFeMn to represent an Fe and Mn rich gypsum product) from the clarifier, is recycled back to the reactors to enhance densification of the sludge and the other portion is transferred into storage tanks. From the filters the solution passes through self-cleaning strainers to remove coarse and finer particles, the solution is then passed through ultra-filtration membranes (reverse osmosis pretreatment) to a storage tank. From this point the solution is pumped through reverse osmosis membranes, where desalinization occurs producing a permeate and reject water of low total dissolved solids (TDS < 200 mg L^{-1}). The permeate is transferred to limestone saturators to raise its pH and the reject water proceeds to Stages 2 and 3 underflows (Hutton et al. 2009 and Steele 2010).

Stages 2 and 3 underflow treatment involves neutralization of rejected solution with $Ca(OH)_2$ in reactor where the pH is raised to 10.5, encouraging the precipitation of magnesium hydroxide ($Mg(OH)_2$). The solution is then pumped through hydro-cyclones that separate solids into fine and coarse particles. The coarse fraction contains approximately 98% pure gypsum (designated as Gyp). Part of this material is recycled back to the reactor and the rest is transferred into a gypsum pond. From the reactor the solution overflows into a clarifier and follows the same steps as in Stage 1, the reject water proceeds to the stages 2 and 3 fines treatment process (Hutton et al. 2009 and Steele 2010).

The fines treatment process for stages 2 and 3 is the same process whereby the coarse fraction (underflow) is produced. The fines are produced when the solution is pumped through hydro-cyclones separating them from coarser particles. The separated fine fraction contains approximately 90% $CaSO_4 \cdot 2H_2O$ and 10% $Mg(OH)_2$ (designated as GypB to represent gypsum with brucite). Most of this material is recycled back into the reactor and the rest transferred into a storage facility. From the clarifier the solution follows the same steps as in stage 1, some of the rejected water is transferred back to reactors and some to the brine pond (Hutton et al. 2009 and Steele 2010).

It is important to note that the focus of HDS plants is on the quality of water required by a third party with an offtake agreement and not on ensuring that the HDS produced is of a particular quality. There are no plant specific or international criteria followed to ensure quality of generated sludge.

In light of the focus on the quality of water discharged, HDS plants use natural mined limestone from nearby sedimentary sources and avoid using alkaline industrial byproducts as limestone or hydrated lime substitutes.

6.2.3. Chemical characterization of HDS products

To achieve the objectives, total concentrations (TC) determined using X-Ray fluorescence (XRF) and leachable concentrations (LC) determined using Toxicity Characteristic Leaching Procedure (TCLP-1311) for HDS products (inorganic solid wastes) were obtained from literature and from collieries in the South African Coalfields, Mpumalanga Province, eMalahleni (Witbank) (Table 6.1). Data for Limestone–Site 1, an HDS plant that uses limestone alone to treat AMD, was obtained from our own chemical characterization undertaken at the University of Pretoria. Data for Limestone–Site 2, an HDS plant that also uses just limestone to treat AMD, was obtained from a South African Water Research Commission (WRC) report (Johnson and Hallberg 2005). The data for the Limestone ($CaCO_3$) plus hydrated Lime ($Ca(OH)_2$) treatment facility was obtained from Anglo American Thermal Coal (2015).

Table 6.1: Sources of data used for HDS.

Site	**HDS**	**Sludge Characterization**	**Sources of Data**
[1] Limestone ($CaCO_3$)–Site 1	GypFeMnNi	HDS–Mainly Gypsum with Fe oxides (own characterization)	This study
[2] Limestone ($CaCO_3$)–Site 2	GypFeNi	HDS–Mainly Gypsum with Fe oxides, high environmental risk, deposited in a lined pond to prevent leaching of metals	(Maree et al. 2004)
	GypFe	HDS–Mainly Gypsum with Fe oxides, low environmental risk, deposited in a large area, leaching not a concern	
Limestone ($CaCO_3$) plus hydrated Lime ($Ca(OH)_2$) Site	GypFeMn	HDS–Mainly Gypsum with Fe & Mn oxides	(Anglo American Thermal Coal 2015)
	GypB	HDS (Fine textured)–90% Gypsum and 10% Brucite ($Mg(OH)_2$)	
	Gyp	HDS (Coarse textured)–approximately 98% Gypsum	

[1,2] Limestones Sites 1 and 2 are HDS Plants/Processes that use limestone alone to treat AMD.

6.2.4. HDS sample collection from Limestone–Site 1 Plant

Samples were sourced in May 2016 from this site that neutralizes AMD using $CaCO_3$ (Günther et al. 2003). Three representative HDS samples were collected directly from the disposal pipe into the storage facility.

6.2.5 Total elemental analyses of HDS from Limestone–Site 1 using X-ray Fluorescence (XRF)

Total elemental content was determined using an ARL 9400XP+ Wavelength Dispersive XRF Spectrometer (Manufactured by XOS^{R}, New York, NY, USA) as described by Loubser and Verryn (2008).

6.2.6 Solubility assessment of HDS from Limestone–Site 1 using the USEPA TCLP-1311 Procedure

The Toxicity Characteristic Leaching Procedure (TCLP 1311): from the Solid Waste Manual 846 (SW-846), used by the US Environmental Protection Agency (USEPA) (1992) to assess the solubility of elements in solid wastes, was used in this study.

6.2.7 Regulatory guidelines used to assess HDS

The various hazardous waste classification systems (as discussed in chapter 2) were the "instruments" of this study. This section attempts to give a brief overview of the basic principles the various systems are based on. The following classification systems were considered: The Republic of South Africa (RSA) Guideline; Australian (New South Wales) Guidelines; The United States of America (USEPA) Guidelines; as well as the Chinese and Canadian (Alberta, British Columbia, Ontario and Manitoba) Guidelines. In the results and discussion section, their respective criteria are used to classify the six HDS products considered.

6.2.7.1 Systems using total and soluble concentrations to classify wastes

Republic of South Africa (RSA) Guidelines

The RSA guidelines consider 20 constituents, with 6 of them (Mn, Sb, V, Cl, SO_4, NO_3) appearing only in this system (National Environmental Management: Waste Act No. 59 2008, Costley 2017 and Department of Water Affairs and Forestry 1998). The guidelines compare TCLP analysis of the material against what is called Leachable Concentration Thresholds (LCTs) (Table 6.2, summarized in Fig. 6.1). These thresholds are divided into LCT0 (minimum threshold), LCT1 and LCT2 (both as intermediate thresholds), and LCT3 (the maximum threshold). According to the National Environmental Management: Waste Act No. 59 (2008) and Costley (2017), the LCT1 values were derived from the minimum values (LCT0) of the Standards for Human Health Effects for Drinking Water in RSA, by multiplying them by 50 (a generic Dilution Attenuation Factor (DAF)). This factor was suggested by the "Industrial Waste Resource Guidelines: Solid Industrial Waste Hazard Categorization and Management" of June 2009. The LCT2 values were derived by doubling the LCT1 values, while the maximum threshold (LCT3) values were derived by multiplying the LCT2 values with a factor of 4 to raise the thresholds, and this factor is also used by the

Environment Protection Authority (EPA) of Australia, Victoria State, to calculate some of their thresholds from drinking water values.

The RSA regulation further compares total elemental analysis of the material against stipulated Total Concentration Thresholds (TCTs). The TC thresholds are divided into TCT0 (minimum threshold), TCT1 (intermediate threshold), and TCT2 (maximum threshold). The TCT0 values were obtained from South African Soil Screening Values that are protective of water resources, while TCT1 values were derived from the Land Remediation Values for Commercial/Industrial Land determined by the Department of Environmental Affairs' "Framework for the Management of Contaminated Land", of March 2010. TCT2 values were derived by multiplying TCT1 values by a factor of 4 (National Environmental Management: Waste Act No. 59 2008, Costley 2017). After the total and soluble concentrations of the waste have been compared to the various TCT and LCT levels, the waste is classified into one of five types, as outlined in Table 6.2.

Table 6.2: Classification of waste according to the Republic of South Africa (RSA) system (National Environmental Management: Waste Act No. 59 2008, Costley 2017 and Department of Water Affairs and Forestry 1998).

Element or Chemical Substance Concentration	**Waste Type**	**Risk**	**Management**
LC > LCT3 or TC > TCT2	Type 0	Very high risk	Direct landfilling not allowed, needs to be treated first, reassessed/classified, needs structure with lining ([1]H:H facility) for disposal to prevent leaching
LCT2 < LC ≤ LCT3 or TCT1 < TC ≤ TCT2	Type 1	High risk	Treatment not a pre-requisite, needs a structure with lining ([1]H:H facility) for disposal to prevent leaching
LCT1 < LC ≤ LCT2 and TC ≤ TCT1	Type 2	Moderate risk	Needs a structure with lining ([1]H:H facility) for disposal to prevent leaching
LCT0 < LC ≤ LCT1 and TC ≤ TCT1	Type 3	Low risk	Leaching is not a major concern, as such a structure without lining ([2]H:h facility) is used for disposal (can be explored for use in construction industry and agriculture)
LC ≤ LCT0 and TC ≤ TCT0	Type 4	Inert	A structure without lining ([2]H:h facility) is used for disposal as leaching is not a major concern (can be explored for use in construction industry and agriculture)

[1]H:H = Hazardous Waste Landfill with lining to prevent leaching, can receive from 1 up to 4 rated wastes; but [2]H:h = Hazardous Waste Landfill without lining to prevent leaching, can only receive 3 and 4 rated wastes.

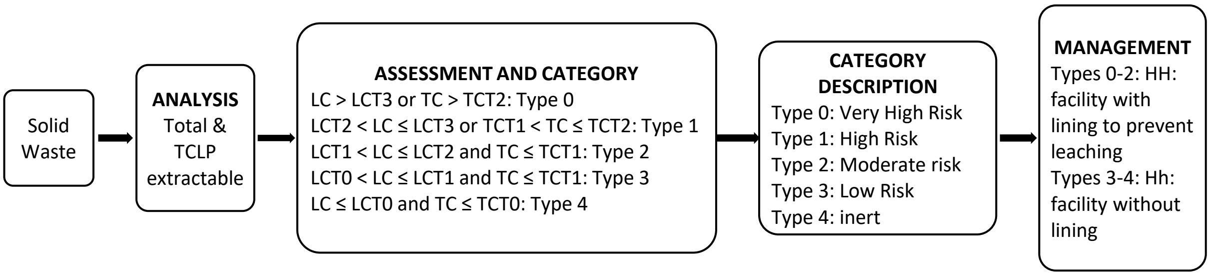


Figure 6.1: Simplified solid waste classification system of the Republic of South Africa (RSA).

Australian (New South Wales) Guidelines

The New South Wales (NSW) guidelines were considered as they are partially aligned to the National Waste Classification system that forms part of the Australian Waste Database (AWD). These guidelines consider a total of 9 (Table 6.3) elements (New South Wales Environment Protection Authority (EPA) 2014). Some of these elements (F, Mo, and Ni) were sourced from the Australian Drinking Water Guidelines (National Health and Medical Research Council (NHMRC) 2011, New South Wales Environment Protection Authority (EPA) 2000), but As, Cd, Cr(VI), Pb, and Ag were adapted from USEPA 2012b. The threshold for Be was calculated based on Be in The Health Risk Assessment and Management of Contaminated Sites. Waste is initially screened (1st screening stage) by considering total content only (referred to as Specific Contaminant Concentrations (SCC)) (Fig. 6.2). In the case of General Solid Waste, i.e., putrescible (liable to decay), non-putrescible (equivalent to Types 3 and 4 of the South African system) the TC ≤ Minimum Specific Contaminant Concentrations (SCC1). Restricted Solid Waste (TC ≤ Maximum Specific Contaminant Concentrations (SCC2)) refers to wastes that have the potential to pollute the environment (equivalent to Types 1 and 2 of the RSA system). If the TC of a constituent exceeds SCC1, further assessment with TCLP may be carried out, and if TCs are equal to or exceed SCC2 thresholds, then a TCLP assessment (2nd screening stage) must be done. At the second screening, using both SCC and TCLP thresholds, final clarity on the status of the waste is obtained, that is if TC > SCC1. At the second screening, TCLP is divided into TCLP1 (minimum threshold) and TCLP2 (maximum threshold). Hazardous solid waste is equivalent to Type 0 of the RSA system (Department of Water Affairs and Forestry (DWAF) 1998). The application of this system for HDS classification can be seen under the results section.

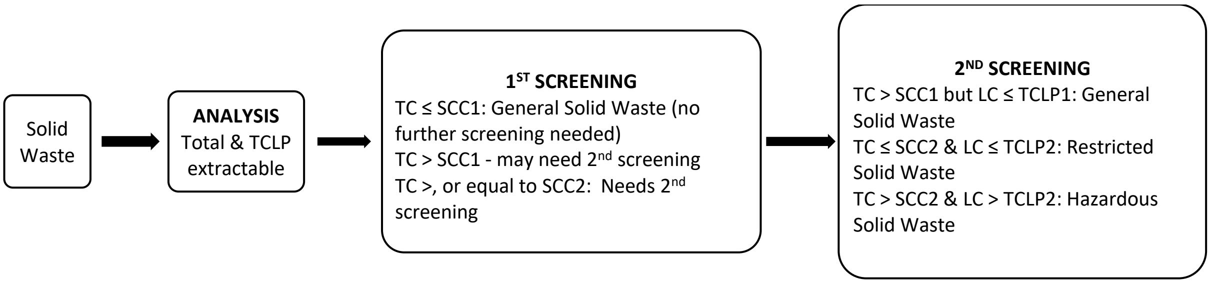


Figure 6.2: Simplified solid waste classification system for Australia (New South Wales).

6.2.7.2 Systems using only soluble concentrations of constituents to classify waste

The United States of America (USEPA) Guidelines

The USEPA regulation is managed by the Resource Conservation and Recovery Act (RCRA) of 1976, and classifies wastes based on hazardous properties (USEPA 1990). It considers 8 elements (Table 6.3) of concern (Environment Protection Authority (USEPA 1990). These elements are considered to cause acute or chronic health effects via the groundwater route and were sourced from the National Interim Primary Drinking Water Standards (NIPDWS) (USEPA 1990). The consideration of these inorganic constituents was further facilitated by available and appropriate chronic toxicity reference levels (CTRLs) on which to base the calculation of thresholds. These elements also had adequate data for the fate and transport model used to establish element specific dilution attenuation factors used to convert CTRLs to thresholds. Furthermore, these constituents have been shown to have toxic, carcinogenic, mutagenic or teratogenic effects (USEPA 1990). The main concern is the solubility of these constituents, and the only analysis performed is a TCLP extraction, after which the data are evaluated against threshold level (summarized in Fig. 6.3).

The critical difference between the USEPA guidelines and the other guidelines considered is that essential trace elements for plants/crops do not form part of their hazardous waste classification. These are B, Mn, Fe, Zn, and Cu. The USEPA regulation, therefore, opens the possibility for waste materials/by-products from industry and mining that have low solubilities of non-essential elements for plants and environmentally harmful constituents, to be considered for use in agriculture.

Chinese and Canadian (Alberta, British Columbia, Ontario and Manitoba) Guidelines

The Canadian and Chinese regulations also only require a TCLP extract, after which the data is compared against leachability thresholds (summarized in Fig. 6.3). China adopted the USEPA guidelines (Liu et al. 2015), except that they consider Cu, Ni, Be and Zn in addition, but do not consider Se (Table 6.3). Thresholds for all other elements, except for Hg, in both guidelines (Chinese and USEPA) are identical. The Canadian guidelines are also similar to those of the USEPA, except that in addition, Alberta considers B, Co, Cu, Ni, Fe, U and Zn; British Columbia considers B, Cu, U and Zn, while Ontario and Manitoba consider B and U.

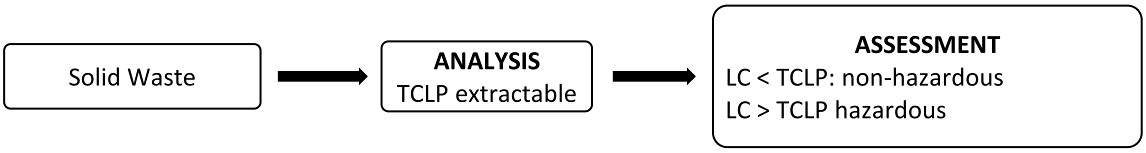


Figure 6.3: Simplified solid waste classification system for USEPA, China and Canada (Alberta, British Columbia, Ontario and Manitoba).

In summary, the RSA system considers the most elements (20) and is the most stringent. Both the total elemental content (referred to as "Total Concentration" determined by XRF) and the solubilities of the elements are assessed (referred to as "Leachable Concentration"). Five hazardous categories have been established (Types 0–4). Currently all waste, including Type 4 (inert waste), must go to a managed storage facility. The Australia system has two screening levels. The first uses only total elemental content (referred to as "Specific Contaminant Concentration, or SCC" divided into SCC1 and SCC2 determined by XRF. If the total elemental content of a waste exceeds SCC1 thresholds, further assessment against TCLP thresholds (2nd screening stage) may be carried out, but, if the total concentration exceeds SCC2 thresholds, then TCLP assessment must be done. A material can therefore be classified as a General, Restricted or Hazardous Solid Waste. With the USEPA, Canadian, and Chinese guidelines, the main concern is solubility of constituents in a waste, and as such, the approach adopted considers leachable concentration data that are evaluated against TCLP thresholds. The elements considered by the various systems are summarized below (Table 6.3).

Table 6.3: Summary of elements considered by each system.

Constituent	**RSA**	**Australia (New South Wales)**	**Canada**			**USEPA**	**China**
			Ontario & Manitoba	**British Columbia**	**Alberta**		
As	X	X				X	X
Ag		X	X	X	X	X	X
B	X		X	X	X		
Ba	X		X	X	X	X	X
Be		X					X
Cd	X	X	X	X	X	X	X
Co	X				X		
Cr	X	X	X	X	X	X	X
Cu	X			X	X		X
Fe					X		
Hg	X		X	X	X	X	X
Mn	X						
Mo	X	X					
Ni	X	X			X		X
Pb	X	X	X	X	X	X	X
Sb	X						
Se	X		X	X	X	X	
U			X	X	X		
V	X						
Zn	X			X	X		X
Cl	X						
SO_4	X						
NO_3	X						
F	X	X					
Total	20	9	9	11	14	8	11

6.3 RESULTS AND DISCUSSION

6.3.1 HDS elemental content and solubility

The most abundant of all metals in the sludges was Fe, which is not considered in the South African guidelines. This is followed by Mn which is included in the guidelines (on both a mass and molar basis) (Table 6.4). This was expected based on the natural abundance of elements in geological materials and soils in this province. AMD dissolves and mobilises Mn as it percolates through geological formations and soil. The limestone/ hydrated lime Site HDS was particularly rich in total Mn, but with low Mn solubility compared to Limestone–Sites 1 and 2 HDS. The Mn content varied across the sludges considered and deemed to be an AMD treatment signature. An HDS process without hydrated lime treatment generates HDS with appreciable amounts of soluble Mn (TCLP extractable). Examples of this are the GypFeMnNi and GypFeNi sludges, with soluble Mn. The mechanism for immobilisation is rapid oxidation of Mn^{2+} to Mn^{4+} and subsequent precipitation of sparingly soluble Mn(IV) oxides under high pH (9–9.5) conditions (Skousen 2014). The kinetics of oxidation is appreciably slower at the pH or alkalinity levels created by limestone alone, which results in incomplete oxidation of Fe^{2+} and Mn^{2+}. Due to the specific interaction of Mn^{2+} and Fe^{2+} with carbonates, there is also the risk that these metals will temporarily precipitate with carbonates, most likely as surface precipitates on limestone particles, which will further decrease their propensity to be oxidized. X-ray diffraction (XRD) analysis (data not shown) for GypFeMnNi, detected ankerite, $Ca(Mg,Fe,Mn)(CO_3)_2$, confirming the presence of ferrous iron and Mn(II), as well as incomplete oxidation of the Fe and Mn in the sludges.

6.3.2 Assessment of HDS using the RSA guidelines

Assessment with the South African guidelines was achieved by comparing HDS data (on the right) to thresholds (on the left) in Table 6.5. For the sludge GypFeMnNi, from Limestone–Site 1, the only element not classified as Type 3 or 4, was Mn (Table 6.6). The TCLP extractable Mn of 259 mg L^{-1} in Table 6.5 exceeded LCT3 (200 mg L^{-1}) resulting in a Type 0 (Table 6.6) classification of this sludge, requiring treatment and reassessment according to RSA regulations before disposal in a lined facility. As discussed earlier, the high Mn solubility was attributed to the fact that the Limestone–Site 1 process only uses limestone. The higher total Mn for GypFeMnNi sludge can be attributed to various factors, for example, (1) the Mn concentration of the AMD may have been higher as a result of a general increasing trend or seasonal change in mine water quality; (2) the limestone source used in the HDS process at the time of sampling. The Ni content of GypFeMnNi was more in-line with the GypFeMn and can either be related to temporal changes in AMD or quality of limestone used (Wang 2012). A more detailed discussion of this is beyond the scope of this study. A consistent and characteristic signature of the GypFeMnNi sludge was Ba, as GypFeMn exhibited low levels of this element. This could also have been a limestone signature.

Table 6.4: HDS data from own characterization and literature (Maree et al. 2004 and Anglo American Thermal Coal 2015).

Constituents	Limestone–Site 1		Limestone–Site 2			Limestone/ Hydrated Lime Site					
	GypFeMnNi			GypFeNi	GypFe	GypFeMn		GypB		Gyp	
	^{1}TC (mg kg^{-1})	^{2}TCLP (mg L^{-1})	^{1}TC (mg kg^{-1})	^{2}TCLP (mg L^{-1})	^{2}TCLP (mg L^{-1})	^{1}TC (mg kg^{-1})	^{2}TCLP (mg L^{-1})	^{1}TC (mg kg^{-1})	^{2}TCLP (mg L^{-1})	^{1}TC (mg kg^{-1})	^{2}TCLP (mg L^{-1})
As	0.1	<0.01	N.R.	0.2	0.003	0.5	<0.05	<0.5	<0.05	<0.5	<0.05
B		<0.01	N.R.	N.R.	N.R.	4.87	<0.24	6.39	<0.24	0.96	<0.24
Ba	465	<0.01	N.R.	N.R.	N.R.	12	<0.1	4	<0.1	1	<0.1
Ca	182,961	626	40,000	N.R.	N.R.	180,300	557	237,000	559	224,500	628
Cd	<1	<0.01	N.R.	0.3	0.01	<0.1	<0.04	<0.1	<0.01	<0.1	<0.01
Co	73	2.9	N.R.	13	0.2	97.2	<0.04	2.9	<0.04	0.6	<0.04
Cu	80	< 0.01	N.R.	0.1	0.002	3	<0.14	1	<0.14	<1	<0.14
Cr	68	0.03	60	2	0.03	2.5	<0.03	<0.5	<0.03	<0.5	<0.03
Fe	124,500	<0.01	40,000	26	0.4	42,040	<0.4	651	<0.4	152	<0.4
Hg	N.A.	N.A.	N.R.	N.R.	N.R.	<0.1	<0.02	<0.1	<0.01	<0.1	<0.02
K	83	9.9	200	N.R.	N.R.	116	4.8	68	10.9	61	<2.0
Mg	6513	61	3000	N.R.	N.R.	47,310	107	35,190	115	2736	12
Mn	7590	259	1000	211	4	6473	<0.04	949	<0.04	95	<0.04
Mo	3.3	<0.01	N.R.	N.R.	N.R.	<0.1	<0.04	0.1	<0.04	<0.1	<0.04
Na	74	<0.04	3000	N.R.	N.R.	612	<0.04	588	<0.04	279	<0.04
Ni	108	2.9	N.R.	16.5	0.3	104.9	<0.04	2.2	<0.04	<0.7	<0.04
P	44	0.05	N.R.	N.R.	N.R.	N.R.	<0.1	N.R.	<0.1	N.R.	<0.1
Pb	<1	<0.1	N.R.	N.R.	N.R.	143	<0.1	*163*	<0.1	40	<0.1
Sb	N.A.	N.A.	N.R.	N.R.	N.R.	<1	<0.04	<1	<0.04	<1	<0.04
Se	25	<0.01	N.R.	N.R.	N.R.	2	<0.06	<1	<0.06	<1	<0.06
V	56	<0.01	N.R.	N.R.	N.R.	4	<0.03	<1	<0.03	<1	<0.03
Zn	285	3.7	400	20.3	0.3	330	<0.1	7	<0.1	5	<0.1
Cl^-		7		N.R.	N.R.		10.2		25		1.3
SO_4^{2-}	55,343	2270		N.R.	N.R.		1761		1946		1456
NO_3^-		0.1		N.R.	N.R.		<0.2		0.9		<0.2
F^-		0.8		N.R.	N.R.		1.2		0.3		<0.3

^{1}TC = Total Concentration; ^{2}TCLP = Toxicity Characteristic Leaching Procedure, N.A. = Not analysed, N.R. = Not Reported.

Table 6.5: Waste classification of HDS using the RSA guidelines (Chandra and Garson 2010, Bortonea et al. 2015, Tepanosyan et al. 2017).

Const.	**TC Standards (mg kg^{-1})**			**LC Standards (mg L^{-1})**				**HDS TC and LC Data Compared to Standards on the Left**											
								Limestone–Site 1		**Limestone–Site 2**				**Limestone/ hydrated Lime Site**					
	^{1}TCT0	**^{1}TCT1**	**^{1}TCT2**	**^{2}LCT0**	**^{2}LCT1**	**^{2}LCT2**	**^{2}LCT3**	**GypFeMnNi**		**GypFeNi**		**GypFe**		**GypFeMn**		**GypB**		**Gyp**	
								mg L^{-1}	**mg kg^{-1}**	**mg L^{-1}**	**mg kg^{-1}**	**mg L^{-1}**	**mg kg^{-1}**	**mg L^{-1}**	**mg kg^{-1}**	**mg L^{-1}**	**mg kg^{-1}**	**mg L^{-1}**	**mg kg^{-1}**
As	5.8	500	2000	0.01	0.5	1	4	<0.01	0.1	0.2	N.R.	0.003	N.R.	<0.05	0.5	<0.05	<0.5	<0.05	<0.5
B	150	15,000	60,000	0.5	25	50	200	<0.01		N.R.	N.R.	N.R.	N.R.	<0.24	4.87	<0.24	6.39	<0.24	0.96
Ba	62.5	6250	25,000	0.7	35	70	280	<0.01	465	N.R.	N.R.	N.R.	N.R.	<0.1	12	<0.1	4	<0.1	1
Cd	7.5	260	1040	0.003	0.15	0.3	1.2	<0.01	<1	0.3	N.R.	0.01	N.R.	<0.04	<0.1	<0.01	<0.1	<0.01	<0.1
Co	50	5000	20,000	0.5	25	50	200	2.9	73	13	N.R.	0.2	N.R.	<0.04	97.2	<0.04	2.9	<0.04	0.6
Cr	46,000	800,000	N/A	0.1	5	10	40	0.03	68	2	60	0.03	60	<0.03	2.5	<0.03	<0.5	<0.03	<0.5
Cr(VI)	6.5	500	2000	0.05	2.5	5	20		-	-	-	-	-	-	-	-	-	-	-
Cu	16	19,500	78,000	2.0	100	200	800	<0.01	80	0.1	N.R.	0.002	N.R.	<0.14	3	<0.14	1	<0.14	<1
Hg	0.93	160	640	0.006	0.3	0.6	2.4	N.A.	N.A.	N.R.	N.R.	N.R.	N.R.	<0.02	<0.1	<0.01	<0.1	<0.02	<0.1
Mn	1000	25,000	100,000	0.5	25	50	200	259	7590	211	1000	4	1000	<0.04	6473	<0.04	949	<0.04	95
Mo	40	1000	4000	0.07	3.5	7	28	<0.01	3.3	N.R.	N.R.	N.R.	N.R.	<0.04	<0.1	<0.04	0.1	<0.04	<0.1
Ni	91	10,600	42,400	0.07	3.5	7	28	2.9	108	16.5	N.R.	0.3	N.R.	<0.04	104.9	<0.04	2.2	<0.04	<0.7
Pb	20	1900	7600	0.01	0.5	1	4	<0.1	<1	N.R.	N.R.	N.R.	N.R.	<0.1	143	<0.1	*163*	<0.1	40
Sb	10	75	300	0.02	1.0	2	8	N.A.	N.A.	N.R.	N.R.	N.R.	N.R.	<0.04	<1	<0.04	<1	<0.04	<1
Se	10	50	200	0.01	0.5	1	4	<0.01	25	N.R.	N.R.	N.R.	N.R.	<0.06	2	<0.06	<1	<0.06	<1
V	150	2680	10,720	0.2	10	20	80	<0.01	56	N.R.	N.R.	N.R.	N.R.	<0.03	4	<0.03	<1	<0.03	<1
Zn	240	160,000	640,000	5.0	250	500	2000	3.7	285	20.3	400	0.3	400	<0.1	330	<0.1	7	<0.1	5
Cl				300	15,000	30,000	120,000	7		N.R.		N.R.		10.2		25		1.3	
SO$_4$				250	12,500	25,000	100,000	2270	55,343	N.R.		N.R.		1761		1946		1456	
NO$_3$				11	550	1100	4400	0.1		N.R.		N.R.		<0.2		0.9		<0.2	
F				1.5	75	150	600	0.8		N.R.		N.R.		1.2		0.3		<0.3	

^{1}TCT = Total concentration Threshold values, ^{2}LCT = Leachable Concentration Threshold values, N.A. = Not Analysed and N.R. = Not Reported

Table 6.6: Classification results obtained from Table 5 using the RSA guidelines.

Constituents	**Limestone–Site 1**	**Limestone–Site 2**		**Limestone/ Hydrated Lime Site**		
	GypFeMnNi	**GypFeNi**	**GypFe**	**GypFeMn**	**GypB**	**Gyp**
As	4	3	4	Inconcl	Inconcl	Inconcl
B	-	-	-	4	4	4
Ba	3	-	-	4	4	4
Cd	Inconcl	Inconcl	Inconcl	Inconcl	Inconcl	Inconcl
Co	3	3	4	3	4	4
Cr	4	3	4	4	4	4
Cr(VI)	-	-	-	-	-	-
Cu	3	4	4	4	4	4
Hg	-	-	-	Inconcl	Inconcl	Inconcl
Mn	0	0	3	3	4	4
Mo	4	-	-	4	4	4
Ni	3	1	3	3	4	4
Pb	Inconcl	-	-	Inconcl	Inconcl	Inconcl
Sb	-	-	-	Inconcl	Inconcl	Inconcl
Se	3	-	-	Inconcl	Inconcl	Inconcl
V	4	-	-	4	4	4
Zn	3	3	3	3	4	4
Cl	4	-	-	4	4	4
SO_4	3	-	-	3	3	3
NO_3	4	-	-	4	4	4
F	4	-	-	4	4	4
Overall Type	0	0	3	3	4	4

Note: Inconcl = Inconclusive analysis.

The only total analyses given for Limestone–Site 2 were for Cr, Mn, Zn, and the TCLP analyses reported were also limited for both GypFeNi and GypFe sludges. The Limestone–Site 2 HDS classification was therefore largely incomplete. However, some general trends were evident. Similar to GypFeMnNi, soluble Mn (Table 5) was the element condemning the GypFeNi in a lined pond to Type 0 (Table 6.6). However, the main difference between the two sludges was the higher soluble Ni in GypFeNi compared to that of GypFeMnNi. Maree et al. (2004) reported TCLP extractable Mn (211 mg L^{-1}) in GypFeNi sludge that exceeded LCT3 (200 mg L^{-1}) and Ni exceeded its LCT2 threshold (7 mg L^{-1}).

The sludge, GypFeMn from Limestone/ Hydrated Lime process had higher Co, Mn, Ni and Zn content than GypFeMnNi sludge and all these metals exceeded the TCT0 thresholds. For this sludge, GypFeMn, it seemed that Pb persists and is not effectively removed by the neutralization process. For both GypB and Gyp sludges, Pb content exceeded the TCT0 threshold of 20 mg kg^{-1} (Table 5). The RSA guidelines have set low minimum TCLP values (LCT0), especially for As, Cd, Pb, Hg, and Se. Due to detection limit difficulties, this has resulted in inconclusive results and technically also an incomplete classification (Table 6.6) of the Limestone–Site 1, Limestone/ Hydrated Lime Site HDS for some of more important elements from an environmental point of view. A TCLP extract (or any other extract) from soil or solid waste at fairly low solution to solid ratios (20:1) creates a substantially more saline and a complex matrix. As a result, method detection limits (MDLs) are always higher (often an order of a magnitude) for extracts than for drinking water. The MDL is the lowest concentration of an element in a specific extractant/matrix where its signal is statistically separable from background "noise". The elements As, Cd, Pb, Hg and Se are especially prone to matrix and spectral interferences, resulting in false positive interferences. In order to measure LCT0 concentrations repeatedly with high confidence, the TCLP MDLs for these elements should be below LCT0 concentrations. Lead in general shows higher MDLs in TCLP and other extracts. Kavouras et al. (2003) reported 0.3 mg L^{-1} (Pb determined by atomic absorption spectroscopy using a graphite furnace), the Laboratory analysis of the Limestone/Hydrated Lime Site, reported 0.1 mg L^{-1}, while Lin and Chang (2006) reported 0.016 mg L^{-1} for Pb in TCLP. Apart from the latter article, all the other detection limits in TCLP were an order of a magnitude higher than the LCT0 for Pb. It is believed that a more extensive investigation into TCLP MDLs for commercial laboratories for these elements will confirm the trend that LCT0 levels set for some or all these elements are below typical TCLP MDLs, and are therefore, of no practical meaning and should be revised.

6.3.3. Assessment of HDS using the Australian (New South Wales) guidelines

The Australian guidelines define total F, Ag and Be levels, where the RSA guidelines do not. As a result, analysis of these elements is not required for hazardous waste characterisation in RSA and a judgement on these elements with the Australian system could not be made. At the 1st screening stage (Table 6.7), Australian regulations indicate that Ni (108 mg kg^{-1}) for GypFeMnNi, from Limestone–Site 1, exceeded SCC1 (40 mg kg^{-1}) allocating a Restricted Solid Waste status to the material, meaning it can pollute the environment. The material was then assessed against both SCC and TCLP, the 2nd Screening stage (Table 6.8). The elements considered for this sludge were found to be below SCC1 thresholds, but when compared against TCLP thresholds, only Ni (2.9 mg L^{-1}) exceeded TCLP1 (2.0 mg L^{-1}) confirming the classification of the material as a Restricted Solid Waste. This categorization is equivalent to

Types 1 to 2 in the RSA system. Only Ni was highlighted as an element of concern, because the Australian guidelines do not consider Mn.

The sludge, GypFeNi, from Limestone–Site 2 was allocated a hazardous status (equivalent to Type 0 of the RSA system) since its Ni (16.5 mg L^{-1}) exceeded TCLP2 (8.0 mg L^{-1}) and GypFe from the same site was categorized as a General Solid Waste, since all its TCs and LCs were below SCC1 and TCLP1 thresholds (Tables 6.7 and 6.8). The other sludges, GypFeMn, from the Limestone/ Hydrated Lime Site had TCs for Pb (143 mg kg^{-1}) and Ni (104.9 mg kg^{-1}) exceeding their thresholds (only in the 1st screening stage—Table 6.7), GypB also had its TC for Pb (163 mg kg^{-1}) exceeding its threshold (only in the 1st screening stage—Table 6.7), categorising both materials as Restricted Solid Wastes, but Gyp from the same site was categorized as a General Solid Waste (allowing exploration for use by either the construction industry or agriculture).

6.3.4. Assessment of HDS based on Canadian, US, and Chinese guidelines

Guidelines for these countries rely only on TCLP data (Table 6.9). To achieve the assessment, the TCLP extracted data presented on the right of Table 6.9 were compared to the thresholds presented on the left portion of the same Table. When comparing GypFeMnNi sludge to the USEPA, Canadian and Chinese guidelines, all of the LC values considered were below threshold levels, categorizing this material as non-hazardous waste. This suggests that no restrictions are needed for the disposal of this sludge and the potential for its use in agriculture or the construction industry can be explored.

GypFeNi from Limestone–Site 2 had an LC for Ni (16.5 mg L^{-1}) exceeding Canada's (Alberta) and China's TCLP threshold (of 5 mg L^{-1}) thereby classifying the material as hazardous waste. The other three systems classified this sludge as non-hazardous. The source of the acid waters treated in the Limestone–Site 2 has not been confirmed as being solely of coal mining origin, and it should be noted that a major metalliferous processing plant is situated upstream of the Limestone–Site 2 treatment plant. Analyses for GypFe were below TCLP thresholds for all countries, assigning the material a non-hazardous status. When evaluating sludges from the Limestone/ Hydrated Lime Site (GypFeMn, GypB and Gyp) against the USEPA, Canadian, and Chinese guidelines, none of the LCs exceeded TCLP thresholds of any of the guidelines.

Table 6.7: Waste classification without TCLP data (1st Screening stage) (New South Wales Environment Protection Authority (EPA) 2014).

Element	**Standards (mg kg^{-1})**		**HDS TC Data (mg kg^{-1}) Compared to Standards on the Left**				
	[1]SCC1 (mg kg^{-1})	**[1]SCC2 (mg kg^{-1})**	**Limestone–Site 1**	**Limestone–Site 2**	**Limestone/Hydrated Lime Site**		
			GypFeMnNi	**GypFeNi & GypFe**	**GypFeMn**	**GypB**	**Gyp**
Ag	100	400	-	-			
As	100	400	0.1	-	0.5	<0.5	<0.5
Be	20	80	-	-			
Cd	20	80	<1	-	<0.1	<0.1	<0.1
Cr	100	400	68	60	2.5	<0.5	<0.5
F	3000	12,000	-	-			
Pb	100	400	<1	-	143	163	40
Hg	4	16	NA	-	<0.1	<0.1	<0.1
Mo	100	400	3.3	-	<0.1	0.1	<0.1
Ni	40	160	108	-	104.9	2.2	<0.7
Se	20	80	25	-	2	<1	<1
Overall classification			RSW	GSW	RSW	RSW	GSW

[1] SCC = Specific Contaminant Concentrations, N.A. = Not analyzed, RSW = Restricted Solid Waste and GSW = General Solid Waste· *Note:* If TC ≤ SCC1: General Solid Waste (no further screening needed), TC > SCC1: may need 2nd screening, TC ≥ SCC2: Restricted Solid Waste (needs 2nd screening).

Table 6.8: Assessment of sludge hazardous status based on both TCLP and SCC thresholds (2nd Screening stage) [New South Wales Environment Protection Authority (EPA) 2014].

Element	**Standards**				**HDS TCLP Extracted and TC Data Compared to the Standards on the Left**											
	[2]TCLP1	**[1]SCC1**	**[2]TCLP2**	**[1]SCC2**	**Limestone–Site 1**		**Limestone–Site 2**				**Limestone/Hydrated Lime Site**					
	mg L^{-1}	**mg kg^{-1}**	**mg L^{-1}**	**mg kg^{-1}**	**GypFeMnNi**		**GypFeNi**		**GypFe**		**GypFeMn**		**GypB**		**Gyp**	
					mg L^{-1}	**mg kg^{-1}**	**mg L^{-1}**	**mg kg^{-1}**	**mg L^{-1}**	**mg kg^{-1}**	**mg L^{-1}**	**mg kg^{-1}**	**mg L^{-1}**	**mg kg^{-1}**	**mg L^{-1}**	**mg kg^{-1}**
Ag	5.0	180	20	270	-	-	-	-	-	-	-	-	-	-	-	-
As	5.0	200	20	500	<0.01	0.1		-		-	<0.05	0.5	<0.05	<0.5	<0.05	<0.5
Be	1.0	100	4	400	-	-	-	-	-	-	-	-	-	-	-	-
Cd	1.0	100	4	400	<0.01	<1	0.3	-	0.01	-	<0.01	<0.1	<0.01	<0.1	<0.01	<0.1
Cr	5.0	1900	20	7600	0.03	68	2	60	0.03	60	<0.03	2.5	<0.03	<0.5	<0.03	<0.5
F	2.0	75	8	300	0.8	-	-	-	-	-	1.2	-	0.3	-	<0.3	-
Pb	5.0	1500	20	6000	<0.1	<1	-	-	-	-	<0.1	143	<0.1	163	<0.1	40
Hg	0.2	50	0.8	200	N.A.	N.A.	-	-	-	-	<0.02	<0.1	<0.01	<0.1	<0.02	<0.1
Mo	5.0	1000	20	4000	<0.01	3.3	-	-	-	-	<0.04	<0.1	<0.04	0.1	<0.04	<0.1
Ni	2.0	1050	8	4200	2.9	108	16.5	-	0.3	-	<0.04	104.9	<0.04	2.2	<0.04	<0.7
Se	1.0	50	4	200	<0.01	25	-	-	-	-	<0.06	2	<0.06	<1	<0.06	<1
Overall Classif.					RSW		HW		GSW		RSW		RSW		GSW	

[1]SCC = Specific Contaminant Concentrations, [2]TCLP = Toxicity Characteristic Leaching Procedure, N.A. = Not analyzed, RSW = Restricted Solid Waste and GSW = General Solid Waste. *Note:* If TC > SCC1 but LC ≤ TCLP1: General Solid Waste, TC ≤ SCC2 & LC ≤ TCLP2: Restricted Solid Waste, TC > SCC2 & LC > TCLP2: Hazardous.

Table 6.9: Assessment of HDS based on leachable concentrations (LC) using regulatory guidelines for Canada, USEPA and China (Zinck et al. 1997 and United States Environmental Protection Agency (USEPA) 1990).

Constituents	**Standards (mg L^{-1})**					**HDS TCLP Extracted Data (mg L^{-1}) Compared to Standards on the Left**					
	Canada			**USEPA**	**China**	**Limestone–Site 1**	**Limestone–Site 2**		**Limestone/Hydrated Lime Site**		
	Ontario & Manitoba	**British Columbia**	**Alberta**			**GypFeMnNi**	**GypFeNi**	**GypFe**	**GypFeMn**	**GypB**	**Gyp**
Ba	100	100	100	100	100	<0.01	-	-	<0.1	<0.1	<0.1
B	500	500	500	-	-	<0.01	-	-	<0.24	<0.24	<0.24
Cd	5	5	1	1	1	<0.01	0.3	0.01	<0.01	<0.01	<0.01
Cr	5	5	5	5	5	0.03	2	0.03	<0.03	<0.03	<0.03
Co	-	-	100	-	-	2.9	13	0.2	<0.04	<0.04	<0.04
Cu	-	100	100	-	100	<0.01	0.1	0.002	<0.14	<0.14	<0.14
Fe	-	-	1000	-	-	<0.1	26	0.4	<0.4	<0.4	<0.4
Pb	5	5	5	5	5	<0.1	-	-	<0.1	<0.1	<0.1
Hg	0.1	0.1	0.2	0.2	0.1	-	-	-	<0.02	<0.01	<0.02
Ni	-	-	5	-	5	2.9	16.5	0.3	<0.04	<0.04	<0.04
Se	1	1	1	1	-	<0.01	-	-	<0.06	<0.06	<0.06
Ag	5	5	5	5	5	-	-	-	-	-	-
U	2	10	2	-	-	-	-	-	-	-	-
Zn	-	500	500	-	100	3.7	20.3	0.3	<0.1	<0.1	<0.1
As	-	-	-	5	5	<0.01	0.2	0.003	<0.05	<0.05	<0.05
Be	-	-	-	-	0.02	-	-	-	-	-	-

Note: If LC < TCLP: non-hazardous, LC > TCLP hazardous.

6.3.5. Comparison of assessments using US, Australian, Canadian, Chinese and South African classification systems

In summary (Table 6.10), the USEPA classification allocated a non-hazardous status to all six sludges assessed. Accordingly, all would be open for exploration for use in the construction industry or agriculture. Two elements, Mn and Ni, resulted in Type 0 or Type 1 categorization by the RSA system for two of the sludges from the limestone treatment plants. With Australia, Ni and Pb remained the main soluble elements that allocated either a Restricted Solid Waste or hazardous status to some of the sludges. Soluble Ni was the only element that resulted in the allocation of a hazardous status to a sludge from one of the limestone treatment plants with Canadian (Alberta) and Chinese guidelines.

Table 6.10: Summary of elements that influence classification of HDS by the different systems.

Elem	High Density Sludge					
	Limestone–Site 1	Limestone–Site 2		Limestone/Hydrated Lime Site		
	GypFeMnNi	GypFeNi	GypFe	GypFeMn	GypB	Gyp
Mn	RSA	RSA	None	None	None	None
Ni	NSW	RSA, NSW, Alberta & China	None	NSW	None	None
Pb	None	None	None	NSW	NSW	None

Note: NSW = New South Wales; RSA = Republic of South Africa.

6.3.6. Should Mn form part of Hazardous Waste Classification?

The GypFeNi product, from Limestone–Site 2 was flagged by the majority of the guidelines (Canada, China, and Australia) based on soluble Ni (USEPA does not consider Ni). GypFeMnNi, from limestone–Site 1, and GypFeNi were both flagged on the basis of Mn, but only by the RSA guidelines. The RSA guidelines are very thorough in the number of elements they consider, and sensibly omit Fe and Al. However, it is the only system that considers Mn. Like Fe, Mn forms sparingly soluble oxides and this is most likely the reason why most countries do not consider it to be an element of major concern. The critical aspect at HDS plants is whether hydrated lime or limestone has been used in the neutralizing process. Lime accelerates oxidation kinetics because of the higher pH. If limestone is used, more time is needed at the lower pH for complete oxidation and formation of Mn (IV) oxides. Once formed, Mn (IV) oxides are exceedingly insoluble as demonstrated by the GypFeMn sludge, which had almost 7000 mg kg^{-1} of Mn, yet the solubility was below 0.04 mg L^{-1}.

Mn is also a common soil constituent, especially in the South African context. This is another environment where the low solubility of Mn from Mn(IV) oxides is demonstrated. The best example is the manganiferous soils derived from the Malmani dolomites in RSA which have been used for irrigation for 150 years or longer and have been critical in providing food for the large urban and peri-urban Gauteng population. These soils span important agricultural areas in Gauteng, parts of the Northwest and Mpumalanga Provinces of South Africa, and contain up to 13000 mg Mn kg^{-1} soil, more than double the total Mn content of the GypFeMn sludge (Mudaly 2016). This means that these soils would be Type 1 (high risk) wastes if they were to be classified using the RSA system based on TC.

Apart from their low solubility, Mn (IV) oxides also have various other benefits. Their metal scavenging abilities are well-known and have a particularly high affinity for B-type cations (soft metals), especially Pb (Feng et al. 2007). They also have the ability to oxidize organic pollutants in the soil and are more likely to play a critical role in protecting environmental quality, rather than harming it. Furthermore, the oxidizing propensity it lends to environments is well-known in soil research and commonly observed in dolomite derived soils (Skousen 2014). Mn(IV) oxides will not only help buffer ferric oxide reduction and dissolution, but also actively oxidize (or re-oxidize) ferrous iron and Mn^{2+}. If As occurs in the waste, the presence of Mn will result in its oxidation to the less soluble As(V) arsenate (Fischel et al. 2015).

Based on the arguments made on the low solubility of Mn(IV) oxides and of the potential environmental benefits, it seems prudent to omit total Mn content from the South African system, as has already been done with Fe.

6.4 CONCLUSIONS

This chapter attempted to address a pertinent question currently asked about HDS from coalmine water neutralization. The approach followed was to determine the hazardous waste classification of various sludges generated from HDS processes, using various international waste classification systems. One consistency between the Canadian, Chinese, Australian, and RSA systems was the classification of GypFeNi sludge from limestone–Site 2 as hazardous waste. In the case of the Canadian, Chinese, and Australian systems, it was due to Ni solubility.

For the RSA system, it was due to both Ni and Mn solubility, because it is the only system that considers Mn, and the wisdom of its inclusion is questioned. Apart from this HDS, the Canadian and Chinese systems did not consider any other of the sludges assessed to be hazardous. None of the sludges was considered by the USEPA guidelines as hazardous, because Ni is not included in their system. The Australian system further classified three other sludges (GypFeMnNi, GypFeMn, GypB) as Restricted Solid Wastes, based on Ni solubility, while two (GypFe, Gyp) were classed as General Solid Wastes. One other sludge (GypFeMnNi) was classified as highly hazardous due to Mn and Ni solubility by the RSA system and needs to be retreated before deposition in a lined facility. The remaining sludges were classed as Type 3 or 4. The LCT0 values for several elements in TCLP extracts are below detection limits using methods available in South Africa. Consequently, incomplete classification of waste is at risk. Changing the LCT0 values for these elements to >MDL TCLP (below the Method Detection Limit in TCLP) would still be lower than the single soluble screening levels of the other systems. Considering all the systems, the probability for the HDS investigated to be classified as hazardous waste increases if the material is only subjected to limestone treatment. The element flagged for the specific sludges considered, was Ni. As a recommendation, the RSA should exclude Mn from its waste classification system as it is an essential plant nutrient and also align the constituents' thresholds with those of international systems

CHAPTER 7

CAN PHOSPHATE BE USED TO REDUCE METAL SOLUBILITY IN HIGH DENSITY SLUDGE AND TRANSFORM IT INTO A USABLE PRODUCT?

ABSTRACT

High Density Sludge (HDS) is often classified as hazardous due to its chemical composition and metal solubility. The objective was therefore to investigate if phosphate (PO_4) treatment can reduce the solubility of metals in HDS. A ferriferous gypseous sludge from a limestone only Acid Mine Drainage (AMD) treatment plant (designated as GypFeMnNi) and another ferriferous gypseous sludge dominated by Mn from a hydrated lime/limestone treatment plant (designated as GypFeMn) were treated with 0, 50, 250, 2000, 4000 and 6000 mg l^{-1} P, and then subjected to the Toxicity Characteristic Leachability Procedure (TCLP). The phosphated sludges were also assessed for redox stability and oxidation capacity. Results showed that phosphating substantially reduced the solubility of Al, Fe, Mn, Zn and Ni in both sludges through precipitation into phosphate minerals of low solubility. However, some of the metals such as Pb, Cd, Cu, Cr, including As and Se were of no concern because their TCLP extracted concentrations were below detection limits (BDL). GypFeMn showed resistance to chemical reduction by dithionite and oxalate, with the result that the extraction of Fe, Al and Ni were lower than in GypFeMnNi. However, with Mn extraction, GypFeMnNi showed more resistance to chemical reduction than GypFeMn. Manganese Electron Demand (MED) showed an increase in the oxidation of Mn in GypFeMn, but in GypFeMnNi, it indicated that this element was already oxidised to either Mn(III) or Mn(IV). Total Electron Demand (TED) showed an increase in GypFeMnNi than in GypFeMn and the reason was that phosphate facilitated the oxidation of Mn(II). Therefore, phosphating substantially prevented the reduction of both materials and thus reduced metal solubility and their hazardous status.

Keywords: High Density Sludge, TCLP, AMD

7.1 INTRODUCTION

High density sludge (HDS) is generated during acid mine drainage (AMD) treatment by recycling sludge and a combination of limestone ($CaCO_3$) and hydrated lime ($Ca(OH)_2$) (Aubé and Zinck 1999). HDS can be alkaline and contains varying concentration of transition metals such as Ni, Pb, Hg, Co, Cr, Cd, Zn and Cu. The origin of these metals can either be the AMD treated and/or the liming material used in the treatment process (Johnson and Hallber 2005, Kalin et al. 2006).

A large part of HDS is gypsum ($CaSO_4.2H_2O$) because of the use of a Ca based liming material and the fact that the AMD is high in sulfate. Iron oxides are another important constituent. The material is also known to contain 10 – 30% residual lime depending on the efficiency of the treatment process (Maree et al. 2004 and Zinck 2006). Using phosphate (PO_4) to chemically decrease the solubility of metals the waste contains is a well-established practice. Metal solubility reduction by PO_4 was demonstrated; in bottom ash of municipal solid wastes (Crannell et al. 2000), in polymineralic mine wastes (Harris and Lottermoser 2006), and in soils (Kumpiene et al. 2006). Transition metals form phosphates of low solubility (Barthel and Edwards, 2004), Kumpiene at al., 2008). For instance, lead is known to form lead hydroxypyromorphite ($Pb_5(PO_4)_3OH$) (Crannell et al. 2000). Phosphate minerals, for example, $Ca_5(PO_4)_3OH$, can also reduce the solubility of transition metals (e.g. Zn, Cu, Cd etc) through either sorption or by isomorphous substitution for Ca in the mineral structure (Eighmy et al. 1997 and Crannell et al. 2000). HDS contains a fair amount of ferric oxides, and ferric iron is a strong electron acceptor and susceptible to reductive dissolution. Phosphate is not redox active, and the redox stabilisation of metals phosphate can introduce to the sludge has not yet been studied. Hence the objective of this study was to investigate the effectiveness of phosphate (PO_4) to reduce metal solubility in HDS. That is, if phosphating decreases the susceptibility of HDS to reduction, and if this decreases the solubility of the constituents of HDS, for example, metals such as Ni and Pb.

7.2 METHODS AND MATERIALS

7.2.1 Types of HDS used and their sources

Two gypseous sludges from the Mpumalanga Coalfields in South Africa, sampled in 2016, were considered. Both sludges were generated from the High Density Sludge Process (HDSP), known to treat AMD with a mixture of recycled sludge and liming material (Aubé and Zinck 1999, Günther et al. 2003). The sludge generated consists of 20 – 30% solids (Günther et al. 2003). The difference between the two sludges was that one was sourced from an HDSP that uses Limestone alone – $CaCO_3$, a Ferriferous gypseous material (GypFeMnNi) dominated by gypsum and Fe oxides, and the other was from a process that uses a combination of Limestone and lime – $CaCO_3$ / $Ca(OH)_2$, a Ferriferous gypseous material (GypFeMn) material, dominated by gypsum, Fe oxides and Mn. These processes were described in Chapters 2 and 6. The sludges, GypFeMnNi and GypFeMn were selected because they were allocated a hazardous status due to solubility of toxic metals in chapter 6. The sludge, GypFeMnNi had soluble Mn and Ni, while GypFeMn had soluble Ni and Pb.

7.2.2 Determination of mineralogy

Mineralogy of HDS was determined with X-ray Diffraction (XRD) before and after phosphating, with a PANalytical X'Pert Pro Powder Diffractometer. The procedure described by Loubser and Verryn (2008) was followed. Details of the mineralogy of both sludges have been discussed in Chapter 4.

7.2.3 Acid-base chemistry of the sludges

The pH was determined before and after phosphating as described by Thomas (1996) on both HDS types. Details of the mineralogy of both sludges have been discussed in Chapter 4.

7.2.4 Phosphating of HDS and solubility assessment

The two types of HDS were treated with solutions spanning a wide phosphate concentration range: 0, 50, 250, 2000, 4000 and 6000 mg P l^{-1}. In each case, one gram of material was reacted with 25 ml of solution prepared from KH_2PO_4. Equilibration was allowed to occur for two days at constant temperature (25 ^{o}C). During this time the stoppered tubes were shaken end to end at 180 oscillations per minute for 2 hours per day. After 48 hours the samples were centrifuged at 3000 revolutions per minute for 10 minutes and filtered through Whatman No. 42 filter paper and 0.45 µm EconoClear membrane filters. Standard P solutions; 0, 5, 10, 50, 100 and 250 mg l^{-1} were prepared and read through ICP-OES before the determination of P in the filtered solutions. The phosphated material was then oven-dried at 30 ^{o}C until attaining a constant mass.

7.2.5 Determination of total elemental content before and after phosphating

Microwave assisted acid digestion, EPA method 3052 (EPA SW-846 2014) was followed. After digestion, elements were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). X-ray Fluorescence (XRF), which uses an ARL 9400XP+ Wavelength dispersive XRF Spectrometer, was also used to determine total elemental content following the procedure described by Loubser and Verryn (2008).

7.2.6 Redox stability assessments

Susceptibility to reductive dissolution was investigated by using reductants to extract Fe, Mn, Al, Pb and Ni. As discussed by Courchesne and Turmel (2007), dithionite-citrate, was used to determine amorphous inorganic forms of Al, Fe and Mn. Similarly, acid ammonium oxalate and acid hydroxylamine were also used to estimate the same elements and forms as with dithionite-citrate. Furthermore, acid ammonium oxalate and acid hydroxylamine also determine Al, Fe and Mn in crystalline forms.

7.2.7 Determination of Total Electron Demand (TED) and Manganese Electron Demand (MED) before and after phosphating

Ferric oxides are electron acceptors and redox stabilisation brought about by phosphate should decrease this electron accepting propensity. Total Electron Demand (TED) and Manganese Electron Demand (MED) were used to assess this by following procedures described by Bartlett and James (1995).

7.3 RESULTS AND DISCUSSION

7.3.1 Mineralogy and basic chemical properties of non-phosphate HDS

Understanding the mineralogy and chemical composition of the materials was important in understanding their response to phosphating. Chemical analysis revealed that GypFeMnNi was slightly acidic with a pH of 5.5 and 250 mg kg^{-1} alkalinity (Table 7.1). The pH is that of a solution in equilibrium with atmospheric CO_2, which shows this HDS contained virtually no soluble acidity or alkalinity. The material GypFeMn had a more alkaline pH because of the use of $Ca(OH)_2$. The acidic pH in GypFeMnNi was due to the use of $CaCO_3$ alone to treat AMD that has slow reaction kinetics and there was possibility of particles being coated by Fe precipitates making it unable to achieve a higher pH (Lottermoser 2007), or it could be that limited limestone was unable to neutralize all the acidity present in the solution.

Table 7.1: Basic chemical properties of HDS

Parameter	GypFeMnNi	GypFeMn
pH(H_2O) at 2.5 solution /solid ratio	5.5^{a}	8.2^{b}
Total Alkalinity as $CaCO_3$ (mg kg^{-1})	250^{a}	617^{b}
Total major elements (mg kg^{-1}) by XRF		
Ca	182961^{b}	235849^{a}
Mg	6513^{b}	46015^{a}
S	142089^{a}	132356^{b}
Total trace elements (mg kg^{-1}) by XRF		
Al	29319^{a}	22439^{b}
As	0.1^{a}	0.5^{a}
B	379.7^{a}	329^{a}
Ba	465^{a}	118^{b}
Cd	< 0.1	< 0.1
Co	73^{b}	149^{a}
Cu	80^{a}	15.5^{b}
Cr	68^{b}	134^{a}
Fe	146319^{a}	114570^{b}
Hg	< 0.1	< 0.1
Mn	7590^{a}	7847^{a}
Mo	3.3^{a}	2.8^{b}
Ni	108^{b}	167^{a}
Pb	< 1	143^{a}
Sb	< 0.1	< 0.1
Se	25^{a}	21^{b}
V	56^{a}	4^{b}
Zn	285^{b}	611^{a}

Note: $\alpha < 0.05$; CV = 8 – 17%. Means of elements with the same letter across sludges are not significantly different from each other. Values with the smaller than sign (<) indicate Method Detection Limits (MDL) of those elements

The mineralogy of these sludges was dealt with in detail in Chapter 4. The material GypFeMnNi was dominated by $CaSO_4.2H_2O$ (72 – 77%). According to Zinck et al. (1997), Aubé and Lee (2015) the only minerals often identified in HDS are $CaSO_4.2H_2O$ and $CaCO_3$. In addition, the semi-quantitative XRD further showed a carbonate mineral – ankerite ($Ca(Fe,Mg,Mn)(CO_3)_2$) and hematite (Fe_2O_3). In this material there was also evidence of amorphous hydrous Fe oxides. The other sludge, GypFeMn, was also shown to be dominated by $CaSO_4.2H_2O$ (70 – 90%). It is worth noting that in the case of GypFeMn, although Fe made-up >11% on a mass basis, Fe mineral phases seemed to be below XRD detection levels (<2%) suggesting Fe resides in amorphous phases (Appendix C). Both materials were also rich in Mg. Amongst the transition metals of environmental concern, GypFeMn contained appreciably more Pb and Ni than did GypFeMnNi. Lead content was extremely low (< 1 mg kg^{-1}) in GypFeMnNi. This was an indication that these materials were generated from two mine waters that were treated differently.

7.3.2 Phosphate effect on the TCLP extractable elements in HDS

The sludge GypFeMn, sorbed more P than GypFeMnNi (Fig. 7.1 B and 7.2). This is to be expected, since GypFeMn had a substantially greater specific surface area (1.1 m^2 g^{-1}) due to the high content of Fe oxides that could facilitate P sorption. In addition, this material was dominantly $CaSO_4.2H_2O$, that also contributes to phosphate immobilization through precipitation by soluble Ca. Increasing P substantially reduced the solubility of Al, Mn, Ni and Zn in GypFeMnNi (Fig. 7.1, A & B), and of Al and Fe in GypFeMn (Fig. 7.2). This possibly suggests precipitation with PO_4 or sorption on the reactive surfaces of this material (Eighmy et al. 1997, Crannell et al. 2000 and Karna et al. 2017). The initial increase in the solubility of Fe evident in GypFeMnNi (Fig. 7.1 B) could possibly be that PO_4 influenced the release of this element from both Fe oxides and carbonate mineral present in this sludge. Phosphate also resulted in an initial increase in the solubility of Mn and Ni in GypFeMn (Fig. 7.2). The change in pH was marginal (< 0.6) in both materials after adding PO_4, as such, PO_4 could not influence any changes in metal solubility. It should be noted that Mn and Fe oxides are important matrices where other elements like Ni and Zn reside; this justifies the focus on Mn and Fe. No conclusions could be made for both sludges about the effect of PO_4 on the solubility of Pb and As, including other metals (e.g. Cd, Cu, Cr, Hg, Se) using this extractant (TCLP), because extracted concentrations were below detection limits (BDL). For Zn in GypFeMn as well, no conclusions could be made because its concentration was below detection limit.

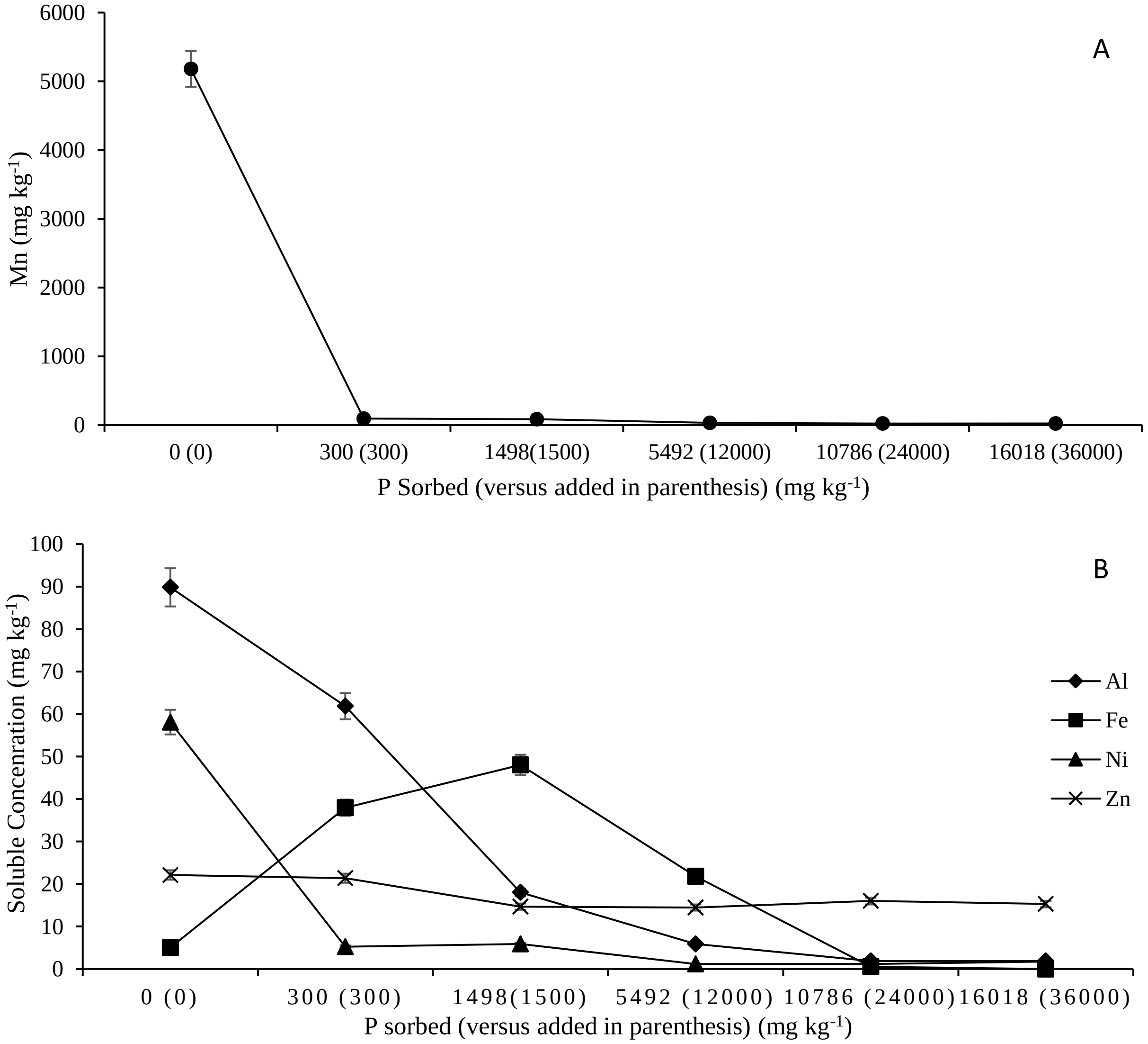


Figure 7.1: GypFeMnNi: A) Mn solubility reduction by phosphate B) Al, Fe, Ni solubility reduction by phosphate based on TCLP extractant.

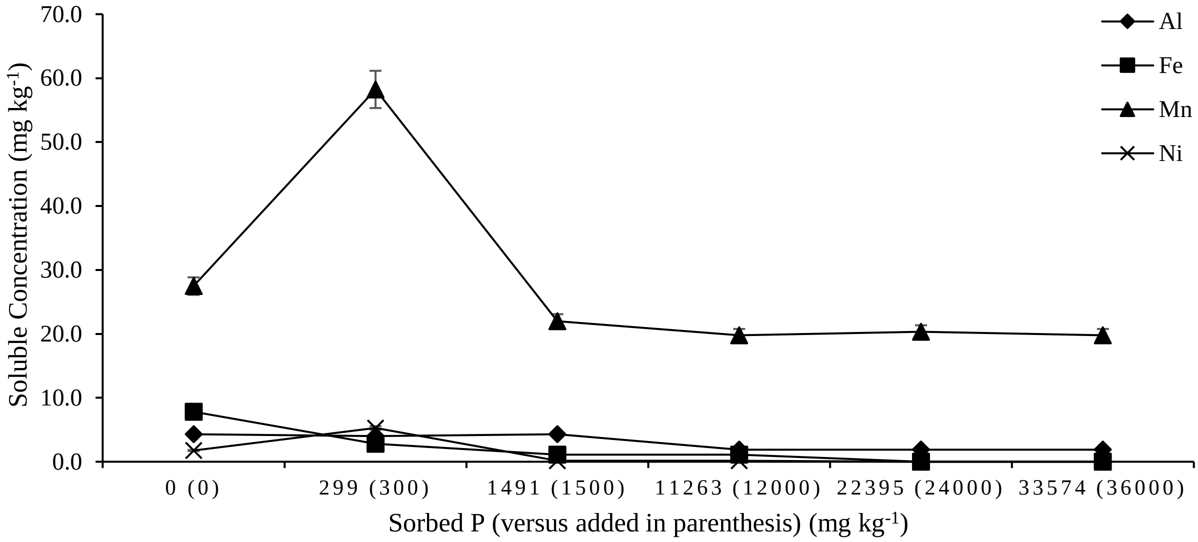


Figure 7.2: GypFeMn: Al, Fe, Mn, Ni solubility reduction by phosphate based on TCLP extractant

7.3.3 Does phosphating HDS make it more stable against reduction?

Manganese electron demand was expected to determine the oxidation capacity of Mn oxides in HDS, while TED was to estimate the oxidation capacity of both Mn and Fe (Van Bodegom et al. 2002 and Sparks 1993). Amorphous ferrihydrite in the GypFeMnNi remained as the predominant Fe source of Fe. The sorption of PO_4 by GypFeMnNi resulted in a significantly ($P < 0.01$) decrease in TED from 28 to 0.9 mg e^- kg^{-1} (Fig. 7.3). The added PO_4 was possibly sorbed and formed sparingly soluble complexes with ferrihydrite decrease its electron accepting ability (Cornell and Schwertmann 2003). However, GypFeMn, showed an increase in both TED (from 2.6 to 7 mg e^- kg^{-1} and MED 0.2 to 1.7 mg e^- kg^{-1} (Figure 7.4).

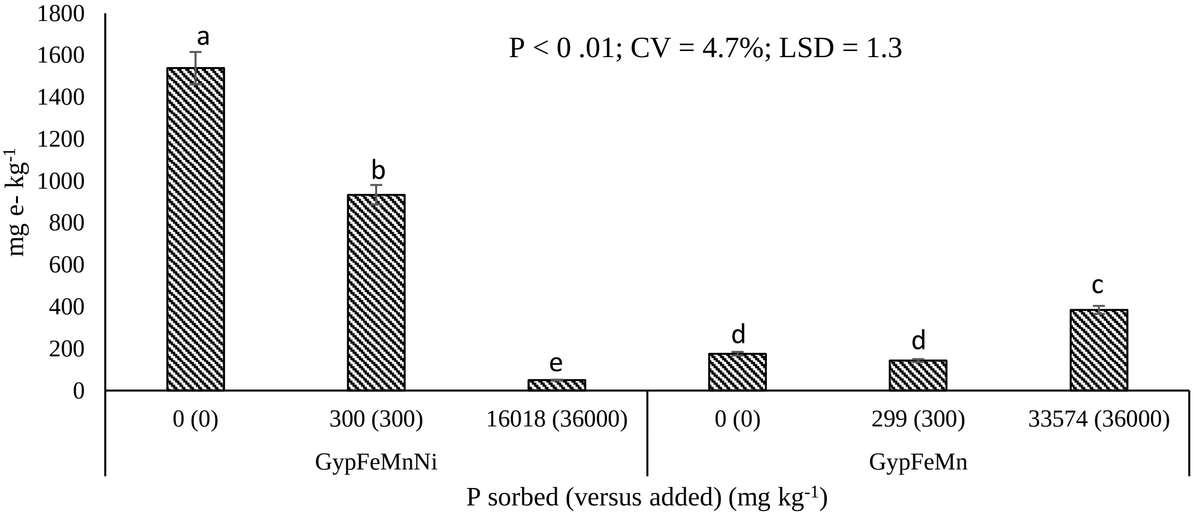


Figure 7.3: Total electron demand (TED) for HDS as influenced by P sorption. Note: Values in parenthesis are the loading rates of phosphate and values with same letter are not significantly different from each other.

The MED of GypFeMnNi was unaffected by any rate of PO_4 addition. The reason was that Mn was already oxidised to Mn(III) or Mn(IV). The reason why TED increased is because it seemed that phosphate actually facilitated the oxidation of Mn(II). The observed effects on GypFeMnNi could be due to the slightly alkaline conditions in this material that facilitated the oxidation of Mn(II), which possibly resided with carbonates, such as rhodochrosite and ankerite.

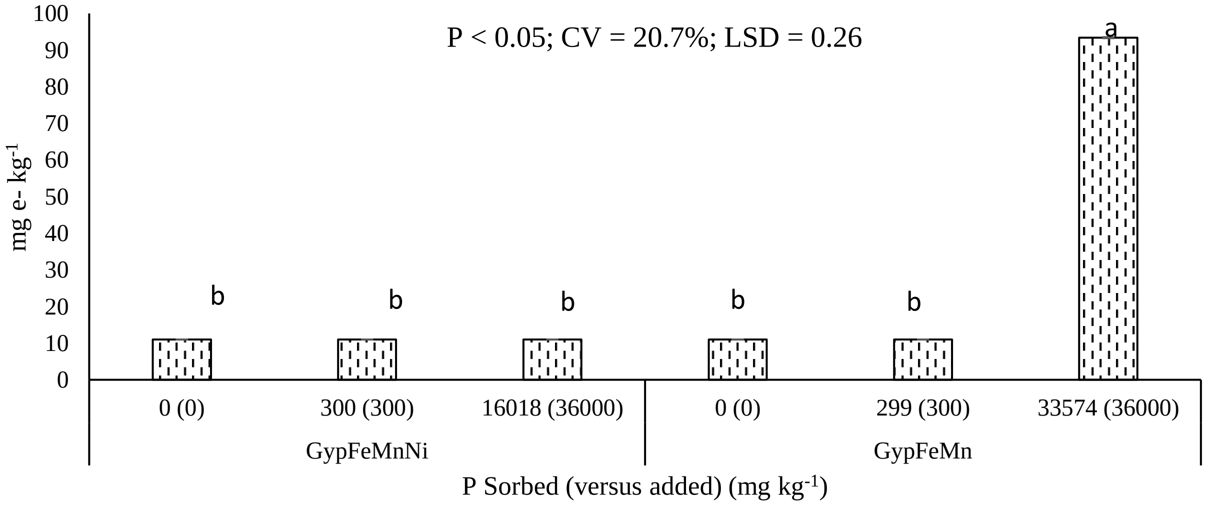


Figure 7.4 Mn electron demand (MED) for HDS as a function of P sorption. Note: Values in parenthesis are the loading rates of phosphate and values with same letter are not significantly different from each other.

7.3.4 Reductive promoted dissolution of HDS before and after phosphating

Comparing the control treatments (zero P addition), Fe oxides in GypFeMn were less resistant against chemical reduction with dithionite than in GypFeMnNi (Fig. 7.5 and Appendix F). Also, this suggested that for GypFeMnNi a greater fraction of the total Fe content resided in crystalline forms. Dithionite is a stronger reductant than oxalate employed in Soil Chemistry to extract all iron oxides (in crystalline and amorphous forms). It is therefore expected that the difference between dithionite and oxalate will increase with increasing crystallinity of iron oxides. GypFeMnNi had similar dithionite and oxalate extractable Fe supporting the fact that the Fe resides largely in less crystalline forms. GypFeMn showed a trend often seen in soils, that is, higher extractable Fe with dithionite than with oxalate. Generally, acid ammonium oxalate extracted the most Fe in both materials. Phosphate sorption had overall little impact on the susceptibility of Fe to reductive dissolution. It was only with GypFeMn and at highest P sorption level where a significant decrease in dithionite extractable Fe was observed.

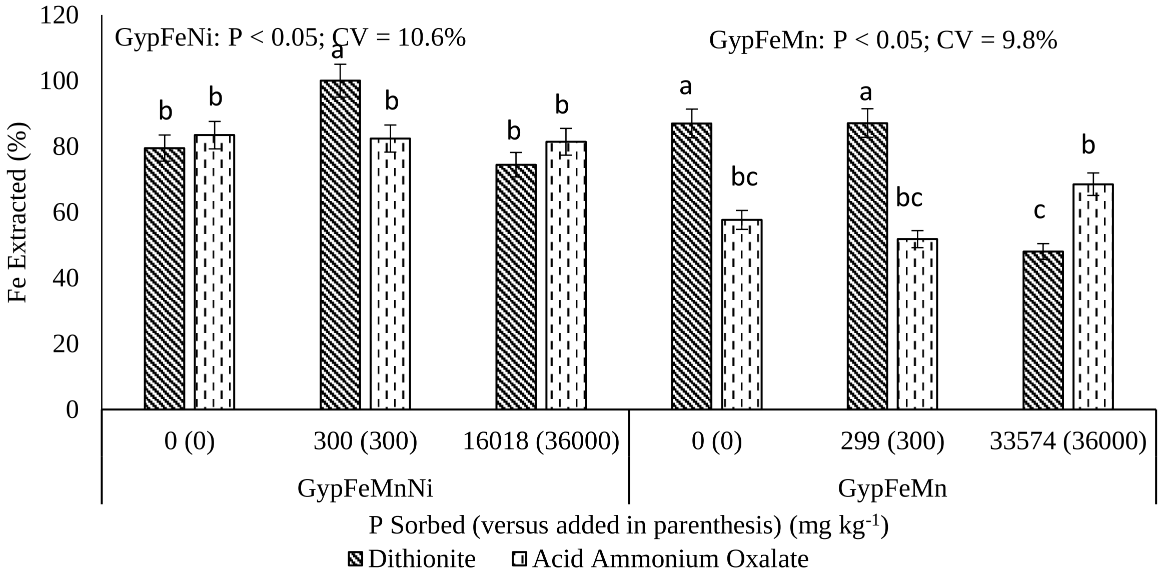


Figure 7.5: Fe extraction by dithionite and acid ammonium oxalate in HDS. Note: Values in parenthesis are the loading rates of phosphate and values with same letter are not significantly different from each other.

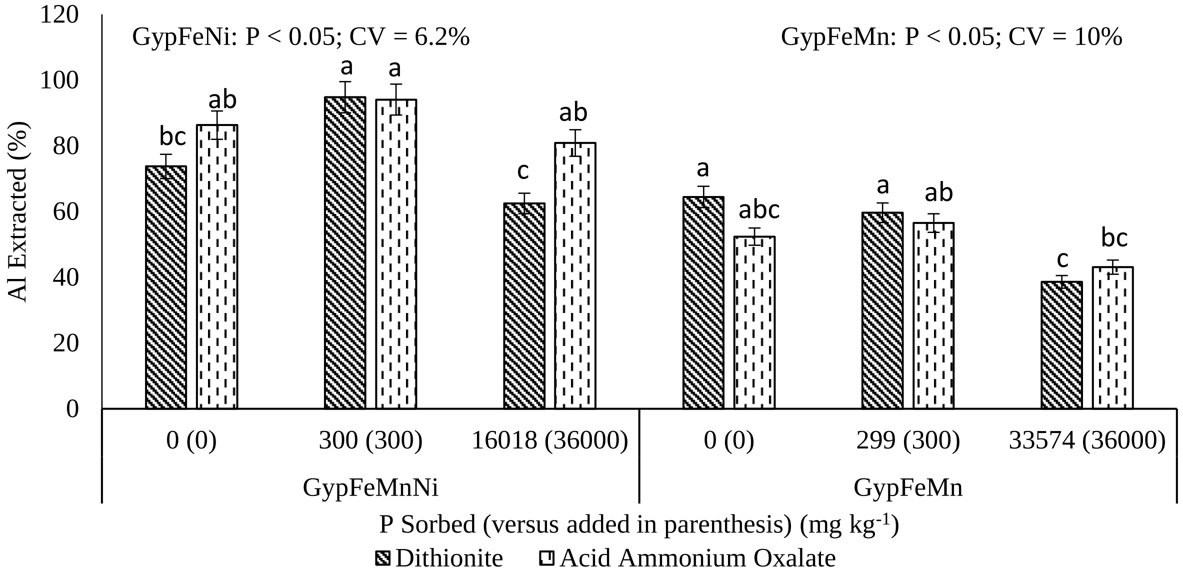


Figure 7.6: Al extraction by dithionite and acid ammonium oxalate in HDS. Note: Values in parenthesis are the loading rates of phosphate and values with same letter are not significantly different from each other

Aluminium data (Fig. 7.6 and Appendix F) showed that this element in GypFeMn was less soluble than in GypFeMnNi. This was because Al is not redox active and could not be extracted by reduction, also it could be residing in Fe oxides. Similar to Fe, Al was extracted mostly where PO_4 was added at 50 mg kg^{-1} by both extractants in GypFeMnNi. This concentration of PO_4 facilitated the increased solubility of HDS, whereas increasing it to 6000 mg kg^{-1} potentially prevented not only the reduction of GypFeMnNi, but also that of GypFeMn. With respect to Ni, this element was less soluble in GypFeMn than in GypFeMnNi (Fig. 7.7 and Appendix F) showing resistance to chemical reduction. Adding PO_4 at 50 mg kg^{-1} induced reduction of both sludges and enhanced Ni extraction by dithionite. Whereas increasing PO_4 to 6000 mg kg^{-1} prevented the reduction of both sludges.

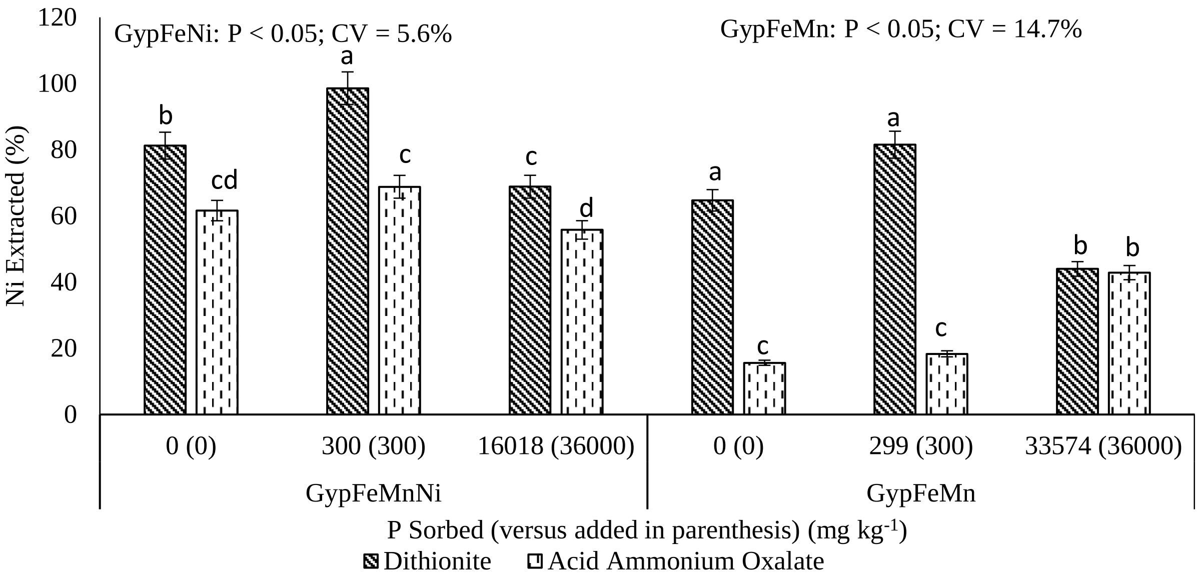


Figure 7.7: Ni extraction by Dithionite and Acid ammonium oxalate in HDS. Note: Values in parenthesis are the loading rates of phosphate and values with same letter are not significantly different from each other

With respect to Mn, the data shows that the Mn oxides of GypFeMnNi were more resistant against chemical reduction (Fig. 7.8 and Appendix F). Most of this metal was extracted from GypFeMn by both extractants. There were significant differences in the extraction of Mn amongst the extractants in GypFeMn. Both extractants showed less capability to extract Mn from both phosphated and non-phosphated GypFeMnNi. Increasing the addition of PO_4 to 36000 mg kg^{-1} prevented the reduction of GypFeMn which reduced extractable Mn by dithionite.

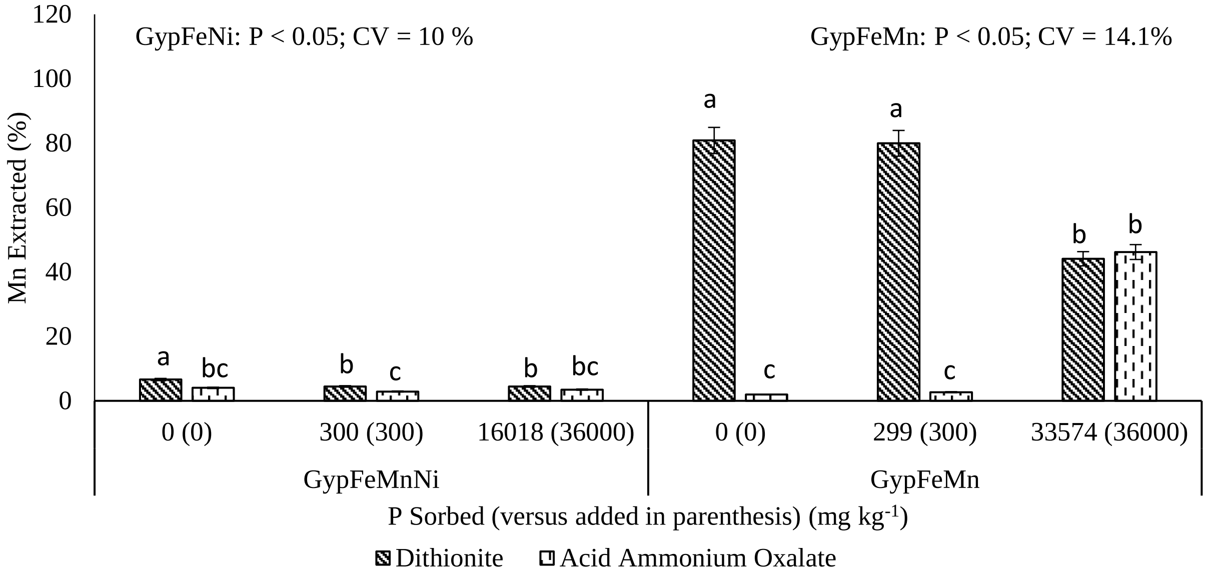


Figure 7.8: Mn extraction by dithionite and acid ammonium oxalate in HDS. Note: Values in parenthesis are the loading rates of phosphate and values with same letter are not significantly different from each other.

Generally, GypFeMn showed resistance to chemical reduction, as such, the extraction of Fe, Al, Ni was lower than in GypFeMnNi. GypFeMnNi showed more resistance to chemical reduction than GypFeMn for the extraction of Mn. It is worth noting that a lower concentration of PO_4 (300 mg kg^{-1}) has the potential of increasing the reduction of both sludges and increasing the extractability of metals. Generally, increasing PO_4 addition to 36000 mg kg^{-1} substantially prevented the reduction of both sludges, decreasing the solubility of metals.

7.4 CONCLUSIONS

Phosphating both materials from 300 to 36000 mg P kg^{-1} substantially reduced the solubility of Al, Fe, Mn, Zn and Ni (based on TCLP extraction) through adsorption on reactive surfaces of amorphous $Fe(OH)_3$ and possibly precipitation into phosphate minerals. No conclusions could be made for some of the metals such as Se, Hg, As and Pb since the focus was on selected elements. Also, there is difficulty in determining these elements with ICP-AES. GypFeMn showed resistance to chemical reduction by dithionite and oxalate, as such, the extraction of Fe, Al, Ni was lower than in GypFeMnNi. GypFeMnNi showed more resistance to chemical reduction than GypFeMn for the extraction of Mn. MED showed an increase in the oxidation of Mn in GypFeMn, but in GypFeMnNi, it indicated that this element was already oxidised to

Mn(III) or Mn(IV). Total Electron Demand showed a decrease in GypFeMnNi and the reason was that phosphate actually facilitated the oxidation of Mn(II). GypFeMn showed a greater propensity to release Mn to extraction by dithionine-citrate than acid oxalate increasing the risk of this material to the environment. Phosphating substantially minimized the reduction of both materials and further reduced metal solubility. For future research, phosphated sludges should be used as soil amendments and assess the solubility of metals in the soil/phosphate sludge mixtures.

CHAPTER 8

HIGH DENSITY SLUDGE AS A SOIL AMENDMENT – SOIL AMELIORATION EFFECTS

ABSTRACT

High Density Sludge is a gypseous material making it a potential soil amendment. Currently, this material is stored as it contains metals (e.g. Mn, Ni, Pb) of environmental concern and maybe classified as hazardous. The study therefore, envisaged that the gypsum contained in the sludge can contribute Ca and S to soils deficient of these elements, will also contribute to salinity reduction through sorption of elements by Fe oxides contained and will increase soil pH as some of the sludges may contain alkalinity. If hazardous, a potential approach was to add phosphate to the sludge since this has been shown before to immobilize toxic metals. There is a possibility that phosphate can also immobilize some of the essential plant nutrients released from the material. Therefore, the influence of phosphate on the release of plant nutrients was also investigated. The main objective of the study was to assess the impact on the soil when phosphate was co-applied with sludge, and when phosphate and sludge were applied on their own. A pot trial was conducted, where, a ferriferous gypseous sludge (GypFeMnNi) from a limestone treatment and a refined product, gypseous sludge (Gyp) from a limestone plus hydrated lime treatment were considered. Both were applied at 10 and 20 t ha^{-1} equivalents, to a soil with pH of 3.75. Phosphate was applied at 40 and 100 kg ha^{-1} equivalents. Positive (soil limed to pH 6.0) and negative (unlimed soil) controls were included. Maize was planted and harvested at physiological maturity. Co-application of phosphate with either sludge and application of sludges and phosphate on their own marginally increased soil pH and applying GypFeMnNi at 20 t ha^{-1} and P at 100 kg ha^{-1}, increased soil pH the most by 0.46. Both sludges on their own significantly ($\alpha < 0.05$) increased soil salinity, with Gyp applied at 20 t ha^{-1} increasing it the most from 7.8 mS m^{-1} to 728 mS m^{-1} (suitable only for salt tolerant crops). This was because the elements removed by reverse osmosis used to further treat the neutralised mine water from AMD treatment to drinking water are returned to the sludge. The application of either sludge increased the availability of Ca and S, but unfortunately reduced P availability due to sorption by GypFeMnNi and/or precipitation with Ca released from both sludges. Increasing the application of GypFeMnNi to 20 t ha^{-1} increased the availability of trace elements (Fe, Mn and Ni) verified through chemical extraction. Increasing Gyp to its maximum rate (20 t ha^{-1}) increased soluble Pb. Zinc availability was reduced by both sludges. Both sludges showed to be potential sources of Ca and S, but cannot be used solely to raise soil pH since an increase in their application can substantially increase salinity.

Keywords: AMD, HDS, Salinity, pH

8.1 INTRODUCTION

Treating Acid Mine Drainage (AMD) with a mixture of recycled sludge and either limestone ($CaCO_3$) or a combination of $CaCO_3$ plus hydrated lime ($Ca(OH)_2$) aims at producing a neutral solution that can be of low risk to the environment. However, this process also produces a gypseous by-product referred to as High Density Sludge (HDS) (Aubé and Zinck 1999, Tsang et al. 2013). The combination of $CaCO_3$ and $Ca(OH_2)$ enhances oxidation and precipitation of transition metals present in AMD into hydroxides forming part of the flocculants settling during solid/liquid separation. Because of the sludge chemical composition and solubility of metals (e.g. Hg, Pd, Ni, Cd, As, Se) contained it is of high risk to the environment. Although the material maybe hazardous, it possesses chemical and mineralogical properties that make it a potential soil amendment. Its mineralogy shows that it is dominated by gypsum ($CaSO_4.2H_2O$) that can release Ca and S upon solubility, and such can benefit acid soils that are often deficient of these elements. Also present in the material is amorphous ferric hydroxide that can provide an opportunity for sorption of metals and some of the solutes through surface complexation (Aubé and Zinck 1999, Tsang et al. 2013). The sorption of solutes in soils can substantially reduce availability of such solutes to plants, reduce environmental contamination and soil salinity. This material also contains substantial amount of Mg that can be traced back to the alkaline chemicals used to treat AMD. This is another element usually deficient in dystrophic acid soils. According to Maree et al. (2004) and Zinck (2006) HDS may contain substantial alkalinity that can increase pH of acid soils.

Evidence of metals and metalloids immobilization in soils treated with HDS was demonstrated by Tsang and Yip (2014), Tsang et al. (2013). There was an almost complete sorption of As, Cu and Cr after 9 months of incubation due to the Fe oxides contained in HDS that has an extremely high surface area (163 – 212 m^2 g^{-1}) and reactive hydroxyl groups. The HDS investigated was composed of 16.4 – 21.2% Fe oxides. This showed that HDS has the potential to reduce leachability and bioavailability of not only metals of environmental concern even essential plant nutrients in soils. According to Zinck (2005) & Zinck (2006) Fe oxides present in alkaline sludges can render plant nutrients applied as inorganic fertilizers unavailable for plant uptake through adsorption.

Based on the potential of HDS to sorb metals and metalloids this study envisaged that it can improve soil fertility. Therefore, the objectives of this study were to determine if HDS is a liming material, a source of Ca, S and other nutrients, decreases plant availability of some essential elements, encourages the accumulation of non-essential or harmful elements, and encourages any salt sequestration.

8.2 MATERIALS AND METHODS

Greenhouse and laboratory investigations were conducted as discussed in Chapter 9. A pot trial was set up to allow the assessment of the response of an acid soil when treated with HDS. The study focussed on three aspects; the response of soil, the response of crop and the uptake of metals, Pb and Ni present in HDS. This part (Chapter 8) of the study therefore, reports only on soil effects. The laboratory investigations were conducted to determine possible changes in the chemical status of the soil.

8.2.1 Sources of sludges and soil used

Two sludges were considered selected based on different treatment processes described in Chapter 6 generated from Mpumalanga coalfields of the Republic of South Africa (RSA), sampled in 2017. One of the sludges was sourced from a limestone treatment plant, ferriferous gypseous (GypFeMnNi) containing gypsum, Fe oxides, Mn and Ni. The other was collected from a Limestone plus Hydrated Lime treatment plant, gypseous (Gyp), a refined product dominated by gypsum. To assess their effects as soil amendments an acid soil with a pH of 3.75, low in bases was selected. The intention here was to assess the liming effect of these materials in increasing soil pH, their effect on soil salinity and if they can contribute to soil Ca and S.

8.2.2 Basic chemical properties of sludges and soil used

Analysis

Before the establishment of HDS-Soil mixtures, the individual sludges and soil (Table 8.1) were analysed for chemical status and after harvesting of the crop the HDS-Soil mixtures were assessed for changes in chemical properties. Total elemental content in sludge and soil was determined following acid digestion method 3052, described by Environmental Protection Agency (EPA) of The United States of America (USA). A 0.3 g sample was treated with concentrated nitric acid (HNO_3) at a solid to solution ratio of 1:30 and transferred into a digestion tube. The sample was digested at 180 $^oC \pm 5$ ^oC by the Anton Paar Multiwave 3000 digester for 15 to 19.5 minutes after which was transferred into a 50 ml centrifuge tube. Extractable elements in the sample were determined with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Plant available elements were also determined in the HDS-Soil mixtures and soil using Ammonium Acetate (NH_4OAc) to extract Fe, Mn, Ni, Zn, Pb, Cd, S; using ethylene diamine tetra acetic acid (EDTA) or Mehlich 3 to extract K, Ca, Na, Mg and P-Bray 1 solution to extract P.

Standard methods as described by Thomas (1996) and Rhoades (1996) in Methods of Soil Analysis Part 3 Chemical Methods (1996) were followed to determine pH and electrical conductivity (EC) of HDS-Soil mixtures (after harvesting), individual sludges and soil. A multi-parameter analyser (Consort C830) with a 0.01 pH resolution coupled with epoxy electrode was used and an electrical conductivity meter (Consort C861) with a 0.001 µS cm^{-1} resolution coupled with conductivity electrode was used.

Physical and chemical status of soil used (a brief description)

The soil used was extremely acidic with a pH of 3.75 and showed an extremely low salinity (7.8 mS m^{-1}) indicative of the substantially low salts contained (Table 8.1). This soil was collected from a field that was intentionally acidified over the years for research purposes. This soil was therefore expected to positively respond to the liming effects of the sludges. With regards to elemental content this soil was dominated by Fe, while other elements such as Ca, Mg, S, Pb, Ni and Cd were substantially low. The low Ca content suggests that this element was possibly exchanged and leached out from the topsoil.

Table 8.1: Selected physicochemical soil properties

pH(H_2O)	3.75		
Salinity (EC) (mS m^{-1}) at 2.5 soil /solid ratio	7.8		
CEC (cmol$_c$ kg^{-1})	7.98		
Texture	Clay Loam		
	Acid digestion (mg kg^{-1})	Extractable elements (mg kg^{-1})	Extraction methods
Major elements			
Ca	26	18	NH_4OAc
K	894	68	NH_4OAc
Mg	338	12	NH_4OAc
P	244	8	P-Bray 1
S	69	25	EDTA
Metals			
Cd	< 0.18	< 0.01	EDTA
Fe	37363	25	EDTA
Mn	301	167	EDTA
Na	38	< 0.01	EDTA
Ni	35	0.9	EDTA
Pb	36	7.2	EDTA
Zn	20	1.2	EDTA

Note: NH_4OAc = Ammonium acetate, EDTA = Ethylenediaminetetraacetic acid. Values with the smaller than sign (<) indicate Method Detection Limits (MDL) of those elements.

Chemical and mineralogy status of HDS materials used (a brief description)

The determination of basic chemical properties of each sludge was meant to aid in understanding their possible contribution to liming. Chemically, GypFeMnNi was slightly acidic with a pH of 5.5 and an alkalinity of 250 mg kg^{-1} (Table 8.2) and this was because the material was from the limestone treatment where the limestone is capable of increasing the pH of the solution to close to neutral. The increase in pH of the solution is usually prevented by armouring where insoluble precipitation of metals, especially Fe and Mn, occurs on the surfaces of the limestone particles preventing further dissolution and chemical reactions (Sun et al. 2000). While Gyp showed to be alkaline with a pH of 9.4 due to the use of $CaCO_3$ plus $Ca(OH)_2$ during treatment and had an alkalinity of 617 mg kg^{-1}. The $Ca(OH)_2$ was capable of increasing solution pH to >10.5 with a potential of precipitating most of the metals into hydroxides (Balintova and Petrilakova 2011). Gyp was therefore expected to be a better liming material than GypFeMnNi. In terms of total elemental content both sludges showed substantially high Ca and S concentrations and Mg contributed mainly by the neutralizing material (Table 8.2). GypFeMnNi also indicated more total Fe concentration and Mn compared to Gyp. Cadmium concentration was extremely low (< 0.18 mg kg^{-1}) in both sludges, Ni content was more in GypFeMnNi, whereas, Pb content was mostly in Gyp. AMD was the main source of these metals.

As discussed in Chapter 4, the mineral composition indicated that both sludges were largely gypsum. The gypsum in the sludges precipitated from Ca contributed by either hydrated lime or limestone used for the treatment and S from AMD. The gypsum in GypFeMnNi accounted for 72 – 77% of the material, with amorphous Fe oxides making-up 17.8% (as determined by XRF), 4% of carbonate minerals (e.g. ankerite) and Hematite (Fe_2O_3). Ankerite formation was facilitated by the lower pH (5.5) in GypFeMnNi and the increased concentrations of Fe, Mg, Mn and Ca (Hendry et al. 2000). Coprecipitated P/Fe with ferrihydrite at pH 3 – 6 promoted transformation of ferrihydrite into Fe_2O_3 (Cornell and Schwertmann 2003). Gyp was composed of a single mineral phase, that of gypsum.

Table 8.2: Selected chemical sludge properties and selected total elemental content

Parameter	GypFeMnNi	Gyp
pH(H_2O) at 2.5 solution /solid ratio	5.5^{b}	9.4^{a}
Salinity (EC) (mS m^{-1}) at 2.5 solution /solid ratio	364^{a}	274^{b}
Total Alkalinity as $CaCO_3$ (mg kg^{-1})	250^{b}	617^{a}
Concentrations extracted by acid digestion (mg kg^{-1})		
Major elements		
Ca	182961^{b}	224500^{a}
K	83^{a}	61^{b}
Mg	6513^{a}	2736^{b}
P	44^{b}	129^{a}
S	132974^{b}	216189^{a}
Metals		
Cd	< 0.18	<0.18
Fe	124500^{a}	152^{b}
Mn	7590^{a}	95^{b}
Na	74^{b}	279^{a}
Ni	108^{a}	0.7^{b}
Pb	< 0.2	40^{a}
Zn	285^{a}	5^{b}

Note: Note: $\alpha < 0.05$; CV = 4 – 12%. GypFeMnNi = Ferriferous gypseous with Mn and Ni; Gyp = Gypseous. Means with the same letter across sludges are not significantly different from each other. Values with the smaller than sign (<) indicate Method Detection Limits (MDL) of those elements.

8.2.3 Determination of exchangeable acidity and exchangeable hydrolysable cations (EHC) of soil.

Potassium Chloride (KCl) extraction to determine exchangeable Al, soluble and exchangeable acidity in the soil was carried out as described by Thomas (1982) in Standard Methods of Soil Analysis Part 2. This was meant to assess the initial soil acidity and changes at the end of the season.

8.2.4 Development of Sludge-Soil mixtures

A homogeneous mixture of sludge and soil was required intended for plant growth. Each of the sludges was applied at two rates (10 and 20 t ha^{-1}) and each level was thoroughly mixed on a mass/mass basis with 8.8 kg of soil (prepared by sieving through a 5 mm sieve). The highest application rate adopted was 10 t ha^{-1} of commercial agricultural gypsum reported by Food and Agriculture Organization of the United Nations (1990). This rate was then doubled to assess the effect on soil and plant. The mass of soil per hectare was estimated to be 2.1 x 10^6 kg assuming a 0.15 depth and a density of 1400 kg m^{-3}. Each HDS-Soil mixture was then transferred into pots with 26 cm top and 20 cm bottom diameters and a height of 25 cm. They also had three small openings at the bottom to allow for drainage.

8.2.5 Experimental design adopted

This was a two-factor experiment arranged in a Randomized Complete Block Design (RCBD). The experiment had 18 treatments with a total of 6 controls. Three of the controls received hydrated lime ($Ca(OH_2)$) at 3.7 t ha^{-1} and different levels of P and were considered "positive controls", while the other 3 received no hydrated lime at three P levels and were considered to be "negative controls" (Table 8.3). The other 12 treatments were made up of the two HDS materials, each at three levels of P application. All treatments were replicated 3 times.

Table 8.3: Treatments included

Treatments	Comments	Description of treatments
Soil + H lime	Positive control	3.7 t ha^{-1} H lime
SoilP40 + H lime		40 kg ha^{-1}P; 3.7 t ha^{-1} H lime
SoilP100 + H lime		100 kg ha^{-1}P; 3.7 t ha^{-1} H lime
Soil	Negative control - Soil unlimed	
SoilP40		40 kg ha^{-1}P
SoilP100		100 kg ha^{-1}P
10GypP0		10 t ha^{-1} Gyp; 0 kg ha^{-1}P
10GypP40		10 t ha^{-1} Gyp; 40 kg ha^{-1}P
10GypP100		10 t ha^{-1} Gyp; 100 kg ha^{-1}P
20GypP0		20 t ha^{-1} Gyp;0 kg ha^{-1}P
20GypP40		20 t ha^{-1} Gyp; 40 kg ha^{-1}P
20GypP100		20 t ha^{-1} Gyp; 100 kg ha^{-1}P
10GypFeMnNiP0		10 t ha^{-1} GypFeMnNi; 0 kg ha^{-1}P
10GypFeMnNiP40		10 t ha^{-1} GypFeMnNi; 40 kg ha^{-1}P
10GypFeMnNiP100		10 t ha^{-1} GypFeMnNi; 100 kg ha^{-1}P
20GypFeMnNiP0		20 t ha^{-1} GypFeMnNi;0 kg ha^{-1}P
20GypFeMnNiP40		20 t ha^{-1} GypFeMnNi; 40 kg ha^{-1}P
20GypFeMnNiP100		20 t ha^{-1} GypFeMnNi; 100 kg ha^{-1}P

Note: Gyp (t ha^{-1}) = Gypseous; GypFeMnNi (t ha^{-1}) = Ferriferous gypseous with Mn and Ni; P (kg ha^{-1}) = Phosphate; H = hydrated

8.2.6 Statistical analysis

All statistical analysis was carried out using SAS Version 9.4. ANOVA was carried out to establish differences amongst treatments and to separate means, Least Significant Difference Mean Separation Test was used. To assess main effects averages were calculated across the sludges and P added.

8.3 RESULTS AND DISCUSSION

Chemical and biological reactions in the soil are controlled by pH (Hendershot and Lalande 2008). Under strong acidity conditions the bioavailability of some of the elements (e.g. Ca, P, K, and Mg) essential for plant growth are reduced, but some such as Mn and Al are increased (Agegnehu et al. 2019). Acidity is composed of exchangeable H^+, exchangeable Al as either Al^{3+} or partially neutralized compounds (Al-OH) for example $AlOH^{2+}$, $Al(OH)_2^+$ and organic acids (Hendershot and Lalande 2008). When the acidity is coupled with Al^{3+} toxicity, this leads to poor soil fertility and reduces soil productivity (Han et al. 2019). Liming is generally used to increase the bioavailability of essential plant nutrients and reduce the toxicity of Al^{3+}. In this study, therefore, the sludges were expected to ameliorate the acid soil used since they contain solid phases of $CaCO_3$ and $Mg(OH)_2$ that contribute to alkalinity. It was on these bases that this discussion was included to help understand the amelioration effects of the sludges on soil pH, exchangeable acidity and exchangeable hydrolysable cations as these influence the availability and uptake of elements by the plant.

8.3.1 Liming effect of the different sludges

Co-application of sludge with phosphate effected an increase in pH, but this increase was marginal. The addition of phosphate from 40 to 100 kg ha^{-1} significantly ($\alpha < 0.05$) increased soil pH (Table 8.4). This was due to phosphate sorption which involves the co-sorption of hydrogen ions (H^+) and cations. A significant ($\alpha < 0.05$) increase in soil pH was also evident when the application of sludge on its own was increased to 20 t ha^{-1}. The interaction of phosphate with either of the sludges also significantly ($\alpha < 0.05$) increased soil pH. This was an indication that phosphate was able to precipitate H^+ which lead to pH increase. But this increase in pH was predominantly where phosphate was added at 100 kg ha^{-1} and when the sludges were applied at 20 t ha^{-1}. Increasing phosphate to 100 kg ha^{-1} influenced GypFeMnNi and Gyp to increase soil pH by 0.31 and 0.46 relative to the pH of the soil (3.75). But still this increase in pH was marginal, not suitable for the growth of plants. This soil pH was expected to increase further since both sludges either applied at 10 or 20 t ha^{-1} had their alkalinity (2500 – 12340 kg ha^{-1}) exceeding soil exchangeable acidity (945 kg ha^{-1}). This suggested some mechanism was responsible for buffering pH. In the presence of abundant Fe oxides, armouring was the most possible mechanism which reduced the potential of the sludges to increase pH. The pH exhibited by GypFeMnNi was influenced mostly by alkalinity present in the material and the co-sorption of H^+ by phosphate. However, this increase in pH by both sludges was significantly lower than the pH value shown by the limed soil. Liming alone increased soil pH to > 5 as expected. A further increase in pH in the limed soil was obtained when the phosphate rate was increased to 100 kg ha^{-1}. Applying sludges on their own and co-application of phosphate with sludge significantly increased soil pH. Applying phosphate on its own did not significantly increase soil pH.

Table 8.4: Effect of treatments on soil pH

P	Sludges (t ha^{-1})						
	Soil	Soil (Limed)	10Gyp	20Gyp	10GypFe MnNi	20GypFe MnNi	*Average*
P0	3.75^{fgh}	5.10^{c}	3.56^{h}	3.79^{fgh}	3.83^{efg}	3.74^{fgh}	*3.8^{c}*
P40 (kg ha^{-1})	3.63^{gh}	5.68^{b}	3.81^{efgh}	3.91^{ef}	3.90^{ef}	3.90^{ef}	*3.89^{b}*
P100 (kg ha^{-1})	3.80^{efgh}	5.95^{a}	3.91^{ef}	4.06^{de}	3.93^{ef}	4.21^{d}	*4.04^{a}*
Average	*3.73^{c}*	*5.43^{a}*	*3.73^{c}*	*3.91^{b}*	*3.88^{b}*	*3.91^{b}*	

$\alpha < 0.05$, CV = 0.2%, LSD = 0.1375. Note: Gyp (t ha^{-1}) = Gypseous; GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; S = Soil, SL = Soil Limed, P (kg ha^{-1}) = Phosphate.

8.3.2 Sludge effects on exchangeable acidity and Al

The soil initially showed an exchangeable acidity of 14.7 $mmol_c$ kg^{-1} (Fig. 8.1 A), whereas GypFeMnNi as it had an acidic pH of 5.5 showed an extremely low acidity of 2.1 $mmol_c$ kg^{-1}. The co-application of phosphate with either sludge significantly ($\alpha < 0.05$) reduced soil acidity. This decrease was more evident where the treatments had sludge on its own or had a combination of sludge and phosphate. Amongst treatments with sludges, the treatments that had a co-application of Gyp or GypFeMnNi at 20 t ha^{-1} with phosphate at 100 kg ha^{-1} reduced acidity the most by 74 and 67% and these percentages were not statistically significantly different ($\alpha < 0.05$) from each other. Generally, treatments with Gyp reduced acidity more than those with GypFeMnNi. However, an increase in the application of either sludge to 20 t ha^{-1} significantly ($\alpha < 0.05$) reduced acidity. For instance, increasing the sludge Gyp on its own to 20 t ha^{-1} reduced acidity relative to the initial soil acidity by 55% and GypFeMnNi by 33%. Applying phosphate on its own at 40 and 100 kg ha^{-1} significantly ($\alpha < 0.05$) reduced acidity by 3 and 16% relative to the initial acidity of 14.7 $mmol_c$ kg^{-1}. This was expected because phosphate is known to precipitate protons in soils and facilitates an increase in soil pH. Excluding phosphate, sludge and hydrated lime especially in the treatment, SP0, increased acidity relative to the initial soil acidity by 11% at the end of the season possibly by the addition of $(NH_4)_2HPO_4$. As expected, liming reduced soil acidity the most from 92 to 94% relative to the initial soil acidity.

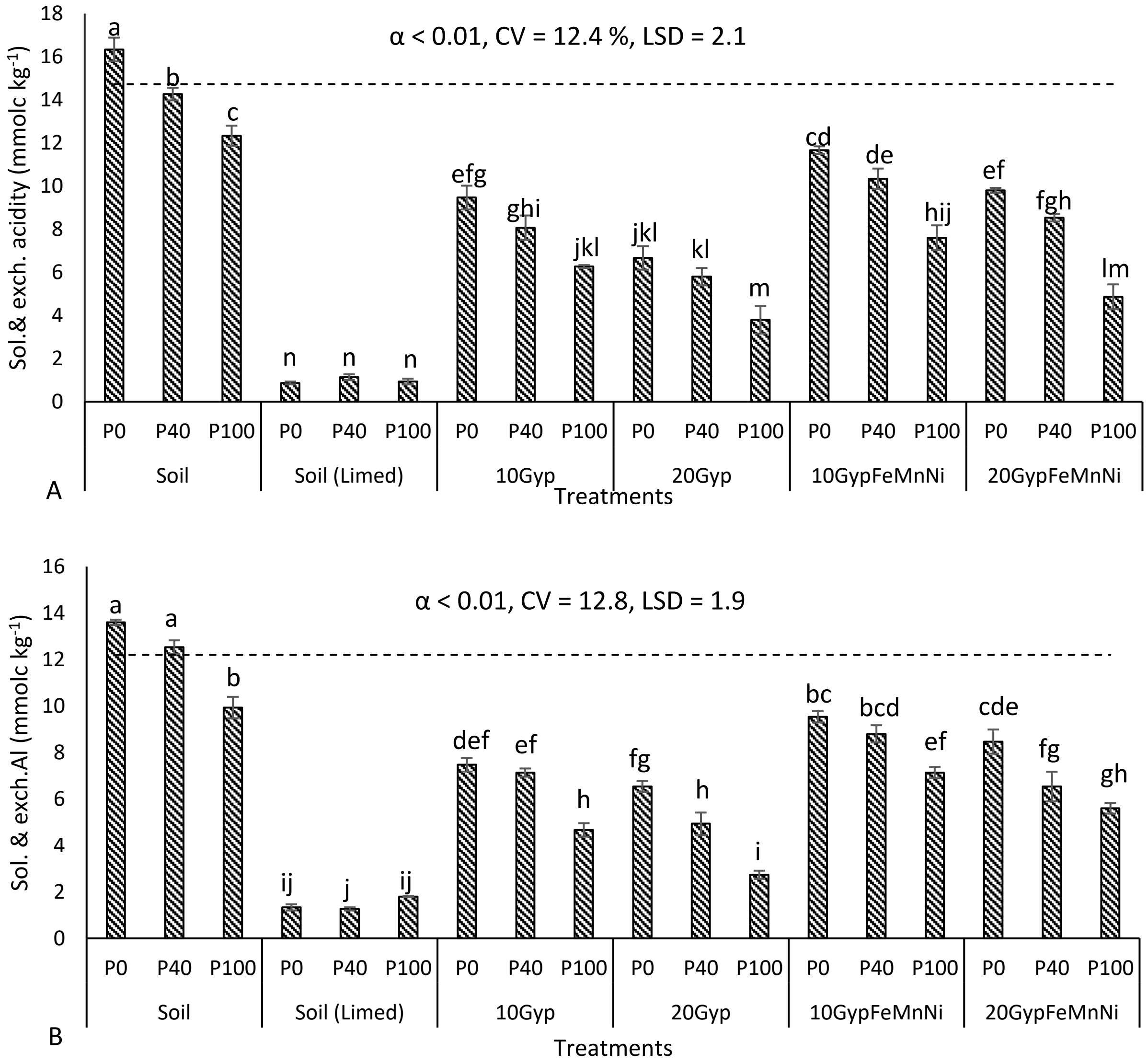


Figure 8.1: A) Exchangeable Acidity reduction, dotted line indicates initial exchangeable acidity, B) Exchangeable Hydrolysable Cations, dashed line indicates initial exchangeable hydrolysable cations, Note: Gyp (t ha^{-1}) = Gypseous; GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; P (kg ha^{-1}) = Phosphorus

The soil showed an initial exchangeable hydrolysable cations (EHC) of 12.2 mmol$_c$ kg^{-1}, with GypFeMnNi showing a substantially low EHC of 1.3 mmol$_c$ kg^{-1}. The application of phosphate on its own or either sludge significantly ($\alpha < 0.05$) reduced EHC (Fig. 8.1 B). However, the decrease in EHC was more evident where sludge on its own or in combination with phosphate was applied. It should be noted that treatments with Gyp generally, reduced EHC more than those with GypFeMnNi. The combination effect of the sludge Gyp applied at 20 t ha^{-1} with phosphate at 100 kg ha^{-1} reduced EHC the most by 78% and was statistically significant ($\alpha <$

0.05). An increase in the application of either sludge (on its own) to 20 t ha^{-1} significantly ($\alpha < 0.05$) reduced EHC. For example, increasing the application of Gyp on its own to 20 t ha^{-1} reduced EHC by 46% relative to the initial EHC and GypFeMnNi reduced EHC by 31%. Increasing phosphate on its own to 100 kg ha^{-1} in the treatments without sludge and hydrated lime significantly ($\alpha < 0.05$) reduced EHC by 19 % relative to the initial EHC (12.2 mmol$_c$ kg^{-1}). This was expected because phosphate is known to precipitate soluble Al under acidic soil conditions forming a sparingly soluble mineral, such as variscite ($AlPO_4{\cdot}2(H_2O)$. Excluding phosphate, sludge and hydrated lime in the treatments, Soil P0 and Soil P40 increased EHC by 3 and 11% relative to the initial EHC by the end of the season due to slight reduction in pH and an increase in exchangeable acidity. Liming as expected, reduced EHC more than any other treatment, it reduced it by 90% relative to the initial EHC.

8.3.3 pH influence on Soil Exchangeable Acidity and Exchangeable Hydrolysable Cations

The influence of pH on soil acidity and EHC was assessed based only on treatments with sludges. The marginal increase in pH facilitated by the sludges and phosphate reduced both soil acidity and EHC (Fig. 8.2: A & B) showing a negative correlation. pH accounted for 21 and 32% in the reduction of EHC and exchangeable soil acidity, suggestion that 79 and 68% reduction in EHC and exchangeable soil acidity was accounted for by other factors such as natural variation or experimental error.

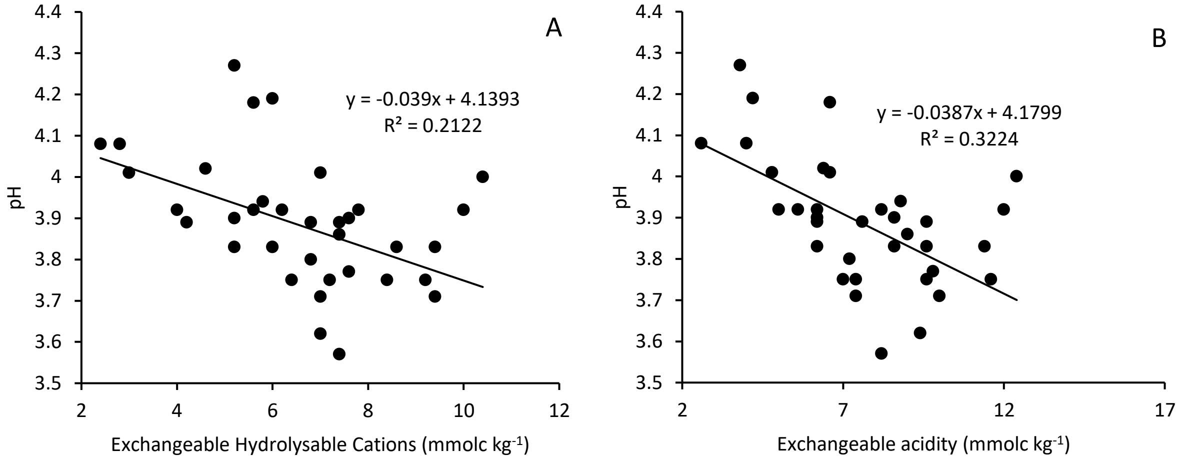


Figure 8.2: A) pH influence on Exchangeable Hydrolysable Cations (EHC), B) pH influence on Exchangeable Soil Acidity

8.3.4 Salt sequestration/salting out in soil-sludge mixtures

Although the sludges contained Fe oxides known to adsorb elements, they also contained a myriad of salts, e.g. Ca, Mg, Na, SO_4, Mn, CO_3, Al and K, as indicated in Chapter 4, that can possibly increase soil salinity to levels toxic to plants. It was on this background that this discussion was included focusing on the potential of the sludges to influence soil salinity. The application of phosphate on its own significantly ($\alpha < 0.05$) reduced soil salinity (Table 8.5) due to sequestration of salts through precipitation and co-sorption. There was a significant ($\alpha < 0.05$) increase in salinity with the addition of either sludge when applied at 20 t ha^{-1}. The minerals gypsum and ankerite in the sludges were the sources of salts. The combination effect of either sludge with phosphate was also significant ($\alpha < 0.05$). However, the significant differences were more evident when either of the sludges was applied at 20 t ha^{-1} either on its own or in combination with phosphate. When Gyp and GypFeMnNi were applied on their own they significantly increased initial soil salinity of 7.8 mS m^{-1} the most by 813 mS m^{-1} and 560 mS m^{-1}, levels suitable only to salt tolerant plants. It should be noted that there was an increase in the initial salinity of soil alone from 7.8 mS m^{-1} to 160 mS m^{-1} probably due to the fertilizers applied (Table 8.5 & Fig. 8.3). The reduction in the increase in salinity by GypFeMnNi was because this material was composed of Fe oxides that possibly sequestrated some of the soluble salts through surface precipitation, complexation or co-sorption. Liming the soil drastically reduced soluble salts as expected hence salinity was extremely low in these treatments (Table 8.5 & Fig. 8.3).

Table 8.5: Effect of treatments on salinity (mS m^{-1}) in soil-sludge mixtures

P	Sludges (t ha^{-1})						
	Soil	Soil (Limed)	10Gyp	20Gyp	10GypFeMnNi	20GypFeMnNi	*Average*
P0	160^{ghi}	13^{i}	576^{cde}	981^{a}	348^{efgh}	728^{bc}	*468*^{a}
P40 (kg ha^{-1})	122^{hi}	14^{i}	443^{def}	865^{ab}	338^{fgh}	644^{bcd}	*404*^{b}
P100 (kg ha^{-1})	161^{ghi}	14^{i}	347^{efgh}	818^{ab}	371^{efg}	449^{def}	*360*^{b}
Average	*148*^{d}	*14*^{e}	*455*^{c}	*888*^{a}	*352*^{c}	*607*^{b}	

$\alpha < 0.05$, CV = 2.1%, LSD = 126, Note: Gyp (t ha^{-1}) = Gypseous; GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; P (kg ha^{-1}) = Phosphorus

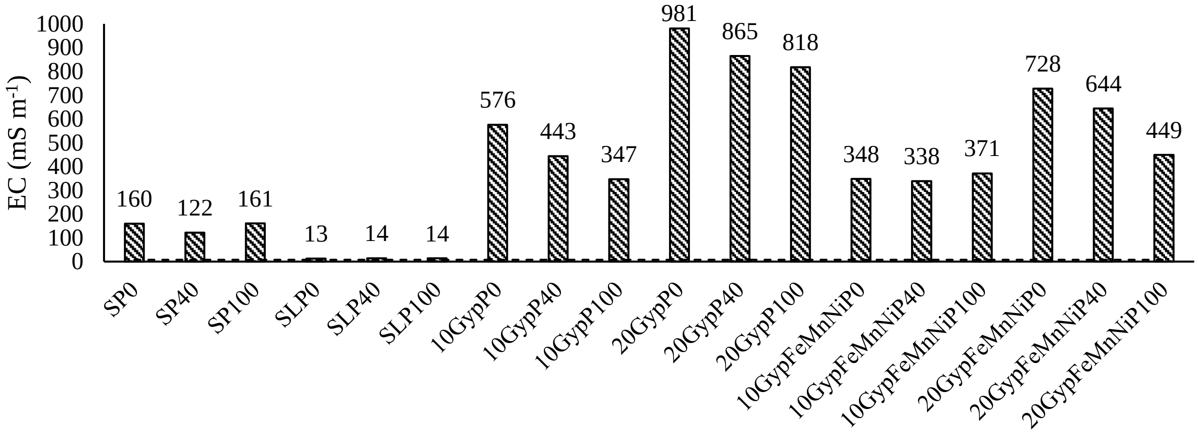


Figure 8.3: Soil salinity as influenced by sludges, phosphate and hydrated lime applied. Dotted line represents initial salinity for soil without hydrated lime, P and sludge (7.8 mS m^{-1}). Note: S = Soil; SL = Soil Limed; Gyp (t ha^{-1}) = Gypseous; GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; P (kg ha^{-1}) = Phosphorus

8.3.5 Are the sludges sources of Ca, S and other nutrients?

Availability of Ca, S and other nutrients contributed by the sludges was of main focus here. Total S was extremely low in soil (SP0, SP40, SP100) and in treatments with hydrated lime (SLP0, SLP40, SLP100) compared to those with sludges (Fig. 8.4: A). Total S increased with an increase in the addition of either sludge from 10 to 20 t ha^{-1} due to the gypsum contained. Gyp contributed more total S compared to the same rates of GypFeMnNi and this was because Gyp contained > 95% gypsum compared to GypFeMnNi which contained 72 – 77% of this mineral. The availability of this element (S) relative to total S increased with an increase in the addition of either sludge. However, in treatments with sludges either applied at 10 or 20 t ha^{-1}, the S released was approximately half. There was evidence of a decrease in the S released where phosphate was increased to 100 kg ha^{-1} in treatments that received 10 t ha^{-1} of Gyp and 20 t ha^{-1} of GypFeMnNi. Similarly, total Ca increased with an increase in the addition of either sludge and this trend was also observed with its availability (Fig. 8.4: B). Gyp contributed more total and soluble Ca compared to GypFeMnNi to the soil and this was due to the differences in gypsum composition. With both sludges and for each application rate (10 and 20 t ha^{-1}), Ca released was approximately half of the total Ca. The Ca observed in the treatments with hydrated lime was contributed mostly by the $Ca(OH)_2$ added to raise the soil pH to > 5 and Ca in the soil released by increasing pH. Both total and available Ca was extremely low in all treatments with soil alone and those with phosphate (SP0, SP40 and SP100).

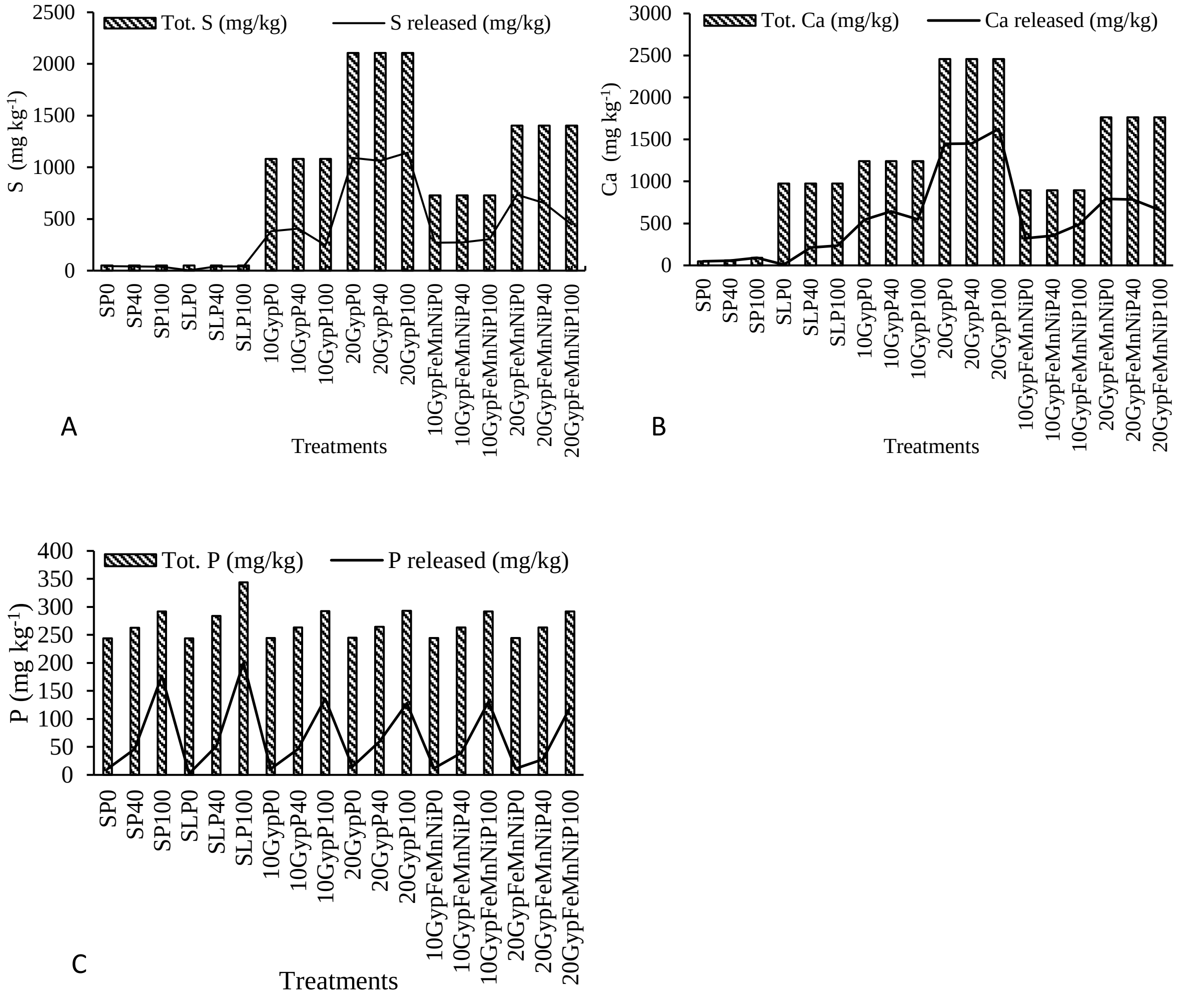


Figure 8.4: Selected major plant nutrients, total and available; A) S, B) Ca, C) P. Note: Gyp (t ha^{-1}) = Gypseous; GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; P (kg ha^{-1}) = Phosphorus

An increase in the addition of phosphate increased its total content and its availability in all treatments (Fig. 8.4: C). Although this trend was maintained by all treatments, but the addition of both sludges gradually reduced both total and available phosphate. This could be due to the precipitation of phosphate with Ca and other elements especially from Gyp and possibly adsorption onto the Fe oxides present in GypFeMnNi. On the hydroxylated surfaces of ferric hydroxides, phosphate is adsorbed as binuclear bridging complex occurring on OH groups in one coordination with Fe atoms (Guzman et al. 1994) reducing its bioavailability in the process.

With respect to trace metals, Mn, Fe and Zn the focus was influenced by their availability in the sludges, especially in GypFeMnNi. Total Mn in treatments with soil without phosphate (SP0), soil with hydrated lime (SLP0, SLP40, SLP100) and treatments with Gyp, this element was contributed mostly by soil (Fig. 8.5, A). The soil had 277 mg kg^{-1} of Mn. Thus, Gyp and the phosphate source used had extremely low Mn. Manganese in treatments with GypFeMnNi increased with an increase in the application of this sludge since it contained the most Mn (7590 mg kg^{-1}). The solubility trend for Mn showed that keeping the soil acidic (pH 3.75) facilitated the solubility of this element, but liming the soil to pH > 5 drastically reduced its availability. The addition of either sludge as well reduced the solubility of this element either through precipitation or sorption on reactive mineral surfaces.

Similarly, total Fe in treatments with soil alone, soil and phosphate, soil with hydrated lime and treatments with Gyp was contributed mostly by soil (Fig. 8.5, B) as it contained 37363 mg kg^{-1} of this element. Gyp and phosphate applied had minimal Fe concentration. Increasing the application of GypFeMnNi in treatments with this material increased total Fe as this material contained the most Fe (124500 mg kg^{-1}). In terms of solubility, generally Fe was extremely low in all treatments (Fig. 8.5, B). The acidity of treatments with soil without sludge (SP0, SP40 and SP100) increased Fe solubility, but liming drastically reduced it. The solubility of this element (Fe) increased with an increase in the application of the sludges.

Total Zn in treatments with soil (SP0, SP40, SP100), soil with hydrated lime and treatments with Gyp, was contributed mostly by soil (Fig. 8.5, C) as it contained more (20 mg kg^{-1}) Zn. Total Zn concentration increased with an increase in the application of GypFeMnNi as it contained the most Zn (285mg kg^{-1}). Keeping the soil acidic increased the solubility of this element (Zn). Liming and increasing phosphate application gradually increased Zn solubility as well. The application of sludges slightly reduced Zn solubility into almost a constant concentration. In these treatments the different sludge rates could not substantially influence an increase in soluble Zn.

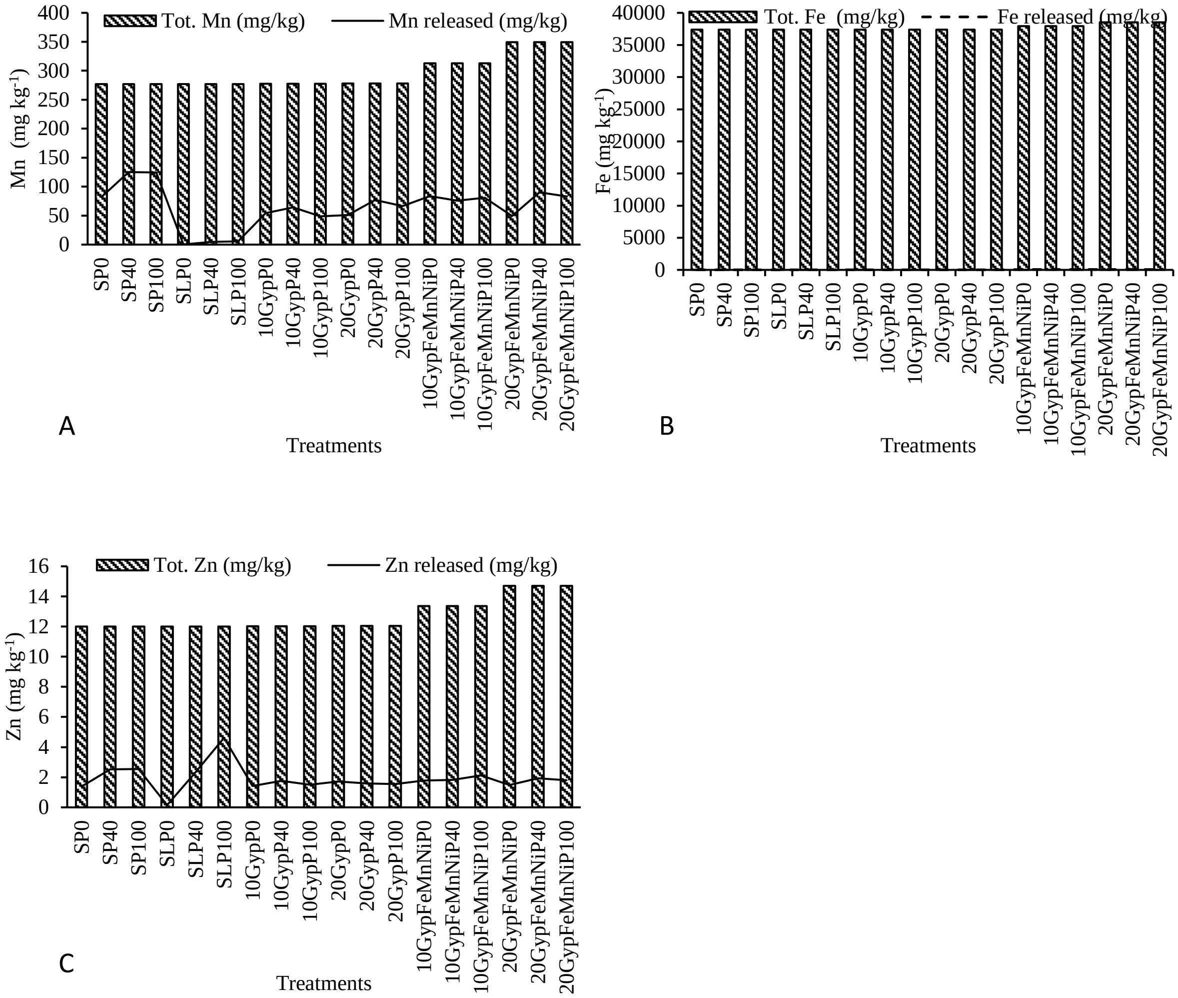


Figure 8.5: Total and available trace elements; A) Mn, B) Fe, C) Zn. Note: Gyp (t ha^{-1}) = Gypseous; GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; P (kg ha^{-1}) = Phosphorus

The discussion of Ni and Pb was influenced by their abundance in the sludges and their reported risk to the environment. In treatments with soil (SP0, SP40, SP100), soil with hydrated lime (SLP0, SLP40, SLP100) and treatments with Gyp, Ni was contributed mostly by soil (Fig. 8.6, A) as it contained 35 mg kg^{-1}) which was more than in the source of phosphate applied and Gyp. Total Ni concentration increased with an increase in the application of GypFeMnNi as this material contained 108 mg kg^{-1} total Ni Relative to total concentration soluble Ni was extremely low in all treatments. However, the solubility trend indicated that the low soil pH (3.75) increased Ni solubility but liming drastically reduced its availability. Increasing the application of either sludge gradually increased the solubility of Ni. The application of phosphate could not substantially influence Ni availability.

With respect to Pb (Fig. 8.6, B) in treatments with soil (SP0, SP40, SP100), soil with hydrated lime (SLP0, SLP40, SLP100) and treatments with GypFeMnNi, Pb in these treatments was contributed mostly by soil. Total Pb concentration increased with an increase in the application of Gyp as this material contained 40 mg kg^{-1} which was more than in GypFeMnNi, soil and source of phosphate. keeping the pH of the soil at 3.75 facilitated the solubility of this element but liming drastically reduced its availability. Adding either sludge increased Pb solubility to even above that shown by the acid soil (SP0, SP40, SP100). As such, treatments with 20 t ha^{-1} of Gyp had the most soluble Pb than any other treatment. This was because Gyp contained the most Pb (40 mg kg^{-1}) than the Pb in GypFeMnNi (< 0.27 mg kg^{-1}) and soil (36 mg kg^{-1}).

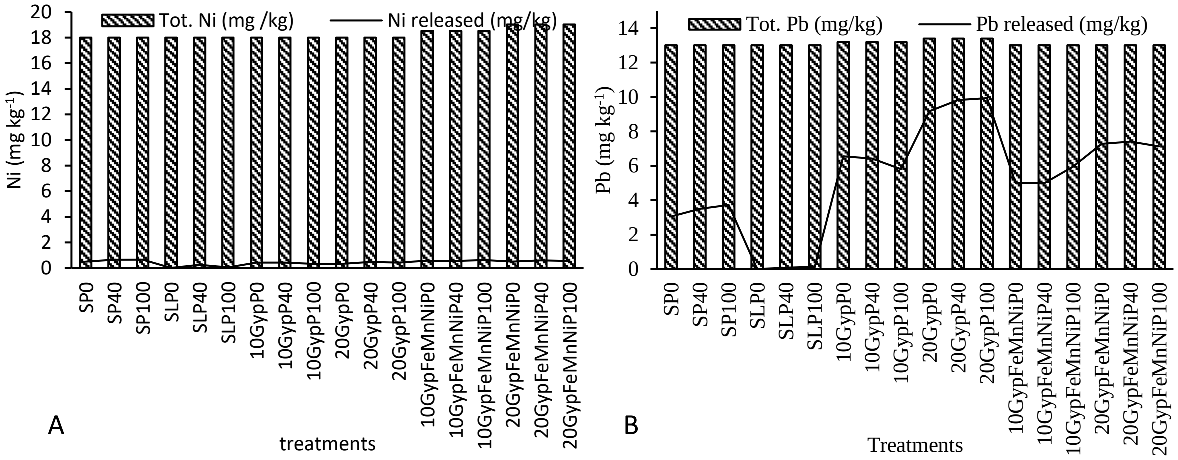


Figure 8.6: Total and available metals; A) Ni, B) Pb. Note: Gyp (t ha^{-1}) = Gypseous; GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; P (kg ha^{-1}) = Phosphorus

Generally, liming increased the availability of Ca but reduced that of trace nutrients (Mn, Fe, Zn) and transition metals (Ni and Pb). But under acidic conditions the solubility of these elements (Mn, Fe, Zn, Ni and Pb) increased. Adding either sludge at 10 and 20 t ha^{-1} increased the solubility of all the elements considered for some of them (Ca, S, Fe and Pb) to even above that observed in soil without sludge or hydrated lime. This was due to the dissolution of the sludge materials.

8.4 CONCLUSIONS

The focus was to investigate the influence of sludge on soil fertility and availability of elements. Applying either sludge with phosphate increased soil pH (3.75) marginally. Applying GypFeMnNi at 20 t ha^{-1} with phosphate at 100 kg ha^{-1} increased soil pH to 4.21 and Gyp to 4.06. Therefore, to use these sludges solely to raise soil pH to > 5 would require quantities > 20 t ha^{-1} but such can increase salinity, metal solubility and sorption of added inorganic plant nutrients like phosphate. HDS also reduced exchangeable soil acidity and exchangeable hydrolysable cations. The sludges on their own significantly increased soil salinity, with Gyp at 20 t ha^{-1} increasing it the most to 728 mS m^{-1} (suitable only for salt tolerant crops). Generally, the application of either sludge increased the availability of Ca and S (through gypsum solubility) but reduced that of phosphate due to sorption by Fe oxides in GypFeMnNi and precipitation with Ca from both sludges. Increasing the application of GypFeMnNi also increased the availability of Fe, Ni and Mn as these were abundant in this material, whereas increasing Gyp increased Pb availability. Irrespective of the sludge sources, both are only suitable for the supply of Ca and S deficient in acid soils. Higher application rates or continuous use of these sludges can possibly increase soil pH to a certain threshold value; Ca and S; however, higher rates may potentially increase salinity, metal accumulation, such as Pb and Ni. Based on the supply of Ca and S by the sludges, application rates above 20 t ha^{-1} maybe recommended in future to further increase their availability and such research should be on a field scale to assess the response of soil. However, the accumulation of Ni in the soil should be monitored (as it is the limiting element in the sludges), so that its threshold of 50 mg kg^{-1} is not exceeded. It is recommended therefore, that the application rate of the sludge, GypFeMnNi, does not exceed 1042 t ha^{-1} per single application to avoid exceeding Ni threshold in the soil. The application rate of Gyp should not exceed 3375 t ha^{-1} per single application. Long term trials may also be recommended.

CHAPTER 9

HIGH DENSITY SLUDGE AS A SOIL AMENDMENT – CROP RESPONSE

ABSTRACT

Unlike other hazardous industrial solid wastes, High Density Sludge (HDS), a gypseous material generated by the neutralization of Acid Mine Drainage (AMD) has not yet been investigated for its potential use in agriculture. This material from the coalfields of the Republic of South Africa (RSA) may be classified as hazardous due to its metal content (Mn, Ni and Pb) and, therefore, is destined for storage facilities. However, this material has some value for use as a soil amendment since it consists largely of gypsum and contains Fe oxides. The Fe oxides have the potential to adsorb phosphate, which can also precipitate some of the elements reducing their phyto-availability, therefore, these aspects were also investigated in this study. Hence, the objective was to assess the response of a crop grown in a soil (pH 3.75) treated with phosphate co-applied with HDS, phosphate and HDS on their own. Further, the impact of phosphate on nutrient phyto-availability and uptake was assessed. A pot trial was conducted, where a ferriferous gypseous sludge (GypFeMnNi) with Mn and Ni from limestone treatment and another gypseous sludge (Gyp), a refined product from limestone plus hydrated lime treatment were considered, each applied at 10 and 20 t ha^{-1}. Phosphate was applied at either 40 or 100 kg ha^{-1}. Positive (soil limed to pH 6.0) and a negative (unlimed soil) controls were included. Maize was planted, grown to physiological maturity and harvested. Results showed that phosphate co-applied with sludge, sludges and phosphate on their own contributed marginally in increasing soil pH, and consequently seed germination was reduced due to soil acidity. Co-application of phosphate with either sludge slightly reduced plant height, biomass and leaf area index (LAI), compared to limed soil. All these parameters were still better than those of the negative control. GypFeMnNi applied at 20 t ha^{-1} and phosphate at 100 kg ha^{-1}, increased plant height the most. Calcium, S, Fe and Mn were concentrated mostly in the foliage. Co-application of phosphate with either sludge increased the concentration of Ca and Mn, but reduced that of S and Fe in the foliage. Phosphate on its own reduced the uptake of Ca and Fe, but increased that of S and Mn. Grain was present only in treatments with phosphate. Co-application of phosphate with either sludge increased yield the most, Gyp applied at 20 t ha^{-1} with phosphate at 100 kg ha^{-1} gave the highest yield. The results suggested that these materials have the potential to improve maize grain yield, especially when phosphate is co-applied with

either sludge. This is because P is an indispensable essential plant nutrient in the development of a plant that is involved in the synthesis of proteins, nucleotides, enzymes, and also plays a vital role in photosynthesis and other physiological and biochemical reactions.

Keywords: AMD, HDS, Maize

9.1 INTRODUCTION

The potential of some inorganic and organic wastes (e.g. waste water treatment sludges, fly ash, biochar, cattle manure) to be used as soil amendments with the intention to improve soil fertility and plant growth has been explored by various researchers (Jala and Goyal 2006, Utomo et al. 2011, Karami et al. 2011, Zornoza et al. 2016, Dotaniya et al. 2016). This is because these materials have some value for use in agriculture. For example, some contain soluble macro and micronutrients, including alkalinity that can reduce soil acidity. High Density Sludge (HDS) is a gypseous by-product of AMD treatment that consists largely of gypsum but may be classified as hazardous by the Republic of South African (RSA) guidelines due to its chemical composition and solubility. This material has value for use as soil amendment since it contains gypsum that can release Ca and S to the soil upon dissolution. These elements, Ca and S, including some bases (e.g. K and Mg) are generally deficient in acid soils. Also, it has been reported to contain Fe-oxides that can provide an opportunity for the adsorption, surface complexation, surface precipitation and co-precipitation of metals and salts in soils (Wei et al. 2008, Tsang et al. 2013). These Fe-oxides can also be a valuable source of Fe. However, as a disadvantage, Fe oxides can render plant nutrients applied as inorganic fertilizers unavailable for plant uptake through adsorption, especially phosphate (Guzman et al. 1993, Zinck, 2005, Zinck, 2006). Zinck (2006) suggested that rapid adsorption of P can be reduced by using organic fertilizers.

Because of the Fe oxides contained, sludge has often been used to remove phosphate and other metals from wastewater (Keefer and Sack, 1983, Wei et al. 2008, Sibrell et al. 2009, Fernando et al. 2018), rather than being used as a soil ameliorant to produce a specific crop. Therefore, the application of this material to soils on its own and the impact it can have when co-applied with phosphate to the phyto-availability of nutrients and uptake has not yet been investigated.

This is simply because the material is often classified as hazardous due to its metal content and as such has limited agricultural use. The chemical composition of the sludge and elemental content suggests that any plant to be grown in a soil treated with it should be carefully selected, based on salinity tolerance and metal toxicity.

Based on the mineralogy (largely gypsum) and chemical composition of this material, the study envisaged that if used as a soil amendment, it can increase crop yields through soil fertility improvement. Hence, the objective of the study was to assess the response of a cereal crop (maize) when planted in a soil treated with sludges, one from limestone and another from limestone plus hydrated lime treatments, co-applied with phosphate, and further apply phosphate and sludges on their own. Further, to assess the impact on nutrient phyto-availability and uptake as influenced by phosphate.

9.2 MATERIALS AND METHODS

The focus in this part of the study was only on crop response, since literature reported that the solubility of gypsum in the sludge can contribute soluble Ca and S to soils that are deficient of these elements, it can also provide trace elements (e.g. Fe, Mn), and can also increase soil pH as it contains alkalinity. The study, therefore, involved both greenhouse and laboratory investigations.

9.2.1 Sources of sludges and soil used

Two sludges from the Mpumalanga coalfields of RSA, selected on the basis of different processes used to generate them, were sampled in 2017 (details of processes of generating them have been discussed in Chapters 2 and 6). One of the sludges was sourced from a limestone treatment plant, designated as Ferriferous Gypseous (GypFeMnNi) sludge, since it was largely gypsum and Fe-oxides. The other designated as Gypseous (Gyp) sludge, was refined from limestone plus hydrated lime treatment and was dominated by gypsum. To assess their full potential as soil amendment, an acid soil with a pH of 3.75, low in base elements was selected.

9.2.2 Determination of basic chemical properties of both sludges and soil

Basic chemical properties of both sludges and soil were determined before and after the establishment of HDS-Soil mixtures. The individual sludges and soil were analysed for chemical status. Total elemental content was determined following acid digestion as recommended by United States (US) Environmental Protection Agency (EPA) Method 3052. Extractable macro and micro-elements were determined by using standard extraction methods, ammonium acetate (1 mo l^{-1}, pH 7) and di-ammonium EDTA, and P-Bray 1 solution, as discussed by the Soil Science Society of South Africa (1990). These extractants aimed at extracting plant available elements. Alkalinity was determined after a dialysis procedure of both sludges with 0.0001 M HCl at pH 4 (procedure details discussed in Chapter 4). A total of 30 ml of the sample/leachate was titrated with 0.001 M NaOH. A blank, 0.0001 M HCl was also titrated with the NaOH. Alkalinity was then calculated following equation 9.1:

$$Alkalinity = \frac{(0.001\ M\ NaOH)*Volume\ used\ (l)-[0.0001\ M\ HCl(blank)]*Volume\ of\ NaOH\ used(l)}{Volume\ of\ sample\ (l)} \quad \text{Eq. 9.1}$$

Determination of pH and EC were done after harvesting in the Soil-Sludge mixtures and before the start of the experiment in the individual sludges and soil, using standard methods described by Thomas (1996) and Rhoades (1996) in Methods of Soil Analysis Part 3 Chemical Methods (1996) were followed.

Physical and chemical status of soil used (brief description)

An acid soil of the Hutton soil form, according to the Soil Classification Working Group (2018), correlated to Ferralsols and Arenosols in the World Reference Base (WRB) classification system (Fanourakis 2012), with a pH of 3.75 and low in bases was selected (Table 9.1). This soil was collected from a field that was intentionally acidified over the years for research purposes. It was dominated by Fe and Mn, while total concentrations of other elements such as, Ca and S were low (Table 9.1). The low Ca content suggests that this element was possibly exchanged and leached out from the topsoil. The soil also had low initial salinity of 7.8 mS m^{-1} before the addition of fertilizers and sludges (Table 9.1) indicative of the substantially low salts contained. Extractable elements by Ammonium acetate (NH_4OAc), ethylenediaminetetraacetic acid (EDTA) and P-Bray 1 solution were also low. Furthermore, the acid soil was selected because the sludges contained some alkalinity and the intention here was to assess their ameliorating effects.

Table 9.1: Some selected physicochemical properties of the soil used for the pot trial

pH(H_2O)	3.75		
Salinity (EC) (mS m^{-1}) at 2.5 soil /solid ratio	7.8		
CEC ($cmol_c$ kg^{-1})	7.98		
Texture	Clay Loam		
	Acid digestion (mg kg^{-1})	Extractable elements (mg kg^{-1})	Extraction methods
Major elements			
Ca	26	18	NH_4OAc
K	894	68	NH_4OAc
Mg	338	12	NH_4OAc
P	244	8	P-Bray 1
S	69	25	EDTA
Metals			
Cd	< 0.18	< 0.01	EDTA
Fe	37363	25	EDTA
Mn	301	167	EDTA
Na	38	< 0.01	EDTA
Ni	35	0.9	EDTA
Pb	36	7.2	EDTA
Zn	20	1.2	EDTA

Note: NH_4OAc = Ammonium acetate, EDTA = Ethylenediaminetetraacetic acid. Values with the smaller than sign (<) indicate Method Detection Limits of those elements.

Chemical and mineralogy of sludges used (brief description)

The basic chemical and mineralogy analysis carried out were an attempt to understand possible contribution of each material to both soil and plant. Details of the mineralogy have been discussed in Chapter 4. Mineral composition indicated that both sludges were dominated by gypsum. The gypsum precipitated from Ca contributed by either hydrated lime or limestone used by HDSP and S from AMD. The sludge, Gyp, was composed mainly of gypsum. The gypsum in GypFeMnNi accounted for 72 – 77% of the material, with amorphous Fe-oxides making-up 17.8% (as determined by XRF), 4% of carbonate minerals (e.g. ankerite) and Hematite (Fe_2O_3). The carbonate formation was facilitated by the lower pH (5.5) of the material and the increased concentrations of Fe, Mg, Mn and Ca (Hendry et al. 2000). The presence of a carbonate confirmed the presence of Fe^{2+} and Mn^{2+} in the material. The Mg, like Ca, could be traced back to dolomite ($CaMg(CO_3)_2$) used to treat AMD. Mineralogy, therefore, revealed that these sludges contained essential plant nutrients in the form of soluble minerals, especially gypsum. The sludge, GypFeMnNi, showed a slightly acidic pH of 5.5, alkalinity of 250 mg kg^{-1} and salinity of 364 mS m^{-1} (Table 9.2). The low pH was because the material was generated by the HDS process that used only limestone, which is only capable of increasing the pH of the solution to close to neutral. The increase in pH is usually prevented by armouring during treatment, whereby precipitation of metals, especially Fe, occurs on the surfaces of the limestone particles, preventing further dissolution and chemical reactions (Skousen, 2014). Gyp showed an alkaline pH of 9.4 due to the use of $CaCO_3$ / $Ca(OH)_2$ combination during treatment. The hydrated lime could increase the solution pH to >10, precipitating most of the metals into hydroxides (Skousen, 2014). This material also had an alkalinity of 617 mg kg^{-1} and a salinity of 274 mS m^{-1}. Both sludges contained substantial salts and they, therefore, had higher salinity values, which suggested that addition of either sludge could increase soil salinity. Due to the dominance of gypsum, both sludges showed substantially high total Ca and S concentrations, while there was also high Mg content contributed by the liming material. The sludge GypFeMnNi also had higher total Fe and Mn concentration, compared to Gyp.

Table 9.2: Some selected chemical properties and total elemental content of the two sludges used in the pot trial

Parameter	GypFeMnNi	Gyp
pH(H_2O) at 2.5 solution /solid ratio	5.5^{b}	9.4^{a}
Salinity (EC) (mS m^{-1}) at 2.5 solution /solid ratio	364^{a}	274^{b}
Total Alkalinity as $CaCO_3$ (mg kg^{-1})	250^{b}	617^{a}
Concentrations extracted by acid digestion (mg kg^{-1})		
Major elements		
Ca	182961^{b}	224500^{a}
K	83^{a}	61^{b}
Mg	6513^{a}	2736^{b}
P	44^{b}	129^{a}
S	132974^{b}	216189^{a}
Metals		
Cd	< 0.18	< 0.18
Fe	124500^{a}	152^{b}
Mn	7590^{a}	95^{b}
Na	74^{b}	279^{a}
Ni	108^{a}	0.7^{b}
Pb	< 0.2	40^{a}
Zn	285^{a}	5^{b}

Note: $\alpha < 0.05$; CV = 4 – 12%. GypFeMnNi = Ferriferous gypseous with Mn and Ni; Gyp = Gypseous. Means with the same letter across sludges are not significantly different from each other. Values with the smaller than sign (<) indicate Method Detection Limits (MDL) of those elements

9.2.3 Development of HDS-Soil mixtures

The intension was to attain a homogenous mixture that could support plant growth. Each of the sludges was added at two rates (10 and 20 t ha^{-1}), and each level was thoroughly mixed on a mass/mass basis with 8.8 kg of soil that was prepared by sieving through a 5 mm sieve. The highest application rate adopted was 10 t ha^{-1} of commercial agricultural gypsum, which was reported by Food and Agriculture Organization of the United Nations (1990) as maximum allowable rate. This rate was then doubled to assess the effect on soil and plant. The mass of soil per hectare was estimated to be 2.1 x 10^{6} kg, assuming a 0.15 depth and a density of 1400 kg m^{-3}. Each HDS-Soil mixture was then transferred into pots with 26 cm top and 20 cm bottom diameters and a height of 25 cm (approximately 0.00785 m^{3}). Pots had three small openings at the bottom to allow for drainage.

9.2.4 Fertilizer choice, application and planting

GypFeMnNi had the potential to sequestrate some of the essential applied plant nutrients, especially phosphate due to the abundance of ferric hydroxide. To test this, a prior phosphate sorption study was carried out and the sludge showed to have the ability to sequester 27 kg of phosphate per ton. These results, therefore, were considered in this study, so phosphate availability had to be assessed at different application rates of the sludge material. Three phosphate application rates were adopted; a control (0 kg ha^{-1}), a recommended rate of 40 kg ha^{-1} (Mengel and Kirkby 2001 and MIG 2017) and a rate (100 kg ha^{-1}) well above the recommendation. Phosphate was also added to test if it can aid in decreasing the uptake of Ni and Pb from HDS. To minimize the introduction of any impurities, a reagent grade potassium dihydrogen phosphate (KH_2PO_4) was used as the source of phosphate. This source also provided some of the K needed by the maize but was insufficient to supply the 40 kg K ha^{-1} recommended. So, to achieve this recommended rate for K, additional K was applied as reagent grade potassium chloride (KCl). Nitrogen (N) was applied at a recommended rate of 100 kg ha^{-1} as reagent grade diammonium hydrogen phosphate ($(NH_4)_2HPO_4$). Also, this source of N provided additional phosphate that was considered to achieve the 40 and 100 kg P ha^{-1} rates selected. To benefit from the addition of N and K, KH_2PO_4 (70%) and 30% $(NH_4)_2PO_4$ were added to the HDS-Soil mix. As an application strategy, sources of P and K were applied in a single dose and spread 5 mm below seed, while N application was split into two applications during vegetative growth. Maize (*Zea mays*) (variety DKC73 – 74BRGEN) was selected based on its acidity (pH 5.5 – 6.5) and salinity (1.8 dS m^{-1}) tolerance and since it is the most common crop planted in Mpumalanga, RSA. A total of 5 seeds were planted in each pot at 5 mm depth. The five seeds were intended to allow plant sampling at different time intervals. The maize was harvested at physiological maturity (after 140 days) to determine final yield and enable food safety assessment of the grain.

9.2.5 Experimental design

This was a two-factor experiment arranged in a Randomized Complete Block Design (RCBD). All treatments were randomly laid out on a glasshouse table. The experiment had 18 treatments with a total of 6 controls. Three of the controls received hydrated lime ($Ca(OH_2)$) at 3.7 t ha^{-1} and different levels of P and were considered "positive controls", while the other 3 received no hydrated lime at three P levels and were considered to be "negative controls" (Table 9.3). The other 12 treatments were made up of the two HDS materials, each at two levels of P application. All treatments were replicated 3 times.

Table 9.3: Treatments included in the pot trial

Treatments	Comments	Description of treatments
Soil + H lime	Positive controls	3.7 t ha^{-1} H lime
SoilP40 + H lime		40 kg ha^{-1}P; 3.7 t ha^{-1} H lime
SoilP100 + H lime		100 kg ha^{-1}P; 3.7 t ha^{-1} H lime
Soil	Negative controls - Soil un-limed	
SoilP40		40 kg ha^{-1}P
SoilP100		100 kg ha^{-1}P
10GypP0	Sludge treatments	10 t ha^{-1} Gyp; 0 kg ha^{-1}P
10GypP40		10 t ha^{-1} Gyp; 40 kg ha^{-1}P
10GypP100		10 t ha^{-1} Gyp; 100 kg ha^{-1}P
20GypP0		20 t ha^{-1} Gyp;0 kg ha^{-1}P
20GypP40		20 t ha^{-1} Gyp; 40 kg ha^{-1}P
20GypP100		20 t ha^{-1} Gyp; 100 kg ha^{-1}P
10GypFeMnNiP0		10 t ha^{-1} GypFeMnNi; 0 kg ha^{-1}P
10GypFeMnNiP40		10 t ha^{-1} GypFeMnNi; 40 kg ha^{-1}P
10GypFeMnNiP100		10 t ha^{-1} GypFeMnNi; 100 kg ha^{-1}P
20GypFeMnNiP0		20 t ha^{-1} GypFeMnNi;0 kg ha^{-1}P
20GypFeMnNiP40		20 t ha^{-1} GypFeMnNi; 40 kg ha^{-1}P
20GypFeMnNiP100		20 t ha^{-1} GypFeMnNi; 100 kg ha^{-1}P

Note: Gyp (t ha^{-1}) = Gypseous; GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; P (kg ha^{-1}) = Phosphate; H = hydrated

9.2.6 Crop management and data collection

Tap water was used for irrigation. Initially all treatments were irrigated to field capacity, which was calculated to be 2.55 L per pot, but water added to reach field capacity (FC) after 3 days was calculated to be approximately 1 L, which was determined as a difference through weighing of pots. During active vegetative growth the 1 L of water to refill the pots to FC was required after every 2 days. This amount of water was then applied after every 2 days until harvesting. Samples were collected by destructive sampling, cutting one of the plants off at soil level at the following development stages; V3 (third leaf collar evident), V7 (seventh leaf collar evident), V10 (tenth leaf collar evident), VT (tasselling) and R6 (physiological maturity, milk line no longer evident, black layer formed). Data collected at V3 – VT stages included; plant height, leaf area, plant biomass and assessment of metal uptake in leaves. At R6, data collected included, number of cobs, yield (leaves, stems and grains), and concentrations of potentially toxic metals in leaves and grains.

9.2.7 Grain and foliage chemical composition

The grain was harvested at physiological maturity. To assess nutritional value the chemical composition of both grain and leaves were determined following the USEPA 3052 Method, as described under the section on the determination of total elemental status of sludges and soil. The focus was on selected major plant nutrients (Ca, S and P) and trace elements (Mn and Fe), as Ca, S, Mn and Fe were expected to be a contribution of both sludges, except for P. The P was included to assess the potential of ferrihydrite and other mechanisms to adsorb this element.

9.2.8 Statistical analysis

All statistical analysis was carried out using SAS Version 9.4. ANOVA was carried out to establish differences amongst treatments and to separate means, the Least Significant Difference (LSD) Separation Test was used. To assess main effects, averages were calculated across the sludges and phosphate applied.

9.3 RESULTS AND DISCUSSION

In the soil, chemical and biological reactions are controlled by pH (Hendershot and Lalande 2008). For instance, under strong acidity conditions the bioavailability of some of the elements (e.g. Ca, P, K, and Mg) essential for plant growth are reduced, but others, such as, Mn and Al are increased (Agegnehu et al. 2019). In this study, therefore, sludges were expected to ameliorate the acid soil used since they contain solid phases of $CaCO_3$ and $Mg(OH)_2$ that can contribute to alkalinity. It was on these bases that this discussion was included to help understand the amelioration effects of the sludges on soil pH, as it is capable of influencing the availability of nutrients.

9.3.1 Influence of sludges on soil pH

Soil chemical reactions and eventual release of plant nutrients is controlled by pH. An increase in soil pH was realised after the co-application of phosphate and either sludge, but this increase was marginal, relative to that of negative control. The incremental addition of phosphate on its own from 40 to 100 kg ha^{-1} significantly ($\alpha < 0.05$) increased soil pH (Fig. 9.1). A significant ($\alpha < 0.05$) increase in soil pH was also evident when the application of either sludge on their own was increased from 10 to 20 t ha^{-1}. The combination effect of phosphate with either sludge was significant ($\alpha < 0.05$), but this change in pH was predominantly where phosphate was added at 100 kg ha^{-1} and when the sludges were applied at 20 t ha^{-1}. Increasing phosphate to 100 kg ha^{-1} influenced GypFeMnNi and Gyp to increase soil pH by 0.41 and 0.26 relative to the pH of the soil (3.75), but this pH increase could be sufficient for acid tolerant crops only. The pH was expected to increase further since both sludges either applied at 10 or 20 t ha^{-1} had alkalinity values (2500 – 12340 kg ha^{-1}) exceeding soil exchangeable acidity (945 kg ha^{-1}). This suggested some mechanism was responsible for buffering pH. In the presence of abundant Fe oxides, armouring was the most possible mechanism, which reduced the potential of the sludges to increase pH. The pH exhibited by GypFeMnNi was influenced mostly by alkalinity present in the material. However, this increase in pH by both sludges was significantly lower than the pH value shown by the limed soil. Liming the soil (as part of the positive control) and applying phosphate at 100 kg ha^{-1} increased pH the most by 2.1 units relative to that of soil (pH 3.75). Non application of phosphate (i.e. applying sludges on their own and no liming), and co-application of phosphate at 40 kg ha^{-1} with either sludge at 10 t ha^{-1} did not significantly increase soil pH.

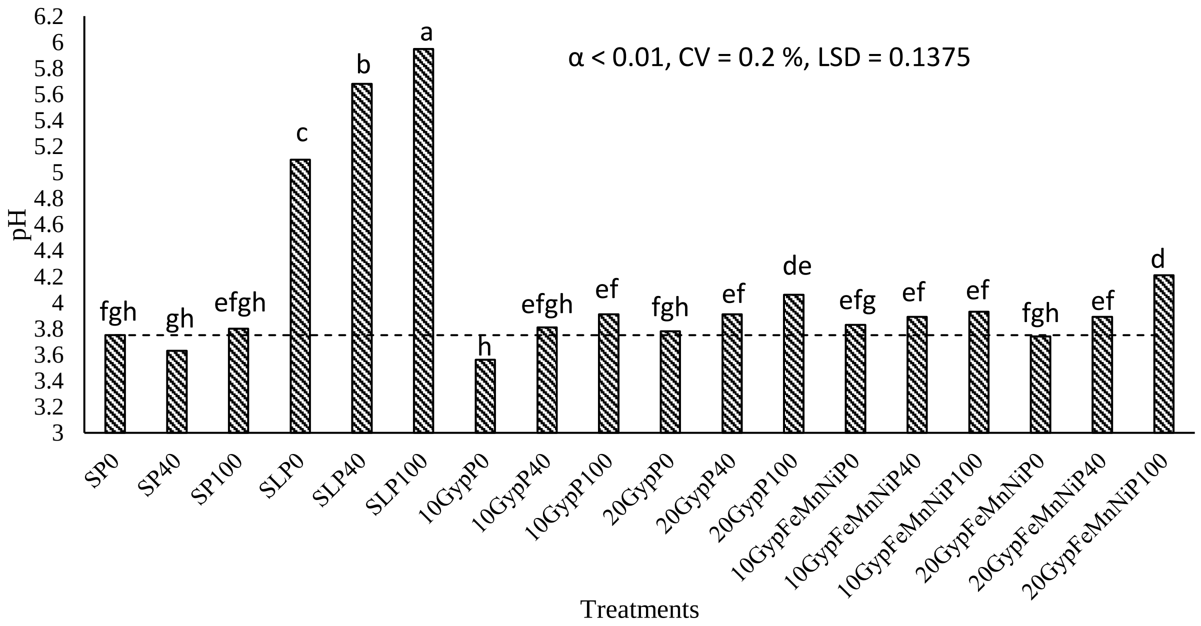


Figure 9.1: Soil pH as influenced by either sludge, phosphate and hydrated lime. Dotted line represents initial soil pH (3.75). Note: S = Soil; SL = Soil Limed; P (kg ha^{-1}) = phosphate; GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; Gyp (t ha^{-1}) = Gypseous.

9.3.2 Sludge effects on the germination of maize seeds

The germination of seed suggested a conducive environment. Seeds in the limed soil treatments took the shortest duration of time (4 days) to germinate, compared to 5 – 8 days taken by all other treatments. This was expected, as the soil was limed to a pH > 5, which is conducive for plant growth, whereas the other treatments were still acidic with an initial pH of 3.75. There was no clear trend in the percent germination of seeds by the different treatments (Fig. 9.2), however, all treatments with hydrated lime and treatments with GypFeMnNi applied at 20 t ha^{-1} combined with phosphate at 40 kg ha^{-1} showed 100% germination. There was a substantial reduction in germination in all treatments that received 100 kg ha^{-1} phosphate either in combination with sludge or on its own, except for treatments with hydrated lime and treatments with GypFeMnNi applied at 10 t ha^{-1} and 100 kg ha^{-1} phosphate. However, a general improvement in the germination percentage of all treatments that received 40 kg ha^{-1} phosphate was evident.

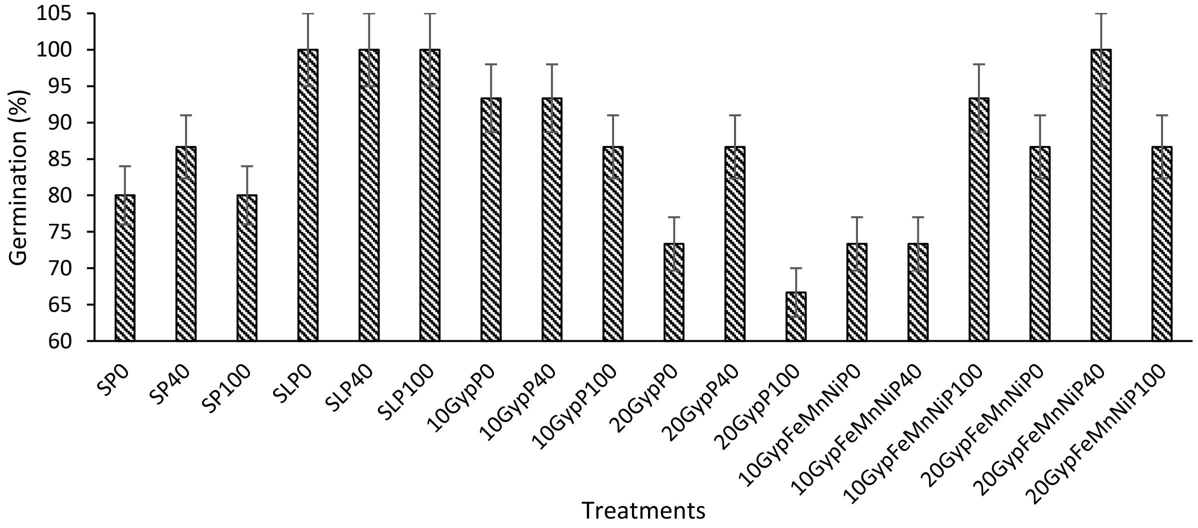


Figure 9.2: Germination assessment (%) in the pot trial with different sludge-soil treatment combinations as growth medium. Note: S = Soil; SL = Soil Limed; P (kg ha^{-1}) = phosphate; GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; Gyp (t ha^{-1}) = Gypseous.

9.3.3 Sludge influence on plant growth of maize

Adding sludges on their own at both rates (10 and 20 t ha^{-1}) or in co-application with phosphate increased average plant height (Table 9.4). When GypFeMnNi was applied at 20 t ha^{-1} with P at 100 kg ha^{-1} increased plant height the most ($\alpha < 0.05$). This increase in plant height was probably a benefit from the addition of Ca and S released by the solubility of gypsum in this material by the water added and reduction of acidity by the alkalinity contained. The application of phosphate on its own significantly increased plant height, but the heights recorded at 40 and 100 kg ha^{-1} P were not significantly different from each other.

Table 9.4: Final height (cm) of maize plants in a pot trial with different sludge-soil treatment combinations as growth medium

Sludge	Soil	SL	10Gyp	20Gyp	10GypFeMnNi	20GypFeMnNi	*Average*
P0	65^{e}	63^{e}	96d^{e}	141^{abcd}	118^{bcde}	102^{cde}	*97^{b}*
P40	133^{abcd}	184^{a}	132^{abcd}	131^{abcd}	130^{abcd}	151^{abcd}	*143^{a}*
P100	136^{abcd}	182^{a}	149^{abcd}	160^{abc}	123^{abcde}	166^{ab}	*153^{a}*
Average	*111^{b}*	*143^{a}*	*126^{ab}*	*144^{a}*	*124^{ab}*	*140^{a}*	

$\alpha < 0.05$, CV = 3.6%, LSD = 33.2, SL = soil limed, P (kg ha^{-1}) = phosphorus, GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; Gyp (t ha^{-1}) = Gypseous

The increase in crop height was rapid from germination for all treatments except for treatments SP0 and SLP0 until the 90th day (Fig. 9.3: A – D) after which some started exhibiting slowed growth responses. However, as expected from a determinate crop, all treatments stopped increasing height after tasselling, which occurred after 100 days (Fig. 9.3: A, B & C). Tasselling occurred earlier, that is, after 90 days for the limed soil where phosphate was applied at 40 and 100 kg ha^{-1} P (Fig. 9.3: D). The addition of phosphate or any of the sludge products on their own, increased plant growth significantly compared to soil receiving neither phosphate nor sludge. The crop growing in treatments without phosphate and sludge were only able to reach a height of 65 cm (Table 9.4). This suggested that the individual sludges had the potential to increase plant growth. Any combination of either sludge and phosphate, increased growth more than when phosphate or sludge were applied on their own. For instance, the treatment with GypFeMnNi at 20 t ha^{-1} with phosphate at 100 kg ha^{-1} P showed the tallest plants (166 cm) than any other treatment, followed by 160 cm for treatments with Gyp and phosphate at the highest rates (Table 9.4). Applying phosphate on its own, at 100 kg ha^{-1} P exhibited somewhat a lower growth of 136 cm, which was close to the 141 cm for the treatment with Gyp at 20 t ha^{-1} on its own. Generally, Gyp contributed more to plant growth than GypFeMnNi and phosphate when considered on their own, but the sludge GypFeMnNi showed greater potential than Gyp when combined with phosphate.

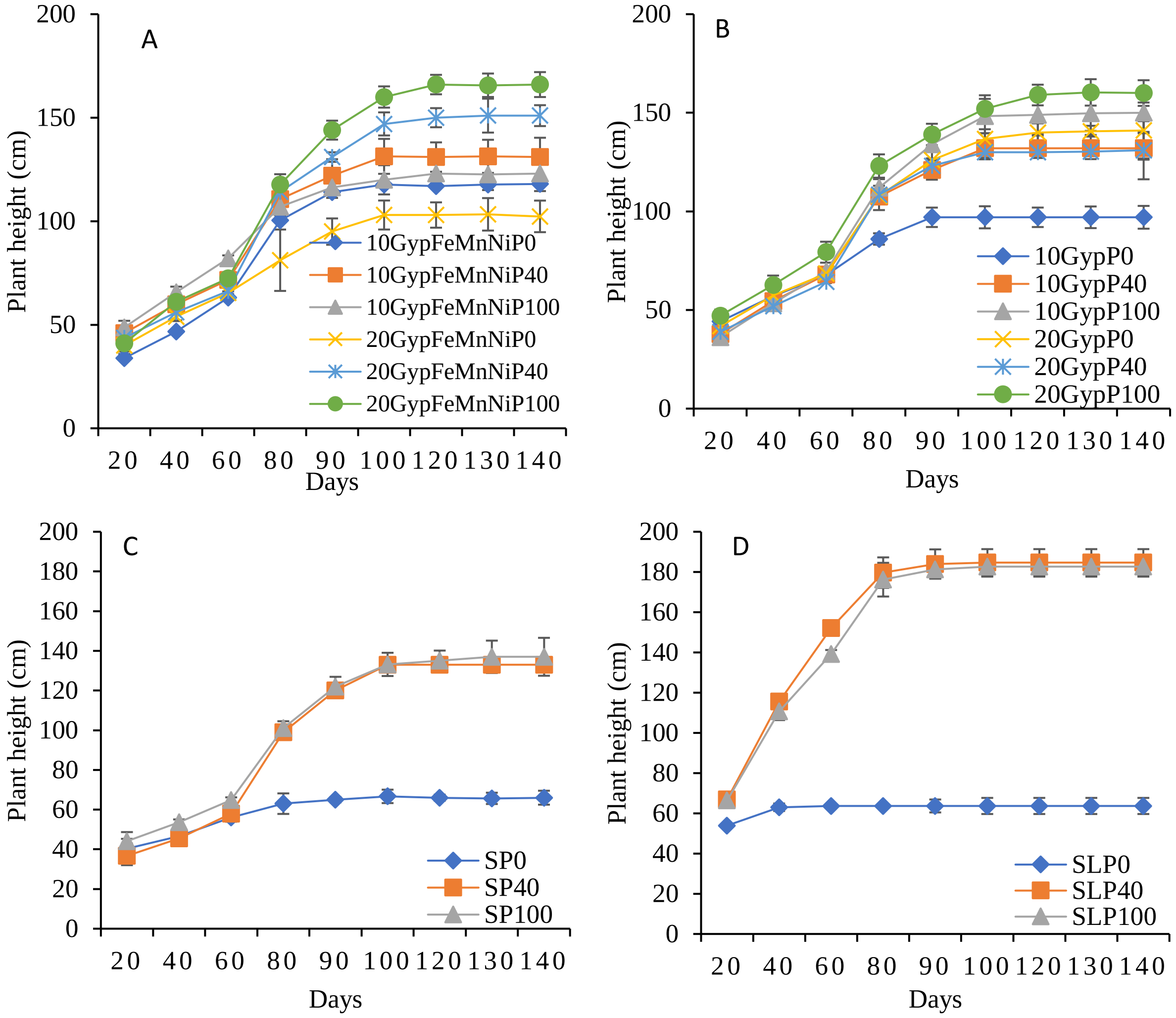


Figure 9.3: Plant height for: A) GypFeMnNi and phosphate; B) Gyp and phosphate; C) phosphate; D) Limed soil with phosphate. Note: Gyp (t ha^{-1}) = Gypseous, GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous (t ha^{-1}) with Mn and Ni, S = Soil, SL = Limed Soil, P (kg ha^{-1}) = Phosphorus. Vertical bars=?

9.3.4 Sludge influence on Leaf Area Index (LAI) of maize

There was a gradual increase in leaf area index (LAI) from 40 to 120 days of plant growth in all treatments (Fig. 9.4: A – D). This parameter (LAI) dropped at physiological maturity of the crop, i.e. at 140 days of growth due to drying and loss of leaves. The treatments with hydrated lime and phosphate at 40 and 100 kg ha^{-1} P (Fig. 9.4, d) showed the highest LAI (8.9 – 9.1 m^{2} m^{-2}), compared to any other treatment. The crop in these treatments were growing rapidly due to the adequate pH increase by the added hydrated lime and phosphate. Applying either sludge combined with phosphate generally improved crop growth, compared to treatments with phosphate on its own. As such, LAI was substantially higher in these treatments (Fig. 9.4: A & B) than for soil without sludge and hydrated lime (Fig. 9.4: C). A soil without sludge and phosphate, whether limed or not, exhibited plants with an extremely low LAI (max 0.67) (Fig. 9.4: C & D). This suggested that either sludge in combination with phosphate were important in increasing LAI. Treatments that received the highest application of sludge and phosphate (Fig. 9.4, a & b) had LAI ranging from 1.5 to 1.8 m^2 m^{-2} at harvest.

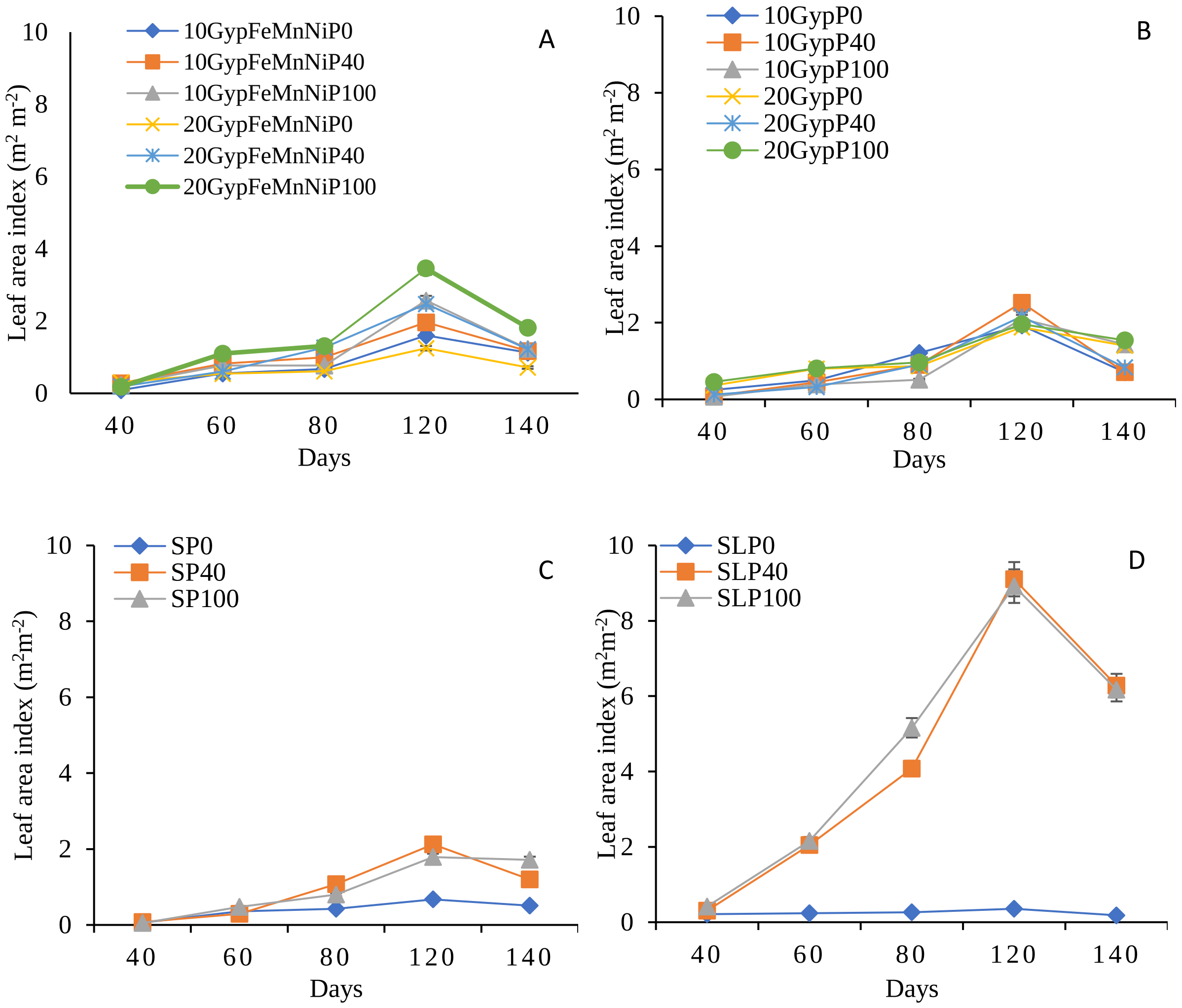


Figure 9.4: Leaf Area Index (LAI m^2 m^{-2}) for: A) GypFeMnNi and phosphate; B) Gyp and phosphate; C) phosphate; D) Limed soil with phosphate. Note: Gyp (t ha^{-1}) = Gypseous, GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous (t ha^{-1}) with Mn and Ni; S = Soil, SL = Limed Soil, P (kg ha^{-1}) = Phosphorus.

9.3.5 Sludge influence on total biomass of maize

Generally, the application of phosphate, whether on its own or in combination with sludge, increased total plant biomass (Fig. 9.5). This was more evident and significant ($\alpha < 0.05$) in treatments with and without hydrated lime and where the sludge GypFeMnNi was applied at 20 t ha^{-1} with P at 100 kg ha^{-1} (Fig. 9.5). The insignificant ($\alpha > 0.05$) increase evident in the rest of the treatments was due to reduced availability of phosphate, possibly by precipitation with Ca and adsorption on the reactive surfaces of the sludges. The addition of either sludge at 20 t ha^{-1} (on its own as well as in combination with P) showed a slight increase in plant biomass, however this increase was statistically not significant, compared to the lower rate (10 t ha^{-1}). Applying the sludges Gyp and GypFeMnNi at 20 t ha^{-1} on their own increased biomass by 132% and 37.5% relative to that of soil, whereas, when applied with phosphate at 100 kg ha^{-1} the biomass increased by 808% and 670%, respectively. Liming the soil and applying phosphate at 40 and 100 kg ha^{-1} significantly increased biomass by 606% and 754%, relative to that of soil. This was due to the increase of soil pH to > 5, a pH that facilitated the availability of most nutrients for plant uptake.

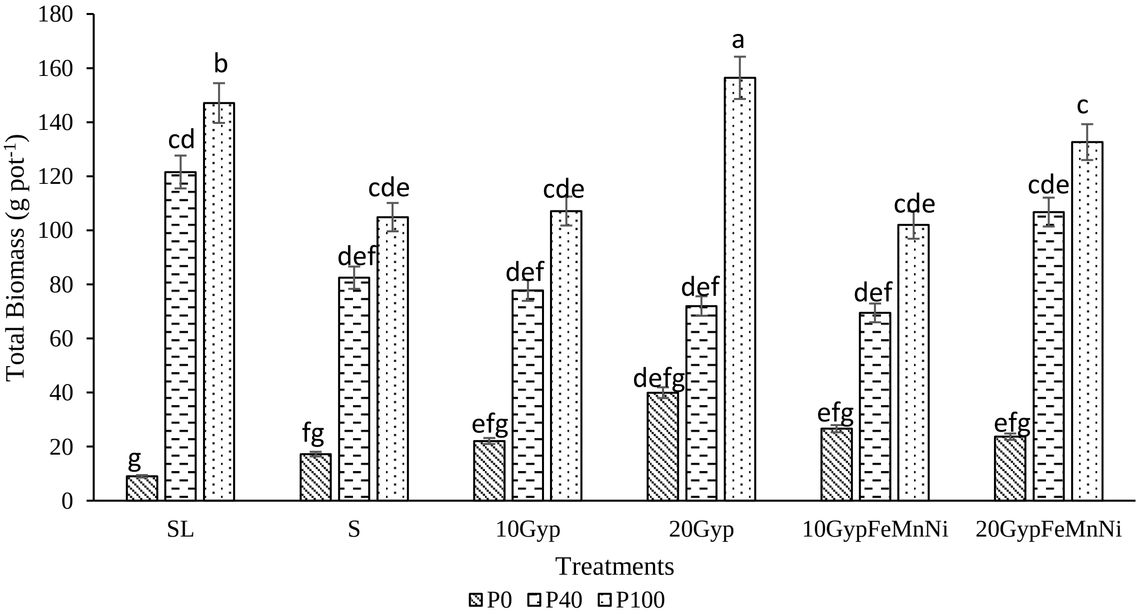


Figure 9.5: Total plant biomass comparisons. Note: Gyp (t ha^{-1}) = Gypseous, GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; S = Soil, SL = Soil Limed, P (kg ha^{-1}) = phosphate

9.3.6 Ca, S and P uptake by foliage, stem and tassels of maize

Calcium

Calcium showed low translocation to the stem and tassels as it was concentrated mostly in the foliage by all treatments (Table 9.5). The addition of sludge had a significant effect on the concentration of Ca in all parts of the plant caused by the solubility of gypsum by water during irrigation. When Gyp was applied at 20 t ha^{-1} combined with phosphate at 40 kg ha^{-1}, it contributed the most Ca to foliage, stem and tassels, but when this material was combined with phosphate at 100 kg ha^{-1} P, it contributed Ca in the foliage, more than any other treatment (Table 9.5). The Ca contribution by Gyp was expected because this material is largely gypsum. Although increasing either sludge increased the concentration of Ca in all plant parts, there was evidence of a slight reduction in Ca when phosphate was increased to 100 kg ha^{-1} in most of the treatments. The phosphate applied at 100 kg ha^{-1} P interfered slightly with Ca uptake or translocation within plant tissues. However, the concentration of Ca in the dry matter for all treatments with sludges was above 5000 mg kg^{-1}, which was reported as adequate for plant growth (Jones, 2012, Bindraban et al. 2015).

Phosphorus application on its own showed a significant ($\alpha < 0.05$) effect on the concentration of Ca in all plant parts. When P was applied at 40 kg ha^{-1}, it significantly ($\alpha < 0.05$) increased Ca concentration in all plant parts relative to that contributed by treatments without phosphate (Table 9.5). Increasing phosphate to 100 kg ha^{-1} could not significantly increase Ca concentration, compared to that at 40 kg ha^{-1} P in foliage and tassels. Also, 100 kg ha^{-1} P could not significantly increase Ca concentration in the stem, relative to that contributed by treatments without sludge. This suggests that increasing phosphate concentration in the soil reduced the mobility of Ca through precipitation into sparingly soluble minerals. Some chemical interactions that can reduce Ca uptake can also occur within the plant tissues, reducing its translocation (Fageria, 2002).

Table 9.5: Calcium (mg kg^{-1}) in biomass of maize, also showing sludge and phosphate effects

Plant part	Calcium							
	Sludge	**S**	**SL**	**10**Gyp	**20**Gyp	**10**GypFe MnNi	**20**GypFe MnNi	***Average***
foliage	P0	3404^{f}	4384^{ef}	6581^{cdef}	8740^{abcde}	7356^{bcdef}	7025^{bcdef}	***6248^{b}***
	P40	6290^{cdef}	8615^{abcde}	10175^{abc}	10930^{ab}c	8692^{abcde}	11537^{ab}	***9373^{a}***
	P100	4738^{def}	7338^{bcdef}	10377^{abc}	13257^{a}	9202^{abcd}	9724^{abc}	***9106^{a}***
	Average	***4811^{d}***	***6779^{cd}***	***9044^{abc}***	***10976^{a}***	***8417^{bc}***	***9429^{ab}***	
Stem	P0	1178^{ef}	BMDL	3923^{ab}	3515^{abc}	3419^{abc}	2594^{cd}	***2438^{b}***
	P40	1158^{ef}	2118de	3672^{abc}	4468^{a}	2802^{bcd}	3177^{bcd}	***2899^{a}***
	P100	1240^{e}	1239^{e}	3116^{bcd}	3948^{ab}	2967^{bcd}	2679^{cd}	***2532^{b}***
	Average	***1192^{d}***	***1119^{d}***	***3570^{ab}***	***3977^{a}***	***3063^{bc}***	***2817^{c}***	
Tassel	P0	538^{ef}	BMDL	2052de	2954^{abcd}	2522^{bcde}	2223^{cde}	***1715^{b}***
	P40	2779^{abcd}	2801^{abcd}	3383^{abcd}	4622^{a}	2712^{abcd}	4331^{ab}	***3438^{a}***
	P100	2455^{bcde}	2454^{bcde}	4097^{abc}	4381^{ab}	3454^{abcd}	3300^{abcd}	***3357^{a}***
	Average	***1924^{c}***	***1752^{c}***	***3177^{ab}***	***3986^{a}***	***2896^{b}***	***3285^{ab}***	

Foliage: $\alpha < 0.05$, CV = 3.3%, LSD = 2537, Stem: $\alpha < 0.05$, CV = 3.3%, LSD = 667, Tassel: $\alpha < 0.05$, CV = 2.1%, LSD = 1093, Note: : Gyp (t ha^{-1}) = Gypseous, GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; S = Soil, SL = Soil Limed, P (kg ha^{-1}) = Phosphorus; BMDL = below method detection limit.

Sulphur

Similar to the concentration of Ca, S was mostly concentrated in the foliage, compared to the stem and tassels (Table 9.6). The application of either sludge significantly increased the concentration of S in all plant parts. The application of Gyp at 20 t ha^{-1} on its own contributed to most S in the foliage, however this S significantly decreased with an increase in phosphate application. This suggests that there was a dilution effect on the uptake of S. The concentration of S in the stem and tassels showed no significant (> 0.05) changes by incremental phosphate applications when Gyp was applied at 20 t ha^{-1}. The application of phosphate on its own had a significant ($\alpha < 0.05$) effect on the concentration of S in both foliage and tassels (Table 9.6). In the foliage, increasing phosphate on its own to 40 kg ha^{-1} significantly ($\alpha < 0.05$) reduced the content of S, but this rate significantly ($\alpha < 0.05$) increased the content of this element in the tassel, however it did not significantly ($\alpha > 0.05$) change S concentration in the stem relative to that of the SP0 treatment. Although there was a dilution effect on S concentration in the plant, the S concentration for all the treatments still exceeded 1000 mg kg^{-1}, which is considered adequate for plant growth (Jones, 2012, Bindraban et al. 2015).

Table 9.6: Sulphur (mg kg^{-1}) in biomass of maize, also showing sludge and phosphate effects

Plant parts	**Sulphur**							
	Sludge	**S**	**SL**	**10**Gyp	**20**Gyp	**10**GypFe MnNi	**20**GypFe MnNi	***Average***
foliage	P0	1957^{e}	1582^{e}	4601^{bcd}	8567^{a}	4217^{bcd}	5989^{b}	***4486^{a}***
	P40	2572de	1564^{e}	4233^{bcd}	4998^{bc}	3325^{cde}	4491^{bcd}	***3531^{b}***
	P100	2389de	1865^{e}	3194^{cde}	4907^{bc}	3201^{cde}	3455^{cde}	***3169^{b}***
	Average	***2306^{c}***	***1670^{c}***	***4009^{b}***	***6158^{a}***	***3581^{b}***	***4645^{b}***	
Stem	P0	712^{cde}	BMDL	1699^{ab}	1879^{a}	1399^{abc}	1348^{abc}	***1173^{a}***
	P40	825^{bcde}	279de	1604^{abc}	1849^{a}	975^{abcd}	1537^{abc}	***1178^{a}***
	P100	686^{cde}	352de	1443^{abc}	1801^{a}	1515^{abc}	1599^{abc}	***1233^{a}***
	Average	***741c***	***210^{d}***	***1582^{ab}***	***1843^{a}***	***1296^{b}***	***1495^{ab}***	
Tassel	P0	714de	BMDL	1384^{bcd}	2110^{ab}	1420^{bcd}	1482^{bcd}	***1185^{b}***
	P40	1730^{abc}	929^{cd}	1613^{abc}	2425^{a}	1554^{bcd}	1866^{ab}	***1686^{a}***
	P100	1909^{ab}	977^{cd}	1999^{ab}	2156^{ab}	1954^{ab}	2022^{ab}	***1836^{a}***
	Average	***1451^{b}***	***635^{c}***	***1665^{b}***	***2230^{a}***	***1643^{b}***	***1790^{b}***	

Foliage: $\alpha < 0.05$, CV = 4.6%, LSD = 1212.8, Stem: $\alpha < 0.05$, CV = 5.5%, LSD = 504, Tassel: $\alpha < 0.05$, CV = 1.7%, LSD = 464, Note: Gyp (t ha^{-1}) = Gypseous, GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; S = Soil, SL = Soil Limed, P (kg ha^{-1}) = phosphate, BMDL = below method detection limit.

Phosphorus

Generally, the application of phosphate showed a substantial increase in the concentration of this element in all plant parts (Table 9.7). The application of either sludge had no significant ($\alpha > 0.05$) effect on the phosphate concentration in the stem and tassels, but incremental sludge application significantly ($\alpha < 0.05$) reduced P level in the foliage. The application of sludges, therefore, generally reduced the availability of phosphate uptake through precipitation and adsorption thereof by Fe-oxides. Applying phosphate on its own at 100 kg ha^{-1} P showed a significant ($\alpha < 0.05$) increase in the element's content in the foliage and stems. Tassels instead showed that phosphate content increased with an increase in phosphate application. Soil with or without hydrated lime, as long as it had phosphate at 100 kg ha^{-1}, significantly increased phosphate content in all parts of the plant, compared to any other treatment.

Table 9.7: Phosphorus (mg kg^{-1}) in maize biomass also showing sludge and phosphate effects

Plant parts	**Phosphorus**							
	Sludge	**S**	**SL**	**10**Gyp	**20**Gyp	**10**GypFe MnNi	**20**GypFe MnNi	***Average***
Foliage	P0	709^{b}	1087^{b}	940^{b}	874^{b}	749^{b}	925^{b}	***881***^{b}
	P40	1602^{b}	521^{b}	1195^{b}	840^{b}	781^{b}	690^{b}	***938***^{b}
	P100	3750^{a}	1709^{b}	1675^{b}	1366^{b}	1859^{b}	1544^{b}	***1984***^{a}
	Average	***2020***^{a}	***1106***^{b}	***1270***^{ab}	***1027***^{b}	***1130***^{b}	***1053***^{b}	
Stem	P0	625^{bc}	BMDL	578^{bc}	498^{bc}	640^{bc}	749^{bc}	***515***^{b}
	P40	1018^{bc}	270^{c}	660^{bc}	707^{bc}	703^{bc}	527^{bc}	***648***^{b}
	P100	1454^{b}	2684^{a}	739^{bc}	596^{bc}	706^{bc}	964^{bc}	***1191***^{a}
	Average	***1032***^{a}	***985***^{a}	***659***^{a}	***600***^{a}	***683***^{a}	***747***^{a}	
Tassel	P0	522^{bc}	BMDL	620^{bc}	857^{bc}	715^{bc}	929^{bc}	***607***^{c}
	P40	1964^{ab}	1281^{bc}	1232^{bc}	1251^{bc}	927^{bc}	760^{bc}	***1236***^{b}
	P100	3487^{a}	3617^{a}	1957^{ab}	2172^{ab}	2005^{ab}	2164^{ab}	***2567***^{a}
	Average	***1991***^{a}	***1633***^{a}	***1270***^{a}	***1427***^{a}	***1216***^{a}	***1284***^{a}	

Foliage: $\alpha < 0.05$, CV = 9.6%, LSD = 938, Stem: $\alpha < 0.05$, CV = 10.9%, LSD = 635, Tassel: $\alpha < 0.05$, CV = 10.8%, LSD = 973, Note: Gyp (t ha^{-1}) = Gypseous, GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; S = Soil, SL = Soil Limed, P (kg ha^{-1}) = phosphate, BMDL = below method detection limit.

Generally, the application of Gyp at 20 t ha^{-1} increased the concentration of Ca and S significantly in all parts of the plant. The addition of either sludge significantly reduced phosphate uptake, but all treatments without sludge significantly increased phosphate content in the plant.

9.3.7 Phosphorus and pH influence on the uptake of Ca and S by foliage of maize

The correlations of phosphate with Ca and S in the foliage indicated weak relationships (Fig. 9.6; A & B). Co-application of phosphate with either sludge positively facilitated the uptake of Ca by 1.1% (Fig. 9.6 A) whereas, phosphate applied on its own showed a negative relationship and reduced Ca uptake by 0.2% (Fig 9.6 B). This indicated that other mechanisms in the plant were responsible for the uptake of this element. For instance, a slight increase in soil pH facilitated by co-application of phosphate with either sludge increased the uptake of Ca in the foliage by 20.4% (Fig. 9.6 C).

There was a negative and weak relationship when phosphate was correlated with S in the foliage. Co-application of phosphate with either sludge reduced the uptake of S by 8.7% (Fig.

9.6; A), whereas applying phosphate on its own showed a positive correlation, facilitating the uptake of S by 15.9% (Fig. 9.6 B). Similar to the reduction by co-applying phosphate with either sludge, the slight increase in pH reduced the uptake of S by 10.3% (Fig. 9.6 C). This was also an indication that there are some other mechanisms, either in the soil or plant that were responsible for the uptake of S.

The application of sludges was expected to increase soluble S due to the dissolution of gypsum, but the tendency of cereals to prefer to accumulate one-third less of this element (S) than phosphate, reduced its uptake (Jones 2012). In conditions of low pH values (< 4), S is adsorbed by both Fe and Al oxides (Jones 2012), reducing its availability. In this respect, all the treatments without hydrated lime had pH values close to 4 and the sludges, especially GypFeMnNi, contained Fe-oxides that adsorbed part of the S. In case mass flow provided soluble S at a rate more than what could be absorbed by the plant, it then precipitated as $CaSO_4$ with Ca around the roots (Jones 2012) as the sludges had abundant Ca.

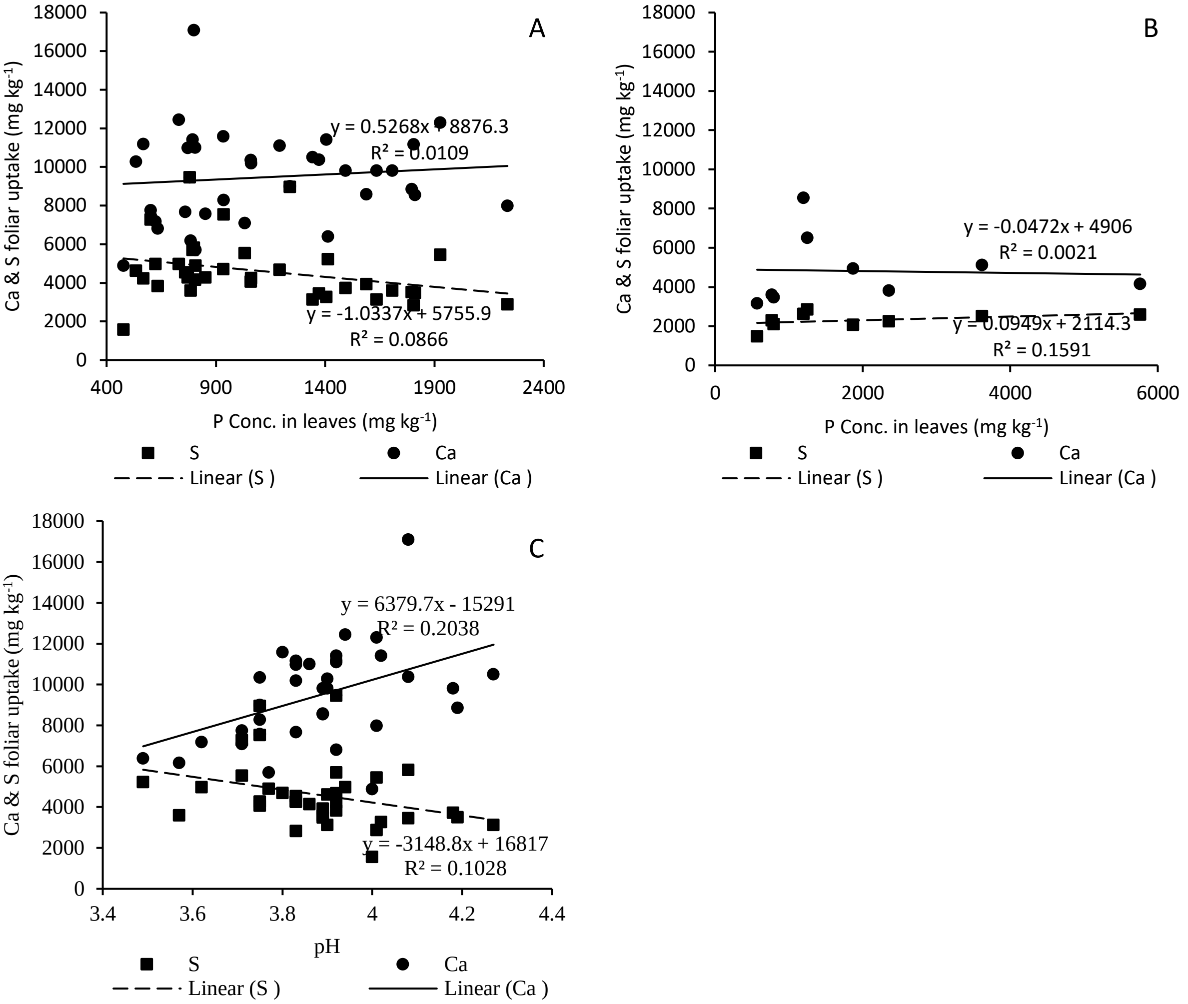


Figure 9.6: A) Phosphate-Sludge influence on Ca and S uptake was insignificant ($P < 0.05$), B) Phosphate influence on Ca and S uptake, C) pH influence on Ca & S uptake

9.3.8 Sludge influence on the uptake of trace elements (Fe and Mn) by plant parts

Iron

Iron was more concentrated in the foliage than in the stem and tassels (Table 9.8). Phosphorus application on its own effected significant ($\alpha < 0.05$) changes on the concentration of Fe in the foliage and tassels only but did not significantly ($\alpha > 0.05$) influence any change in the stem Fe content (Table 9.8). In the tassel, Fe was significantly increased by an increase in the application of phosphate, but in foliage it was significantly reduced. The sludge GypFeMnNi on its own applied at 10 t ha^{-1} had significantly higher Fe in the foliage amongst treatments with sludges. Similar to soils, the mobility and uptake of Fe by plants in GypFeMnNi was controlled by the solubility of Fe-oxides (Pendias and Pendias, 2001). According to these authors, the uptake and transport of Fe amongst plant parts is also affected by the concentration of Ca, phosphate and competition with other metals. An excess amount of Mn reduces the uptake of Fe, while phosphate forms a precipitate ($FePO_4.2H_2O$) with Fe under acid conditions. Due to the abundance of Fe in the soil and sludges, the concentration of this element in the plant exceeded 100 mg kg^{-1}, which was reported by Jones (2012) and Bindraban et al. (2015) as adequate for plant growth. Limed soil with phosphate at 40 or 100 kg ha^{-1} indicated significantly higher Fe concentration in the foliage.

Table 9.8: Iron (mg kg^{-1}) in biomass of maize

		Iron						
Plant parts	**Sludge**	**S**	**SL**	**10**Gyp	**20**Gyp	**10**GypFe MnNi	**20**GypFe MnNi	***Average***
Foliage	P0	265^{b}	1231^{a}	132^{b}	187^{b}	308^{b}	181^{b}	***384***^{a}
	P40	168^{b}	370^{b}	132^{b}	137^{b}	176^{b}	188^{b}	***195***^{ab}
	P100	131^{b}	436^{b}	123^{b}	150^{b}	142^{b}	129^{b}	***185***^{b}
	Average	***188***^{b}	***679***^{a}	***129***^{b}	***158***^{b}	***209***^{b}	***166***^{b}	
Stem	P0	36a^{b}	BDL	53^{a}	14^{b}	17^{ab}	23^{ab}	***24***^{a}
	P40	24a^{b}	15^{ab}	16^{ab}	13^{b}	11^{b}	15^{ab}	***16***^{a}
	P100	17^{ab}	15^{ab}	15^{ab}	15^{ab}	30^{ab}	10^{b}	***17***^{a}
	Average	***26***^{a}	***10***^{a}	***28***^{a}	***14***^{a}	***20***^{a}	***16***^{a}	
Tassel	P0	26^{b}	BDL	24^{b}	37^{b}	32^{b}	23^{b}	***24***^{b}
	P40	37^{b}	140^{a}	31^{b}	49^{b}	47^{b}	45^{b}	***58***^{a}
	P100	48^{b}	140^{a}	35^{b}	51^{b}	32^{b}	52^{b}	***60***^{a}
	Average	***37***^{b}	***93***^{a}	***30***^{b}	***45***^{b}	***37***^{b}	***40***^{b}	

Foliage: $\alpha < 0.05$, CV = 4.8%, LSD = 397, Stem: $\alpha < 0.05$, CV = 12.5%, LSD = 21.4, Tassel: $\alpha < 0.05$, CV = 2.5%, LSD = 33.6, Note: Gyp (t ha^{-1}) = Gypseous, GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; S = Soil, SL = Soil Limed, P (kg ha^{-1}) = phosphate; BMDL = below method detection limit

Manganese

Most of the Mn was concentrated in the foliage than in the stem and tassels (Table 9.9). The stem showed substantially lower Mn content than the foliage and tassels. Phosphate application effected significant ($\alpha < 0.05$) changes on the concentration of Mn in all plant parts (Table 9.9). The concentration of Mn was significantly increased in all parts of the plant when phosphate was applied from 40 to 100 kg ha^{-1}, indicating synergism between the two elements. Applying either sludge slightly reduced the concentration of Mn in the foliage due to either the slight increase in pH and the phosphate applied that prevented the reduction of the sludges. The Mn could also be precipitated by phosphate and adsorbed on the Fe oxides in the sludges (Eighmy et al. 1997, Crannell et al. 2000 and Karna et al. 2017). Soil with either phosphate at 40 kg ha^{-1} or without phosphate showed significantly higher Mn content. This is because the soil had its pH maintained at low levels, which encouraged Mn solubility. In the stem, soil with either phosphate at 40 or 100 kg ha^{-1} P showed significantly high Mn. In the tassel as well, soil with either phosphate at 40 or 100 kg ha^{-1} showed significantly higher Mn content. As such, the concentration of Mn exceeded 50 mg kg^{-1}, which was reported by Jones, (2012), Bindraban et al. (2015) as adequate for plant growth.

Table 9.9: Manganese (mg kg^{-1}) in biomass of maize

	Manganese							
Plant parts	**Sludge**	**S**	**SL**	**10**Gyp	**20**Gyp	**10**GypFe MnNi	**20**GypFe MnNi	***Average***
Foliage	P0	1592^{bcd}	102^{e}	1243^{cde}	1935^{abc}	1178^{cde}	1178^{cde}	***1205^{b}***
	P40	3100^{a}	207^{de}	1583^{bcd}	1596^{bcd}	1548^{bcd}	1760^{abc}	***1632^{a}***
	P100	2697^{ab}	198^{de}	1964^{abc}	1954^{abc}	1881^{abc}	1536^{bcd}	***1705^{a}***
	Average	***2463^{a}***	***169^{c}***	***1597^{b}***	***1828^{ab}***	***1536^{b}***	***1491^{b}***	
Stem	P0	163^{ab}	BDL	135^{bc}	116^{bc}	114^{bc}	71^{cde}	***100^{ab}***
	P40	160^{ab}	7^{de}	100^{bc}	85^{bcde}	69^{cde}	92^{bc}	***86^{b}***
	P100	241^{a}	3^{de}	123^{bc}	86^{bcd}	125^{bc}	85^{bcde}	***110^{a}***
	Average	***188^{a}***	***3^{c}***	***120b***	***96^{b}***	***103^{b}***	***83^{b}***	
Tassel	P0	319^{cde}	<0.001	344^{cde}	489^{cde}	346^{cde}	234^{cde}	***289^{b}***
	P40	1257^{a}	65^{de}	587^{cd}	658^{bc}	427^{cde}	535^{cde}	***588^{a}***
	P100	1179^{ab}	59^{de}	699^{bc}	619^{c}	570^{cd}	578^{cd}	***617^{a}***
	Average	***918^{a}***	***41^{c}***	***543^{b}***	***589^{b}***	***448^{b}***	***449^{b}***	

Foliage: $\alpha < 0.05$, CV = 3.3%, LSD = 760, Stem: $\alpha < 0.05$, CV = 7.3%, LSD = 46, Tassel: $\alpha < 0.05$, CV = 2.0%, LSD = 291, Note: Gyp (t ha^{-1}) = Gypseous, GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous, S = Soil, SL = Soil Limed, P (kg ha^{-1}) = phosphate. BMDL = below method detection limit

In summary, Fe and Mn were concentrated mostly in the foliage and increased with an increase in phosphate application. However, the addition of either sludge reduced their concentration in all plant parts.

9.3.9 Phosphate and pH influence on the uptake of Fe and Mn by maize foliage

Correlations indicated that co-applying phosphate with either sludge reduced the uptake of Fe by 8.3% in the foliage (Fig. 9.7; A). This showed that co-application of phosphate and either sludge rendered Fe less available for plant uptake and this suggested that it existed in sparingly soluble forms. Applying phosphate on its own also reduced the uptake of this element by 22.5% (Fig. 9.7; B). According to Jones (2012), Kabata-Pendias and Pendias (2001) phosphate competes with plants for Fe, forming a sparingly soluble mineral, Strengite ($FePO_4.2H_2O$) with Fe as all these treatments had low pH values. Phosphate in this case directly reduced the availability of Fe for plant uptake. Further, phosphate is often reported to be in antagonism with Fe for plant uptake (Kabata-Pendias and Pendias 2001). Slightly increasing the pH by co-applying phosphate with either sludge did not increase the uptake of this element either, instead it was reduced by 0.6% (Fig. 9.7 C). This suggested that there are some mechanisms both in the plant and soil that were responsible for the uptake of this element. For instance, maize and grasses can use the chelation-based strategy if Fe is deficient. The maize releases mugineic acid (MA) that has high affinity for Fe, it efficiently binds it and improves its uptake by the plant (Kim and Guerinot 2007).

Co-application of phosphate with either sludge, applying phosphate on its own and slightly increasing pH by co-applying phosphate with either sludge increased the uptake of Mn in the foliage, as indicated by the correlations (Fig. 9.7; A). However, the correlations were weak. Co-application of phosphate with either sludge, applying phosphate on its own and slightly increasing pH increased the uptake of Mn by 1.5, 4.6 and 5.2% (Fig. 9.7; A-C). This suggested that > 94.8% uptake of Mn was a responsibility of other mechanisms. The increase in Mn uptake by phosphate facilitation was expected, because phosphate is reported to increase Mn uptake through synergism (Jones 2012, Kabata-Pendias and Pendias 2001).

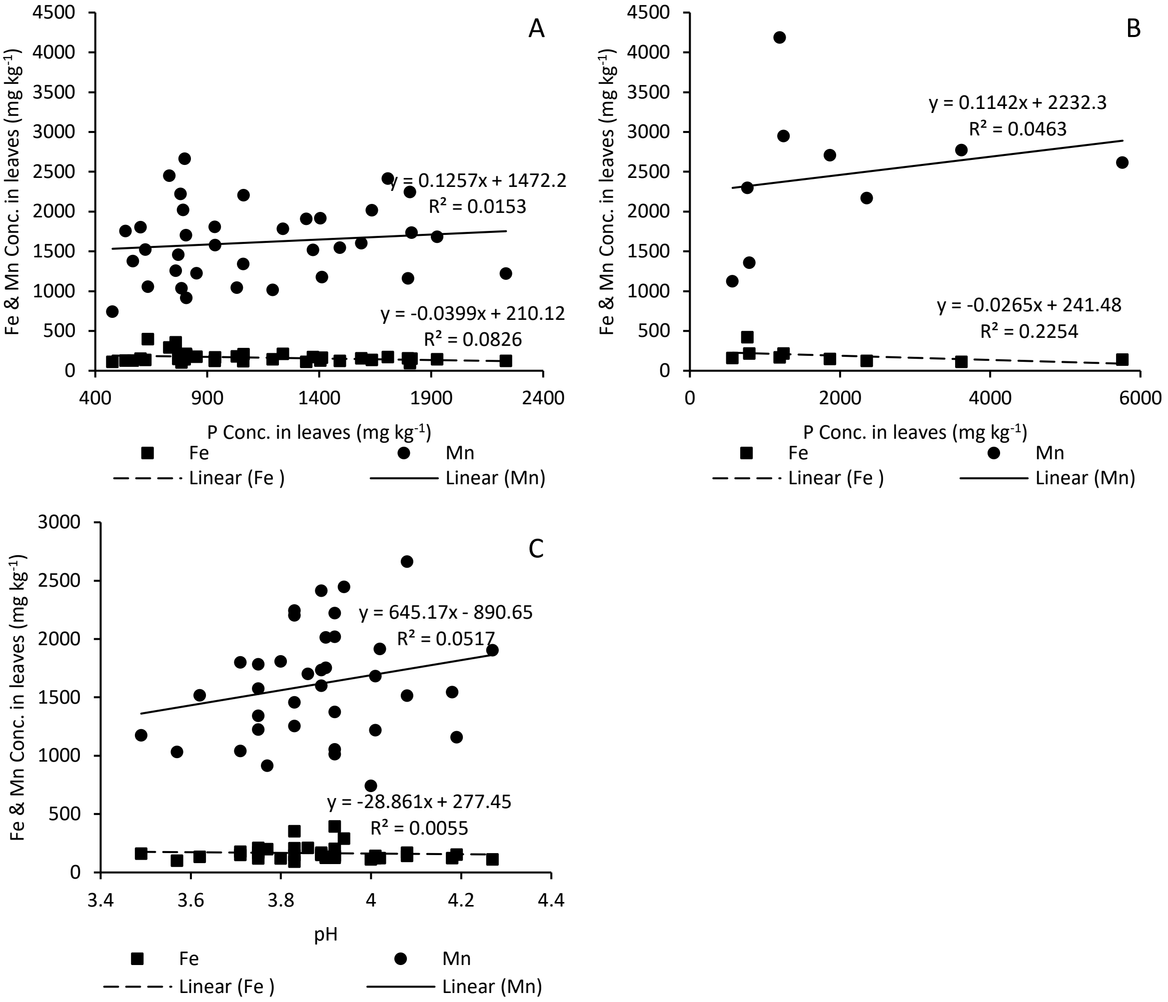


Figure 9.7: A) Phosphate-Sludge influence on Fe & Mn uptake, B) Phosphate influence on Fe & Mn uptake, C) pH influence on Fe & Mn uptake

9.3.10 Sludge influence on maize yield

Grain harvested was available only in treatments that received phosphate on its own and those where phosphate was co-applied with either sludge, thus there was no grain assessment in all treatments that had no phosphate (Table 9.10). The addition of phosphate from 40 to 100 kg ha^{-1} increased grain yield significantly by 45%, relative to that of soil and adding either of the sludges slightly increased the yield, compared to treatments without sludge, but this increase was non-significant. The differences in yield evident amongst sludge rates and among those of phosphate suggested an interaction between these factors. Gyp applied at 20 t ha^{-1} with phosphate at 100 kg ha^{-1} showed the highest yield of 101.7 g pot^{-1}, but this yield was not significantly different from that indicated by the same sludge at 10 t ha^{-1}, also by GypFeMnNi at 10 and 20 t ha^{-1} and when phosphate was applied at 100 kg ha^{-1} on its own. The slight increase in yield by treatments with sludges was an indication that these materials improved soil fertility. Applying phosphate at 40 kg ha^{-1} with either of the sludges at any rate or adding phosphate to a limed soil did not significantly increase the yield.

Table 9.10: Yield of maize planted in different sludge-soil mixtures (g pot^{-1})

Sludge	Soil	Soil (Limed)	10Gyp	20Gyp	10GypFe MnNi	20GypFe MnNi	***Average***
P40	40.4^{b}	41.2^{b}	39.3^{b}	31.4^{b}	32.1^{b}	66.3^{b}	***41.8^{b}***
P100	58.4^{ab}	43.5^{b}	65.5^{ab}	101.7^{a}	61.3^{ab}	82.18^{ab}	***68.8^{a}***
Average	***49.4^{b}***	***42.3^{c}***	***52.4^{b}***	***66.6^{a}***	***46.7^{b}***	***74.23^{a}***	

$\alpha < 0.05$, CV = 14.4%, LSD = 2.4, Note: Gyp (t ha^{-1}) = Gypseous, GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous, S = Soil, SL = Soil Limed, P (kg ha^{-1}) = phosphate. Note: Means of the same letter are not significantly different from each other across rows and columns

9.3.11 Sludge influence on Harvest Index (HI) for maize

Limed soil showed the lowest HI (0.30 – 0.34) due to liming that contributed mostly to plant biomass than to the grain (Fig. 9.6). Increasing phosphate application to 100 kg ha^{-1} showed to contribute more to grain than to biomass for all other treatments. Applying phosphate on its own showed an HI of 0.49. Co-application of phosphate with either sludge contributed more to the grain as such HI (0.44 – 0.65) increased for these treatments. The general contribution of the phosphate and sludges combinations to soil fertility resulted to an increase in grain yield. However, the upper limit (0.65) of the HI values for treatments with sludge combined with phosphate slightly exceeded the upper limit of the HI range, 0.49 – 0.57 reported by Djaman et al. (2013) and the HI range 0.41 – 0.62 reported by Unkovich et al. (2010) for maize. However, the lower limit (0.44) of the HI values for treatments with sludge combined with phosphate slightly exceeded the lower limit (0.41) of the range reported by Unkovich et al. (2010) for maize, but slightly below the lower limit (0.49) of the HI range reported by Djaman et al. (2013). What should be noted is that these Authors were not investigating the contribution of HDS to a soil and crop.

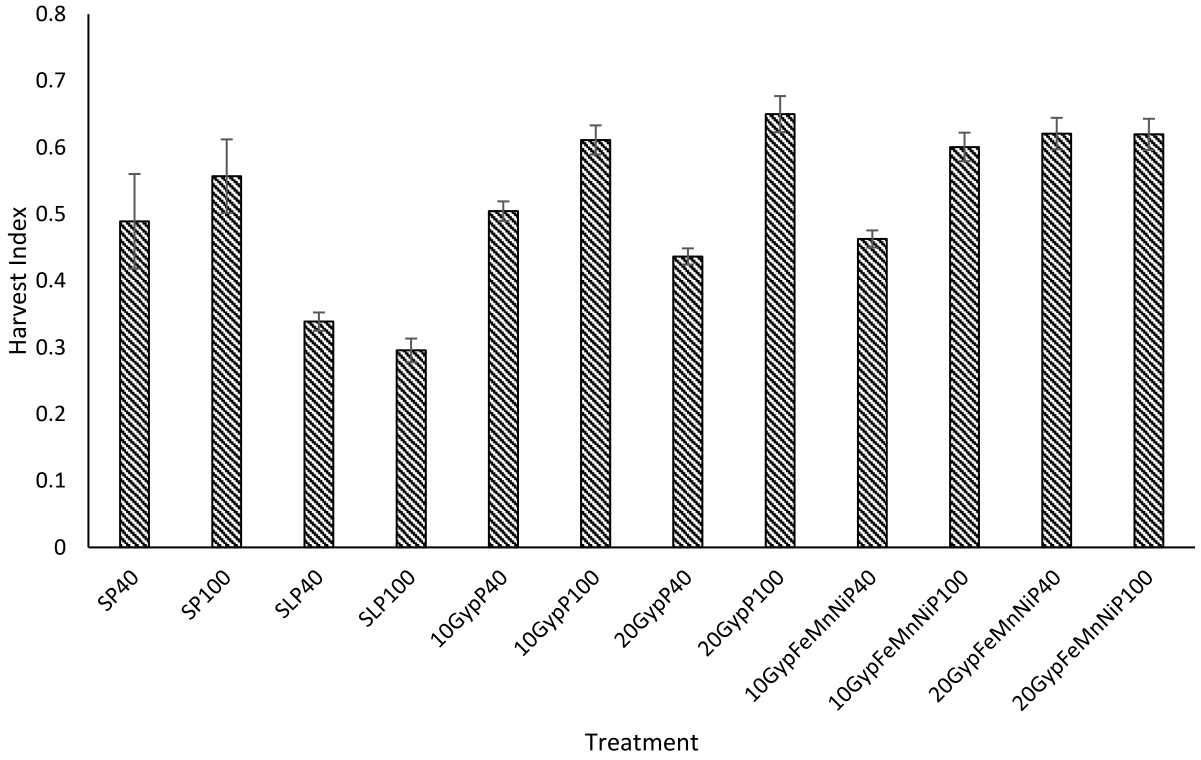


Figure 9.8: Harvest Index for maize. Gyp (t ha^{-1}) = Gypseous, GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; S = Soil, SL = Soil Limed, P (kg ha^{-1}) = phosphate

9.3.12 Sludge influence on the concentration of Ca, S and P in maize grain

Applying phosphate from 40 to 100 kg ha^{-1} had a non-significant effect on the concentration of Ca in the grain but showed a significant effect on the concentration of S and P (Table 9.11). Increasing the application of phosphate to 100 kg ha^{-1} significantly increased the concentration of phosphate but reduced that of S in the grain. Applying either of the sludges at both rates did not have a significant effect on the concentration of the elements in the grain, but there was an evidence of a slight increase. There is a possibility that the phosphate concentration in the grain was a contribution of the added fertilizer, while S and Ca were contributed through solubility of the gypsum in the sludges by irrigation water. Calcium concentration showed to be extremely low for all treatments, indicating a possibility of reduced availability in the soil. There is a possibility that there was precipitation of this soluble element (Ca) with the added phosphate into a thermodynamically stable phosphate mineral; hydroxyapatite ($Ca_5(PO_4)_3OH$), a sparingly soluble mineral (Ma et al. 2019). Liming significantly increased the concentration of all the elements in the grain. The concentration of elements in the grain in descending order were as follows; P>S>Ca in treatments without sludge and a similar trend was evident where sludges were added. This concentration trend of P, S and Ca in the grain differed from that of foliage, which was generally as follows; Ca<S<P. Calcium in foliage is needed more that S and P to maintain cell integrity and membrane permeability also important for protein synthesis and carbohydrate transfer (Jones 2012). This makes Ca to be more concentrated in foliage than in the grain. While P is a component of enzymes and proteins, adenosine triphosphate (ATP), ribonucleic acids (RNA), deoxyribonucleic acids (DNA), and phytin in the plant (Jones 2012).

Table 9.11: Major elements in maize grain (mg kg^{-1})

	Sludge	S	SL	10Gyp	20Gyp	10GypFe MnNi	20GypFe MnNi	*Average*
S	P40	94^{cd}	937^{a}	108^{c}	114^{c}	110^{c}	105^{c}	***245^{a}***
	P100	93^{cd}	789^{b}	89^{cd}	94c^{d}	99^{cd}	98^{cd}	***210^{b}***
	Average	***93^{b}***	***863^{a}***	***99^{b}***	***104^{b}***	***104^{b}***	***102^{b}***	
P	P40	285^{c}	2023^{b}	289^{c}	302^{c}	300^{c}	262^{c}	***577^{b}***
	P100	312^{c}	3043^{a}	317^{c}	287^{c}	349^{c}	374^{c}	***780^{a}***
	Average	***299^{b}***	***2533^{a}***	***303^{b}***	***295^{b}***	***325^{b}***	***318^{b}***	
Ca	P40	0.5^{a}	63.6^{a}	2.8^{a}	4.3^{a}	4.3^{a}	4.0^{a}	***13^{a}***
	P100	0.8^{a}	56.4^{a}	2.2^{a}	2.0^{a}	2.1^{a}	4.7^{a}	***11^{a}***
	Average	***0.7^{b}***	***60.0^{a}***	***2.5^{b}***	***3.1^{b}***	***3.2^{b}***	***4.4^{b}***	

S: $\alpha < 0.05$, CV = 3.6%, LSD = 55.9, P: $\alpha < 0.05$, CV = 4.1%, LSD = 213 , Ca: $\alpha < 0.05$, CV = 17%, LSD = 8.3, Note: Gyp (t ha^{-1}) = Gypseous, GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; S = Soil, SL = Soil Limed, P (kg ha^{-1}) = phosphate

9.3.13 Sludge influence on the concentration of Fe and Mn in maize grain

The addition of phosphate showed no significant effects on the concentration of Mn and Fe (Table 9.12). The addition of either sludge at any rate slightly reduced the concentration of Mn in the grain. The only reduction which was significant was that of Mn when compared to that of soil without sludge and hydrated lime. The limed soil showed an increased concentration of Fe in the grain. The increase in pH to 6.0 by the added hydrated lime increased the solubility of these elements from clay minerals, which were available for plant uptake. However, it was only the increase in Fe concentration that was significantly different. In descending order, the trace element concentrations were as follows: Mn < Fe in the grain for all treatments. This Mn < Fe trend in grain differed from that of foliage, which was generally as follows; Fe < Mn. Manganese is involved in the photosynthetic electron transport system within the plant and acts as a bridge for ATP and enzyme complex phosphokinase and phosphotransferases (Jones 2012) making it less concentrated in the grain.

Table 9.12: Transition metals in maize grain (mg kg^{-1})

	Sludge	S	SL	10Gyp	20Gyp	10GypFe MnNi	20GypFe MnNi	***Average***
Mn	P40	0.798^{a}	BMDL	0.381^{bc}	0.427^{bc}	0.528^{abc}	0.352^{bcd}	***0.41***^{a}
	P100	0.683^{ab}	BMDL	0.387^{bc}	0.292^{cd}	0.532^{abc}	0.480^{abc}	***0.40***^{a}
	Average	***0.741***^{a}	*BMDL*	***0.384***^{b}	***0.360***^{b}	***0.530***^{ab}	***0.416***^{b}	
Fe	P40	1.090^{b}	16.680^{a}	0.890^{b}	0.990^{b}	0.660^{b}	2.530^{b}	***3.81***^{a}
	P100	1.040^{b}	18.090^{a}	0.770^{b}	0.660^{b}	0.650^{b}	0.880^{b}	***3.68***^{a}
	Average	***1.065***^{b}	***17.385***^{a}	***0.830***^{b}	***0.825***^{b}	***0.655***^{b}	***1.705***^{b}	

Fe: $\alpha < 0.05$, CV = 13.2%, LSD = 2.45, Mn: $\alpha < 0.05$, CV = 15.5%, LSD = 0.19, Note: Gyp (t ha^{-1}) = Gypseous, GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; S = Soil, SL = Soil Limed, P (kg ha^{-1}) = phosphate, BMDL = below method detection limit

9.3.14 Nutrient concentration in soil, grain, foliage (foliage, stem and tassel) of maize

Major elements (Ca, S and P)

Only treatments with phosphate were considered for this discussion since they were the only treatments with harvestable grain. All concentrations reported as retained or absorbed were calculated relative to total (residual and added) in the soil. Generally, most of the nutrients remained below ground, accounting for leached, sorbed by the soil and unanalysed roots (Fig. 9.7: A, B & C). This was evident mostly in treatments with sludges. There is a possibility that some of the nutrients formed non-soluble precipitates in the soil or were sorbed by the sludges. However, in the unlimed soil, approximately half of S was absorbed by the plant. With Ca, 79% of it (relative to total) was absorbed by the plant in the unlimed soil with 40 kg ha^{-1} phosphate but increasing phosphate to 100 kg ha^{-1} P drastically reduced its uptake (Fig. 9.7 C). Finally, absorbed nutrients generally remained mostly in the biomass and there was minimal transfer to the harvested grain. Limed soil potentially facilitated the transfer of phosphate and S from biomass to the grain as their content in the grain relative to total in the soil ranged from 3.3 to 8.95% (Fig. 9.9: A & B).

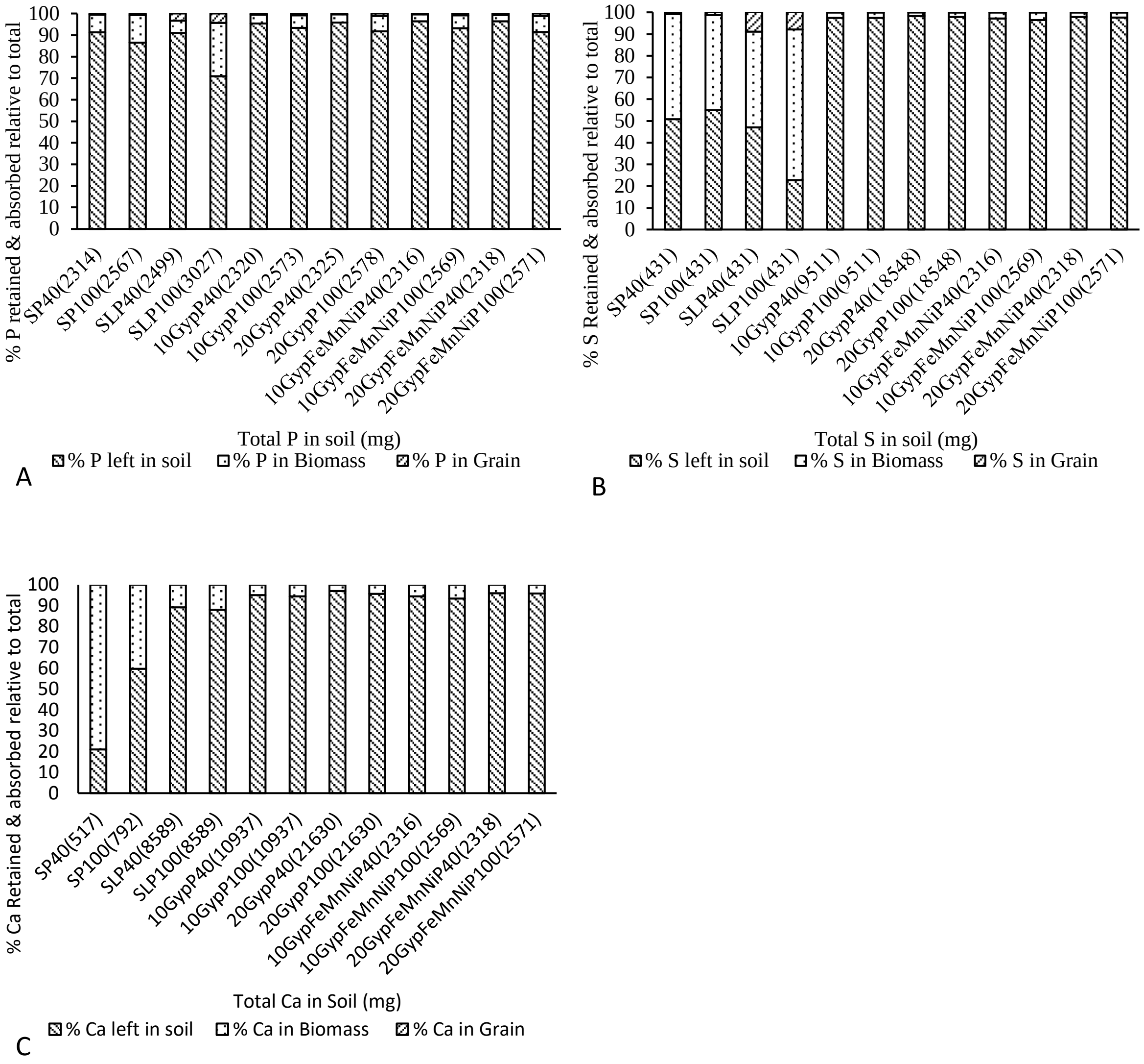


Figure 9.9: Nutrients retained in soil and taken up by plants; A) P; B) S; C) Ca, Note: Gyp (t ha^{-1}) = Gypseous, GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni;, S = Soil, SL = Soil Limed, P (kg ha^{-1}) = phosphate

Trace elements (Fe and Mn) in maize

Most of Fe and Mn remained below ground mostly in treatments with sludges (Fig. 9.8: A – D). However, limed soil facilitated mostly the uptake of Fe (Fig. 9.8: B, C & D), while the unlimed soil facilitated that of Mn (Fig. 9.8 A & C). Both trace elements, Mn and Fe were expected to be more soluble and be available for plant uptake in the unlimed soil with a pH of 3.75. Absorbed portions generally remained mostly in the biomass and there was minimal transfer to the grain.

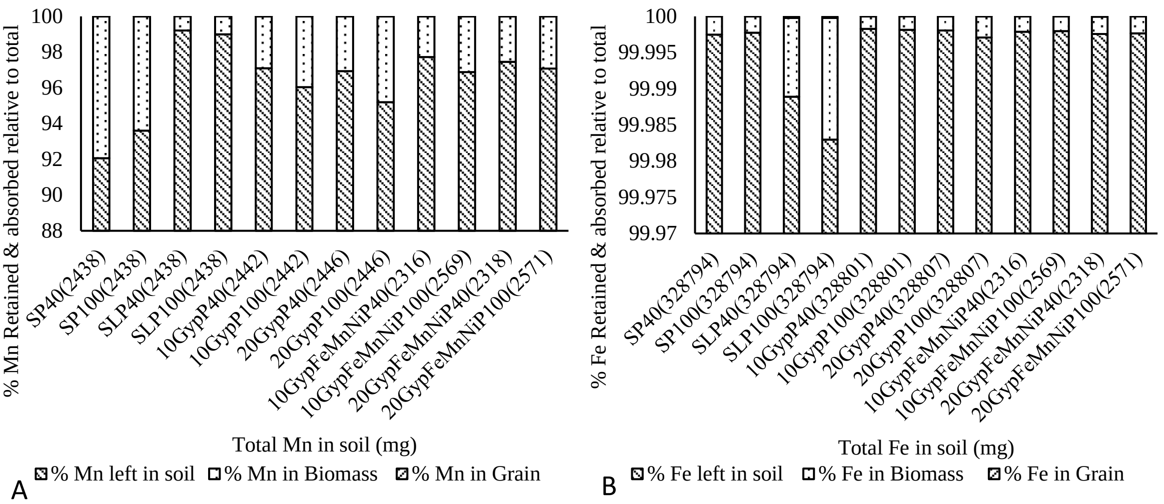


Figure 9.10: Metals retained in soil and taken up by plants; A) Mn; B) Fe; C) Ni: D) Pb. Note: Gyp (t ha^{-1}) = Gypseous, GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; S = Soil, SL = Soil Limed, P (kg ha^{-1}) = phosphate

9.4 CONCLUSIONS

Co-application of phosphate with either sludge, for instance applying GypFeMnNi at 20 t ha^{-1} with phosphate at 100 kg ha^{-1} increased plant height (166 cm) the most. Adding either sludge on its own slightly increased plant height and biomass relative to the treatments without hydrated lime and sludge. Leaf Area Index increased more when phosphate was co-applied with either sludge than when phosphate or either sludge was applied on its own. In terms of nutrient content, Ca and S concentrated mostly in the foliage, whereas, phosphate substantially concentrated in all plant parts. Adding either sludge increased the concentration of both Ca and S in all plant parts, relative to treatments without sludge and hydrated lime. Co-application of phosphate with either sludge increased the uptake of Ca by 1.1%, whereas applying phosphate on its own reduced Ca uptake by 0.2% in the foliage. With S, co-application of phosphate with either sludge reduced its uptake by 8.7 %, whereas applying phosphate on its own increased its uptake by 15.9%. With respect to trace elements, Fe and Mn were concentrated mostly in the foliage. Co-applying phosphate with either sludge reduced the uptake of Fe by 8.3% in the foliage and applying phosphate on its own as well reduced its uptake by 22.5%. Co-application of phosphate with either sludge, applying phosphate on its own and slightly increasing pH increased the uptake of Mn by 1.5, 4.6 and 5.2%. Nutrient concentrations indicated that Ca, Fe, Mn, S and phosphate were retained as follows; below ground > biomass > grain for all treatments. With respect to the yield, grain was present only in treatments that were fertilized with phosphate, whereas sludges contributed mostly to the grain yield than to foliage. For instance, Gyp applied at 20 t ha^{-1} with phosphate at 100 kg ha^{-1} had the highest yield of 20.7 t ha^{-1}, but this yield was not significantly different from that produced by the same sludge treatment at 10 t ha^{-1}, also by GypFeMnNi at 10 and 20 t ha^{-1} and by soil with 100 kg ha^{-1} of phosphate. This suggested that these sludge materials have the potential to improve plant biomass and yield, especially when they are applied at 20 t ha^{-1} and combined with phosphate at 100 kg ha^{-1}. Phosphate is an indispensable essential plant nutrient in the development of crops that is involved in the synthesis of proteins, nucleotides, enzymes, and also plays a vital role in photosynthesis and other physiological and biochemical reactions. Therefore, the crops in all the treatments without P had limited phenological development. For future work, it is recommended that application rates > 20 t ha^{-1} of the sludges incorporated with P are investigated and such research should be on a field scale to assess the response of different crops. The accumulation of Ni in the soil should be monitored (as it is the limiting element in the sludges), so that it does not exceed its threshold of 50 mg kg^{-1}. It is recommended therefore, that the application rate of the sludge, GypFeMnNi, does not exceed 1042 t ha^{-1} per single application to avoid exceeding Ni threshold in the soil. The application rate of Gyp should not exceed 3375 t ha^{-1} per single application. Long term trials may also be recommended.

CHAPTER 10

FOOD SAFETY OF MAIZE GRAIN PRODUCED WITH HIGH DENSITY SLUDGE FROM ACID MINE DRAINAGE NEUTRALIZATION AS A SOIL AMENDMENT: UPTAKE AND TRANSLOCATION OF Pb AND Ni

ABSTRACT

High Density Sludge (HDS), is a gypseous material from Acid Mine Drainage (AMD) treatment with hydrated lime and/or limestone. These materials may be classified as hazardous based on Mn, Ni and Pb derived from AMD, therefore requiring expensive disposal management. The potential use of HDS as an agricultural gypsum, depends on the phyto-availability of non-essential elements. Phosphate influence on phyto-availability was also investigated. The objective of this study was to assess food safety of maize produced on soil to which 10 or 20 t ha^{-1} HDS was applied, with or without phosphate at 40 and 100 kg ha^{-1}. A pot trial with an acidic soil (pH 3.75), considering two HDS materials, a Ni containing ferriferous gypseous sludge from limestone treated AMD, and a Pb containing gypseous sludge from a hydrated lime plus limestone treated AMD. Maize was grown to physiological maturity and food safety of grain assessed. Applying sludges on their own and co-application with phosphate reduced Ni and Pb concentrations in grain, which were below the Codex Alimentarius Pb threshold of 0.2 mg kg^{-1} and the 1 mg kg^{-1} threshold for Ni of the National Standards of the People’s Republic of China for all treatments. HDS should not pose a food safety risk if used responsibly, that is, considering the sludge application rates suggested in this study and the crop. Larger application rates and continuous use of the sludges may possibly lead to Ni and Pb accumulation exceeding their thresholds of 50 and 60 mg kg^{-1} in the soil.

Keywords: AMD; HDS; Gypseous; Maize; Food Safety; Nickel; Lead

10.1 INTRODUCTION

Neutralization of Acid Mine Drainage (AMD) by High Density Sludge Process (HDSP) generates a gypseous product (composed of mainly gypsum) referred to as High Density Sludge (HDS). The material from the Coalfields of Mpumalanga, South Africa contains various transition metals (e.g. Ni & Pb) that can be of environmental concern (Kalin et al. 2006, Chen et al. 2018). As such, it is often classified as hazardous and destined for storage facilities. An extensive evaluation of the HDS from the Coalfields Mpumalanga, in Chapter 6, using five different hazardous waste classification systems (South Africa, Australia, USA, Canada and China), it was established that a ferriferous gypseous product (consists of gypsum and contains Fe oxides in the percentage range), can accumulate Ni levels considered hazardous by various global waste classification systems (South Africa, Australia, Canada and China). The South African system, which is the only system considering Mn, also suggested that Mn accumulation can reach the level that can be considered hazardous. The reason why most systems do not consider Mn is because it forms sparingly soluble oxides and a common constituent of soil. It was also found that a gypseous product from which Fe oxides were removed was flagged based on Pb concentration, (albeit only by the South Africa (RSA) system). However, the material is largely composed of gypsum, therefore has some value as a soil amendment. Further, if it contains ferric oxides it can sorb metals and the material also has alkalinity that can possibly reduce soil acidity (Aubé and Zinck 1999, Tsang et al. 2013).

But if used as a soil amendment the major concern would be the accumulation of toxic metals especially Ni and Pb in food, a risk to food safety. Such contaminants are non-biodegradable, therefore, remain a health risk to humans and animals longer and at low concentrations (Sharma et al. 2018). Nickel and Pb meet this criterion and are amongst metals of environmental concern due to their toxicity, bioaccumulation and persistence (Shahid et al. 2017). Their risk to the food chain depends on their solubility which, in turn, influences their bioavailability (Shahid et al. 2017, Kabata-Pendias 2004). Root uptake is expected to be the main mechanism of uptake and therefore understanding soil control on this is important. Important controlling factors in the soil include pH, redox conditions, soil mineralogy, metal speciation, moisture to facilitate solubility and soil texture (Shahid et al.2017, Kabata-Pendias 2004, Martınez and Motto 2000). Kabata-Pendias (2004) reported that pH coupled with redox potential can influence the phyto-availability of Ni, Pb and other metals. In the case of HDS, metal availability is influenced largely by redox conditions because they are associated with ferric oxides. Under oxidizing soil conditions, the solubility of Ni increases at pH < 3 (a pH not suitable for the growth of most plants). The solubility of Pb decreases at pH > 5 when in association with ferric oxides and under oxidizing conditions. Martinez and Motto (Martınez and Motto 2000) reported that the solubility of metals including Ni and Pb increased with a decrease in soil pH in a study that involved amending several soils with metals.

Interaction of transition metals including Ni and Pb with phosphate, reduces their mobility as well and this has been studied by several researchers (Bolan et al. 2003, Cao et al. 2004, Tangahu et al. 2011, Mignardi et al. 2012, Seshadri at al. 2017, Zeng et al. 2017). For example, Cao et al. (2004) in an experiment that was meant to characterize the mono-metal and multi-metal interactions of Pb, Cu, and Zn on the surface of phosphate rock, found that, phosphate rock had a great affinity for Pb and formed sparingly soluble fluoropyromorphite ($Pb_{10}(PO_4)_6F_2$).

During uptake and translocation, elemental interaction occurs (Malvi 2011), synergism (where the excess of one element improves the uptake of another) and antagonism (where the excess of one element suppresses the uptake of another). The main antagonistic elements to the uptake of metals in general are Ca, Mg and P (Kabata-Pendias 2004). According to Shahid et al. (2017), after root uptake, translocation of metals within the plant is basically through chelation assistance and their transportation is controlled mainly by transpiration (a passive uptake method). The authors further pointed-out that most absorbed metals, especially Pb (approximately 95%) accumulate in the roots due to a blockage by the Casparian strip, a physical barrier existing around cell walls in the roots (Ahmad 2016) or by precipitation as metal-solid phases within the tissues of the plant or accumulation in the vacuoles. This limits translocation of metals within plant tissues.

Tsang et al. (2013), Tsang and Yip (2014) provided evidence of metal immobilization in soils treated with HDS that was composed of 16.4 – 21.2% Fe oxides and contained 45% of amorphous oxides/hydroxides of Fe. Their study showed nearly complete sequestration of As, Cu and Cr after 9 months of incubation of the Soil-HDS mixture. This was attributed to sorption by ferric oxides, in the case of As and Cr strong inner sphere complexation with low exchangeability. This showed that HDS has the potential to reduce solubility and phyto-availability of elements in soils. But as a disadvantage, ferric oxides can also sequestrate plant nutrients applied (Zinck 2005 and Zinck 2006).

With human food and animal feed safety, metals are only one of the concerns along with; natural contaminants (e.g. mycotoxins), process contaminants (e.g. acrylamine) and residues (e.g. pesticides) that are also considered (Thielecke and Nugent 2013). However, the focus is on Ni and Pb because this was a follow-up to Chapter 6 where some of the sludges were found hazardous due to the solubility of these elements. Waste classification is based purely on chemical extractability and/or total content and the assessment procedures do not include any direct environmental (bio)availability assessment. Therefore, the objectives were to assess; 1) Food and feed safety of maize when using HDS as an agricultural gypsum, 2) The phyto-availability of Ni and Pb from HDS; 3) The impact of the co-application of phosphate fertilizer with HDS on their phyto-availability.

10.2. MATERIALS AND METHODS

To achieve these objectives, greenhouse and laboratory investigations were conducted. A pot trial was set-up to allow the assessment of Pb and Ni uptake by a plant and their translocation within the tissues of the plant. Metal concentration intended to determine translocation within the plant tissues was assessed through chemical analysis.

10.2.1 Sources of sludges and soil used

Two sludges were selected based on the different AMD treatment processes detailed in Chapter 6. These materials were collected from the Mpumalanga coalfields, eMalahleni (Witbank) in South Africa, in 2017. One of them was sourced from a HDSP that uses limestone only, designated as ferriferous gypseous (GypFeMnNi) since it contained mainly gypsum and ferric oxides. Mn remain soluble in this material since limestone does not have the potential to increase pH to levels > 9 which facilitates Mn^{2+} oxidation and precipitation of Mn (IV) oxide (Skousen 2014). However, once added to an aerated agricultural soil the expectation is that it will be oxidized with time to Mn(IV) oxides. The other was collected from an HDSP that uses a combination of limestone plus hydrated lime and was designated as gypseous (Gyp) because the iron oxides were removed. The use of limestone plus hydrated lime increases the pH of the AMD solution to alkaline levels facilitating the precipitation of most metals including Mn (Skousen 2014).

Gypsum accounted for 72 – 77% of the crystalline phases in GypFeMnNi, with Fe oxides making-up 17.8% (calculated from XRF analysis) these were amorphous ferric oxides which could not be identified by the XRD technique and carbonate minerals (e.g. ankerite) 4%. Gyp was largely gypsum (> 95%), because iron oxides were removed during its refinement. With respect to metals, Ni (108 mg kg^{-1}) was concentrated mostly in GypFeMnNi, whereas, Pb concentration was more abundant (40 mg kg^{-1}) in Gyp (Table 10.1). In chapter 4, Ni was shown to reside in ferric oxides present in GypFeMnNi since it was only extracted by acid solutions and reductive extractants (dithionite and oxalate) and not by water. Lead extracted from this material by these solutions was below the detection limit (BDL) of 0.2 mg kg^{-1}.

Table 10.1: Selected chemical properties of Ferriferous gypseous (GypFeMnNi) and Gypseous (Gyp) materials

Parameter	GypFeMnNi	Gyp
pH(H_2O) at 2.5 solution /solid ratio	5.5^b	9.4^a
Salinity (EC) (mS m^{-1}) at 2.5 solution /solid ratio	364^a	274^b
Total Alkalinity as $CaCO_3$ (mg kg^{-1})	250^b	617^a
Concentrations extracted by acid digestion (mg kg^{-1})		
Major elements		
Ca	182961^b	224500^a
K	83^a	61^b
Mg	6513^b	9528^a
P	44^b	129^a
S	132974^b	216189^a
Metals		
Cd	< 0.18	< 0.18
Fe	124500^a	152^b
Mn	7590^a	95^b
Na	74^b	279^a
Ni	108^a	0.7^b
Pb	< 0.2	40^a
Zn	285^a	5^b

Note: Note: Note: $\alpha < 0.05$; CV = 4 – 12%. GypFeMnNi = Ferriferous gypseous with Mn and Ni; Gyp = Gypseous. Values with the smaller than sign (<) indicate Method Detection Limits (MDL) of those elements. Means with the same letter across sludges are not significantly different from each other. Values with the smaller than sign (<) indicate Method Detection Limits (MDL) of those elements

An acid soil, Hutton soil form according to the South African Soil Classification Working Group (1991) correlated to Ferralsols and Arenosols in the World Reference Base (WRB) classification system (Fanourakis 2012) with a pH of 3.75 and low in bases was selected (Table 10.2). It is a highly weathered soil derived from andesite and quartzite, with the clay fraction dominated by kaolinite (>75% of clay fraction) and iron oxides (approximately 10 and 6% goethite and hematite) (Mudaly 2016). This soil was collected from a field that was intentionally acidified over the years for research purposes. Total and exchangeable Ca and S were especially low (Table 10.2). This acid soil was selected because the sludges contained some alkalinity and the intention was to assess their ameliorating effect and, in turn, the impact this has on Pb and Ni uptake and translocation. This Ca and S deficient or borderline deficient soil was also a good candidate to assess crop response to gypseous HDS.

Table 10.2: Selected chemical and physiological soil properties

pH(H_2O)	3.75		
Salinity (EC) (mS m^{-1}) at 2.5 soil /solid ratio	7.8		
CEC ($cmol_c$ kg^{-1})	7.98		
Texture	Clay Loam		
	Acid digestion (mg kg^{-1})	Extractable elements (mg kg^{-1})	Extraction methods
Major elements			
Ca	26	18	NH_4OAc
K	894	68	NH_4OAc
Mg	338	12	NH_4OAc
P	244	8	P-Bray 1
S	69	25	EDTA
Metals			
Cd	< 0.18	< 0.01	EDTA
Fe	37363	25	EDTA
Mn	301	167	EDTA
Na	38	< 0.8	EDTA
Ni	35	0.9	EDTA
Pb	36	7.2	EDTA
Zn	20	1.2	EDTA

Note: NH_4OAc = Ammonium acetate, EDTA = Ethylenediaminetetraacetic acid. Values with the smaller than sign (<) indicate Method Detection Limits (MDL) of those elements.

10.2.2 Development of HDS-Soil mixtures

The HDS was applied at two rates, 10 and 20 t ha^{-1} (equivalent to 42 and 84 g/pot) to 8.8 kg soil (prepared by sieving through a 5 mm sieve) and thoroughly mixed on a mass-basis. The highest application rate adopted was 10 t ha^{-1} of commercial agricultural gypsum reported by Food and Agriculture Organization of the United Nations (1990). This rate was then doubled to assess the effect on soil and plant. The mass of soil per hectare was estimated to be 2.1 x 10^6 kg assuming a 0.15 m depth and a density of 1400 kg m^{-3}. Each HDS-Soil mixture was then transferred into pots with 26 cm top and 20 cm bottom diameter and a height of 25 cm. They also had three small openings at the bottom to allow for drainage.

10.2.3 Experimental design

This was a two-factor experiment arranged in a Randomized Complete Block Design (RCBD). All treatments were laid out on a rotating table to ensure exposure of treatments to similar conditions (sunlight, temperature and air blown by conditioners). The experiment had 18 treatments with a total of 6 controls that had no HDS applied (Table 10.3). Three of the controls received hydrated lime at 3.7 t ha^{-1} and different levels of phosphate and were considered "positive controls", while the other 3 received no hydrated lime at three phosphate levels and were considered to be "negative controls". The other 12 treatments were made up of the two HDS materials, each applied at 10 and 20 t ha^{-1}, and phosphate at 40 and 100 kg ha^{-1}. All treatments were replicated 3 times.

Table 10.3: Treatments included

Treatments	Comments	Description of treatments
Soil + H lime	Positive control	3.7 t ha^{-1} H lime
SoilP40 + H lime		40 kg ha^{-1}P; 3.7 t ha^{-1} H lime
SoilP100 + H lime		100 kg ha^{-1}P; 3.7 t ha^{-1} H lime
Soil	Negative control - Soil unlimed	
SoilP40		40 kg ha^{-1}P
SoilP100		100 kg ha^{-1}P
10GypP0		10 t ha^{-1} Gyp; 0 kg ha^{-1}P
10GypP40		10 t ha^{-1} Gyp; 40 kg ha^{-1}P
10GypP100		10 t ha^{-1} Gyp; 100 kg ha^{-1}P
20GypP0		20 t ha^{-1} Gyp;0 kg ha^{-1}P
20GypP40		20 t ha^{-1} Gyp; 40 kg ha^{-1}P
20GypP100		20 t ha^{-1} Gyp; 100 kg ha^{-1}P
10GypFeMnNiP0		10 t ha^{-1} GypFeMnNi; 0 kg ha^{-1}P
10GypFeMnNiP40		10 t ha^{-1} GypFeMnNi; 40 kg ha^{-1}P
10GypFeMnNiP100		10 t ha^{-1} GypFeMnNi; 100 kg ha^{-1}P
20GypFeMnNiP0		20 t ha^{-1} GypFeMnNi;0 kg ha^{-1}P
20GypFeMnNiP40		20 t ha^{-1} GypFeMnNi; 40 kg ha^{-1}P
20GypFeMnNiP100		20 t ha^{-1} GypFeMnNi; 100 kg ha^{-1}P

Note: Gyp (t ha^{-1}) = Gypseous; GypFeMnNi (t ha^{-1}) = Ferriferous gypseous with Mn and Ni; P (kg ha^{-1}) = Phosphate; H = hydrated

10.2.4 Fertilizer choice, application and planting

GypFeMnNi had the potential to sequestrate some of the essential applied plant nutrients especially phosphate, Ni and Zn due to the abundance of ferric hydroxide. To test this, a phosphate sorption study was carried out prior and the sludge showed to have the ability to sequester 27 kg of phosphate per ton of HDS. These results, therefore, were considered in this study, so phosphate availability had to be assessed at different application rates of the sludge material. Three phosphate application rates were adopted; a control, at a recommended rate of

40 kg ha^{-1} (Mangel and Kirby 2001, MIG 2017) and a rate (100 kg ha^{-1}) well above the recommendation. Phosphate was also added to test if it can aid in decreasing the uptake of Ni and Pb from HDS. To minimize the introduction of any impurities, a reagent grade potassium dihydrogen phosphate (KH_2PO_4) was used as the source of phosphate. This source also provided some of the K needed by the maize but was insufficient to supply the 40 kg K ha^{-1} recommended. So, to achieve this recommended rate for K, additional K was applied from potassium chloride (KCl), a reagent grade. Nitrogen (N) was applied at a recommended rate of 100 kg ha^{-1} as diammonium hydrogen phosphate ($(NH_4)_2HPO_4$), in the form of a reagent grade chemical. Also, this source of N provided additional phosphate that was considered to achieve the 40 and 100 kg P ha^{-1} rates selected. To benefit from the addition of N and K, KH_2PO_4 (70%) and 30% $(NH_4)_2PO_4$ were added to the Soil-HDS mix. As an application strategy, sources of P and K were applied in a single dose and spread 5 mm below seed, while N application was split into two applications during vegetative growth.

Maize (*Zea mays*) variety DKC73 – 74BRGEN was selected based on its acidity (pH 5.5 – 6.5) and salinity (1.8 dS m^{-1}) tolerance and the fact that it is a commonly planted crop in Mpumalanga, RSA. A total of 5 seeds were planted in each pot at 5 mm depth. This number of seeds was intended to allow plant sampling at different time intervals. This maize was harvested at physiological maturity (125 – 140 days) to enable food safety assessment of the grain.

10.2.5 Crop management

Tap water was used for irrigation. All treatments were irrigated to field capacity (FC) which was calculated to be 2.55 L per pot. The frequency of irrigation was every third day. Additional water required to reach field capacity after the third day was determined as a difference in mass through weighing of pots. During active vegetative growth, 1 L of additional water was required every third day. One of the plants was cut off at soil level at the following development stages; V3 (third leaf collar evident), V7 (seventh leaf collar evident), V10 (tenth leaf collar evident), VT (tasselling) and R6 (physiological maturity, milk line no longer evident, black layer formed). Data collected at V3 – VT stages included assessment of metal (Pb and Ni) uptake in foliage and at R6 the concentration of these metals in the grain.

10.2.6 Soil, HDS and plant digestions, and analyses

Nickel and Pb as well as Cd, Fe, Mn, Na, Zn, Ca, K, Mg, P and S of the sludge, soil, HDS - Soil mixtures, foliage, tassels and grains were determined following the microwave assisted acid digestion method by the United States (US) Environmental Protection Agency (EPA) Method 3050 (1996). In the case of the Soil-HDS mixtures, it was done before and after harvesting. Tassels and grains were analyzed at the physiological maturity stage (R6).

When EPA 3050 digestion were performed, a solution to solids ratio of 1:30 was used (solid sample weight = 0.3 g). The samples were digested with 65% Merck SupraPur HNO_3 at 180 $^oC \pm 5\ ^oC$ using an Anton Paar Multiwave 3000 (USA) digester for 15 to 19.5 minutes after which the digestants were transferred to a 50 ml centrifuge tube. Elements extracted were determined with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES). The ICP was calibrated using standards for the different elements.

Method detection limit (MDL) for EPA 3050 in our lab was determined following a standard Procedure by USEPA 40 CFR Appendix A to Part 136 (2011). Seven replicates of the same acid used for the digestions (Merck SupraPur HNO_3) were spiked in order to obtain concentrations of 50 µg L^{-1} for Ni and Pb. An ICP multi-element standard containing Ni and Pb (1000 mg L^{-1}, in diluted HNO_3) was used. The MDL was then calculated as follows:

MDL = Standard deviation of replicates x Student's *t* value $_{(n\text{-}1,\ 1\text{-}\alpha = 0.99)}$

Where: n = number of replicates

α = level of significance

Finally, MDL was converted from mg L^{-1} to mg kg^{-1} by multiplying the value with the following ratio; 0.03 L of the extractant / 0.0003 kg of the sample. The MDL for Ni and Pb were therefore, calculated to be 0.93 mg kg^{-1} (0.01 mg L^{-1}) and 0.2 mg kg^{-1} (0.002 mg L^{-1}).

10.2.7 Determination of KCl extraction of exchangeable Al, and soluble and exchangeable acidity in soil.

Potassium chloride (KCl) extraction, to determine exchangeable Al, soluble and exchangeable acidity in the soil, was carried out as described by Thomas (1982) in Standard Methods of Soil Analysis Part 2. This was meant to assess the initial soil acidity and changes at the end of the season. The method for determining “exchangeable Al”, basically quantified all exchangeable hydrolysable cations (EHC) in the system, i.e. more or less the sum of soluble and exchangeable Fe^{3+}, Mn^{3+} and Al^{3+}.

10.2.8 Food safety assessment

Food safety standards for humans by Codex Alimentarius (2006) was preferred. This was because Codex standards are a collection of internationally adopted standards (developed by different countries) and related texts aimed at protecting consumers’ health and ensuring fair practices in the food trade (Codex Alimentarius Commission 2010). The main concern in this study was the concentration of Pb and Ni in maize. However, it should be noted that in cereal grains contaminants of concern by Codex Alimentarius Commission include Pb, with a threshold set at 0.2 mg kg^{-1} but not Ni. Therefore, a different food safety standard had to be selected to assess Ni toxicity in the grain. Several food standards; European, Canadian, USA, Australian and South African were scrutinized to see if Ni was included but none of them considered it as a toxic contaminant in food except for China. The Chinese food standards assess Ni only in fats and their products, i.e., in hydrogenated vegetable oils and hydrogenated vegetable oil-based products. The threshold for Ni was set at 1.0 mg kg^{-1} on a dry basis (National Standard of the People’s Republic of China 2012).

Also investigated was animal feed safety in case the fodder including the grain are fed to animals. Standards for Food and Agricultural Organization (1997), European Commission (2002) and the Department of Agriculture for South Africa (2006) were considered. The European Commission (2002) together with member States do not consider Ni as toxic in animal feed as such it is excluded in their standards, but the threshold for Pb was set to 40 mg kg^{-1}. Standards for Food and Agricultural Organization (1997) and the Department of Agriculture for South Africa (2006) were considered because they include thresholds for both Ni and Pb. With Pb, both Food and Agricultural Organization (1997) and the Department of Agriculture for South Africa (2006) have set the threshold at 40 mg kg^{-1}. Food and Agricultural Organization (1997) considers Ni as moderately toxic and has set its threshold at 100 mg kg^{-1} while the Department of Agriculture for South Africa (2006) has set it at 50 mg kg^{-1}.

10.2.9 Statistical analysis

All statistical analysis was carried out using SAS Version 9.4. ANOVA was performed to establish differences amongst treatments and to separate means, Least Significant Difference (LSD) was used. To assess main effects, means were calculated across the sludges and phosphate added.

10.3. RESULTS AND DISCUSSION

10.3.1 Possible benefits of HDS as a soil ameliorant

The agricultural soils of the Mpumalanga Highveld (where the HDS is generated) are largely dystrophic (low in Ca, Mg and K) and sensitive to soil acidification (South African Soil Classification Working Group 1991). HDS appeared to be a logical amendment for these nutrient poor soils, because it is enriched, (apart from Ca and S) with most of the elements these soils are deficient in, examples; Mg, K, Zn and P (Table 10.1). The proximity of the treatment plants can also decrease transport costs. The added iron oxide in the case of GypFeMnNi is known to sorb Ni. In addition, GypFeMnNi contains Mn, an essential plant nutrient. Although the material was found hazardous by the RSA classification guidelines based on Mn content (Chapter 6). Considering everything discussed up till this point, the assessment of HDS as a soil ameliorant merited investigation.

10.3.2 The amelioration effect of HDS

Both chemical and biological reactions in the soil are controlled by pH (Hendershot and Lalande 2008). Soil acidification is common in the agricultural soils of the higher rainfall areas of RSA (e.g. Mpumalanga Highveld). This acidity is composed of soluble and exchangeable H^+ and Al^{3+}. When acidity is coupled with Al^{3+} toxicity it leads to poor soil fertility and reduces soil productivity (Han et al. 2019). Under these conditions non-essential elements like Pb are also expected to be highly bio-available. Liming therefore is essential to maintain the bioavailability of Ca, P, K and Mg and reduce the toxicity of Al^{3+} and non-essential elements like Pb (if present). Based on the alkalinity analysis presented in Table 10.1 the sludges were expected to ameliorate the acid soil. It was on these bases that this discussion was included to help understand the amelioration effects of HDS.

Soil pH

An overall marginal increase in pH was evident in treatments with phosphate co-applied with sludge (Table 10.4). A significant ($\alpha < 0.05$) increase was evident when adding either sludge at 10 and 20 t ha^{-1} in combination with phosphate, but still these values were low, and the soils amended with HDS on its own suggested conditions conducive for Ni and Pb uptake. However, the highest pH recorded for HDS – phosphate treatment combination was 4.21 (at 20 t ha^{-1} of GypFeMnNi and 100 kg ha^{-1} P), and although statistically significant ($\alpha < 0.05$) increases were found, but the impact from a nutrition perspective was expected to be negligible. Based on the alkalinity of Gyp and GypFeMnNi, the soil pH was expected to increase since with loading rates of 10 or 20 t ha^{-1} alkalinity added, equivalent of $CaCO_3$ (19 – 94 mmol kg^{-1}) exceeded the soil exchangeable acidity 14.7 mmol$_c$ kg^{-1}. This suggested that some mechanism was responsible for either buffering soil pH or /and preventing the alkalinity in the HDS to react. In the case of GypFeMnNi, both Fe oxide and gypsum could have armoured limestone, whereas with the Gyp product it was possibly armouring due to gypsum (Simón et al. 2005, Skousen et al. 2019). Applying phosphate on its own at 100 kg ha^{-1} slightly increased soil pH as well but was lower than when co-applied with either sludge.

Table 10.4: Effect of treatments on soil pH

P	Sludges (t ha^{-1})					
	Soil	Soil (Limed)	10Gyp	20Gyp	10GypFeMnNi	20GypFeMnNi
P0	3.78^{fgh}	5.10^{c}	3.56^{h}	3.79^{fgh}	3.83^{efg}	3.74^{fgh}
P40 (kg ha^{-1})	3.63^{gh}	5.68^{b}	3.81^{efgh}	3.91^{ef}	3.90^{ef}	3.90^{ef}
P100 (kg ha^{-1})	3.80^{efgh}	5.95^{a}	3.91^{ef}	4.06^{de}	3.93^{ef}	4.21^{d}

$\alpha < 0.05$, CV = 0.2, LSD = 0.14. Note: Gyp = Gypseous; GypFeMnNi = Ferriferous gypseous with Mn and Ni; P = Phosphorus; means of the same letter are not significantly different from each other across rows and columns.

Exchangeable acidity and hydrolysable cations

Initially, the soil had an exchangeable acidity of 14.7 mmol$_c$ kg^{-1} (Figure 10.1). Generally, the addition of phosphate and/or sludge statistically significantly ($\alpha < 0.05$) reduced exchangeable acidity. This decrease was more pronounced for combined sludge and phosphate treatments. When Gyp and GypFeMnNi were applied at 20 t ha^{-1} with phosphate at 100 kg ha^{-1}, exchangeable acidity decreased the most by 74 and 67% respectively, relative to initial soil acidity. It was evident that the phosphate-Gyp combination, reduced acidity more than the combination of phosphate with GypFeMnNi. This was expected since the alkalinity of Gyp (617 mg kg^{-1}) was higher than that of GypFeMnNi (250 mg kg^{-1}) and also could be due to the absence of Fe oxides in Gyp. The application of either sludge (on their own) at 10 and 20 t ha^{-1}, significantly ($\alpha < 0.05$) reduced soil acidity as well. Applying Gyp and GypFeMnNi at 20 t ha^{-1} reduced acidity by 55 and 33% relative to the initial soil acidity. Whereas applying Gyp and GypFeMnNi at 10 t ha^{-1} reduced acidity by 36 and 21% relative to the initial soil acidity. Phosphate on its own significantly reduced exchangeable acidity but did not show an appreciable liming effect than when combined with either sludge. Applying phosphate on its own at 40 and 100 kg ha^{-1}, statistically significantly ($\alpha < 0.05$) decreased exchangeable acidity by 3 and 16% relative to the initial soil acidity (14.7 mmol$_c$ kg^{-1}). Results, therefore, indicated that the combined effect of phosphate and sludge reduced acidity more than when phosphate or sludge were on their own. Soil P0, increased exchangeable acidity by 11% at the end of the season relative to the initial soil acidity. This could be attributed to the application of $(NH_4)_2HPO_4$, a fertilizer known to slightly acidify soils as a result of protons (H^+) generated caused by the oxidation of NH_4. As expected, liming reduced soil acidity the most, from 92 to 94% relative to the initial soil acidity.

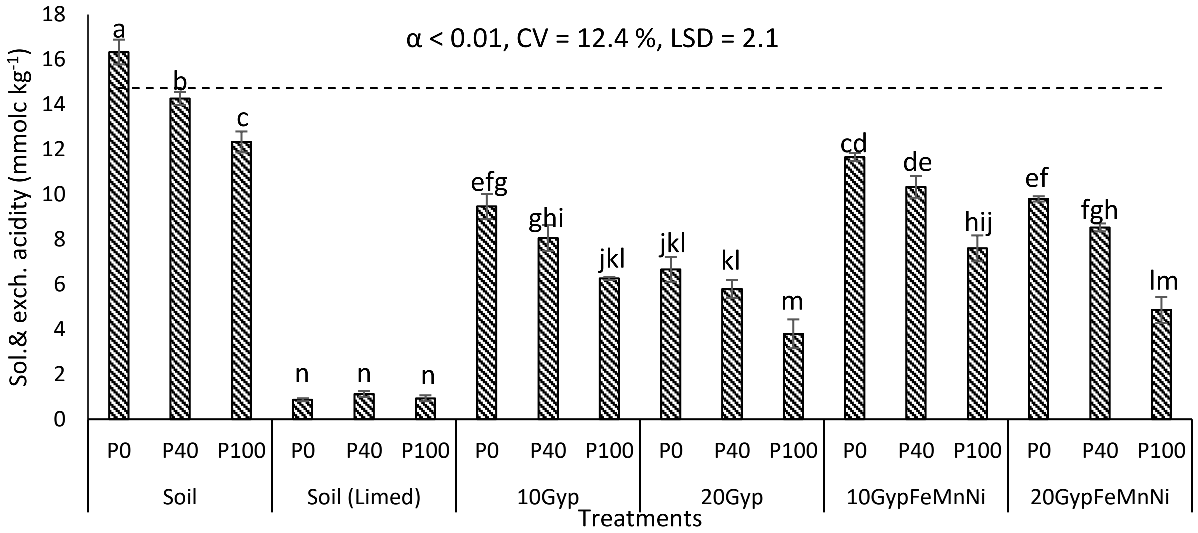


Figure 10.1: Exchangeable acidity, dashed line indicates initial exchangeable acidity (14.73 mmol$_c$ kg^{-1}). Means with the same letter are not significantly different from each other across treatments. Note: Gyp (t ha^{-1}) = Gypseous; GypFeMnNi (t ha^{-1}) = Ferriferous gypseous with Mn and Ni; P (kg ha^{-1}) = Phosphate

A similar trend as with exchangeable acidity was observed with “exchangeable Al” (Figure 10.2). As explained earlier, the method for “Exchangeable Al” basically quantified all EHC in the system, i.e. more or less the sum of soluble and exchangeable Fe^{3+}, Mn^{3+} and Al^{3+}. The initial EHC for the soil was 12.2 $mmol_c\ kg^{-1}$ and the greatest reductions were observed when phosphate was co-applied with HDS. The EHC decreased with increasing phosphate application and the most pronounced decrease was for the highest HDS and phosphate combinations. In general, treatments with Gyp reduced EHC more than those with GypFeMnNi. Applying Gyp at 20 t ha^{-1} with 100 kg ha^{-1} phosphate reduced EHC the most (78%), relative to the initial soil conditions, whereas, applying GypFeMnNi at 20 t ha^{-1} with phosphate at 100 kg ha^{-1} reduced it by 54% and this could be due to Fe or Al hydroxy sulphate precipitation even though most of these were removed from Gyp by the treatment process. It could also be that some of the lime in GypFeMnNi was locked up by Fe oxides, which was not the case with Gyp. Phosphate as well that could have reacted with the EHC was sorbed by the Fe oxides. Applying Gyp at 20 t ha^{-1}, on its own reduced EHC by 46%, while GypFeMnNi at 20 t ha^{-1} caused a 31% reduction. This EHC reduction at 20 t ha^{-1} was more that when either sludge was applied at a lower rate of 10 t ha^{-1}. Phosphate on its own at 100 kg ha^{-1} P significantly ($\alpha < 0.05$) reduced EHC by 19% relative to the initial EHC. In general, soil that received only phosphate showed negligible changes in hydrolysable cations, in some instances EHC actually increased. For example, treatment without P (Soil P0) and Soil with P at 40 kg ha^{-1} increased EHC by 11 and 3% relative to initial soil conditions. Liming as expected, reduced EHC more than any other treatment, it reduced it from 85 to 90% relative to the initial EHC.

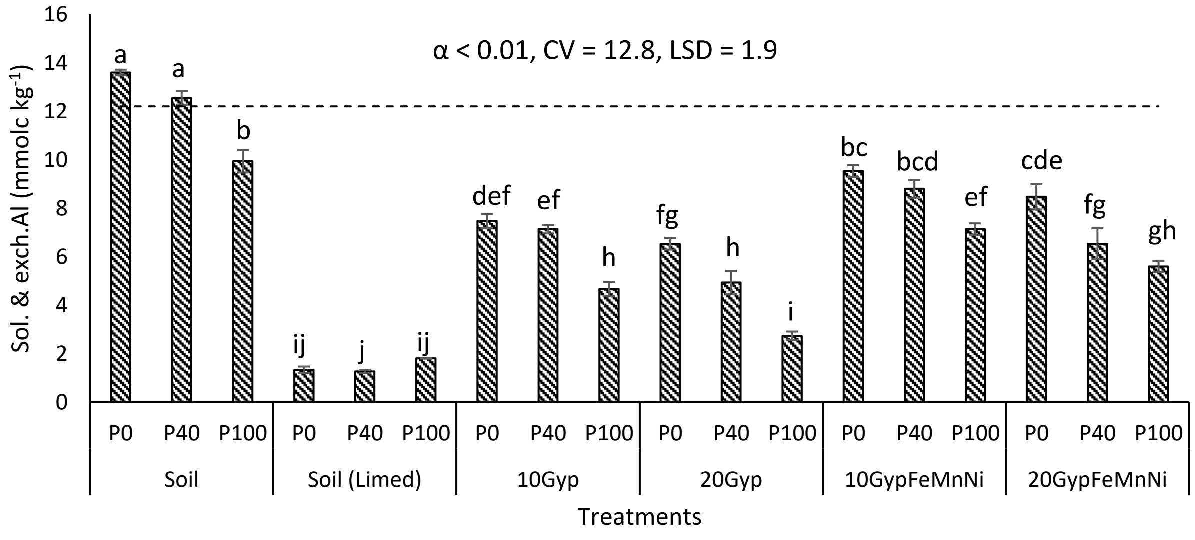


Figure 10.2: Exchangeable hydrolysable cations (EHC), dashed line indicates initial EHC (12.2 mmolc kg^{-1}), Note: Means with the same letter are not significantly different from each other across treatments, Note: Gyp (t ha^{-1}) = Gypseous, GypFeMnNi (t ha^{-1}) = Ferriferous gypseous with Mn and Ni; P (kg ha^{-1}) = phosphate.

10.3.3 Salinity effect

The sludges contained elements that can increase soil salinity. Salinity is an abiotic stress that leads to substantial losses in agricultural production by reducing the capacity of a plant to absorb water due to increased osmotic pressure and accumulation of ions such as Na^+ and $Cl^−$ in the organs of the plant (Parida and Das 2005, Hernández 2019, Zanetti et al. 2019). Salinity can possibly increase the solubility of Ni and Pb either through solution complexation or decrease in ion activity. These salinity impacts therefore, necessitated this discussion that focused on the potential of the sludges to induce soil salinity. Generally, there was a significant ($\alpha < 0.05$) increase in salinity with the addition of either sludge. The 20 t ha^{-1} clearly represented an upper application limit (Table 10.5) of the sludges. When Gyp and GypFeMnNi were applied on their own (treatments 20GypP0 and 20GypFeMnNiP0) soil salinity increased the most to 973 and 720 mS m^{-1} respectively, suitable only to salinity tolerant plants. Possibly sulphates of Mg, Na and K in the sludges contributed to this. However, the co-application of phosphate with sludges decreased the salinity of treatments and this could be due to the precipitation of soluble Ca. Also, this decrease in salinity could have been the result of the decrease in EHC discussed earlier. The decreased salinity by GypFeMnNi was because it contained less elements and the fact that it had Fe oxides that sequestrated some of the soluble ions through surface precipitation, complexation or co-sorption. The application of phosphate on its own significantly ($\alpha < 0.05$) reduced soil salinity due to precipitation and co-sorption of the soluble ions. There was evidence of increase in salinity in the control which was due mainly to the addition of fertilizers.

Table 10.5: Effect of treatments on salinity (mS m^{-1})

P	Sludges (t ha^{-1})						
	Soil	Soil (Limed)	10Gyp	20Gyp	10GypFe MnNi	20GypFe MnNi	Average
P0	160^{ghi}	13^{i}	576^{cde}	981^{a}	348^{efgh}	728^{bc}	468^{a}
P40 (kg ha^{-1})	122^{hi}	14^{i}	443^{def}	865^{ab}	338^{fgh}	644^{bcd}	404^{b}
P100 (kg ha^{-1})	161^{ghi}	14^{i}	347^{efgh}	818^{ab}	371^{efg}	527^{def}	360^{b}
Average	148^{d}	14^{e}	455^{c}	888^{a}	352^{c}	633^{b}	

$\alpha < 0.05$, CV = 2.1%, LSD = 126, Note: Gyp (t ha^{-1}) = Gypseous; GypFeMnNi (t ha^{-1}) = Ferriferous Gypseous with Mn and Ni; P (kg ha^{-1}) = Phosphorus

In summary, co-application of sludges with phosphate helps to decrease salinity and this suggested that phosphate co-sorption / co-precipitation some of the soluble ions in HDS.

10.3.4 Uptake, translocation and accumulation of Ni and Pb

Phosphate application on its own and sludges on their own did not significantly ($\alpha > 0.05$) increase the concentration of Ni in all plant parts (Table 10.6). Applying GypFeMnNi and Gyp at 20 t ha^{-1} loaded 2.16 and 0.014 kg ha^{-1} Ni to the soil while 10 t ha^{-1} loaded 1.08 and 0.007 kg ha^{-1} Ni. In descending order Ni concentration could be ranked as follows; foliage > tassel > stem within the plant suggesting a passive uptake of this element as reported by Kebata-Pendias and Pendias (2001). Ni was also reported by Kacálková et al. (2014) to concentrate mostly in the foliage rather than in the stalk of maize. This was an indication that Ni uptake and translocation within the plant tissues were not hindered as most of it was concentrated in the foliage. Phosphate application was expected to reduce Ni phyto-availability due to precipitation or phosphate induced Ni sorption by iron oxides (similar to phosphate induced Zn sorption). However, increasing the application of GypFeMnNi increased Ni concentration in the plant parts, but the concentration was close to the method detection limit. This was because this material contained more fairly soluble Ni and soil acidity was conducive for its solubility. The increase in Ni concentration in the foliage when Gyp was applied at 20 t ha^{-1} either on its own or in combination with phosphate at 40 kg ha^{-1} was not expected, it was contributed by the soil (35 mg kg^{-1}) since Gyp had negligible Ni content (0.7 mg kg^{-1}). This was also evident in treatments like SP0, SP40 and SP100.

Table 10.6: Sludge and phosphate influence on Ni (mg kg^{-1}) in biomass

Plant part	Nickel							
	Trt	S	SL	10Gyp	20Gyp	10GypFe MnNi	20GypFe MnNi	Average
Foliage	P0	1.14^{a}	0.93^{a}	0.98^{a}	1.23^{a}	< 0.93	1.55^{a}	1.17^{a}
	P40	1.25^{a}	< 0.93	< 0.93	1.38^{a}	1.22^{a}	1.28^{a}	1.28^{a}
	P100	1.11^{a}	1.03^{a}	< 0.93	< 0.93	< 0.93	< 0.93	1.07^{a}
	Average	1.17^{a}	0.98^{a}	0.98^{a}	1.31^{a}	1.22^{a}	1.42^{a}	
Stem	P0	1.15^{a}	< 0.93	1.32^{a}	< 0.93	< 0.93	0.25^{a}	0.91^{a}
	P40	<0.93	< 0.93	< 0.93	< 0.93	< 0.93	< 0.93	<0.93
	P100	<0.93	< 0.93	< 0.93	< 0.93	< 0.93	< 0.93	<0.93
	Average	1.15^{a}	< 0.93	1.32^{a}	< 0.93	< 0.93	0.25^{a}	
Tassel	P0	1.66^{a}	< 0.93	<0.93	1.06^{a}	< 0.93	< 0.93	1.36^{a}
	P40	<0.93	1.40^{a}	1.00^{a}	< 0.93	1.07^{a}	< 0.93	1.15^{a}
	P100	2.26^{a}	<0.93	< 0.93	< 0.93	< 0.93	1.36^{a}	1.81^{a}
	Average	1.96a	1.40^{a}	1.00^{a}	1.06^{a}	1.07^{a}	1.36^{a}	

Foliage: $\alpha < 0.05$, CV = 4.3%, LSD = 1.1, Stem: $\alpha < 0.05$, CV = 17.3%, LSD = 0.8, Tassel: $\alpha < 0.05$, CV = 7.8%, LSD = 1.5, Note: Gyp (t ha^{-1}) = Gypseous; GypFeMnNi (t ha^{-1}) = Ferriferous gypseous with Mn and Ni; S = Soil; SL = Soil Limed; P (kg ha^{-1}) = Phosphate, Trt = Treatment, MDL for Ni was 0.93 mg kg^{-1} (0.01 mg L^{-1}).

Lead as well was concentrated mostly in the foliage (Table 10.7) and its concentration could be ranked as follows; foliage > tassel > stem within the plant, also suggesting a passive uptake of this element. GypFeMnNi had total Pb below detection limit while Gyp loaded 0.8 and 0.4 kg ha^{-1} Pb into the soil when applied at 20 and 10 t ha^{-1}. Kacálková et al. (2014) also reported that Pb concentrates more in foliage than in the stalk of maize. The extremely low Pb concentration in the stem was shown by all treatments. The application of phosphate on its own effected a Pb increase which was not statistically significantly different ($\alpha < 0.05$) in foliage, tassels and stem. With respect to the sludges, the application of these materials could not significantly ($\alpha < 0.05$) reduce the concentration of Pb in all the plant parts. According Kumpiene et al. (2008) Ca compounds including gypsum and phosphogypsum, Fe and Mn oxides have the potential to immobilize Pb. As discussed earlier, both materials are composed of gypsum, but GypFeMnNi also contains ferric oxides that can sorb Pb. Shahid et al. (2018) pointed out that more than 95% of absorbed Pb including other metals such as Ni accumulate in the plant roots due to a physical barrier by the Casparian strip and precipitation. Liming the soil also increased the concentration of Pb in the foliage due to the combination effect of $Ca(OH)_2$ used which contained 30 mg kg^{-1} Pb and soil that already had 36 mg kg^{-1} Pb.

Table 10.7: Sludge and phosphate influence on Pb (mg kg^{-1}) in biomass

Plant part	Lead							
	Trt	S	SL	10Gyp	20Gyp	10GypFeMnNi	20GypFeMnNi	Average
Foliage	P0	1.27^{b}	2.4^{ab}	1.21^{b}	1.48^{b}	0.97^{b}	1.1^{b}	1.41^{a}
	P40	3.01^{ab}	3.46^{ab}	1.41^{b}	1.43^{b}	1.9^{ab}	1.79^{ab}	2.17^{a}
	P100	0.96^{b}	4.22^{a}	0.97^{b}	0.93^{b}	1.08^{b}	0.97^{b}	1.52^{ab}
	Average	1.75^{b}	3.36^{a}	1.20^{b}	1.28^{b}	1.32^{b}	1.29^{b}	
Stem	P0	0.46^{ab}	< 0.2	0.29^{ab}	0.43^{ab}	< 0.2	0.29^{ab}	0.37^{a}
	P40	0.93^{a}	0.2^{ab}	0.34^{ab}	0.40^{ab}	0.55^{ab}	0.32^{ab}	0.46^{a}
	P100	0.48^{ab}	< 0.2	< 0.2	0.35^{ab}	< 0.2	0.60^{ab}	0.48^{a}
	Average	0.62^{a}	0.2^{b}	0.32^{ab}	0.40^{ab}	0.55^{ab}	0.40^{ab}	
Tassel	P0	0.65^{bc}	< 0.2	0.33^{c}	0.41^{bc}	0.59^{bc}	0.46^{bc}	0.49^{b}
	P40	0.67^{bc}	1.64^{ab}	0.79^{bc}	0.92^{abc}	0.87^{abc}	0.69^{bc}	0.93^{a}
	P100	0.38^{c}	2.05^{a}	1.01^{abc}	0.81^{bc}	0.31^{c}	1.13^{abc}	0.95^{a}
	Average	0.57b	1.85^{a}	0.71^{ab}	0.71^{ab}	0.59^{b}	0.76^{ab}	

Foliage: $\alpha < 0.05$, CV = 19.4%, LSD = 1.5, Stem: $\alpha < 0.05$, CV = 14.3%, LSD = 0.5, Tassel: $\alpha < 0.05$, CV = 3.7%, LSD = 0.7, Note: Gyp (t ha^{-1}) = Gypseous; GypFeMnNi (t ha^{-1}) = Ferriferous gypseous with Mn and Ni; S = Soil; SL = Soil Limed; P (kg ha^{-1}) = Phosphate. Trt = Treatment, MDL for Pb was 0.2 mg kg^{-1} (0.002 mg L^{-1}).

Generally, the application of either sludge even with a content of 40 mg kg^{-1} Pb did not increase the concentration of Pb in the plant while limed soil with a Pb content of 36 mg kg^{-1} did. Lead was concentrated more in the foliage than in the stem and tassels and generally increased with an increase in phosphate application. This synergism with phosphate occurred within the plant tissues because phosphate in the soil was expected to reduce the solubility of Pb through pH increase and precipitation. It should be noted that no data represented the analysis of roots as it proved difficult to clean them. However, the addition of either sludge slightly reduced Pb phyto-availability and uptake in all plant parts presumably due to pH increase and reduction in acidity. In descending order Pb could be ranked as follows; foliage > tassel > stem. With respect to Ni both sludges and applied phosphate had marginal influence on Ni bioavailability, uptake and translocation.

10.3.5 Nickel and Pb uptake as influenced by Exchangeable Soil Acidity, Exchangeable Hydrolysable Cations (EHC), pH and phosphate

Both soil acidity and EHC showed an extremely weak influence on the uptake of both Ni and Pb in the foliage, where these metals were mostly concentrated (Figure 10.3: A & B). This investigation was based only on treatments with sludges with phosphate at 0, 40 and 100 kg ha^{-1}. Generally, a decrease in either soil acidity or EHC due to a marginal increase in pH slightly decreased the concentration of both metals in the foliage. Soil acidity accounted for only 2.3

and 0.4% of Pb and Ni concentration in the foliage, whereas EHC accounted for only 0.9% for each of the metals in the foliage. This was an indication that there was no relationship between changes in exchangeable acidity, EHC, phosphate (Figure 10.3: D) and the uptake of Ni and Pb. The marginal increase in pH that slightly reduced both soil acidity and EHC also decreased the concentration of both metals in the foliage (Figure 10.3: C). Only 3.1 and 14% of Pb and Ni reduction in the foliage was influenced by pH.

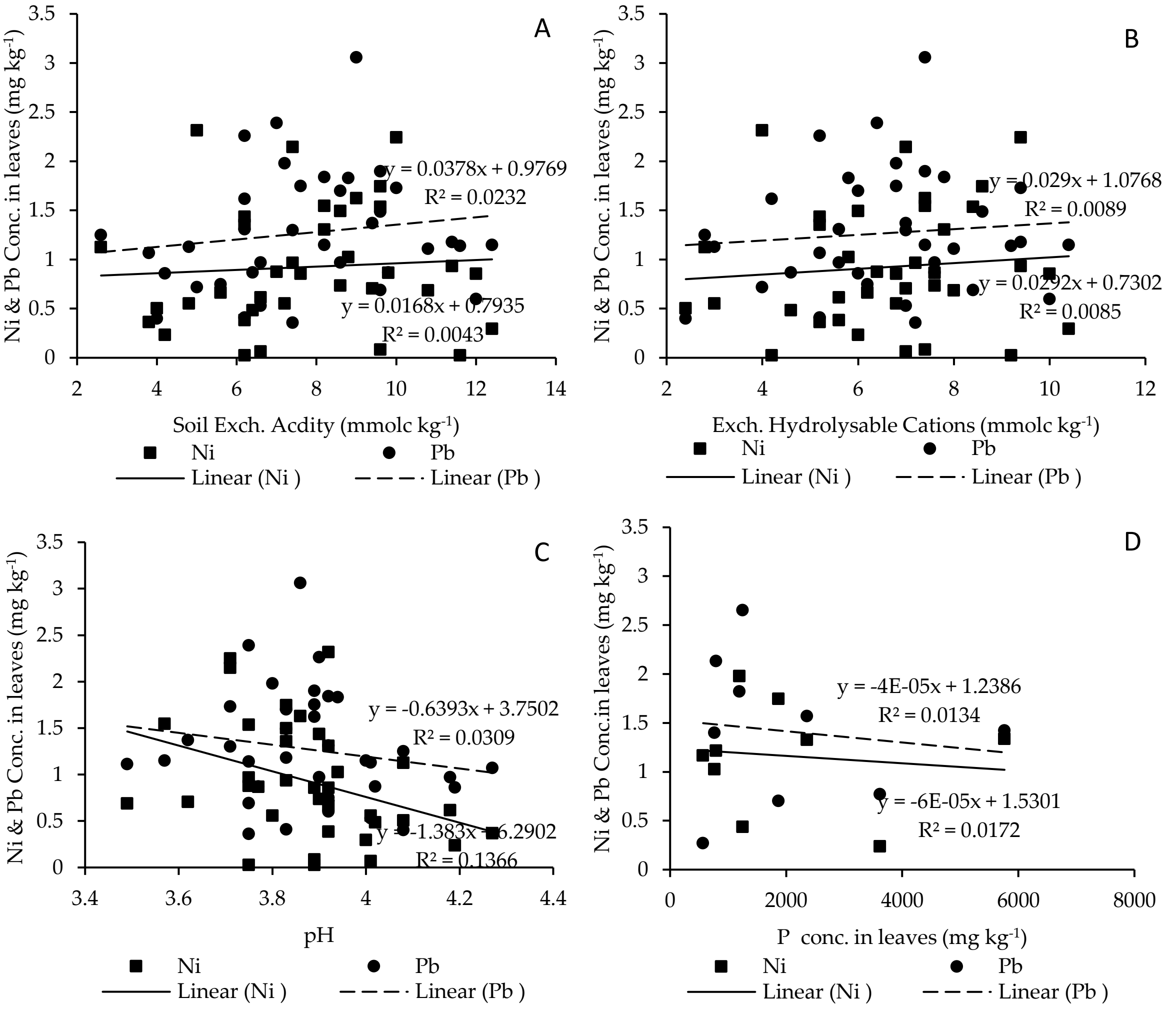


Figure 10.3: A) Soil acidity influence on Ni and Pb in foliage, B) Exchangeable Hydrolysable Cations influence on Ni and Pb in foliage, C) pH influence on Ni and Pb in foliage, D) P influence on Ni and Pb in foliage

10.3.6 Nickel and Pb concentration in the grain

Nickel and Pb in the grain were below the method detection limit for all treatments (Table 10.8). Even loading the soil with 20 t ha^{-1} resulting in loading of 2.16 kg ha^{-1} of Ni in the case of GypFeMnNi and 0.8 kg ha^{-1} of Pb in the case of Gyp did not result in elevating the levels of these elements in the grain relative to the control. This could be a result of either the sorption of these metals by the sludges or precipitation reducing their phyto-availability or remobilization from other plant tissues (especially foliage) to the seed or both (Sankaran and Grusak 2014). It is also possible that most of the Ni and Pb could not react with the soil, for example, the Ni that resided with Fe oxides in the HDS was not released.

Table 10.8: Ni and Pb (mg kg $^{-1}$) in grain

	Sludge	S	SL	10Gyp	20Gyp	10GypFe MnNi	20GypFe MnNi	*Average*
Pb	P40	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
	P100	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
	Average	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	
Ni	P40	<0.93	<0.93	<0.93	<0.93	<0.93	<0.93	<0.93
	P100	<0.93	<0.93	<0.93	<0.93	<0.93	<0.93	<0.93
	Average	<0.93	<0.93	<0.93	<0.93	<0.93	<0.93	

Note: No yield was harvested in all treatments without P; Note: Gyp (t ha^{-1}) = Gypseous; GypFeMnNi (t ha^{-1}) = Ferriferous gypseous; S = Soil; SL = Soil Limed; P (kg ha^{-1}) = Phosphate. Method detection limits for Ni and Pb were 0.93 mg kg^{-1} (0.01 mg L^{-1}) and 0.2 mg kg^{-1} (0.002 mg L^{-1}).

10.3.7 Food and feed safety of the grain and fodder

For all treatments, Pb concentration in the grain was below the threshold (0.2 mg kg^{-1}) stipulated by Codex Alimentarius (2006). This threshold was close to Pb MDL of 0.2 mg kg^{-1}. Using HDS from the coalfields as a soil amendment, even at high application rates of 20 t ha^{-1} did not elevate Pb levels in grain above the Codex threshold. Adding phosphate from 40 to 100 kg ha^{-1} did not increase Pb concentration in the grain above this threshold. Similarly, Ni concentration in the grain by all treatments was below the threshold of 1 mg kg^{-1} stipulated by the National Standard of the People's Republic of China (2012). This threshold was also close to Ni MDL of 0.93 mg kg^{-1}. Applying phosphate and GypFeMnNi containing the most Ni (108 mg kg^{-1}) did not increase the concentration of this element above the threshold. This was an indication that the application of the sludges with the intention to improve crop yields will not induce Ni toxicity if the edible plant part is ingested. However, application of the sludges should not exceed Ni and Pb accumulation thresholds in the soil. Nickel and Pb should not exceed 50 and 60 mg kg^{-1} in the soil (Adagunodo et al. 2018).

With respect to the safety of the fodder and grain as animal feed, applying sludges on their own even at 20 t ha^{-1} or co-applying them with phosphate could not increase the concentration of Pd to above the threshold of 40 mg kg^{-1} stipulated by Food and Agricultural Organization (1997), European Commission (2002) and the Department of Agriculture for South Africa (2006). These treatments also could not increase the concentration of Ni in both fodder and grain to above the thresholds of 50 and 100 mg kg^{-1} stipulated by the Department of Agriculture for South Africa (2006) and Food and Agricultural Organization (1997).

10.4 CONCLUSIONS

Both sludges showed some value as ameliorants, since they contained macro and micronutrients (S, Ca, Mg, K, Mn, Fe and Zn). Both Gyp and GypFeMnNi exhibited a liming effect, marginally increasing soil pH, decreasing acidity and hydrolysable cations. Co-applied with phosphate had the strongest liming effect. With the combination of GypFeMnNi at 20 t ha^{-1} and phosphate at 100 kg ha^{-1} increasing pH the most to 4.21. Also, the combined effect of phosphate and sludge showed that applying Gyp at 20 t ha^{-1} with phosphate at 100 kg ha^{-1} reduced exchangeable hydrolysable cations and exchangeable acidity the most by 78% and 74%. While applying GypFeMnNi at 20 t ha^{-1} with phosphate at 100 kg ha^{-1} reduced exchangeable hydrolysable cations and exchangeable acidity by 54 and 67%. This marginal increase was not expected since the alkalinity added for both sludges either at 10 or 20 t ha^{-1} exceeded exchangeable acidity. This was attributed to armouring by both Fe oxides and gypsum in the case of GypFeMnNi and gypsum in Gyp that protected them from reacting with soil acidity. This, therefore, reduced the alkalinity potential of the sludges. However, the application of these materials on their own at 20 t ha^{-1} increased soil salinity to levels suitable only to salt tolerant plants. GypFeMnNi and Gyp increased it by 720 and 973 mS m^{-1} respectively. There was a slight reduction in the concentration of both Ni and Pd in the foliage due to soil acidity and exchangeable hydrolysable cations reduction. Neither of the sludges even when applied at 20 t ha^{-1} significantly increased plant concentrations of Ni and Pb. With respect to food safety, both Pb and Ni were below the standards set by Codex Alimentarius (2006) and the National Standard of the People's Republic of China (2012) in the grain for all treatments. The application of the sludges on their own and when co-applied with phosphate reduced Ni and Pb phyto-availability, consequent uptake and concentration in the foliage and grain. As such, the levels of Ni and Pb in the foliage and grain could not be clearly separated from the treatments that did not receive additional Ni and Pb. Both fodder and grain showed to be safe as feed for animals since levels of both metals in all treatments were below the thresholds stipulated by the European Commission (2002), Food and Agricultural Organization (1997) and the Department of Agriculture for South Africa (2006). It can be concluded therefore, that the use of HDS on its own as a soil ameliorant or in combination with phosphate, is not a food or feed safety risk and can be used as a nutrient source and sequester of metals. Therefore, HDS should not pose a food safety risk if used responsibly, that is, using the application rates suggested in this study and the crop used. Larger application rates and continuous use of the sludges may possibly lead to Ni and Pb accumulation in the soil that can exceed their thresholds of 50 and 60 mg kg^{-1}. For future research, the response of different crops and their food safety should be assessed on a field scale when these sludges are used as soil amendments.

CHAPTER 11

GENERAL CONCLUSIONS AND RECOMMENDATIONS

11.1 Conclusions

Generally, the study focused on the possibility of using specific mine impacted waters, AMD and its neutralization products, HDS and circum-neutral mine water in agriculture. Both waters were not fit for irrigation due to suspended solids contained, Al, Fe and Mn that exceeded thresholds. If used for irrigation, micro irrigation systems should be avoided since the suspended solids contained can clog them and it will take 3, 2, 0 years for Al, Fe, Mn in AMD; 11, 15, 0 years in circum-neutral mine water to reach soil accumulation thresholds. Root zone effects of salinity by both waters reduced the crop yields and irrigating with AMD contributed > 50% to the removal of N, P, K by a crop; circum-neutral mine water as well to N and K removal, but not to P. AMD was predicted to corrode the irrigation system with a Langelier Index of < -2. However, AMD can be used for irrigation if the soil can be limed to reduce acidity and prevent pH reduction. Both waters can be used for irrigation; if less frequent irrigation scheduling is adopted to increase the number of years to reach soil accumulation thresholds of Al, Fe and Mn; if sprinklers or canons can be used instead of drippers to avoid clogging; and if salt accumulation can be reduced by irrigating with appropriate leaching fraction. salt accumulation can also be reduced through sequestration by precipitated gypsum and amorphous ferric hydroxides.

With respect to characterization of HDS, the approach was to initially understand how the partitioning of elements in HDS is influenced by the two different AMD treatments. The product, GypFeMnNi was found to be slightly acidic (pH 5.5) with $CaCO_3$ equivalent to 250 mg kg^{-1}, while the sludges GypFeMn, GypB and Gyp were alkaline with pH values of 8.2, 9.4, 9.5 and total alkalinity values of 510, 601, 617 mg kg^{-1}. Therefore, all the products have the potential to reduce soil acidity if used as soil amendments due to the alkalinity they possess. All the four products were found to be largely gypsum making them valuable for agricultural use. In addition, GypFeMnNi and GypFeMn had substantial amounts of iron oxides that can supply Fe and possibly sorb metals in soils if used as soil amendments. Sulphur was dominant in all the sludges followed by Ca, Mg and K in descending order. While, Fe was the most dominant amongst trace elements followed by Mn in GypFeMnNi, GypFeMn and Gyp while in GypB, Mn was the most dominant followed by Fe. This indicated that these materials can potentially supply essential plant nutrients to the soil. The concentration of other trace elements was extremely low.

Extractability showed that in general, both major and trace elements were extracted mostly by deionised water from all the sludges. This suggested that deionized water has the potential to facilitate the solubility of all the elements in all the materials than any other extractant considered. Generally, S was the most extracted in the sludges compared to Ca and this reduction in Ca extraction was due to armouring of gypsum in the materials by iron oxides. Amongst trace elements, Mn was the most released from all the sludges except in Gyp which showed to have all trace elements extremely low. The extractant, EDTA solubilized Fe the most than Mn from GypFeMnNi. Both Mn and Fe are more likely to pollute the environment if these materials can be in contact with water, acidic solutions and organic chelators. Both Mn and Fe are part of the constituents of environmental concern by the RSA classification guidelines. Other metals of environmental concern, Cd and Pd were below detection limits by all extractants in all materials. Amongst the anions extracted, all the extractants released SO_4^{2-} the most from all sludges. Phosphate sorption capacity showed that all the materials have the potential to sorb elements, with GypFeMnNi, GypFeMn, GypB and Gyp showing maximum sorption capacities of 1810, 887, 887 and 236 mmol kg^{-1}. Therefore, these results suggested that all sludges can be of low risk to the environment and in addition have the potential for use in agriculture. All the four sludges assessed for agricultural use can be sources of nutrients, especially Ca and S if used as soil amendments, therefore, hypothesis 6 which partly says the sludges can provide S and Ca was accepted.

The focus was now on evaluating the sludges; GypFeMnNi, GypFeMn, GypB and Gyp as soil amendments based on physical properties. Physical assessment of the sludges showed that GypFeMn and GypB had narrower particle size ranges; 0.4 – 168 and 0.5 – 250 µm, whereas both GypFeMnNi and Gyp showed a wider range of 0.4 – 906 µm. Generally, these particle sizes for all the materials were lower than those of natural agricultural gypsum. Gyp was dominated by 75% sand particles and if it can be used as a soil amendment it may be expected to increase macroporosity and improve the movement of water especially in clay or silty soils. Whereas, all the other materials can increase microporosity and water holding capacity of sandy soils. However, this may not be possible since the material is largely gypsum composed which is water soluble. All the materials had their particle densities closer to the lower limit of the Gypsum particle density range of (2300 – 2470 kg m^{-3}). However, Gyp had the least particle density (2312 kg m^{-3}) whereas, densities of GypFeMnNi and GypFeMn were slightly higher, 2354 and 2386 kg m^{-3} due to high content of iron oxides known to have densities of > 5000 kg m^{-3}.

he next step was to assess the hazardous status of the differently generated sludges. There was one consistency between the Canadian, Chinese, Australian and RSA systems it was the classification of GypFeMn as a hazardous waste. In the case of Canada, China and Australia it was based on Ni content, but with RSA it was both Ni and Mn content. None of the sludges was considered by USEPA as hazardous probably because Ni is not included in their system. One other sludge, GypFeMnNi was allocated a hazardous status by RSA due to Mn and Ni content, this was because it is the only system that considers Mn. Considering all the systems, the probability for the sludge investigated to be classified as hazardous waste increases if the material is only subjected to limestone treatment. Although some of the sludges were classified as hazardous due to Mn solubility, but this element is a trace element essential for plant growth. That is the reason why most of the classification systems exclude it as a metal of environmental concern. The RSA system was therefore unnecessarily strict and needs to be revisited because it encourages the storage of these materials in expensive facilities.

The sludges, therefore, needed phosphate to reduce the solubility of metals. As phosphate was used to improve the status of the sludges, it reduced the solubility of Al Fe Mn, Zn and Ni in GypFeMnNi and GypFeMn. The TCLP extracted concentrations of As, Pb, Cd, Cu, Cr, Hg, Se were below method detection limit. This reduced the hazardous status of both materials. When the phosphated sludges were subjected to reductive conditions, GypFeMn showed resistance to reduction by Dithionite and Oxalate as such the extraction of Fe, Al, Ni were lower than in GypFeMnNi. With Mn the sludge, GypFeMnNi showed more resistance to reduction than GypFeMn. MED, showed an increase in the oxidation of Mn in GypFeMn, but in GypFeMnNi, MED indicated that Mn was already oxidized to Mn(III) or Mn(IV). TED showed an increase in GypFeMnNi and the reason was that the phosphate facilitated the oxidation of Mn(II). Phosphate reduced metal solubility and the hazardous status of both materials. Phosphate addition was therefore a useful approach to make an otherwise hazardous gypseous HDS safe to the environment.

Impact on soil when used as soil amendment showed that all treatments with phosphate (on its own) or co-applied with either sludge marginally increased initial soil pH of 3.75, with the combination of GypFeMnNi at 20 t ha^{-1} and phosphate at 100 kg ha^{-1} P increasing it the most to 4.21. The addition of the sludges also reduced exchangeable soil acidity and exchangeable hydrolysable cations significantly ($\alpha = 0.05$). When Gyp and GypFeMnNi were applied at 20 t ha^{-1} acidity was reduced by 74 and 67% and exchangeable hydrolysable cations by 78 and 54%. However, both sludges increased soil salinity, with Gyp at 20 t ha^{-1} increasing it the most to 728 mS m^{-1}, suitable only for salt tolerant crops. It can be concluded that irrespective of the treatment process, both are suitable for the supply of S and Ca, can potentially reduce both acidity and exchangeable hydrolysable cations and improve conditions for plant growth. This further made the materials suitable as soil amendments.

Crop response showed that co-application of phosphate with either sludge increased plant height, for instance applying GypFeMnNi at 20 t ha^{-1} with phosphate at 100 kg ha^{-1} increased plant height (166 cm) the most. Adding either sludge, on its own, slightly increased plant height and biomass relative to the treatments without hydrated lime and sludge. Leaf area index increased more when phosphate was co-application with either sludge than when phosphate or either sludge was applied on its own. Calcium, S and P concentrated mostly in the foliage and adding either sludge increased the concentration of both Ca and S in the plant. Co-application of phosphate with either sludge increased the uptake of Ca by 1.1% but reduced that of S by 8.7%. Applying phosphate on its own reduced Ca uptake by 0.2% but increased that of S by 15.9%. Iron and Mn as well were concentrated mostly in the foliage. Co-applying phosphate with either sludge and applying phosphate on its own reduced the uptake of Fe by 8.3 and 22.5%. Co-application of phosphate with either sludge, applying phosphate on its own and slightly increasing pH increased the uptake of Mn by 1.5, 4.6 and 5.2%. Nutrient concentrations indicated that Ca, Fe, Mn, S and phosphate were retained as follows; below ground > biomass > grain for all treatments. Grain was present only in treatments with phosphate. Whereas, the sludges contributed mostly to the yield than to biomass. For instance, Gyp applied at 20 t ha^{-1} with phosphate at 100 kg ha^{-1} showed the most yield of 102 g pot^{-1} carrying 8.8 kg of soil, but this yield was not significantly different from that indicated by the same sludge at 10 t ha^{-1}, also by GypFeMnNi at 10 and 20 t ha^{-1}. This suggested that these materials have the potential to improve plant biomass and yield especially when they are applied at 20 t ha^{-1} and combined with phosphate at 100 kg ha^{-1}. This was evident that these materials improve soil fertility and uptake of nutrients, especially Ca and S making it a potential soil amendment.

The assessment of food safety based on Ni and Pb uptake showed that the reduction in soil acidity and exchangeable hydrolysable cations reduced the concentration of Ni and Pb in the foliage. Therefore, Pb and Ni concentration were ranked as follows within the plant; foliage > tassel > stem. Ni exceeded the lower limit of the range 0.1-5 mg kg^{-1} in leaf dry matter reported to be toxic to plants, but there was no evidence of toxicity induced by this element. Lead was below the lower limit of the range 5-10 mg kg^{-1} reported toxic to plants. In terms of food safety of the grain, Pb was below the standard (0.2 mg kg^{-1}) set by Codex Alimentarius and Ni was below 1 mg kg^{-1}, standard set by the National Standard of the People’s Republic of China for all treatments. Therefore, co-application of phosphate with either sludge improved crop yields than when phosphate and sludges were applied on their own. The combination effect of phosphate with either sludge reduced Ni and Pb phyto-availability, consequent uptake and concentration in the foliage and grain. Phosphate application was therefore a useful approach to make an otherwise hazardous gypseous HDS useful for agriculture.

11.2 Recommendations

11.2.1 Recommendations for implementation

- Based on this study, it could be recommended that the RSA waste classification system be aligned to other international systems and exclude Mn as it is a trace element essential for plant growth and increase the thresholds for As, Cd, Pb, Hg and Se, such that they are above method detection limits.
- The study evaluated only four sludges from two different AMD treatment plants for use

in agriculture, it is recommended therefore, that more sludges from mine water treatment plants be evaluated for use as soil amendments. This should include chemical, physical and mineralogical characterisation of the sludges and use as soil amendments, where soil and crop responses can be assessed. If successful, the disposal of sludges in expensive storage facilities can be eliminated.

- The study considered maize only to assess the uptake of Pb and Ni, therefore, it is recommended that different crops be considered for their potential uptake of these metals. The accumulation of Ni in the soil should be monitored (as it is the limiting element in the sludges), so that it does not exceed its threshold of 50 mg kg^{-1}. It is recommended therefore, that the application rate of the sludge, GypFeMnNi, does not exceed 1042 t ha^{-1} per single application to avoid exceeding Ni threshold in the soil. The application rate of Gyp should not exceed 3375 t ha^{-1} per single application.

11.2.2 Recommendations for future research

- There are still unknowns regarding field scale trials where AMD and circum-neutral mine water are used for irrigation. Not all crops and cropping systems have been included in the Water Quality Decision Support System to predict the fitness for use of these mine impacted waters. Therefore, more winter and summer crops should be included in the system including different cropping systems. Further, a crop screening field trial is recommended to determine the response of both summer and winter crops on mono, rotational and intercropping systems to these mine waters.
- Nickel is the limiting metal in the sludges and its threshold in soils is 50 mg kg^{-1}, while that of Pb is 60 mg kg^{-1}. It is recommended therefore, that the application rate of the sludge, GypFeMnNi, does not exceed 1042 t ha^{-1} per single application to avoid exceeding Ni threshold in a soil. The application rate for Gyp should not exceed 3375 t ha^{-1} per single application to avoid exceeding Ni threshold in a soil. Field scale trials should be considered for future research, therefore rates exceeding 20 t ha^{-1} per single application of these sludges can be investigated.
- To avoid environmental contamination and improve agricultural usage, both sludges (GypFeMnNi and Gyp) need to be phosphated to reduce metal solubility and avoid contact with water, acid solutions and organic chelators. However, the duration of the

immobilization of metals at this point remains unknown. An experiment where sludge would be phosphated and the solubility of different metals be assessed over time is recommended.

- The application rate of P should be at least 40 mg kg^{-1} to ensure plant growth, it is therefore recommended that higher rates are investigated on field scale trials to assess its influence on metal solubility from the sludges.
- At this point the sludges have not been compared to commercial agricultural gypsum on a field scale, therefore, comparison is recommended. The investigations should include both winter and summer crops.

REFERENCES

Adagunodo TA, Sunmonu LA, Emetere MEE. 2018. Heavy metals' data in soils for agricultural activities. Science direct, 18: 1847-1855.

Agegnehu G, Yirga C, Erkossa T. 2019. Soil Acidity Management. Ethiopian Institute of Agricultural Research (EIAR), Addis Ababa, Ethiopia, p 13

Ahmad P. 2016. *Plant metal interaction: emerging remediation techniques*. Elsevier

Akcil A, Koldas S. 2006. Acid Mine Drainage (AMD): causes, treatment and case Studies. *Journal of Cleaner Production* 14: 1139 – 1145.

Ali MH. 2010. Water: an element of irrigation, *In*: Fundamentals of irrigation and on-farm water management. *Springer* Vol. 1: pp 276-329

Anglo American Thermal Coal. 2015. *Classification and Assessment of Brine and Sludge*; Report Number 1538858-298217-1; Anglo American: EMalahleni, South Africa.

Annandale JG, Jovanovic NZ, Claassens AS, Benadé N, Lorentz SA, Johnston MA, Tanner PD, Aken ME, Hodgson FDI. 2001. The Influence of Irrigation with Gypsiferous Mine Water on Soil Properties and Drainage Water. Water Research Commission Report No. K5/858, Pretoria, South Africa

Annandale JG, Jovanovic NZ, Claassens AS. 2001. The influence of irrigation with gypsiferous mine water on soil properties and drainage water. *Water Research Commission Report No.* 858/1/02

Annandale JG, Jovanovic NZ, Hodgson FDI, Usher BH, Aken ME, Van Der Westhuizen A.M, Bristow KL, Steyn JM. 2006. Prediction of the environmental impact and sustainability of large-scale irrigation with gypsiferous mine-water on groundwater resources. *Water South Africa*. *32*, 21–28.

Annandale JG, Du Plessis HM, Tanner PD, Jo Burgess J 2018. Using a risk based, site-specific Decision Support Systemto determine the suitability of mine water for irrigation. 11th ICARD | IMWA | MWD Conference – “Risk to Opportunity”, pp 239-244

Aubé B. 2004. The science of treating acid mine drainage and smelter effluents. URL: http://www.infomine.com/publications/does/Aube.pdf

Aubé B, Lee D. 2015. The High Density Sludge (HDS) Process and Sulphate Control. 10th International Conference on Acid Rock Drainage and IMWA Annual Conference.

Aubé B, Zinck JM. 1999. Comparison of AMD treatment processes and their impact on sludge characteristics. pp. 261-270

Balintova M, Petrilakova A. 2011. Study of pH influence on selective precipitation of heavy metals from acid mine drainage. *Chem Eng Trans*, 25: 345-350.

Barthel J, Edwards S. 2004. Chemical stabilization of heavy metals. Met. Treat.Technol. MT2 3, 151-162

Bartlett RJ, James BR. 1995. System for categorizing soil redox status by chemical field testing. Geoderma, 68: 211-218.

Beauchemin S, Fiset JF, Poirier G, Ablett J. 2010. Arsenic in an alkaline AMD treatment sludge: Characterization and stability under prolonged anoxic conditions. *Applied Geochemistry* 25: 1487–1499. doi:10.1016/j.apgeochem.2010.07.004

Beuselinck L, Govers G, Poesen J, Degraer G, Froyen L. 1998. Grain-size analysis by laser diffractometry: comparison with the sieve-pipette method. *Catena* 32: 193–208

Bindraban PS, Dimkpa C, Nagarajan L, Roy A, Rabbinge R. 2015. Revisiting fertilisers and fertilisation strategies for improved nutrient uptake by plants. *Biology and Fertility of Soils*, 51: 897-911.

Bolan NS, Adriano DC, Curtin D. 2003. Soil acidification and liming interactions with nutrient and heavy metal transformation and bioavailability. *Advances in agronomy*, 78: 5-272.

Bortonea I, Chianese S, Ertoc A, Di A, Nardob MDN, Santonastasob GF, Musmarrab D. 2015. Risk Analysis for a Contaminated Site in North of Naples (Italy). *Chemical*. *Engineering*. *43*, 777–780, doi:doi:10.3303/CET1543322.

Cao X, Ma LQ, Rhue DR, Appel CS. 2004. Mechanisms of lead, copper, and zinc retention by phosphate rock. *Environmental Pollution*, 131: 435-444.

Ch’ng HY, Ahmed OH, Majid NMA. 2014. Improving phosphorus availability in an acid soil using organic amendments produced from agroindustrial wastes. *The Scientific World Journal*, 2014.

Chandra AP, Gerson AR. 2010. The mechanisms of pyrite oxidation and leaching: A fundamental perspective. *Surf*. *Sci*. *Rep*. 2010, *65*, 293–315, doi:10.1016/j.surfrep.2010.08.003.

Chen Z. Wang X, Ge O, Guo G. 2015. Iron oxide red wastewater treatment and recycling of iron-containing sludge. *J. Clean. Prod.*, *87*, 558–566. doi:10.1016/j.jclepro.2014.10.057

Costley S. 2013. Waste Classification and Management Regulations and Supporting Norms & Standards. Waste Khoro Available online: ttps://www.environment.gov.za/sites/default/files/docs/wasteclassification_regulations_disposalstandards.pdf (accessed on 9 March 2017).

Codex Alimentarius. 2006. Understanding the Codex Alimentarius. 3rd ed. Joint Food and Agricultural Organization of the United Nations (FAO)/World health Organization (WHO) Food Standards Programme, FAO, Rome

Cornell RM, Schwertmann U. 2003. Formation In: The Iron Oxides, Structure, Properties, Reactions, Occurrences and Uses. Second Completely Revised and Extended Addition. Wiley-VCH Verlag GmbH & Co KGaA, Weinheim. pp 345-407

Coulton R, Bullen C, Williams C, Williams K. 2004. The formation of high density sludge from mine waters with low iron concentrations. *Mine Water*: 25-30.

Courchesne F, Turmel MC. 2007. Extractable Al, Fe, Mn, Si, In: Carter RM and Gregory EG (Ed). Soil sampling and methods of analysis, 2nd Ed. Canadian Society of Soil Science. Florida: CRC Press, pp 309-311

Crannell BS, Eighmy TT, Krzanowski JE, Eusden Jr. JD, Shaw EL, Francis. 2000. Heavy metal stabilization in municipal solid waste combustion bottom ash using soluble phosphate Waste Management 20: 135-148.

Dama-Fakir P, Sithole Z, Van Niekerk AM, Dateling J, Maree JP, Rukuni T, Mtombeni T, Ruto S, Zikalala N, Hughes C, Wurster A, Saunders B. 2017. Mine water treatment technology selection tool: Users' Guide. Report No. TT 711/17 to Water Research Commission (WRC). pp 67-68

Demers I, Mbonimpa M, Benzaazoua M, Bouda M, Awoh S, Lortie S, Gagnon M. 2017. Use of acid mine drainage treatment sludge by combination with a natural soil as an oxygen barrier cover for mine waste reclamation: Laboratory column tests and intermediate scale field tests. *Miner. Eng.*, *107*, 43–52.

De Almeida R.P, Leite ADL. 2015. Borghetti Soares, A. Reduction of acid rock drainage using steel slag in cover systems over sulfide rock waste piles. *Waste Manag. Res.*, *33*, 353–362.

Department of Water Affairs and Forestry. 1996. South African Water Quality Guidelines (second edition). Volume 4: Agricultural Use: Irrigation.

Department of Water Affairs (DWA). 2013. Feasibility Study for a Long-Term Solution to Address the Acid Mine Drainage Associated with the East, Central and West Rand Underground Mining Basins. Study Report No. 5.5: Options for the Sustainable Management and Use of Residue Products from the Treatment of AMD. DWA Report No.: P RSA 000/00/16512/5. Available online: http://sawic.environment.gov.za/documents/2177.pdf (accessed on 22 April 2018).

Department of Water Affairs & Forestry (DWAF). 1998. *Waste Management Series. Minimum Requirements for Waste Disposal by Landfill*, 2nd ed. Available online: http://www.dwaf.gov.za/Documents/Other/WQM/ RequirementsWasteDisposalLandfillSep05Part1.pdf (accessed on 16 May 2018).

Djaman K, Irmak S, Rathje WR, Martin DL, Eisenhauer DE. 2013. Maize evapotranspiration, yield production functions, biomass, grain yield, harvest index, and yield response factors under full and limited irrigation. *Transactions of the ASABE*, 56: 373-393.

Dotaniya M, Datta S, Biswas D, Dotaniya C, Meena B, Rajendiran S, Regar K, Lata M. 2016. Use of sugarcane industrial by-products for improving sugarcane productivity and soil health. *International Journal of Recycling of Organic Waste in Agriculture*, 5: 185-194.

Du Plessis M, Annandale J, Benade N, Van Der Laan M, Jooste S, Du Preez C, Barnard J, Rodda N, Dabrowski J, Genthe, B, Nell P. 2017. Risk Based, Site-Specific, Irrigation Water Quality Guidelines. Volume 1: Description of Decision Support System. Water Research Commission Report No TT 727/17. Water Research Commission, Pretoria, South Africa.

Du Plessis HM. 1983. Using lime treated acid mine water for irrigation. Water Science Technology 15 145-154.

Eighmy TT, Crannell BS, Butler LG, Cartledge FK, Emery EF, Oblas D, krzanowski JE, Eusden, Jr. JD, Shaw EL, Francis CA. 1997. Heavy Metal Stabilization in Municipal Solid Waste Combustion Dry Scrubber Residue Using Soluble Phosphate. Environ. Sci. Technol. 31:3330-3338

Eshel, G, Levy GJ, Mingelgrin U, Singer MJ. 2004. Critical Evaluation of the Use of Laser Diffraction for Particle-Size Distribution Analysis. Soil Sci. Soc. Am. J. 68:736–

743

Essington ME. 2004. Organic matter in soils. pp 129-180. *In*: Soil and water chemistry: An integrative approach. CRC Press LLC, 200 N.W. Corporate Blvd., Boca Raton, Florida. Cementation in Deeply Buried Jurassic Sandstone Reservoirs of the Central North Sea. *Journal of sedimentary research* 70:1

Fageria NK. 2002. Influence of micronutrients on dry matter yield and interaction with other nutrients in annual crops. *Pesquisa Agropecuária Brasileira*, 37: 1765-1772.

Feng XH, Zhai LM, Tan WF, Liu F, He JZ. 2007. Adsorption and redox reactions of heavy metals on synthesized Mn oxide minerals. *Environ*. *Pollut*., *147*, 366–373.

Fernando WAM, Ilankoon I, Syed TH, Yellishetty M. 2018. Challenges and opportunities in the removal of sulphate ions in contaminated mine water: A review. *Minerals Engineering*, 117: 74-90.

Fischel MHH, Fischel JS, Lafferty BJ, Sparks DL. 2015. The influence of environmental conditions on kinetics of arsenite oxidation by manganese-oxides. *Geochem. Trans.*, *16*, 15, doi:10.1186/s12932-015-0030-4.

Gaikwad1 RW, Sapkal VS, Sapkal RS. 2010. Ion exchange system design for removal of heavy metals from acid mine drainage wastewater. *Acta Montanistica Slovaca* 15: 298-304

Gan WY, Selomulya C, Tapsell G, Amal R. 2005. Densification of iron(III) sludge in neutralization. *International Journal of Mineral Processing*; 76: 149– 162

Graham RD, Hannam RJ, Uren NC. 1988. Inorganic Reactions of Manganese in Soils, In: Manganese in Soils and Plants. Kluwer Academic Publishers, Netherlands. pp 37 - 50

Günther P, Maree JP, Strobos G, Mtimikulu JS. 2003. Neutralisation of acid leachate in a coal processing plant with calcium carbonate. In Proceedings of the 8th International Congress on Mine Water & the Environment, Johannesburg, South Africa, 20–25 October.

Guzman G, Alcantara E, Barron V, Torrent J. 1994. Phytoavailability of phosphate adsorbed on ferrihydrite, hematite, and goethite. *Plant and soil*, 159: 219-225.

Hamon R, McLaughlin M, Lombi E. 2007. Effects of different amendments on plant growth and contaminant uptake, In: Natural attenuation of trace element availability in soils. The Society of Environmental Toxicology and Chemistry, Florida USA. Pp 207 - 209

Han T, Cai A, Liu1 K, Huang J, Wang B, Li D, Qaswar M, Feng G, Zhang H. 2019. The links between potassium availability and soil exchangeable calcium, magnesium, and aluminum are mediated by lime in acidic soil. *J. Soils Sediments*, 19:1382–1392.

Harris DL, Lottermoser BG. 2006. Evaluation of phosphate fertilizers for ameliorating acid mine waste. Applied Geochemistry 21:1216–1225.

Hendershot WH, Lalande H. 2008. Soil Reaction and Exchangeable Acidity, *In*: Soil Sampling and Methods of Analysis, 2nd Ed. Taylor & Francis Group, LLC, Canadian Society of Soil Science, p 163

Hendry JP, Wilkinson M, Fallick AE, Haszeldine RS. 2000. Ankerite cementation in deeply buried Jurassic sandstone reservoirs of the central North Sea. *Journal of Sedimentary Research*, 70: 227-239.

Hsu PH. 1966. Formation of Gibbsite from Aging Hydroxy-Aluminum Solutions. Division S-2 – SoilChemistry. Soil Science Society of America Proc. 30.

Hutton B, Kahan I, Naidu T, Gunther P. 2009. Operating and maintenance experience at the eMalahleni Water Reclamation Plant. In Proceedings of the International Mine Water Conference, Pretoria, South Africa, 19–23 October.

Idowu OA. 2007. Impact of irrigation with gypsiferous mine water on the water resources of subcatchments in the Upper Olifants basin. PhD Thesis, University of KwaZulu-Natal, Pietermaritzburg. 254 pp.

Jala S, Goyal D. 2006. Fly ash as a soil ameliorant for improving crop production—a review. *Bioresource Technology*, 97: 1136-1147.

Jackson ML, 1958. Cation exchange determination for soils. In: Soil chemical analysis. Constable and LTD. University of Wisconson Madison, USA, pp 57-70

Johnson DB, Hallberg KB. 2004. Acid mine drainage remediation options: A review. *Sci. Total Environ*. 2005, *338*, 3–14, doi:10.1016/j.scitotenv

Jones Jr JB. 2012. *Plant nutrition and soil fertility manual*. CRC press.

Jovanovic NZ, Barnard RO, Rethman NFG and Annandale JG. 1998. Crops can be irrigated with lime-treated acid mine drainage. Water SA 24: 113-122.

Kabata-Pendias A, Pendias H. 2001. Elements of Group II and Elements of Group IV, *In*: Trace elements in soils and Plants, 3rd Edition. CRC Press LLC, United States of America. PP 138 – 234

Kabata-Pendias A. 2004. Soil–plant transfer of trace elements—an environmental issue.

Geoderma, 122: 143-149.

Kacálková L. Tlustoš P, Száková J. 2014. Chromium, Nickel, Cadmium, and Lead Accumulation in Maize, Sunflower, Willow, and Poplar. *Pol. J. Environ. Stud.*, 23: 753-761

Kalin M, Fyson A. 2006. Wheeler, W.N. The chemistry of conventional and alternative treatment systems for the neutralization of acid mine drainage. *Sci. Total Environ. 366*, 395–408. doi:10.1016/j.scitotenv.2005.11.015

Karatza D, Prisciandaro M, Lancia A, Musmarra D. 2010. Sulfite oxidation catalyzed by cobalt ions in flue gas desulfurization processes. *J. Air Waste Manag. Assoc.*, *60*, 675–680, doi:10.3155/1047-3289.60.6.675.

Karna RR, Luxton T, Bronstein KE, Redmon JH, Scheckel KG. 2017. State of the science review: Potential for beneficial use of waste by-products for in situ remediation of metal-contaminated soil and sediment, Critical Reviews in Environmental Science and Technology, 47:2, 65-129, DOI: 10.1080/10643389.2016.1275417

Kavouras P, Kaimakamis G, Ioannidis THA, Kehagias TH, Komninou PH, Kokkou S, Pavlidou E, Antonopoulos I, Sofoniou M, Zouboulis A. 2003. Vitrification of lead-rich solid ashes from incineration of hazardous industrial wastes. *Waste Manag*, *23*, 361–371.

Karami N, Clemente R, Moreno-Jiménez E, Lepp NW, Beesley L. 2011. Efficiency of green waste compost and biochar soil amendments for reducing lead and copper mobility and uptake to ryegrass. *Journal of hazardous materials*, 191: 41-48.

Keefer GB, Sack WA. 1983. Sludge recycle and reuse in acid mine drainage treatment. *Journal (Water Pollution Control Federation)*: 278-284.

Kim SA, Guerinot ML. 2007. Mining iron: iron uptake and transport in plants. *FEBS letters*, 581: 2273-2280.

Kumpiene J, Lagerkvist A, Maurice C. 2008. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments–a review. *Waste management*, 28: 215-225.

Lal R, Shukla MK. 2004. Principles of soil physics. Marcel Dekker, Inc. New York, USA. pp 271 – 275

Li H, Ji H. 2017. Chemical speciation, vertical profile and human health risk assessment of heavy metals in soils from coal-mine brownfield, Beijing, China. *J. Geochem. Explor.*, *183*, 22–32.

Lin KL, Chang CT. 2006. Leaching characteristics of slag from the melting treatment of municipal solid waste incinerator ash. *J. Hazard. Mater.*, *135*, 296–302, doi:10.1016/j.jhazmat.2005.11.064.

Liu A, Ren F, Lin WY, Wang JY. 2015. A review of municipal solid waste environmental standards with a focus on incinerator residues. *Int. J. Sustain. Built Environ.*, *4*, 165–188, doi:10.1016/j.ijsbe.2015.11.002.

Lollar BS, Holland HD, Turekian KK. 2005. Environmental Geochemistry.
Elsevier, The Boulevard, Langford Lane, Kidlington, Oxford OX5, IGB, UK.

Loubser G, Verryn S. 2008. Combining XRF and XRD analyses and sample preparation to solve mineralogical problems. *S. Afr. J. Geol.*, *111*, 229–238, doi:10.2113/gssajg.111.2-3.229.

Lottermoser BG. 2007. Mine water, In: Mine Wastes, Characterization, treatment, environmental impacts, 2nd Ed. Springer-Verlag Berlin Heidelberg, pp 139-140

Lucier CA, Gareau BJ. 2016. Obstacles to preserving precaution and equity in global hazardous waste regulation: An analysis of contested knowledge in the Basel Convention. *Int. Environ. Agreem.*, *16*, 493–508, doi:10.1007/s10784-014-9261-6.

Ma Y, Ma J, Peng H, Weng L, Yongtao Li YC. 2019. Effects of iron, calcium, and organic matter on phosphorus behavior in fluvo-aquic soil: farmland investigation and aging experiments. Journal of Soils and Sediments, *Journal of Soils and Sediments*, 1-11

Mackie AL, Walsh M.E. 2015. Investigation into the use of cement kiln dust in high density sludge (HDS) treatment of acid mine water. *Water Res.*, *85*, 443–450.

Madiseng L. 2018. Crop response to irrigation with acidic and neutralised saline mine water. M.Sc. Dissertation, Department of plant and Soil Sciences, University of Pretoria.

Malvi UR. 2011. Interaction of micronutrients with major nutrients with special reference to potassium. *Karnataka Journal of Agricultural Sciences*, 24.

Mao L, Young S, Tye A, Bailey E. 2017. Predicting trace metal solubility and fractionation in Urban soils from isotopic exchangeability. *Environmental Pollution*, 231: 1529-1542.

Maree JP, Strydom WF, Adlem CJL, De Beer M, Van Tonder GJ, Van Dijk BJ. 2004. Neutralization of Acid Mine Water and Sludge Disposal. Division of Water, Environment and Forestry Technology CSIR. WRC Report No 1057/1/04, November 2004.

http://www.wrc.org.za/Knowledge%20Hub%20Documents/Research%20Reports/1057-1-04.pdf. Accessed 4 May 2016

Martınez C, Motto H. 2000. Solubility of lead, zinc and copper added to mineral soils. *Environmental Pollution*, 107: 153-158.

Marzouk E, Chenery S, Young S. 2013. Predicting the solubility and lability of Zn, Cd, and Pb in soils from a minespoil-contaminated catchment by stable isotopic exchange. *Geochimica et Cosmochimica Acta*, 123: 1-16.

McCarthy TS. 2011. The impact of acid mine drainage in South Africa. S Afr J Sci. 107(5/6), Art. #712, 7 pages. doi:10.4102/sajs.v107i5/6.712

McDonald DM, Webb JA. 2006. Chemical Stability of Acid Rock Drainage Treatment Sludge and Implications for Sludge Management. *Environ*. *Sci*. *Technol*., *40*, 1984–1990.

McDonald DM, Webb JA, Taylor J. 2006. Chemical stability of acid rock drainage treatment sludge and implications for sludge management. *Environmental science & technology*, 40: 1984-1990.

Meissner R, Steyn M, Moyo E, Shadung J, Masangane W, Nohayi N, Jacobs-Mata I. 2018. South African local government perceptions of the state of water security. *Environmental Science & Policy*, 87: 112-127.

Mengel K, Kirkby E. 2001. Fertilizer application. *In*: Principles of plant nutrition. Springer Science+Business Media Dordrecht. pp 337-596

Method 3051A, Revision V 2014 Final Update II to the Third Edition of the Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA publication SW-846.

Mettetal E. 2019. Irrigation dams, water and infant mortality: Evidence from South Africa. *Journal of Development Economics*, 138: 17-40.

Mhlongo SP, Mativenga PT, Marnewick A. 2018. Water quality in a mining and water-stressedregion. *Journal of cleaner production*, 171: 446-456.

MIG. 2017. Fertilization. *In*: Maize Information Guide. Agricultural Research Council (ARC) Grain Crops Institute. pp 69-94

Mignardi S, Corami A, Ferrini V. 2012. Evaluation of the effectiveness of phosphate treatment for the remediation of mine waste soils contaminated with Cd, Cu, Pb, and Zn. *Chemosphere*, 86: 354-360.

Mine Water Coordinating Body. 2019. Annual General Meeting Report. CSIR International

Convention Centre.

Mudaly L. 2016. The Contribution of Manganese Oxides to Redox Buffering in Selected Soils of the South African Highveld. Master's Thesis, University of Pretoria, Pretoria, South Africa,

Nimmo J R. 2004. Porosity and Pore Size Distribution. *in* Hillel, D., ed. Encyclopedia of Soils in the Environment: London, *Elsevier* 3: pp 295-303

National Environmental Management: Waste Act No. 59. 2008. Waste Classification and Management Regulations. Government Gazette No. 10008. Pretoria, South Africa; 578p. Available online: https://www.environment.gov.za/sites/default/files/legislations/nemwa59of2008_wasteclassification.pdf (accessed on 9 March 2018).

National Health and Medical Research Council (NHMRC). 2011. National Resource Management Ministerial Council (NRMMC). Australian Drinking Water Guidelines Paper 6 National Water Quality Management Strategy. Available online: https://nhmrc.gov.au/about-us/publications/australian-drinking-water-guidelines (accessed on 9 March 2017).

New South Wales Environment Protection Authority (EPA). 2000. ACT's Environmental Standards: Assessment & Classification of Liquid & Non-Liquid Wastes. Available online: http://www.act.gov.au/environ/ (accessed on 22 April 2018).

O'Kelly BC. 2005. Sewage sludge to landfill: Some pertinent engineering properties. *J. Air Waste Manag. Assoc.*, *55*, 765–771, doi:10.1080/10473289.2005.10464670.

Petrik LF, White RA, Klink MJ, Somerset VS, Burgers CL, Fey MV. 2003. Utilization of South African fly ash to treat acid coal mine drainage, and production of high quality zeolites from the residual solids. International Ash Utilization Symposium, Centre for Applied Energy Research, University of Kentucky, Paper 61.

Rakotonimaro TV, Neculita CM, Bussière B, Benzaazoua M, Zagury GJ. 2017. Recovery and reuse of sludge from active and passive treatment of mine drainage-impacted waters: a review. *Environmental Science and Pollution Research*, 24: 73-91.

Ravengai1 S, Love1 D, Love I, Gratwicke B, Mandingaisa1 O, Owen RJS. 2005. Impact of Iron Duke Pyrite Mine on water chemistry and aquatic life – Mazowe Valley, Zimbabwe. *Water SA* 31

Rhoades JD, 1996. Salinity: Electrical conductivity and Total dissolved solids. In: Methods of Soil Analysis, Part 3 – Chemical methods. SSSA Book Series No. 5, pp 417

Seshadri B, Bolan N, Choppala G, Kunhikrishnan A, Sanderson P, Wang H, Currie L, Tsang DC, Ok Y, Kim G. 2017. Potential value of phosphate compounds in enhancing immobilization and reducing bioavailability of mixed heavy metal contaminants in shooting range soil. *Chemosphere*, 184: 197-206.

Shahid M, Dumat C, Khalid S, Schreck E, Xiong T, Niazi NK. 2017. Foliar heavy metal uptake, toxicity and detoxification in plants: A comparison of foliar and root metal uptake. *Journal of hazardous materials*, 325: 36-58.

Sharma S, Nagpal AK, Kaur I. 2018. Heavy metal contamination in soil, food crops and associated health risks for residents of Ropar wetland, Punjab, India and its environs. *Food chemistry*, 255: 15-22.

Sheoran AS, Sheoran V. 2006. Heavy metal removal mechanism of acid mine drainage in wetlands: A critical review. *Miner. Eng.*, *19*, 105–116, doi:10.1016/j.mineng.2005.08.006.

Sibrell PL, Montgomery GA, Ritenour KL, Tucker TW. 2009. Removal of phosphorus from agricultural wastewaters using adsorption media prepared from acid mine drainage sludge. *Water research*, 43: 2240-2250.

Skousen JG. 2014. Overview of Acid Mine Drainage Treatment with Chemicals. In *Acid Mine Drainage, Rock Drainage, and Acid Sulfate Soils: Causes, Assessment, Prediction, Prevention, and Remediation*; Jacobs, J.A., Lehr, J.H., Testa, S.M., Eds.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, doi:10.1002/9781118749197.ch29.

Skousen JG, Ziemkiewicz PF, McDonald LM. 2019. Acid Mine Drainage Formation, Control and Treatment: Approaches and Strategies. West Virginia University, Morgantown, WV 26506-6108. doi: 10.1016/j.exis.2018.09.008

Soil Science Society of South Africa. 1990. Handbook of standard soil testing methods for advisory purposes. *The non-affiliated soil analysis work committee. ISBN0620148004.*

Soil Classification Working Group. 1991. Soil Classification – a Taxonomic System for South Africa. Memoirs on the Agricultural Natural Resources of South Africa No. 15. Department of Agricultural Development, Pretoria.

Sposito G. 2008. Mineral stability and weathering. pp119-135. *In*: The Chemistry of Soils. 2nd Ed. Published by Oxford University Press, Inc. 198 Madison Avenue, New York.

Steele MG. 2010. Throughput Improvement at the eMalahleni Water Reclamation Plant. Bachelor's Thesis, University of Pretoria, Pretoria, South Africa.

Sun Q, McDonald Jr LM, Skousen JG. 2000. Effects of armoring on limestone neutralization of AMD. pp. 1-10.

Tabatabai MA. Frankenberger WT. 1996. Liquid chromatography. In: Methods of Soil Analysis, Part 3 – Chemical methods. SSSA Book Series No. 5, pp 225

Tangahu BV, Abdullah S, Rozaimah S, Basri H, Idris M, Anuar N, Mukhlisin M. 2011. A review on heavy metals (As, Pb, and Hg) uptake by plants through phytoremediation. *International Journal of Chemical Engineering*, 2011.

Tepanosyan G, Sahakyan L, Belyaeva O, Maghakyan N, Saghatelyan A. 2017. Human health risk assessment and riskiest heavy metal origin identification in urban soils of Yerevan, Armenia. *Chemosphere*, *184*, 1230–1240.

Thielecke F, Nugent A. 2018. Contaminants in Grain—A Major Risk for Whole Grain Safety? *Nutrients*, 10: 1213.

Thomas GW. 1996. Soil pH and Soil Acidity. In: Methods of Soil Analysis, Part 3 – Chemical methods. SSSA Book Series No. 5, pp 475

Thomas GW. 1982. Exchangeable Cations, In Methods of Analysis, Part 2. American Society of Agronomy, Madison, Wisconsin, USA. PP 159 – 165

Tsang DC, Olds WE, Weber PA, Yip AC. 2013. Soil stabilisation using AMD sludge, compost and lignite: TCLP leachability and continuous acid leaching. *Chemosphere*, 93: 2839-2847.

Tsang DC, Yip AC. 2014. Comparing chemical-enhanced washing and waste-based stabilisation approach for soil remediation. *Journal of soils and sediments*, 14: 936-947.

Tye A, Young S, Crout N, Zhang H, Preston S, Zhao F, McGrath S. 2004. Speciation and solubility of Cu, Ni and Pb in contaminated soils. *European Journal of Soil Science*, 55: 579-590.

USEPA procedure 40 CFR Appendix B to Part 136. 2011. Definition and Procedure for the Determination of the Method Detection Limit—Revision 2. https://www.epa.gov/cwa-methods (Accessed March 2019)

United States Environmental Protection Agency (EPA). SW-846 Test Method 1311. 1992. Toxicity Characteristic Leaching Procedure (TCLP). Available online: https://www.epa.gov/hw-sw846/sw-846-test-method-1311-toxicity-characteristic-leaching-procedure (accessed on 9 March 2018).

United States Environmental Protection Agency (EPA). 1990. Hazardous Waste Management System; Identification and Listing of Hazardous Waste; Toxicity Characteristics Revisions. Federal Register, Rules and Regulations. Available online: https://www.epa.gov/sites/production/files/2016-04/documents/55fr11798.pdf (accessed on 9 March 2017).

United States (US) Environmental Protection Agency (EPA) Method 3052. 1996. Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices, part of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 20 pp, https://www.epa.gov/hw-sw846/sw-846-test-method-3052-microwave-assisted-acid-digestion-siliceous-and-organically-based (Accessed May 2018)

Unkovich M, Baldock J, Forbes M. 2010. Dry Matter, Grain Yield, and Harvest Index Values for Crops In: Variability in Harvest Index of Grain Crops and Potential Significance for Carbon Accounting: Examples from Australian Agriculture. *ADVANCES IN AGRONOMY*, 105: PP 192 - 193

Utomo WH, Kusuma Z, Nugroho WH. 2011. Soil fertility status, nutrient uptake, and maize (Zea mays L.) yield following biochar and cattle manure application on sandy soils of Lombok, Indonesia. *Journal of Tropical Agriculture*, 49: 47-52.

Vahedian A, Asadzadeh Aghdaeib SA, Mahinic S. 2014. Acid Sulphate Soil Interaction with Groundwater: A Remediation Case Study in East Trinity. *APCBEE Procedia* 9: 274 – 279

Van Bodegom PM, Van Reeven J, Van Der Gon HACD. 2003. Prediction of reducible soil iron content from iron extraction data. Biogeochemistry 64:231-245.

Wang LK, Shammas NK, Hung Y. 2009. *Advances in Hazardous Industrial Waste Treatment*; CRC Press: Boca Raton, FL, USA; pp. 1–35.

Wang CY, Liu JQ, Guo P. 2012. *An Analysis of Limestone Gypsum Desulfurization Systems*; Trans Tech Publ.: Zurich, Switzerland; Volume 550–553, pp. 667–670.

Wen X, Luo Q, Hu H, Wang N, Chen Y, Jin J, Hao Y, Xu G, Li F, Fang W. 2014. Comparison research on waste classification between China and the EU, Japan and the USA. *Mater. Cycles Waste Manag*. *16*, 321–334, doi:10.1007/s10163-013-0190-1.

Wei X, Viadero Jr RC, Bhojappa S. 2008. Phosphorus removal by acid mine drainage sludge from secondary effluents of municipal wastewater treatment plants. *Water research*, 42: 3275-3284.

Wei X, Viadero RC, Jr, Buzby KM 2005. Recovery of Iron and Aluminum from Acid Mine Drainage by Selective Precipitation. Environmental Engineering Science, 22: 6

Wilmoth RC. 1977. Limestone and lime neutralization of ferrous iron acid mine drainage. Environmental Protection Technology Series. EPA-600/2-77-101

Jamal HYA. 2015. Removal of Heavy Metals from Acid Mine Drainage: A Review. *International Journal of New Technologies in Science and Engineering* 2: 2349-0780

Zeng G, Wan J, Huang D, Hu L, Huang C, Cheng M, Xue W, Gong X, Wang R, Jiang D. 2017. Zinck JM. 2006. Disposal, reprocessing and reuse options for acidic drainage treatment sludge. American Society of Mining and Reclamation (ASMR), 3134 Montavesta Road, Lexington, KY 40502

Zinck JM, Griffith W. 2006. Utilizing industrial wastes and alterative reagents to treat acidic drainage. The 7th International Conference on Acid Rock Drainage (ICARD), American Society of Mining and Reclamation (ASMR) 3134 Montavesta Road, Lexington, KY 40502. https://nrcca.cals.cornell.edu/soil/CA2/CA0212.1-3.php (accessed 21 August 2017)

Zinck JM, Wilson LJ, Chen TT, Griffith W, Mikhail S, Turcotte A.M. 1997. Characterization and Stability of Acid Mine Drainage Treatment Sludges. Mining and Mineral Sciences Laboratories Report MMSL 96-079 (CR). MEND Project 3.42.2a, Job No. 51144, Canada. http://mend-nedem.org/wp-content/uploads/2013/01/3.42.2a.pdf. Accessed 22 November 2018

Zinck J. 2005. Review of Disposal, Reprocessing and Reuse Options for Acidic Drainage Treatment Sludge. CANMET Report 04-007 CR prepared for MEND (Report 3.42.3)

Zinck JM. 2006. Disposal, reprocessing and reuse options for acidic drainage treatment sludge. In: 7th International Conference on Acid Rock Drainage (ICARD), St. Louis MO. R.I. Barnhisel (ed.) Published by American Society of Mining and Reclamation (ASMR), 3134 Montavesta Road, Lexington, KY 40502, March 26-30, 2006

Zornoza R, Moreno-Barriga F, Acosta J, Muñoz M, Faz A. 2016. Stability, nutrient availability and hydrophobicity of biochars derived from manure, crop residues, and municipal solid waste for their use as soil amendments. *Chemosphere*, 144: 122-130.

APPENDICES

Appendix A: Determination of Method Detection Limits (MDL) in mg kg^{-1}

Spiked sample	Fe	Zn	Ni	Cd	Pb	Mn
1	0.0731	0.0619	0.0603	0.0742	0.0758	0.04932
2	0.0791	0.0612	0.0663	0.0745	0.0751	0.04952
3	0.0833	0.0617	0.0632	0.0748	0.0745	0.04972
4	0.0793	0.0627	0.0603	0.0755	0.0746	0.04942
5	0.0827	0.0623	0.0655	0.0744	0.0752	0.04942
6	0.0834	0.0614	0.0509	0.0733	0.0769	0.04922
7	0.0850	0.0616	0.0627	0.0751	0.0760	0.04942
Stdev	0.004055	0.000522	0.005138	0.000704	0.011918	0.000157
MDL=STDEV*t	0.012746	0.00164	0.016147	0.002214	0.03746	0.000495
Digestion	1.1	0.14	1.3	0.18	0.2	0.04
EDTA	0.01	0.008	0.08	0.01	0.01	0.04
NH4OAc	0.2	0.03	0.3	0.04	0.2	0.04
Dialysis	0.2	0.03	0.3	0.04	0.04	0.04

Appendix B: Mineralogy of sludges before and after solubility with deionized water and diluted HCl to pH 4 using X-Ray Diffraction (XRD) technique

Gypseous material	Solubility	Mineral	Chemical formula	Weight (%)
GypFeMnNi (Ferriferous Gypseous)	Before solubility with any extractant	Gypsum	$CaSO_4.2H_2O$	72 – 77
		Ankerite	$Ca(Fe,Mg,Mn)(CO_3)_2$	4.17
		Calcite	$CaCO_3$	-
		Goethite	$FeO(OH)$	-
		Hematite	Fe_2O_3	-
		Quartz	SiO_2	-
		Jarosite	$KFe^{3+}{}_3(OH)_6(SO_4)_2$	-
	After solubility with deionized H_2O	Gypsum	$CaSO_4.2H_2O$	98.37
		Ankerite	$Ca(Fe,Mg,Mn)(CO_3)_2$	0.2
		Hematite	Fe_2O_3	
		Quartz	SiO_2	1.42
	After solubility with diluted HCl at pH4	Gypsum	$CaSO_4.2H_2O$	99.47
		Hematite	Fe_2O_3	
		Quartz	SiO_2	0.53
GypFeMn (Ferriferous Gypseous with Mn)	Before solubility with any extractant	Gypsum	$CaSO_4.2H_2O$	69.95
		Quartz	SiO_2	0.91
		Calcite	$CaCO_3$	27.4
		Brucite	$Mg(OH)_2$	1.74
	After solubility with deionized H_2O	Gypsum	$CaSO_4.2H_2O$	89.33
		Calcite	$CaCO_3$	10.67
	After solubility with diluted HCl at pH4	Gypsum	$CaSO_4.2H_2O$	90.29
		Quartz	SiO_2	0.15
		Calcite	$CaCO_3$	9.57
GypB (Gypseous with Brucite)	Before solubility with any extractant	Gypsum	$CaSO_4.2H_2O$	90.98
		Quartz	SiO_2	0.2
		Calcite	$CaCO_3$	0.96
		Brucite	$Mg(OH)_2$	7.86
	After solubility with deionized H_2O	Gypsum	$CaSO_4.2H_2O$	Gypsum
	After solubility with diluted HCl at pH4	Gypsum	$CaSO_4.2H_2O$	Gypsum
Gyp (Gypseous)	Before solubility with any extractant	Gypsum	$CaSO_4.2H_2O$	99.08
		Quartz	SiO_2	0.16
		Calcite	$CaCO_3$	0.55
		Brucite	$Mg(OH)_2$	0.21
	After solubility with deionized H_2O	Gypsum	$CaSO_4.2H_2O$	100
	After solubility with diluted HCl at pH4	Gypsum	$CaSO_4.2H_2O$	100

Note: GypFeMnNi = Ferriferous Gypseous with Mn and Ni; GypFeMn = Ferriferous Gypseous with Mn: GypB = Gypseous with Brucite: Gyp = Gypseous

Appendix C: Diffractograms

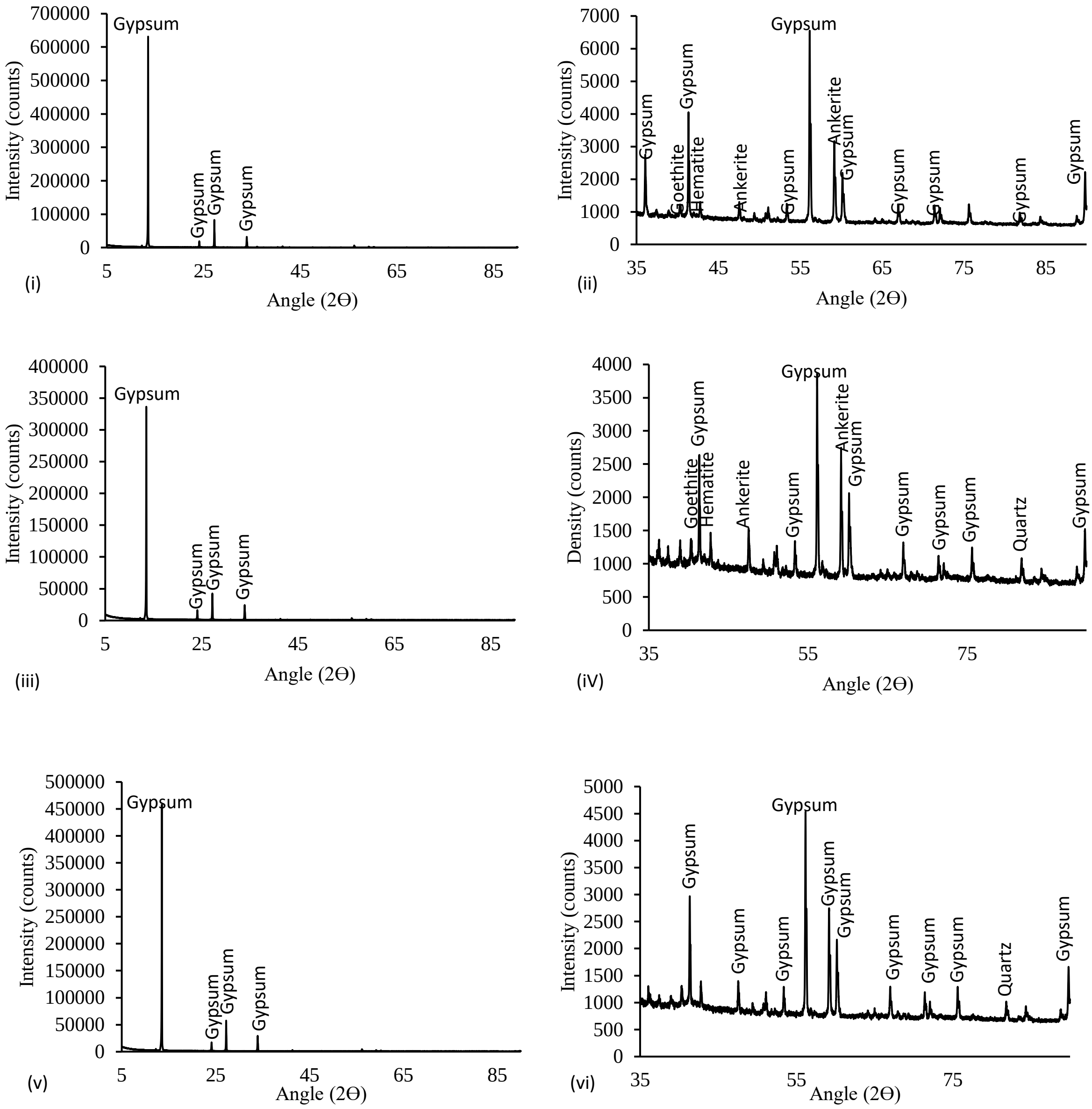


Fig. 1: i & ii) GypFeMnNi before extraction; iii & iv) GypFeMnNi after solubility with deionized water; v & vi) GypFeMnNi after solubility with diluted HCl at pH4

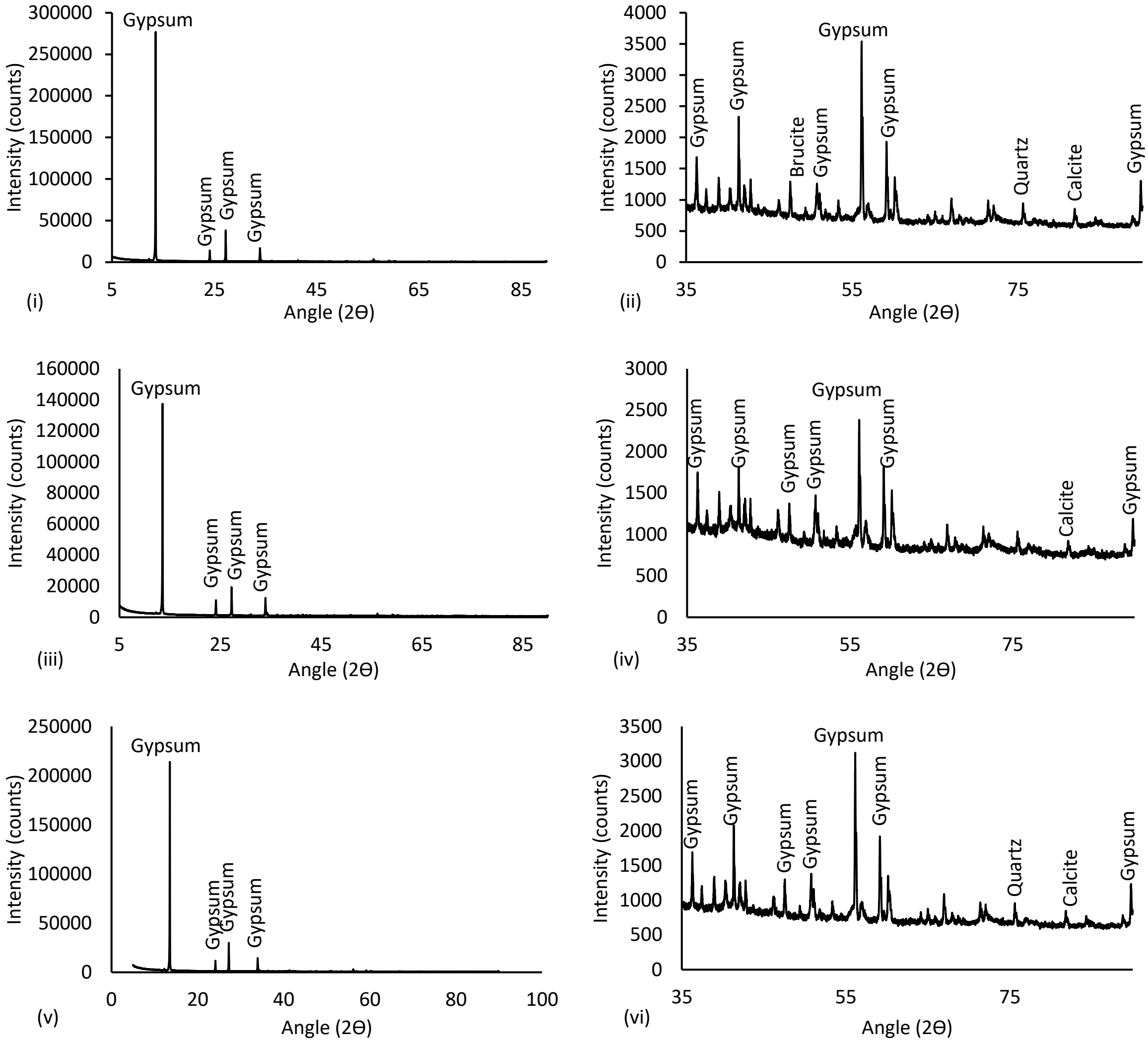


Fig. 2: i & ii) GypFeMn before extraction; iii & iv) GypFeMn after solubility with deionized water; v & vi) GypFeMn after solubility with diluted HCl at pH4

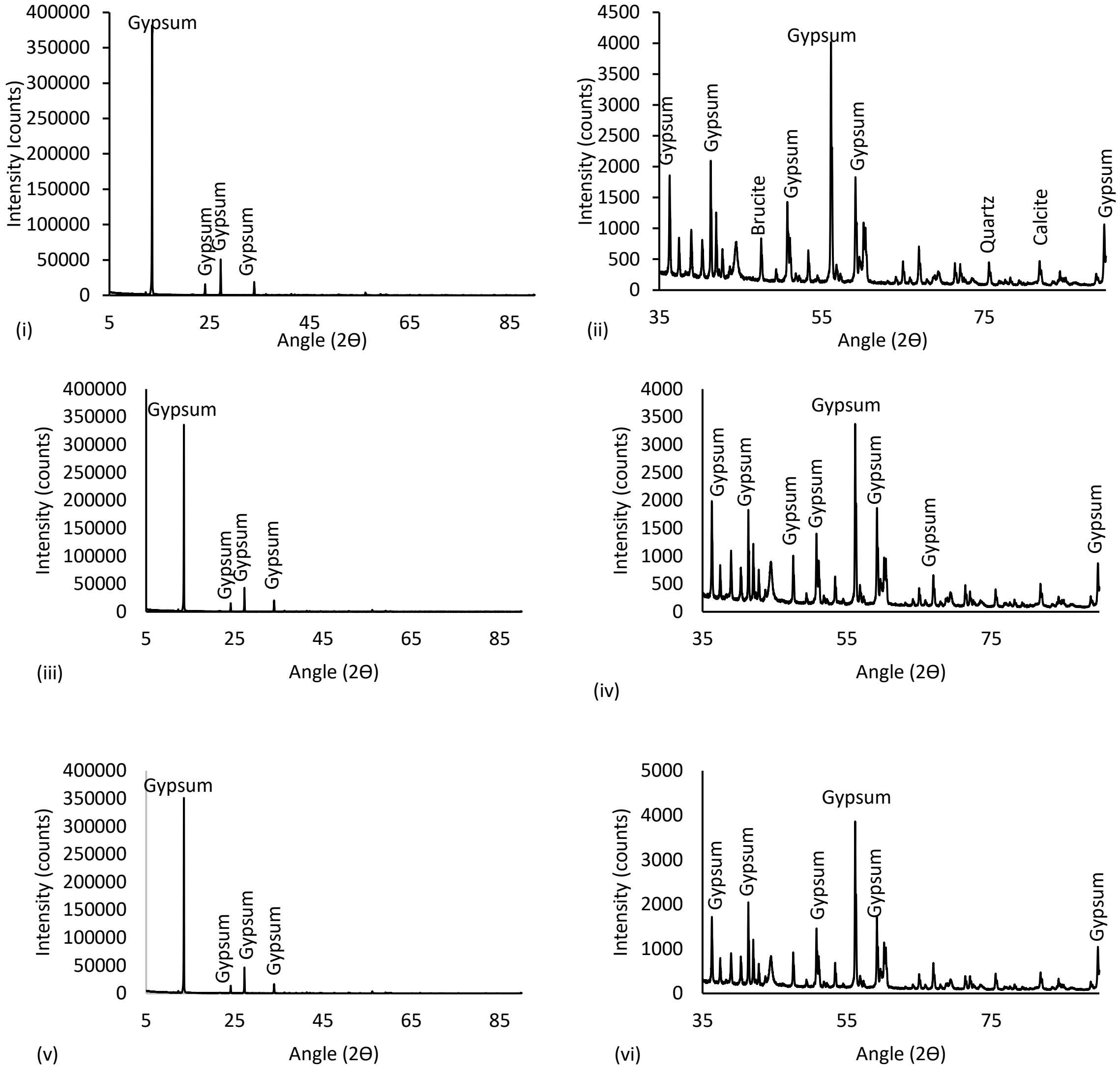


Fig. 3: i & ii) GypB before extraction; iii & iv) GypB after solubility with deionized water; v & vi) GypB after solubility with diluted HCl at pH4

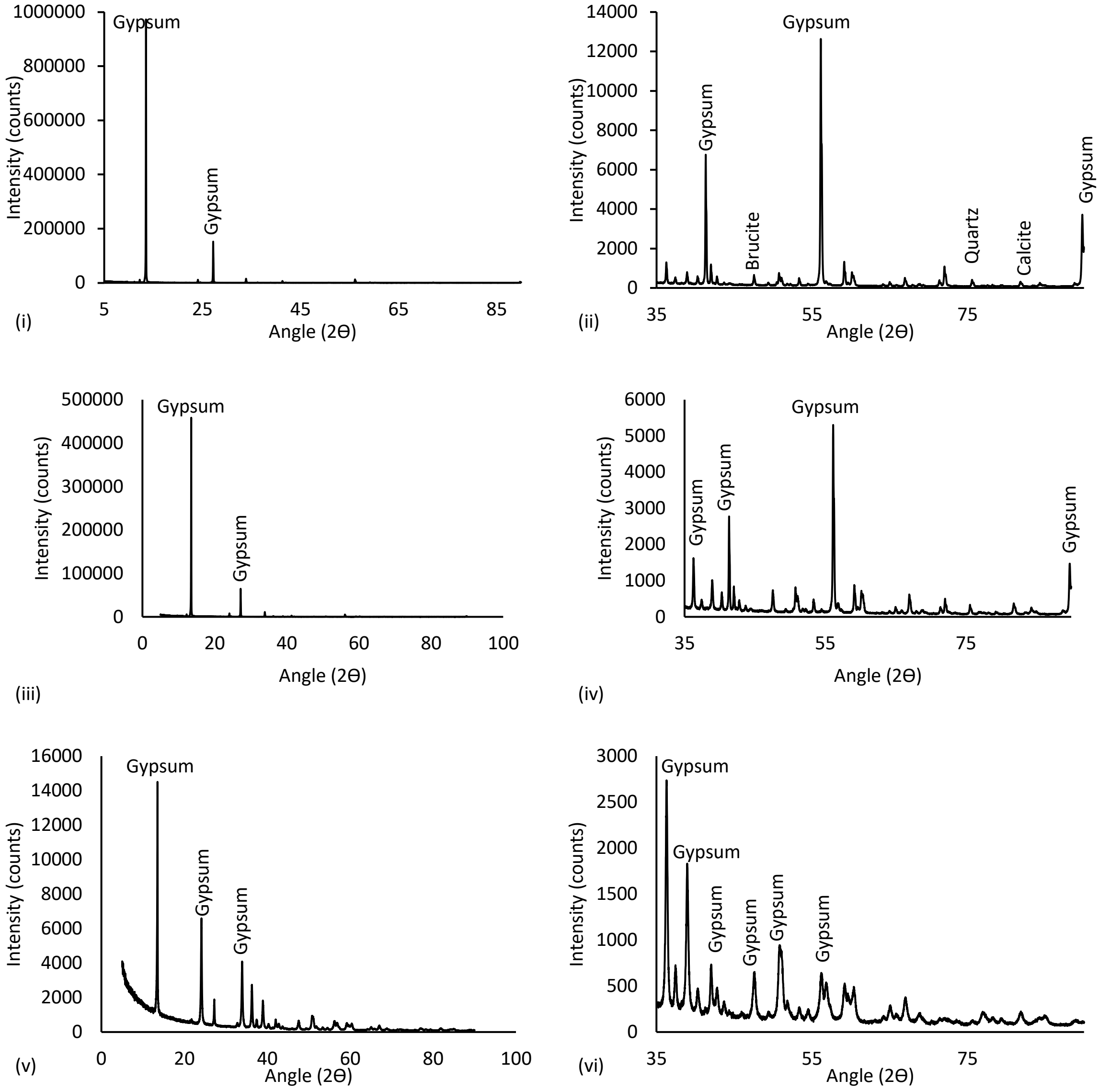


Fig. 4: i & ii) Gyp before extraction; iii & iv); Gyp after solubility with deionized water; v & vi) Gyp after solubility with diluted HCl at pH4

Appendix D: Morphology for gypseous product, GypFeMnNi and armouring of gypsum by amorphous ferrihydrite

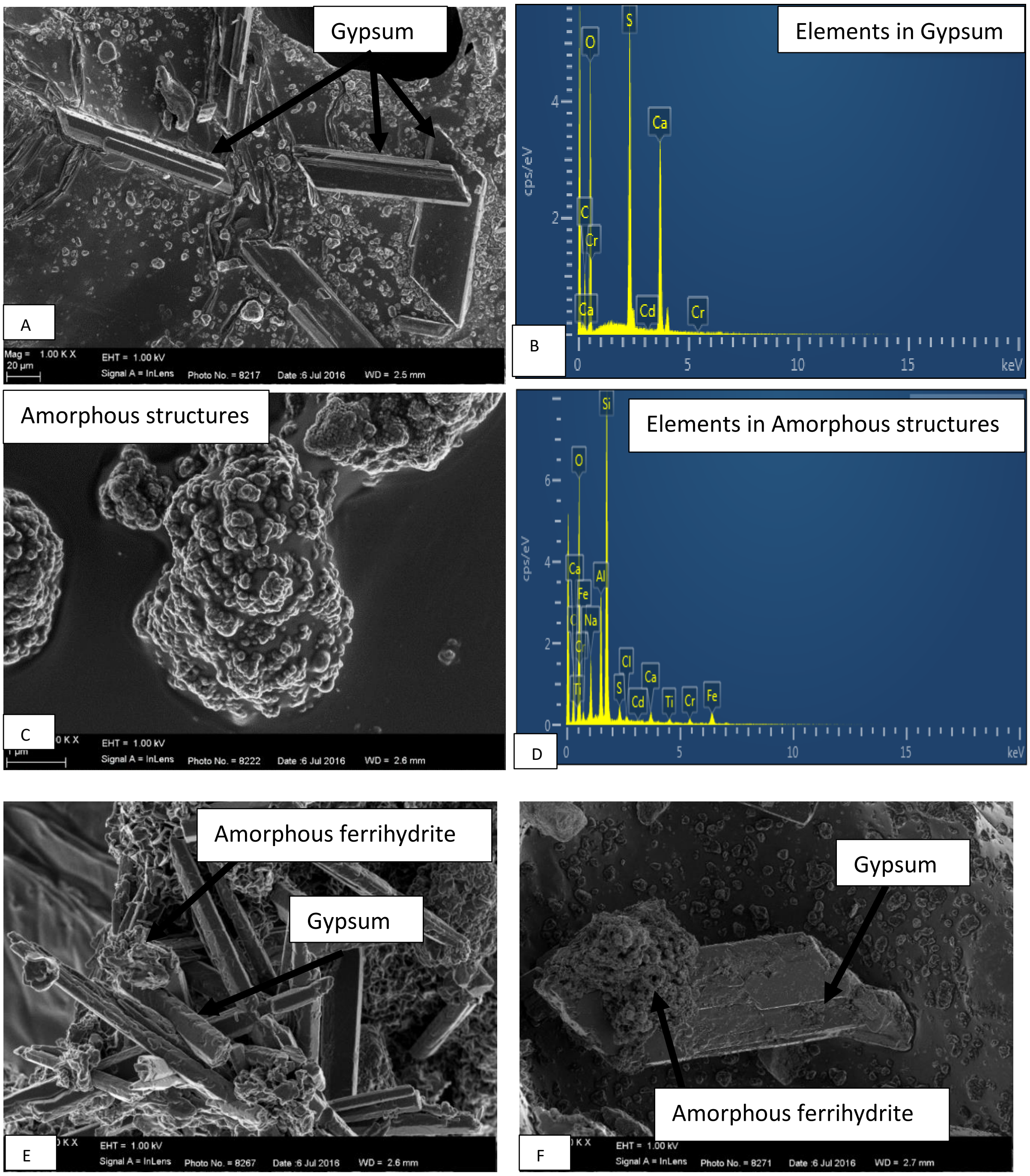


Fig. 1: A & C) Morphology of minerals in HDS using SEM; B & D) Elemental concentrations in minerals using EDS; E & F) Armouring of gypsum by amorphous ferrihydrite

Appendix E: Solubility of HDS through dialysis method

Appendix F

Table 1: Percentages of elements extracted by Acid Ammonium Oxalate and Dithionite in HDS

Extractant	P (mg kg^{-1})	HDS	Fe	Mn	Al	Ni
Oxalate	0	GypFeMn	6.606	0.015	1.175	0.003
	50	GypFeMn	5.937	0.021	1.268	0.003
	6000	GypFeMn	7.851	0.362	0.967	0.007
	0	GypFeMnNi	12.209	0.031	2.530	0.007
	50	GypFeMnNi	12.057	0.022	2.758	0.007
	6000	GypFeMnNi	11.913	0.027	2.370	0.006
Dithionite	0	GypFeMn	9.970	0.634	1.446	0.011
	50	GypFeMn	9.982	0.627	1.338	0.014
	6000	GypFeMn	5.505	0.346	0.866	0.007
	0	GypFeMnNi	11.634	0.050	2.162	0.009
	50	GypFeMnNi	14.931	0.034	2.779	0.011
	6000	GypFeMnNi	10.894	0.034	1.831	0.007

Table 2: Percentage of elements extracted by Dithionite and Acid Ammonium Oxalate relative to total elemental content in HDS

Element	HDS	P sorbed against added (in parenthesis)	Dithionite	Acid Ammonium Oxalate
Fe	GypFeMnNi	0 (0)	79.5	83.4
		300 (300)	100.0	82.4
		16018 (36000)	74.5	81.4
	GypFeMn	0 (0)	87.0	57.7
		299 (300)	87.1	51.8
		33574 (36000)	48.0	68.5
Mn	GypFeMnNi	0 (0)	6.6	4.0
		300 (300)	4.5	2.9
		16018 (36000)	4.5	3.5
	GypFeMn	0 (0)	80.8	2.0
		299 (300)	80.0	2.7
		33574 (36000)	44.1	46.2
Al	GypFeMnNi	0 (0)	73.7	86.3
		300 (300)	94.8	94.1
		16018 (36000)	62.4	80.8
	GypFeMn	0 (0)	64.5	52.4
		299 (300)	59.6	56.5
		33574 (36000)	38.6	43.1
Ni	GypFeMnNi	0 (0)	81.2	61.6
		300 (300)	98.6	68.8
		16018 (36000)	68.8	55.8
	GypFeMn	0 (0)	64.7	15.6
		299 (300)	81.5	18.3
		33574 (36000)	44.0	42.9