Nitrogen dynamics of amending coal gasification ash with organic industrial sludge: implications for dumpsite rehabilitation

by

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Declaration

I, Ikenna Mbakwe declare that the thesis, which I hereby submit for the degree PhD Soil Science at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

SIGNATURE:…………………………

DATE:…………………………………..

Acknowledgement

When an animal wants to scratch an itch it goes to a tree, but when a man wants to scratch an itch, he goes to another man …Igbo proverb

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Abstract

Coal gasification ash (CGA) is the waste by-product of the process of producing synthetic fuel from coal. Every year, millions of tons of this saline, alkaline waste are generated and although alternative uses have been found such as for brick-making purposes, transport costs make it unviable to reuse this bulky material beneficially, leading to the inevitable stockpiling of the waste product. It has thus become increasingly evident that onsite rehabilitation of ash dumps is the most workable waste management option. Use of sludge to amend ash dumps has been suggested since sludge could improve the physical and chemical properties of ash and aid the establishment of vegetation on these dumps. Sludge could add a range of necessary plant nutrients, especially nitrogen. Nitrogen in sludge, however, is bound up in organic forms which have to be mineralized into plant-usable nitrogen species subject to a wide range of physical and chemical processes and reactions. This thesis presents studies exploring nitrogen dynamics in CGA amended with organic industrial sludge. First, it sought to establish a limit above which sludge addition to CGA will be harmful to the environment, based on trace element solubility studies in a column leaching experiment. The study found that with respect to trace element release, up to 5% dry sludge addition may be safe for amending CGA. Incubation experiments aimed at investigating the rate and pattern of nitrogen mineralization from sludge in a CGA medium showed that more N was mineralized in fresh ash than in weathered ash and in soil. Most nitrification occurred in soil while most of the N mineralized in ash was in the form of ammonium, suggesting an inhibition of nitrifying organisms in the ash medium and implying that at least initially, plants used for rehabilitation of CGA dumps may take up N mostly as ammonium. Due to the build up of ammonium, the risk for ammonium leaching was investigated in batch experiments by reacting fresh and weathered CGA with ammonium concentrations in the range found in common sludge materials. Results showed high ammonium sorption in ash with more sorption occurring in weathered ash than in fresh ash. Chemical modelling analysis of leachates from a column experiment indicated that ammonium may also be retained by chemical precipitation as struvite in a sludge-amended CGA medium, but that this will be dissolved as the concentration of P reduces due to precipitation of calcium phosphate, and as pH and ammonium levels drop due to nitrification. Results from a volatilization experiment showed that ammonia volatilization is greater and more rapid in soil than in CGA, and that less nitrogen was volatilized in weathered than in fresh ash, a phenomenon attributed to the high ammonium sorption capacity of CGA which is enhanced by ash weathering. This thesis concludes that with respect to nitrogen, use of sludge to rehabilitate CGA dumps is feasible and when sludge rates do not exceed 5%, and with good management practices, environmental risks will be minimal. As the first in-depth nitrogen study of CGA-sludge mixtures, this study evaluated the risks and benefits of sludge amendment of CGA, proffered practical solutions to rehabilitation of CGA dump sites, and enhanced the understanding of nitrogen dynamics in alkaline, saline environments.

Chapter 1: General introduction

1.1 Background

Management of solid wastes has long been a constant source of concern for environmentalists, governments and industry executives the world over. With the upsurge in industrialization and the numerous legislations on waste disposal, municipalities and industries have sought ways to either reuse their wastes, or dispose of them in such a way that the environment is not harmed (Henry et al., 2006). Improper disposal of wastes could cause various health and environmental problems, and although landfilling and incineration are some of the common waste management strategies, these options come with certain drawbacks, such as contamination of groundwater through leaching of toxic elements, and release of harmful gases into the atmosphere (Rushton, 2003; Wu et al., 2014). As a result, the development of safer and cheaper waste disposal options has become top priority as the world strives to cope with the rise in industrialization and the massive growth in population.

The proper handling of coal combustion byproducts (CCPs) has particularly been problematic, not only because of the huge amounts generated every year (about 500 million tons) (Skousen et al., 2012), but also because they contain elements that can become toxic to both plants and animals. Although some of the CCPs have been used in the cement industry, observations like those of Stevens and Dunn (2004), that carbon contents in coal ash above 6% are not suitable for direct use in concrete due to interactions between the carbon and the chemical admixtures used in concrete, have limited the use of CCPs for construction purposes.

Several authors have also investigated the use of the finer fractions of CCPs, mostly fly ash, as a soil amendment for agricultural soils. They observed that ash could reduce soil acidity (Phung et al., 1978), add nutrients to the soil (Fail and Wochok, 1977), improve soil physical characteristics (Mishra et al., 2007), and improve crop yield (Plank and Martens, 1974). However, the improvement in soil properties and crop yield reported by these authors has been contradicted by other reports (Hammermeister et al., 1998; Singh et al., 2008) which show yield reductions and elemental toxicities as a result of coal ash addition to agricultural land. Fey (2007) also observed that use of coal ash on farms outside of a 50 km radius of an ash source would be unprofitable due to increased transport costs. These impediments have indeed limited the widespread acceptance of coal ash as a viable reusable material, and have resulted in the unsafe practice of piling up ash in dumps around the vicinity of coal-fired power stations.

Coal gasification ash (CGA) generated by the process of producing synthetic fuel from low grade coal, presents similar challenges. Gasification is the reaction of solid fuels with air, oxygen, steam, carbon dioxide, or a mixture of these gases at a temperature exceeding 700 °C, to yield a gaseous product suitable for use either as a source of energy or as a raw material for the synthesis of chemicals, liquid fuels or other gaseous fuels **(**Collot, 2006). There are about 160 modern gasification plants in operation worldwide that produce syngas, oxy-chemicals, methanol, hydrogen, and electricity (Minchener, 2005). South African Coal and Oil (*Suid Afrikaanse Steenkool en Olie,* Sasol) operates such a plant, and in its Lurgi coal gasification process, produces synthesis gas (a mixture of carbon monoxide and hydrogen) from low-grade, medium rank C (bituminous) coal and extraneous rock fragments, usually carbonaceous shale, siltstone, sandstone and mudstone (Matjie et al., 2008). The process which takes place in gasifiers at temperatures greater than 1350 ºC and pressures exceeding 2

MPa, generates the waste coal gasification ash. It has been estimated that at Sasol's Secunda plant, about 7 million tons of CGA is produced annually from gasification of about 28 million tons of coal (Matjie et al., 2005). Gasification ash is a combination of red and white to grey fused clinkers of heterogeneous texture varying from fine material to large irregularly shaped aggregates ranging from 4 mm to 75 mm; and is composed predominantly of quartz, mullite, anorthite diopside, hematite, cristobalite and anhydrite (Matjie et al., 2005).

Coal gasification ash has found usage mostly in the making of cement bricks especially in the Vaal Triangle area where between two to three million ash-containing bricks are made each day (Matjie et al., 2005) using ash mostly from the Sasolburg site. Use of CGA from the Secunda site has been hampered by its geographical location, because of the transport costs involved in moving ash to areas where they can be utilized. Consequently, stockpiling has remained the most practical option for CGA disposal in Secunda (Fig1.1).

Rehabilitation of these ash dumps has become imperative in view of the pollution risks they pose to the environment and human health. Coal ash dumps are a source of air pollution when ash particles are transported by wind. Moreover, the ash heap is a reservoir of toxic elements with potential to leach into and contaminate water systems (Van Rensburg et al., 1998; Jala and Goyal, 2006).

Fig 1.1 A coal gasification ash dump site in Secunda, South Africa

Use of topsoil to cap ash dumps has been suggested (Cairns, 1983; Van Rensburg et al., 1998), however, the consequent removal of arable topsoil and the costs of transporting soil to ash sites are major drawbacks with this rehabilitation option. One of the more recently proposed management options is the amendment of CGA with organic industrial sludge, both to aid rehabilitation of ash dump sites, and as a viable sludge disposal system (Annandale et al., 2004). The sludge originates from the activated sludge treatment of industrial streams from the gasification process. Sludge generated at Sasol’s wastewater treatment plant (WWTP) can potentially be used to ameliorate the surface layer of the ash dumps to stimulate the growth and establishment of vegetation. Although some plant species have naturally sprouted on CGA dumps, the high porosity of CGA makes it impossible for the medium to retain sufficient water during dry periods to sustain a vigorous vegetative cover. As a result, growing plants die back during the dry winter. Apart from supplying essential plant nutrients, the amendment of CGA with sludge is capable of improving the water holding capacity of the medium and ensuring that enough water is stored for the establishment of perennial vegetation. Presently, the sludge generated at Sasol's WWTP is incinerated, a practice that is both costly in terms of energy demands, and unsafe in terms of the toxic gases released during incineration.

Previously, field trials by Annandale et al. (2004) were initiated with the objective of establishing permanent vegetation on CGA dumps in order to reduce the percolation of water through the dump and subsequently minimize salt mobilization. Those trials were aimed primarily at assessing the viability of establishing grasses and trees on ash dumps using additions of sludge instead of a very expensive soil cap. It was envisaged that with time, parent material effects would diminish once the coal ash surface has been stabilized by litter layer development and organic matter accumulation.

1.2 Problem statement and research objectives

Those trials by Annandale et al. (2004) and other studies on rehabilitation of coal ash dumps using organic materials (Cairns, 1983; Van Rensburg et al., 1998) lend credence to the potential of sludge-ash mixtures to support vegetation. Recently, Sukati (2012) in a series of laboratory studies, highlighted the increased availability of plant nutrients as a result of amending CGA with sludge. These pioneer studies form the platform on which a further evaluation of the dynamics of elements in coal gasification ash-sludge mixtures has to be built.

At present, two key issues are priority. First, it is important to determine the changes to the solubility of potentially toxic trace elements with a view to setting limits to sludge amendment of CGA. Secondly, since sludge is a major source of nitrogen, it is pertinent to assess the dynamics of nitrogen in sludge-amended CGA, both to determine the availability of plant-usable nitrogen species, and to evaluate any environmental risks with respect to the inorganic nitrogen species released. Most of the nitrogen in sludge is bound in organic forms (Hseu and Huang, 2005), therefore the success of sustaining vegetation on ash heaps through sludge amendment can only be realized if organic N from sludge is mineralized into plant-usable nitrogen in such a medium that is potentially unfavourable to the microorganisms that carry out the mineralization process.

This study mainly seeks to focus on the second question – the nitrogen issue. The overall purpose of this present research, therefore, is to determine the rate and pattern of nitrogen mineralization from sludge in a coal gasification ash medium so as to assess the potential of such media to release plant-usable nitrogen species from sludge, and consequently evaluate any risks of the inorganic nitrogen forms released. However, in order to do this, the study first estimates safe sludge application rate based on trace element solubility.

1.3 Structure of thesis

This thesis presents a written account of experimental and geochemical modelling work. Chapter 2 reviews relevant literature. Chapters 3 to 7 are research chapters and have been written up in the form of publishable papers. Chapter 3 aimed at establishing a sludge limit for ash amendment which was later used in the nitrogen studies, is a 12 month column leaching study of the effects of amending ash with sludge on trace element solubility. The

CGA that underwent this 12 month leaching/drying cycle was used in subsequent studies as 'weathered ash'; Chapter 4 investigates nitrogen mineralization from sludge in a CGA medium; Chapter 5 evaluates ammonium sorption in CGA; Chapter 6 uses geochemical modelling to estimate ammonium retention in sludge-amended CGA by chemical precipitation; Chapter 7 quantifies ammonia volatilization from sludge-amended CGA; and Chapter 8 summarizes the findings of these studies, and makes recommendations.

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Chapter 2: Sludge use in agriculture and land rehabilitation, with emphasis on nitrogen dynamics: a review of literature

2.1 Introduction

Proper handling of sewage sludge has been problematic not only because of the bulky nature of the large amounts generated every year, but also because improper handling could present serious health, environmental and social challenges. Because of its soil improvement characteristics, the waste material has often been used by farmers as a soil amendment. Recently too, sludge has been used for land rehabilitation purposes. Use of sludge on agricultural soil to improve crop yield has been practised for a very long time and numerous studies have been conducted and reported. However, it is only recently that sludge amendment of non-soil media has gained impetus as a result of waste-land rehabilitation efforts. This review seeks mainly to bring together existing knowledge of sludge use in soil and non soil media. Later, the review focuses on nitrogen release from sludge and the issues surrounding its prediction with mathematical models.

2.2 Sludge generation and use in agriculture

Use of biological faecal material to aid crop growth probably began long before its use was documented. Rudolfs et al. (1950) opined that the economy of highly populated countries like China and India would be wrecked without human manure. Ever since civilization gave birth to the concept of wastewater treatment plants (WWTPs), the notion has evolved into very complicated and specialized processes. Scattered in many municipalities and major cities across the world, these WWTPs stand as concrete epitomes of man’s efforts at safeguarding human health in the midst of increasing human and industrial activities.

Many cities have well established networks of sewers that collect wastewater from homes and industries and channel these to treatment plants, the major goal of which is to detoxify these wastewaters before discharging them into waterways, or before reusing them for various industrial, agricultural and recreational purposes. Mininni and Santori (1987) estimated that the input sewage flow rate to wastewater treatment plants is 2.5-7.5 liters per inhabitant per day.

The process of generation of sewage sludge differs from plant to plant, but the basic principles are the same. Wastewater from homes and industries flowing into a treatment plant is made to pass a screen where large floating objects are intercepted and removed. Next, the sewage passes through a grit chamber where other objects such as stones and large sand fractions settle to the bottom and are removed. After this stage, sewage still contains a variety of organic and inorganic matter which is removed from the sewage in a sedimentation tank where the suspended solids gradually sink to the bottom and form a mass of biosolids commonly called sludge. Sludge produced from this primary treatment process is called primary sludge and typically contains 3 to 7% solids and can be easily thickened or dewatered (Hue, 1995). Sludge is pumped out of the sedimentation tank and is either incinerated, disposed of in a landfill, or processed further into fertilizers (EPA, 1998).

Some WWTPs go a step further to treat the effluent after sludge has been removed, in order to eliminate various contaminants. This usually involves biological processes in the form of an activated sludge system and trickling filter system where bacteria are used. This secondary treatment produces secondary sludge which generally has 0.5 to 2.0% solids and is more difficult to thicken and dewater than the primary sludge. Tertiary treatment usually involves the addition of chemicals such as lime, or Al and Fe salts to wastewater in order to remove dissolved solids (Hue, 1995). Primary and secondary sludges are pathogen rich and odorous. In order to reduce these problems, sludges are stabilized. Stabilization methods include anaerobic digestion, aerobic digestion, lime addition, and composting.

Utilization of treated sewage sludge on croplands has become a common practice because of the many benefits associated with its agronomic use. Land application of sludge has been shown in many cases to improve soil physical characteristics, stimulate microbial activity and add plant nutrients to the soil (Boyle and Paul, 1989; Webber et al., 1996; Peterson et al., 2003; Ojeda et al., 2008). Sewage sludge has also been used to immobilise toxic elements for example, Neunhäuserer et al. (2001) reported that in a molybdenum-contaminated site, sewage sludge reduced plant molybdenum contents by 60% which reduced the possibility of molybdenosis in grazing ruminants.

Agronomic use of sludge saves municipalities landfilling and incineration costs (Fytili and Zabaniotou, 2008). Moreover, it translates to financial benefits for farmers in the form of reduced dependence on commercial fertilizers and possible tipping fees received for accepting the sludge (Bailey, 2013).

Use of sludge on farmland is, however, not without its drawbacks. For example, although the high organic nitrogen contents of many sludges make them important contributors to plant available inorganic forms of nitrogen, the uncertainties about N-mineralization rates from sludges have in many cases caused either an underdose of N or excessive nitrate levels in the soil leading to problems such as poor crop growth in the former, and nitrate leaching and groundwater contamination in the latter (Fumagalli et al., 2013).

Nitrate leaching into groundwater poses huge health risks, especially for infants and pregnant animals. When taken up in drinking water, certain bacteria in the digestive tract of ruminant animals and human infants convert nitrate to nitrite. Nitrite so produced, combines with haemoglobin and reduces the ability of the blood to transport oxygen to body cells. The condition, termed methaemoglobinaemia, can be fatal in many instances (Jahn et al., 2006). Adults could also be at risk because high nitrate concentrations can cause cancer in adults. Positive correlations have been found between nitrate concentrations and cancer risk because nitrite converted from nitrates can react with secondary and tertiary amines to form nitrosamines which are carcinogenic (Fedkiw, 1991; Canter, 1996). The World Health Organisation stipulates a maximum limit of 50 mg/l nitrate in drinking water (WHO, 2008). Excess nitrogen washed off into water bodies could also lead to algal blooms and exacerbate the greenhouse effect due to N_2O (Ehsani et al., 1999). Because of nitrate risks, sludge is usually applied to crop land based on crop nitrogen demand, however, this guideline has been shown to increase soil phosphorus to environmentally unsafe levels, especially in soils with low clay content (Shober and Sims, 2003; Heredia and Fernández Cirelli, 2007; Tesfamariam, 2009).

Added to the possibilities of nitrate leaching, heavy metals, pathogens and social inhibitions have limited the application of sludge to soil. For this reason, authorities have put restrictions on how much sludge can be applied to soil. In South Africa, the guidelines stipulate that not more than 10 tons dry sludge ha^{-1} yr^{-1} can be applied to agricultural soils over a 25 year period (Snyman and Herselman, 2006).

Furthermore, the general public, even those who have no knowledge of the chemical and pathogenic risks of sludge are repelled by the odour of the waste material and by the disease-causing organisms that the odour attracts. Tyson (2002) suggested that the odour of sewage sludge influences public perception to a far greater extent than many other factors. He hypothesized that if sewage sludge did not smell, the public would not complain. Moreover, there are cultural inhibitions in certain areas, with some religions considering human excreta as a spiritual pollutant, and some ethnic groups believing the waste to be a potential material used in witchcraft (Duncker et al., 2007; Jewitt, 2011).

Unfortunately, the main alternative of incineration of sludge not only releases several toxic gases to the atmosphere, but is also expensive considering the energy expended during incineration. Consequently, disposal of sludge has become problematic in South Africa and around the world, with increasing volumes of the material accumulating in the vicinity of wastewater treatment plants. The foregoing has called attention to the possibilities of other non-soil application of sludge, such as in the rehabilitation of degraded land.

2.3 Sludge use in land rehabilitation

The increase in industrialization and the initial management snub of the environment have resulted in many degraded lands around the world. Degraded lands present a depletion of the very small fraction of arable land available for agriculture. As the world's population increases, there is growing concern to manage the earth's resources in such a manner that they can support the growing populace. This had led to various efforts geared towards rehabilitation of degraded lands. Because of its physical and chemical properties, sludge has been used in some of these rehabilitation efforts.

Use of sludge in rehabilitation efforts has been based on the premise that sludge would add necessary nutrients, improve physical attributes such as water holding capacity, and bind metals, thereby reducing their bioavailability and toxicity, thus allowing vegetation to be established. The established vegetation subsequently reduces the spread of pollution by wind or water erosion, and reduces water ingress and accompanying metal leaching (Tandy et al., 2009).

Zanuzzi et al. (2009) reported an increase in pH, total organic carbon, total nitrogen, porosity, and an improvement in aggregate stability after amending mine tailings with a combination of sewage sludge and marble waste, or pig manure and marble waste. Tandy et al. (2009) found that mixing organic waste-derived compost with highly acidic mine soil resulted in amelioration of extreme acidity, making the medium more suitable for plant growth. They also found a significant reduction in plant shoot concentrations of Pb, As and Cu after addition of organic material to mine spoil. However, they reported that mobility of As was increased when mine spoil was amended with organic waste compost and suggested that among other processes, humic substances may compete with elements such as As for binding to Fe and Al oxides.

In a pot trial lasting 30 days, Theodoratos et al. (2000) evaluated the potential of sewage sludge to immobilize Pb, Zn and Cd in a mining-contaminated soil. They found from EPA Toxicity Characteristic Leaching Procedure (TCLP) analysis that 15% w/w sludge application reduced the solubility of Pb by 84%, Zn by 64% and Cd by 76% (Fig 2.1).

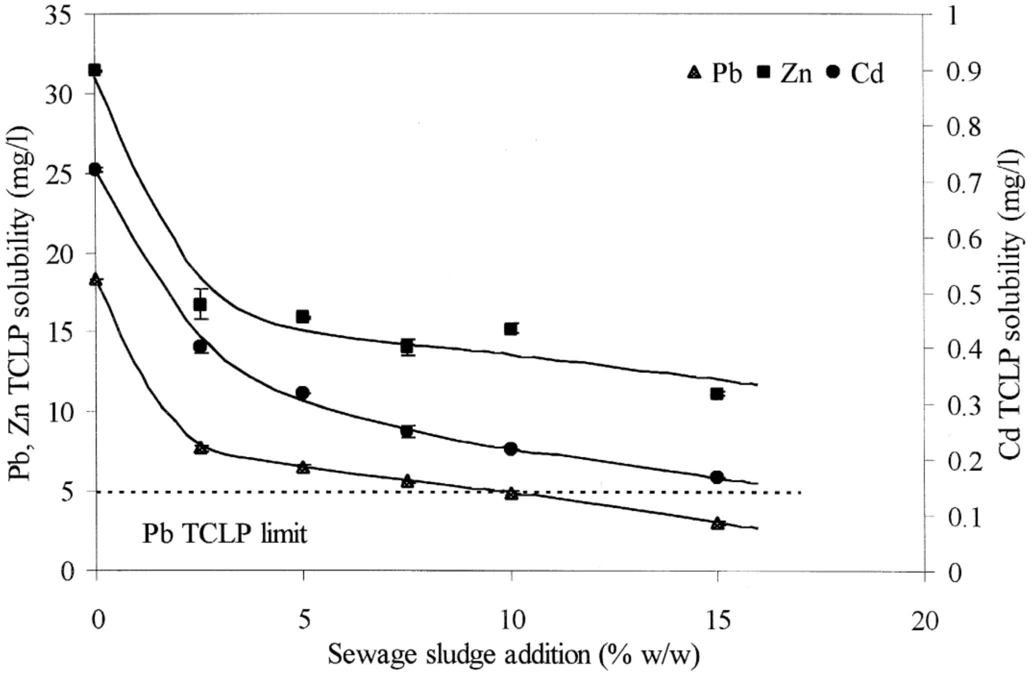

Fig 2.1 Immobilization of Pb, Zn and Cd by sludge in a mining-contaminated soil (Theodoratos et al., 2000)

Juwarkar and Jambhulkar (2008) observed an improvement in nutrient status, microbiological characteristics and a reduction of metal toxicity after coal mine spoil was amended with sludge. Van Rensburg et al. (1998) in an endeavour to revegetate a coal fine ash dump using organic and inorganic amendments, including sludge, reported that the addition of organic material resulted in better growth than inorganic fertilizer treatment alone. That positive effect may have resulted from improved water infiltration, improved water holding capacity, increased macropore space, addition of nutrients and stimulation of microbial populations (Scholl and Pase, 1984). A reduction of pH due to organic matter addition to coal ash may also make for a more conducive medium for plant growth and survival (Van Rensburg et al., 1998).

The benefits of amending coal ash with sludge can also be viewed as a viable sludge disposal system and a way to limit the environmental risks posed by disposing sludge on arable land. Several authors have reported that addition of coal fly ash to sewage sludge can reduce odour from sludge (Wong, 1995), reduce metal availability from sludge (Fang et al., 1999), and prevent a quick drop of pH during composting of sludge (Nakasaki et al., 1993). Wong et al. (1997) reported that the addition of coal fly ash to sewage sludge significantly reduced the Diethylenetriaminepentaacetic acid (DTPA) extractability of the heavy metals Cd, Cu, Mn, Pb, and Zn in sludge. They posited that the high alkalinity of coal fly ash had reduced the extractability of the heavy metals in sludge by forming less soluble carbonate salts.

The effect of a combination of coal ash and sludge on nitrates has also been recorded. For example, Fang et al. (1999) co-composted sewage sludge mixed with fly ash at rates of 0, 10, 25 and 35% (w/w) fly ash for 100 days. They observed lower nitrate levels in the ash-amended composts than the control and attributed this to the inhibition of nitrifiers by the higher salinity and alkalinity levels of ash-amended composts.

Wong and Su (1997) found in a greenhouse experiment where sludge was amended with fly ash at rates of 0, 5, 10, 35 and 50% (w/w) and mixed with loamy soil at either 1:1 or 1:5 (v/v), that *Agropyron elongatum* (tall wheat grass) shoot tissue concentrations of Fe, Mn and Zn decreased with an increase in ash amendment rate. They also found that in all the treatments, tissue N concentrations were more than the deficiency level of 1.5% proposed by Chapman (1966) indicating the ash-sludge mixtures provided sufficient N for the growth of the grass *Agropyron elongatum.*

The increasing demand for aluminium that has led to increased generation of bauxite residues has warranted investigation into reclamation of these bauxite residue sites. Use of sludge in these rehabilitation exercises has yielded positive results (Wong and Ho, 1994; Alifragis et al., 2000). There has also been some effort in using sludge in acid sulphate soils (for example, Parkpian et al., 2003), but there is a high possibility of mobilizing heavy metals from sludge due to the low pH of these soils.

Metal behaviour in sludge-amended growth media is difficult to generalize, since it is strongly dependent on the nature of the metal, sludge, medium properties and crop (McBride, 2003). Addition of sludge can add inorganic fractions such as carbonates, sulphates, sulphides and hydrous oxides which can lead to an increase in the sorption affinity of the medium for metals. Conversely, as it mineralizes, unstabilized organic matter may increase metal mobility due to a high dissolved organic matter (DOM) content that can complex metals and facilitate their movement. However, Tandy et al. (2009) noted that composting stabilizes organic wastes and reduces their DOM content and the potential for metal leaching.

2.4 Fate of nitrogen from sludge

Nitrogen is the element most abundant in the atmosphere, making up 78% of the atmosphere's total gaseous content. It has been estimated that some 300,000 Mg of nitrogen is found in the air above 1 ha of soil (Brady and Weil, 1999). However, because of the very strong triple bond between two nitrogen atoms, the gas is quite inert and can only be used by plants or animals after certain microorganisms have broken this triple bond to form nitrogen compounds.

Nitrogen is by far the most important element in crop production. Brady and Weil (1999) have stated that "More money and effort have been and are being spent on the management of nitrogen than any other mineral element. The world's ecosystems are probably influenced more by deficiencies or excesses of nitrogen than by those of any other essential element." Fertilizer programmes and many environmental policies are weaved around nitrogen because nitrogen deficiency spells crop failure, financial ruin and ensuing hunger, while its excesses trigger off a series of environmental and health risks.

In the soil, nitrogen occurs mainly as part of organic molecules. Soil organic matter (SOM) typically contains about 5% nitrogen but only about 2 to 3% of the nitrogen in SOM is released annually as inorganic nitrogen (Brady and Weil, 1999). About 50-90% of nitrogen in sludge is organic (Hseu and Huang, 2005), while between 95 and 99% of nitrogen in soil is bound in organic compounds (Brady and Weil, 1999). This binding of nitrogen in organic compounds protects it from loss but also makes it largely unavailable to plants. Soil microbes attack these organic compounds producing simple amino compounds which are then hydrolysed and nitrogen is released as ammonium (NH_4^+). The conversion of organically bound nitrogen into inorganic forms is termed mineralization. The process is a step by step procedure in which organic N is converted first to ammonium (NH_4^+), then to nitrites (NO_2^-) by the group of autotrophic bacteria *Nitrosomonas*, and subsequently to nitrates (NO_3^-) by a second group of autotrophs, *Nitrobacter*. The oxidation of ammonium by these groups of autotrophic bacteria to yield nitrites and nitrates is termed nitrification. If conditions favourable to the process prevail, conversion of nitrites to nitrates is rapid, and nitrites do not accumulate.

Loss of nitrogen through ammonia volatilization is an important pathway for significant depletion of plant-available nitrogen from soil amendments such as sludge. Ammonia volatilization has been shown to be enhanced by high pH, temperature, soil water content and wind speed (Søgaard et al., 2002). Especially for sludges with high contents of urea, the hydrolysis of urea by the enzyme urease results in an increase in pH and a consequent increase in ammonia volatilization (Soares et al., 2012). Up to 60% of total nitrogen can be lost through ammonia volatilization (Jiang et al., 2012) and apart from its economic implications, ammonia volatilization poses environmental risks such as soil acidification, N_2O production, and eutrophication of water bodies (Velasco-Velasco et al., 2011). As a result, efforts at minimizing ammonia volatilization have been explored. In this regard, the potential of urease inhibitors and acidifying agents has been reported (Blaise et al., 1996; Soares et al., 2012).

Inorganic nitrogen ions can be converted into organic forms in a process termed immobilization. This occurs when microorganisms decomposing carbonaceous organic residues require more nitrogen than is contained in the residues themselves. In this case, microorganisms incorporate inorganic N from the soil environment into their cellular components. The tendency for immobilization to occur is increased when the residues under decomposition have a high carbon to nitrogen ratio (Cabrera et al., 2005). A schematic representation of the nitrogen cycle (Henry et al., 1999) is shown in Fig 2.2.

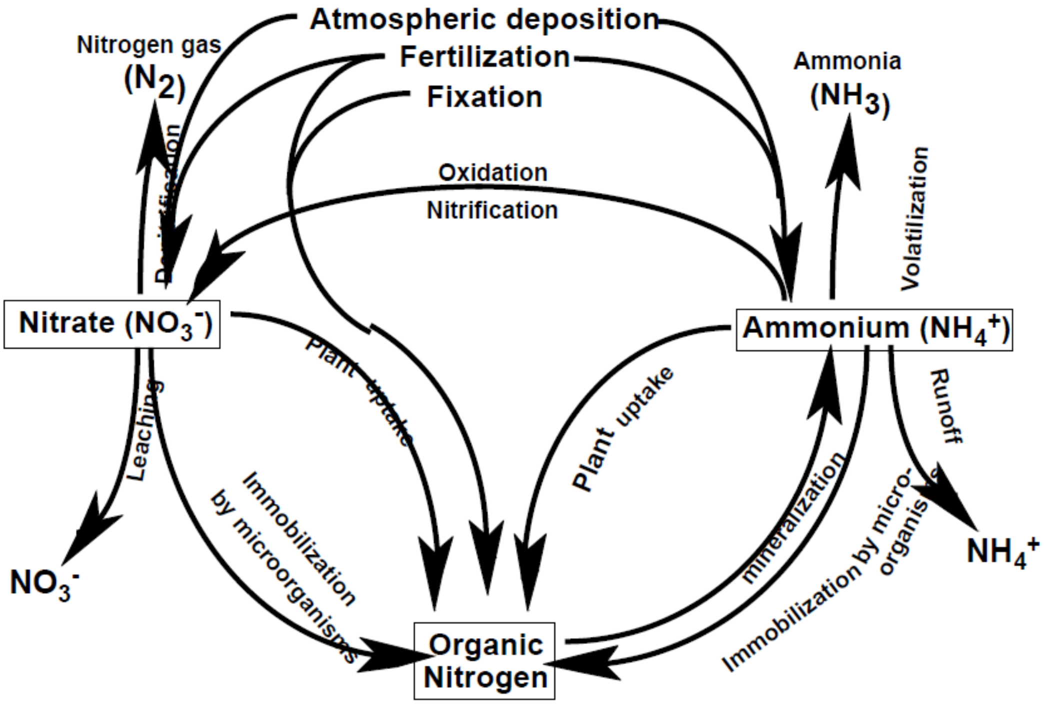

Fig 2.2 The nitrogen cycle (Henry et al., 1999)

Plants take up nitrogen from the soil solution mainly as nitrates (NO_3^-) and ammonium (NH_4^+) ions. The relative amounts of these ions taken up by plant roots affect the pH of the soil solution in close proximity to plant roots. Nitrate anions exchange with HCO_3^- or OH^- at the root surface, thereby causing an increase in the pH of the soil solution around plant roots. When ammonium cations are absorbed, they exchange with hydrogen ions, thereby lowering the pH of the soil solution (Brady and Weil, 1999). Nitrate anions are among the most mobile ions in the soil, and are susceptible to leaching. Therefore, effective fertilizer management programmes aim to regulate its generation, and align its production with crop needs and uptake.

Release of nitrogen from organic materials such as sludge is affected by environmental and substrate conditions, mainly because of the effects these factors have on the activities of soil microorganisms responsible for the mineralization process. Mineralization of organic N in land-applied sludge has been shown to be dependent on soil type, soil pH, temperature, aeration, water content, type of waste, and type of stabilization process employed in the generation of the sludge. These factors are discussed below.

2.5 Factors affecting nitrogen mineralization from sludge

Research shows that the factors that affect nitrogen release from organic materials such as sludge applied to porous media can be broadly categorized under sludge characteristics and media characteristics.

2.5.1 Sludge treatment

The wide range of treatment or stabilization methods among different wastewater treatment plants has been shown to affect the release of inorganic N from sludge. Magdoff and Chromec (1977) were part of the first researchers to report this observation. They noted that aerobically digested sludges gave higher nitrogen mineralization rates than those that were anaerobically digested. In their 13 week study, they observed that while mineralization rates for anaerobically digested sludges ranged from 14 to 25%, aerobically treated ones gave rates of 36 to 41%.

Serna and Pomares (1992) in a 16 week incubation study using 12 sewage sludges also observed that aerobically treated sludges gave higher mineralization rates than those that were anaerobically treated. They reported that N mineralized from aerobically digested sludges ranged from 95 to 428 mg N per kg. Sludges that were anaerobically treated gave N mineralization of 74 to 262 mg N per kg soil. Their results are shown in Fig 2.3.

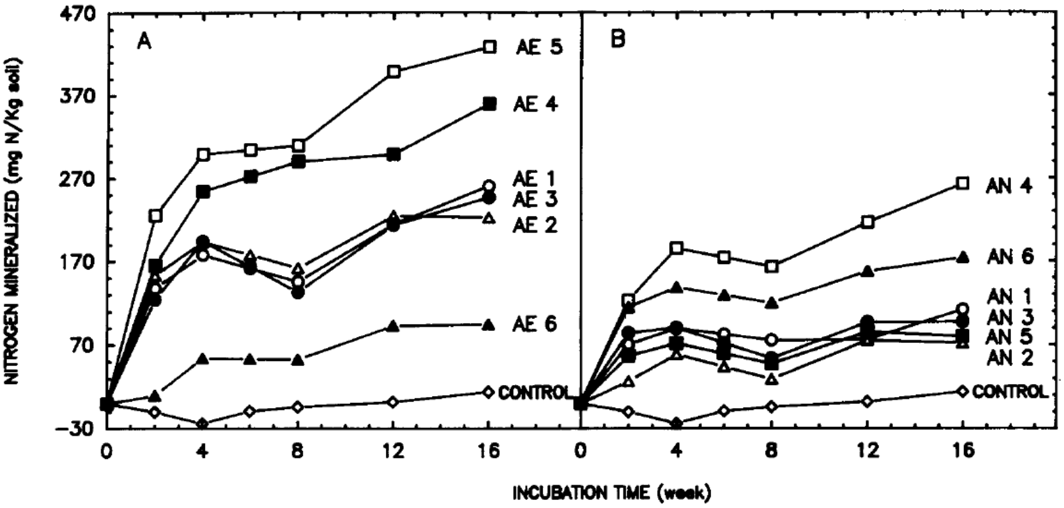

Fig 2.3 Nitrogen mineralization from sewage sludges obtained from different sewage treatment plants in Spain that were either aerobic (A) or anaerobically (B) digested (Serna and Pomares, 1992).

Tarrasón et al. (2008) compared mineralized N from composted sludge and thermally-dried sludge to their parent fresh partially dewatered sludge (Fig 2.4).

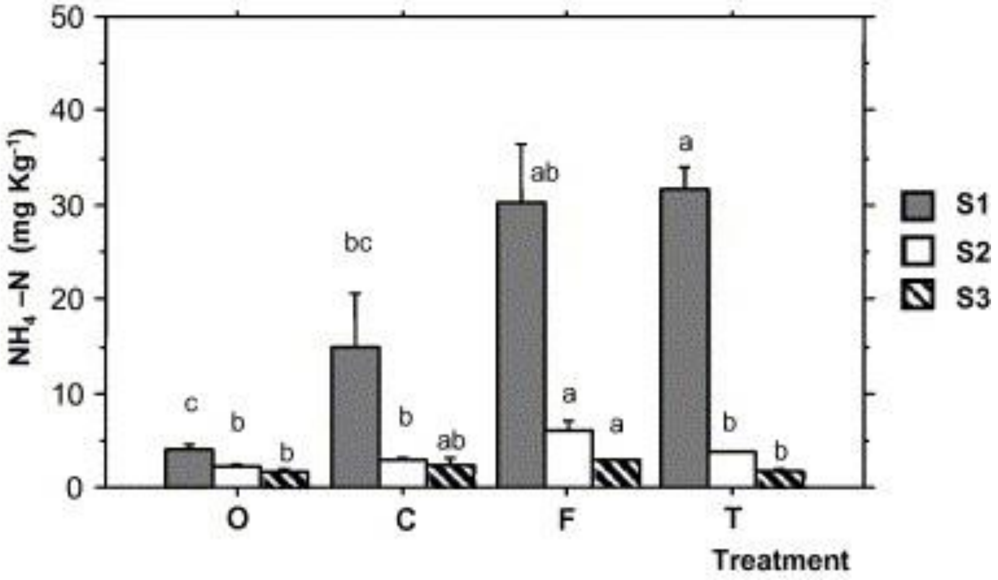

Fig 2.4 Mean concentration of NH_4−N in a soil amended with three types of sludge (O, control; C, composted sludge; F, fresh sludge; T, thermally-dried sludge) with corresponding standard errors, during three samplings (S1= 24 days, S2= 149 days, S3= 401 days after surface application of sludge). Different letters show significant differences of NH_4−N concentration between treatments at $p < 0.05$, in each sampling ($N = 12$) (Tarrasón et al., 2008).

They found that initially, NH_4 –N concentration was greater in plots fertilized with thermally-dried sludge than in plots amended with composted sludge, and attributed this to more intense initial mineralization and an abundance of labile nitrogen organic substances in thermally-dried sludge. However, in the long term, fresh sludge showed the highest concentrations of NH_4-N and NO_3-N. They concluded that since the fresh sludge was the parent material for the thermally-dried and composted sludge, the initial composition of the sludges was the same and the differences in NH_4-N and NO_3-N could only be attributed to the effect of the post-treatment process.

2.5.2 Sludge C/N ratio

The ratio of carbon to nitrogen (C/N ratio) has been shown to be inversely proportional to N mineralization. Barbarika et al. (1985) found that a high C/N ratio of both sludge and soil negatively affected N mineralization.

Serna and Pomares (1992) found a strong negative correlation coefficient r = -0.885 between C/N ratio and N mineralization for aerobically treated sludges. A graph plotted from their results is shown in Fig 2.5.

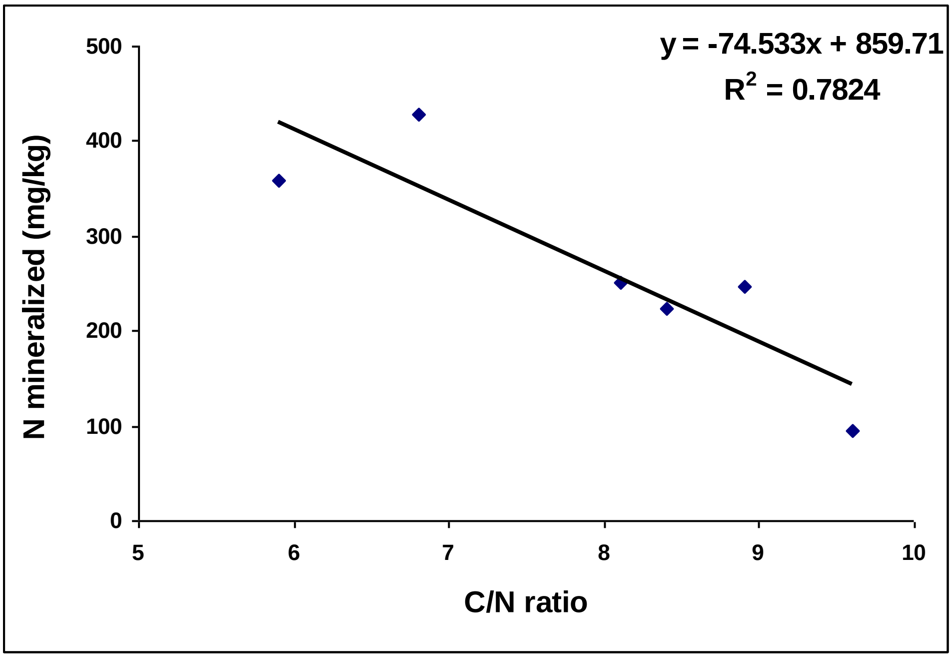

Fig 2.5 Relationship between C/N ratio and mineralized nitrogen from sludge (graph plotted from values obtained from Serna and Pomares, 1992).

Cabrera et al. (2005) explained that for there to be net mineralization with release of inorganic N, the amount of N present in the organic residue must be larger than that required by the microbial biomass involved in the decomposition process. If the amount of N in the residue is smaller than what is required by the microbes responsible for decomposition, then the microbes will have to immobilize inorganic N from the soil to enable them complete the decomposition process. N mineralization may be favoured by C/N ratios less than 20. This thinking is based on the fact that heterotrophic bacteria usually have a lower C/N ratio than the soil they inhabit, and if their cells have a C/N ratio of 10 and respire 50% of their C uptake, then there may be N limited above a soil C/N ratio of 20 (Bengtsson et al., 2003).

2.5.3 Sludge heavy metal content

Sludge heavy metal content may also affect N mineralization. In an experiment to compare nitrification in soil amended with industrial sludge with soil amended with domestic sludge, Wilson (1977) observed that industrial sludge reduced nitrification, and that at the highest rate of 16 mg sludge per gram of soil, industrial sludge completely inhibited nitrification for the first two weeks of the experiment. Wilson (1977) attributed the reduced nitrification observed with industrial sludge to the higher levels of metals in the sludge, particularly Zn, Cd and Pb. High concentrations of metals can cause a reduction in microbial biomass (Chander and Brookes, 1991; Bardgett and Saggar, 1994) leading to reduced mineralization of organic matter. Sandaa et al. (1999) reported a decrease in bacterial diversity from 16 000 bacterial genomes in non contaminated soil to only 2000 (per gram of wet soil) in soil amended with sewage sludge with high metal content.

2.5.4 Texture of the medium

Stevenson (1986) observed that rate of mineralization is reduced by high clay contents, because clay tends to protect organic matter from mineralizing. Hernández et al. (2002) found that organic N mineralization was greater in sludge-amended sandy soil (from 30% to 41% of the initial N) than in the amended clayey soil (from 13% to 17%) (Fig 2.6).

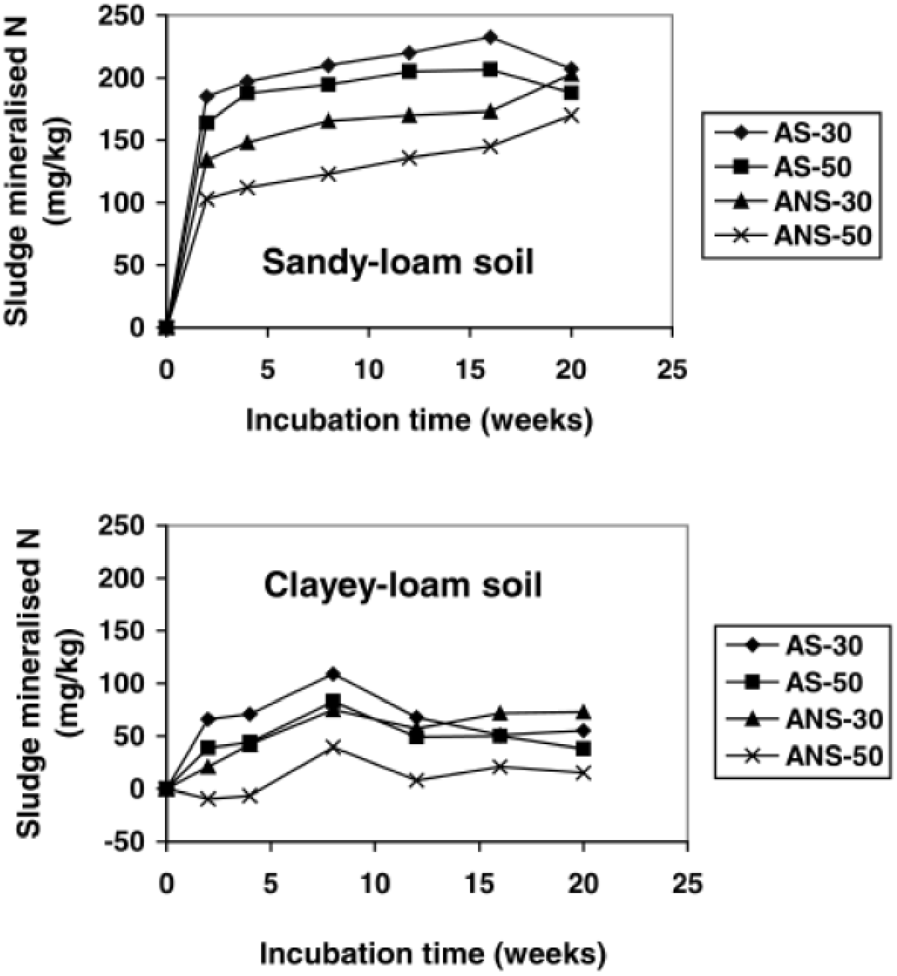

Fig 2.6 Effect of soil texture on nitrogen mineralized from sludge (Hernandez et al., 2002). AS-30 = Soil amended with aerobically digested sludge at 30 g sludge kg^{-1} soil. AS-50 = Soil amended with aerobically digested sludge at 50 g sludge kg^{-1} soil. ANS-30 = Soil amended with anaerobically digested sludge at 30 g sludge kg^{-1} soil. ANS-50 = Soil amended with anaerobically digested sludge at 50 g sludge kg^{-1} soil

This may have been as a result of the improved aeration in sandier soils (Thomsen et al., 1999). It may also be explained by the fixation of NH_4^+ ions by clay minerals (Smith et al., 1998a).

2.5.5 pH and electrical conductivity of the medium

Terry et al. (1981) observed a faster rate of nitrification for sludge-amended soil with initial pH of 7.5 compared to those with initial pH of 6.0 or 5.3. Bauhus et al. (1993) observed that although low pH was not a limiting factor for nitrification, high pH may promote the establishment of autotrophic nitrifiers. Ste-Marie and Paré (1999) studied the relationships between stand types and net nitrification in the forest floor of five stand types (Paper birch: *Betula papyrifera*, trembling aspen: *Populus tremuloides,* white spruce: *Picea glauca*, jack pine: *Pinus banksiana,* white cedar: *Thuja occidentalis*). They found that increase of forest floor pH had a positive effect on net nitrification and that no net nitrification occurred at pH(H_2O) values below 4.5 (Fig 2.7). Kyveryga et al. (2004) also found significant positive relationships between soil pH and percentage nitrification.

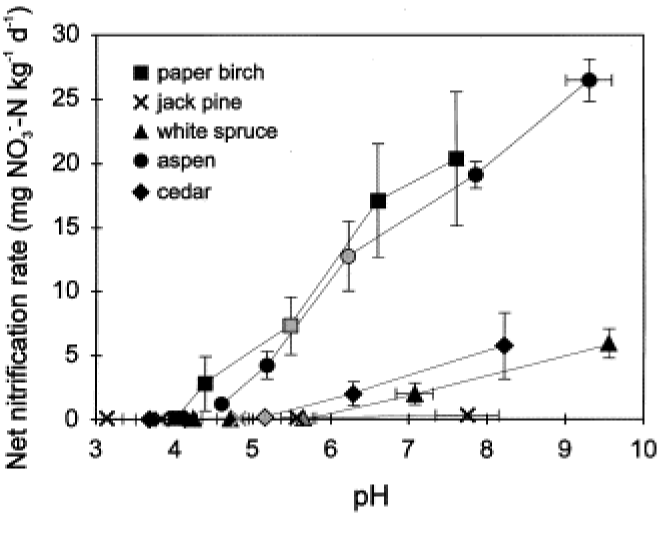

Fig 2.7 Soil pH effect on net nitrification rates in the nitrifying forest floor of different stand types after a 6-week laboratory incubation. Grey symbol represents samples incubated at original pH. Error bars show standard error (Ste-Marie and Paré, 1999).

Ammonification is inhibited by very high salinity, while nitrification is much more sensitive to salinity since ammonifiers are more tolerant of salinity than nitrifiers (McClung and Frankenberger, 1985). Pathak and Rao (1998) found that N mineralization decreased from

351 mg kg^{-1} in a non-saline soil of EC 1.1 dS m^{-1} to 277 mg kg^{-1} at an EC of 97 dS m^{-1}. N mineralization also decreased from about 400 mg kg^{-1} in a soil of pH 8.1, to 317 mg kg^{-1} in a soil of pH 10.0. They also found that while ammonification declined only above an EC of 70 dS m^{-1}, nitrification declined at 16 dS m^{-1} and was undetectable above an EC of 26 dS m^{-1}.

2.5.6 Water content and temperature

Agehara and Warncke (2005) reported that soil water content and temperature are the major physical environmental factors affecting N availability from organic N sources. They observed in their 12 week incubation experiment, that maximum aerobic microbial activity occurred at soil water content between 50 and 70% of water holding capacity. Terry et al. (1981) observed that nitrification was faster in sludge-amended soils adjusted to -0.25 and -0.5 bar moisture tension than in soils at -1 bar. In other words, dry conditions seemed to inhibit nitrogen release from sludge.

Terry et al. (1981) noted that nitrogen mineralization from sludge increased with increase in temperature. Nadelhoffer et al. (1991) found that rate of N mineralization increased by factors of 2 or more between 9 and 15 °C. Increasing temperature up to an optimum seems to enhance the activity of nitrifying bacteria. Maximum nitrification has been shown to occur between 25 and 35 ºC degrees (Breuer et al., 2002). This suggests that the plant availability of nitrogen in sludge-amended soils may follow the daily and annual sinusoidal behavior of temperature. Release of nitrogen in the cold months would be much lower than is released in the warmer months.

Guntiñas et al. (2012) investigated the influence of temperature and moisture content on net nitrogen mineralization in a laboratory experiment in which three soils under different types of use were incubated for 42 days under different moisture conditions and temperature. Their results for forest and grassland soils are shown in Fig 2.8. They found that in general, optimal moisture content for nitrogen mineralization was between 80% and 100% of field capacity and that net mineralization increased with temperature. They noted, however, that the effect of moisture on N mineralization was lower than that of temperature.

Many studies that have investigated the effect of water content and temperature on N mineralization have either investigated the effect of water content at optimum temperature (e.g. Myers et al., 1982) or the effect of temperature at optimum water content (e.g. Ellert and Bettany, 1992). They have assumed that there is no interaction between these variables. But studies such as that by Knoepp and Swank (2002) found a significant interaction effect between water content and temperature for N mineralization. Their experiment was, however, on soil organic matter, and it still has to be ascertained if the same holds true for surface applied residues such as sewage sludge. Indeed Quemada and Cabrera (1997) found that the effects of temperature and water content on N mineralization from soil organic matter were different from the effects those variables had on mineralization of N from surface-applied residues. Agehara and Warncke (2005) concluded from their results, that soil temperature and water content influence N release from organic materials differently depending on source of N. The interaction effects between water content and temperature on the release of nitrogen from sludge is therefore, an area needing research.

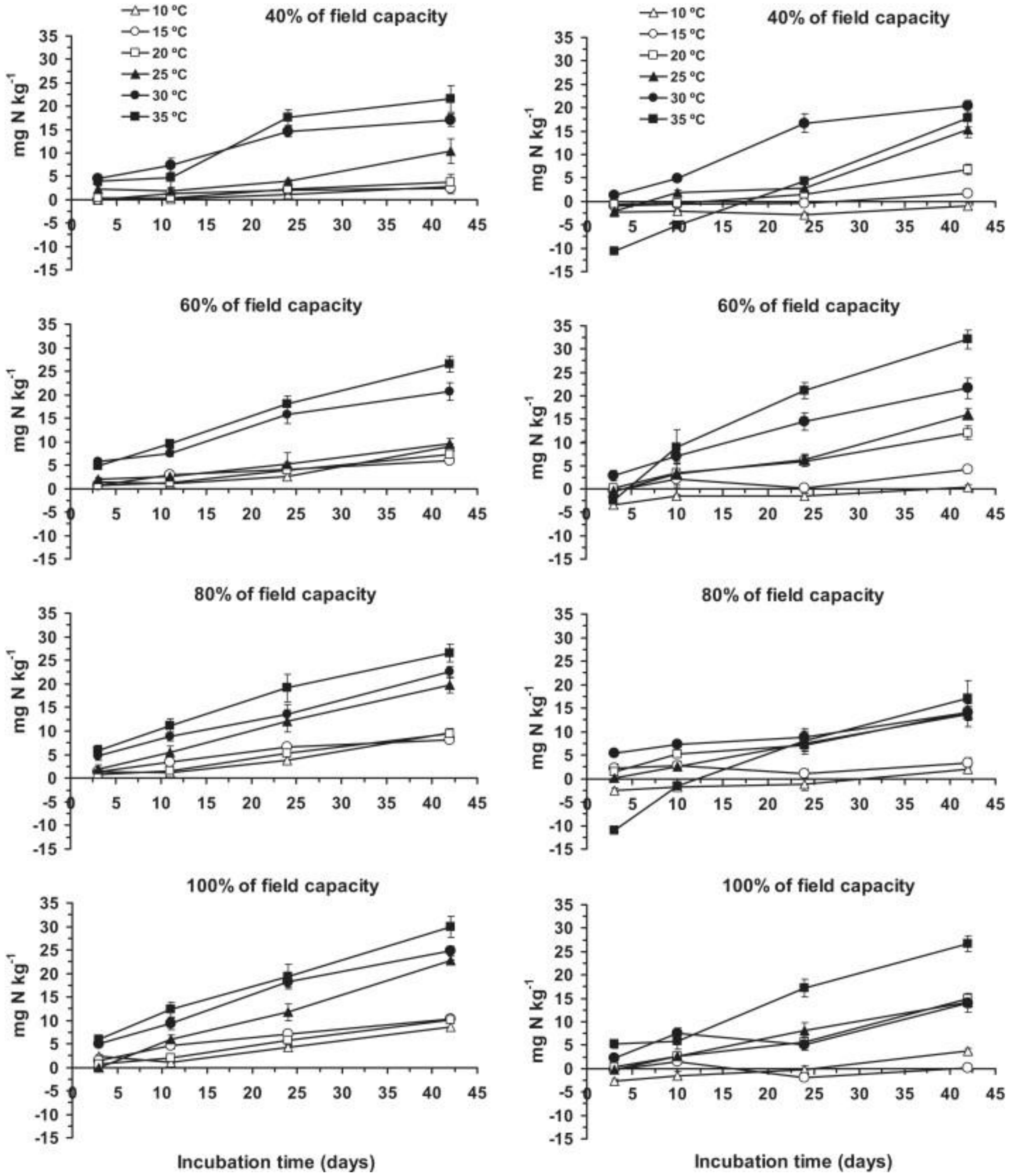

Fig 2.8 Variation in the values of mineralized nitrogen in a 42 day laboratory incubation of forest soils (graphs on left side of page) and grassland soils (graphs on right side of page) kept under different conditions of moisture and temperature (Guntiñas et al., 2012).

2.6 Predicting release and transport of nitrogen using mathematical models

The thin line between beneficial and hazardous implications of applying sludge in agriculture and rehabilitation purposes coupled with the impracticality of continuous experimentation makes use of mathematical modelling a helpful tool to predict the possible consequences of sludge-amending porous media.

Being able to predict future outcomes of management practices is an expertise that has pushed back the frontiers of science in recent years. Many natural processes are complex and the quest to simplify them into predictable pathways has peaked in many fields of science, especially in agriculture and environmental science. Even more important is the fact that some chemical changes, although measurable, may be slow, and it is not always feasible to wait before making decisions and recommendations.

Estimating how much of a nutrient is capable of being released from soil amendments is especially critical, not only because resources are scarce, but also because excess release could create serious environmental challenges. Annandale et al. (1999) pointed out that computer models are useful tools for predicting environmental consequences of management practices.

The development of a mathematical model generally involves three steps (Manzoni and Porporato, 2009):

i. definition of the variables of interest
ii. identification of inputs, outputs, and possible interactions

iii. model verification.

Modelling thus involves detailed experimentation, generation of the model, and more experimentation to validate the model or compare predictions with observations. Elliot et al. (1996) coined the phrase “modelling the measurable and measuring the modelable.”

2.6.1 Modelling nitrogen mineralization from sludge

Models have been used to predict the release of elements from sludge, especially nitrogen because of the importance of this element, its high content in sludge, and the risk for nitrate leaching when nitrate generation exceeds plant uptake. Estimating how much nitrogen is released from organic materials is critical both from an economic and an environmental perspective.

The costs and difficulties associated with measuring N release parameters from soil or organic materials has caused growing interest in the use of mathematical models to guide the application of N to soils (Lotse et al., 1992). Consequently, many nitrogen models have evolved in recent years.

Manzoni and Porporato (2009) have shown the increase over the years, in the number of models that describe carbon and nitrogen release (Fig 2.9). These models differ not only in the teams that developed them, but also in the approaches they follow in predicting N release.

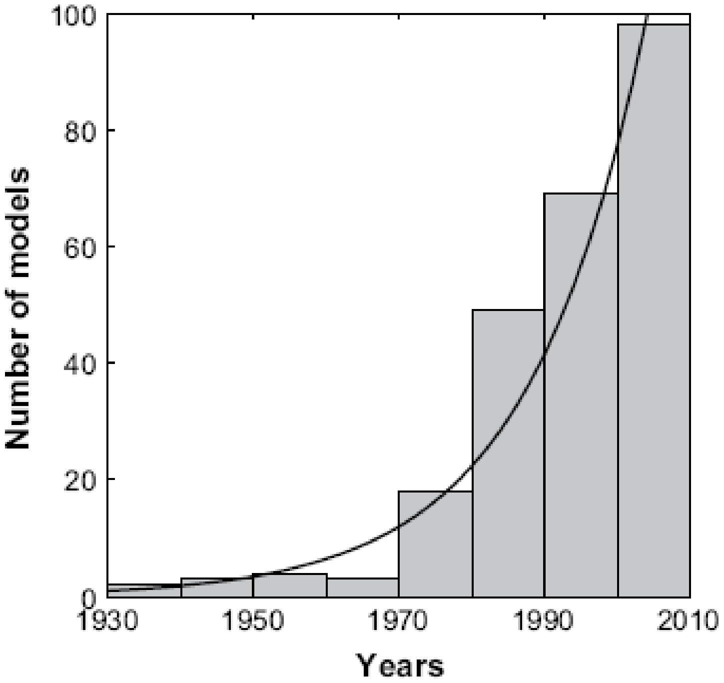

Fig 2.9 Trend in the number of carbon and nitrogen models since 1930 (Manzoni and Porporato, 2009)

Stanford and Smith (1972) were among the first to suggest a mathematical equation to predict nitrogen release from organic materials. However, since then, debate about how best to model nitrogen release has raged among researchers and modelers alike. The problem is exacerbated by the fact that a number of soil and environmental factors, some of which are poorly understood, control the fate of nitrogen in soils and thus complicate its prediction. Researchers have argued over the following important questions: (a) Is N mineralization a zero or first-order kinetic reaction? (b) Is estimation of N mineralization best described by a single or multiple pool approach? (c) Should N modelling follow an empirical or more mechanistic approach? Brief discussions on these questions follow.

(a) Is N mineralization a zero or first-order kinetic reaction?

Chemical kinetics deals with the rate at which a reaction takes place. For most reactions, rate is related in some way to the concentration of the reactants. Order of reaction can only be determined experimentally. For first order reactions, the rate of reaction varies directly with the concentration of the reactant raised to the first power. In other words, the reaction rate will be doubled by doubling the concentration of the reactant.

Rate = k(A)............................. eq (2.1)

Where (A) is concentration of reactant and k is a rate constant derived from experiments and modified to account for changing environmental conditions.

If the rate is increased by a factor of four when the concentration of the reactant is doubled, we have a second order reaction.

Rate = $k(A)^2$…………................eq (2.2)

For a zero-order reaction, rate of formation of product does not depend on the concentration of reactants (Brady and Humiston, 1986).

There has been debate by researchers on the kinetics of mineralization of N from organic materials. A number of researchers have predicted N mineralization by first order kinetics. One of the earliest was Stanford and Smith (1972) who described soil N mineralization potential as the amount of organic N susceptible to mineralization at a rate of mineralization (*k*) according to first-order kinetics:

$dN/dt = -kN$...................................eq (2.3)

Where N is the amount of mineralizable substrate, and t is time. Integration of eq (2.3) between time t_0 and t, gives:

$N_t = N_0\exp(-kt)$…………………….....eq (2.4)

Where N_0 is the initial amount of substrate or the potentially mineralizable N, and N_t is the amount of substrate remaining at time t.

A modification to eq (2.4) may be made by substituting $N_t = (N_0-N_m)$, where N_m is the accumulated N mineralized in time t. This yields

$N_m = N_0\,[1-\exp(-kt)]$……………....eq (2.5)

N_0 is assumed to be a pool of readily-mineralizable N which is mineralized at a rate proportional to the size of the pool (Sierra, 1990; Benbi and Richter, 2002).

The more recent authors who have predicted N release using first order kinetics include: Pansu et al. (1998); Pansu and Thuriès (2003); and Marinari et al. (2010). The models, SUNDIAL, EPIC and SOILN adopt first-order kinetics in simulating nitrification (Cannavo et al., 2008).

However, other studies have reported that first order kinetics does not adequately describe N mineralization. For example, Lindemann and Cardenas (1984) found it unsuited to describe N release from sludge-amended soils. Seyfried and Rao (1988) also report a poor fit of a first order model to experimental data.

Stenger et al. (1995) in a 5 month long incubation experiment reported that N mineralization could best be described by zero-order kinetics. Pansu et al. (1998) also observed that accumulation of nitrates in incubation studies reflected zero-order kinetics. RZWQM, NLEAP and NCSOIL are some of the models that follow zero-order kinetics (Cannavo et al., 2008).

A mixed first and zero order model has also been suggested. For example, Li et al. (2003) found that a two-component mixed first and zero-order exponential model gave better prediction of N mineralization than one-component and two-component first-order exponential models. Seyfried and Rao (1988) also attested to the improved accuracy of predicting N mineralization using a combined first order-zero order model. This combined model can be expressed as:

$N_m = N_1[1-\exp(-k_1t)\ ] + Kt$…………….eq (2.6)

Where N_1 is the amount of mineralizable N in the easily decomposable pool at the start of incubation and k_1 is the rate constant; K is the zero-order rate constant (Benbi and Richter, 2002).

N mineralization following first order kinetics has in fact been suggested to result from wetting of air-dried soil samples at the start of incubation studies. When soil samples are dried, a sizable fraction of microbial biomass is killed. Upon rewetting, there is a flush of mineralization which may arise as a result of mineralization of the dead microbial biomass which is an N fraction that may have a high decomposition rate. This phenomenon explains why a greater flush of mineralization is usually observed in the initial periods of incubation experiments using rewetted dried samples (Benbi and Richter, 2002). As a result, some authors have suggested that this phenomenon will not be observed in soils that did not dry out completely. In that situation, N mineralization may follow zero-order kinetics only (Addiscott, 1983).

The above discussion suggests that first-order kinetics may be suitable for describing N release from organic materials in incubation studies because of the phenomenon of mineralization flush upon rewetting. In reality, however, the goal of incubation studies usually, is to predict N dynamics in agricultural fields kept moist most of the time, a condition for which zero-order kinetics may be better suited. It might be safe to say, however, that a combined first and zero order kinetic model may be more accurate in modelling nitrogen mineralization because of the fluctuating drying and wetting cycles observed in the field. Ducheyne et al. (2001) for example, have found a mineralization flush in a field amended with pig slurry at the beginning of spring, leading to the underestimation of mineralization by their model. The fact that the majority of existing models adopt either first or zero order kinetics calls attention to the need to develop more models that estimate N mineralization from a combination of the two.

(b) Is estimation of N mineralization best described by a single or multiple pool approach?

Models have followed either a single or multiple pool approach in predicting nitrogen release from organic materials. Stanford and Smith (1972) for example, adopted the single-fraction approach when they described soil N mineralization potential as the amount of organic N susceptible to mineralization at a rate of mineralization (*k*) according to first-order kinetics. However, the complexity of organic matter has long been recognized. Nikiforoff (1936) is thought to be the first to suggest that organic matter may contain pools with different turnover times (Manzoni and Porporato, 2009).

Some studies have shown that the single fraction approach may lead to erroneous estimates of the amount of N capable of being mineralized. Results from N release studies suggest that more than one N fraction or pool, with different decomposition rates needs to be considered for organic materials (Serna and Pomares, 1992). Henry et al. (1999) separated decomposition of sludge into rapid breakdown, moderate breakdown and slow breakdown fractions. Rowell et al. (2001) referred to these release pools as extractable, acid-soluble or acid-insoluble fractions. They are also called cellulose, hemicellulose and lignin-like fractions (Jouraiphy et al., 2005).

Smith et al. (1998b) found that a twin-pool approach gave a better description of nitrate production in sludge amended soil than a single pool function. Schomberg and Cabrera (2001) modified the CERES nitrogen model by allowing user input of three pools: carbohydrate, cellulose, and lignin pools. They found that simulations of nitrogen mineralization were improved after this modification to the CERES model (Fig 2.10).

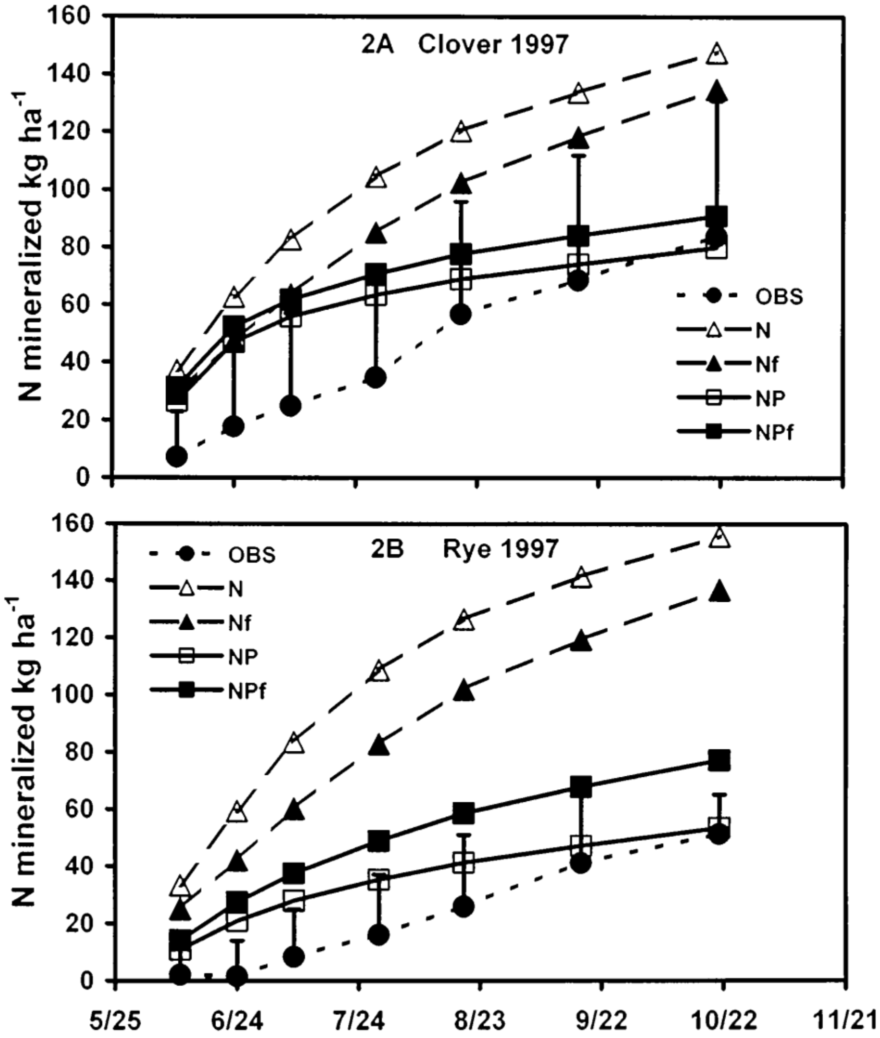

Fig 2.10 Prediction of N mineralization by the CERES model modified to include inputs of three organic matter pools. OBS, measured data; N, the original unmodified version; Nf, original version with field data derived rate constants; NP, version modified to allow user input of residue pool sizes with laboratory derived rate constants; NPf, pool version with field data derived rate constants (Schomberg and Cabrera, 2001)

It has become increasingly evident that better prediction of N release from organic materials may be achieved following a multi-pool approach. Many existing models have been modified in this regard. However, there are still questions regarding how many pools should be included. Should two pools be considered or will a three- pool model be more accurate? It can be argued that since the third pool, usually referred to as the lignified pool, could take decades to mineralize N, its inclusion for modelling N availability in agricultural land may be unnecessary since farms often operate short term fertilizer programmes. Knapp et al. (1983) for example, assumed that the lignin fraction was completely resistant to decomposition and did not include it in their model. Many models, however, lean towards a three-pool approach.

Benbi and Richter (2002) nevertheless warned that validation of models that employ a multi-compartment system is difficult, because most of the functional pools cannot be quantified by physical, chemical and/or biological techniques. Increasingly though, infrared spectroscopy has been shown to aid rapid determination of N fractions in organic amendments, for example Langkilde and Svantesson (1995).

(c) Should N modelling follow an empirical or more mechanistic approach?

Many workers have simulated N mineralization using empirically determined rate coefficients modified to account for changing environmental conditions. The parameters for models that adopt an empirical approach are obtained from laboratory incubation studies by fitting N mineralization data to the time of incubation (Benbi and Richter, 2002).

However, some models have followed a more mechanistic approach. Mechanistic models describe mechanisms and try to integrate N cycle processes and biological parameters into the model. For example, the models LEACHN (Acutis et al., 2000) and DNDC (Li, 1996) include microbial parameters to take nitrifier populations into account (Cannavo et al., 2008). But has the inclusion of processes made mechanistic models more accurate?

Smith et al. (1998b) have pointed out the complexity of mechanistic models integrating processes such as distribution of mineralizable N, cation exchange sites and colonies of microbes. They advised that until mechanistic models have been developed to a robust stage, the empirical approach should suffice to predict mineralization in biosolid-treated soils.

After a review of 62 nitrogen models, Cannavo et al. (2008) stated that whichever N process simulated, they did not observe a lower performance for empirical models compared to the more mechanistic ones. They concluded that empirical approaches, with fewer and more accessible input data, can be as accurate as mechanistic models. They also noted that mechanistic models may lead to a large number of parameters that are difficult to assess and that the biological processes which they include are still not well understood. Pansu et al. (1998) also report that the increase in parameters with mechanistic models makes this approach rather inconvenient. The difficulty in parameterizing mechanistic models has made modelers shift towards adopting an empirical approach. Besides, there is a wide range of disparity between mechanistic models, in the degree of sophistication of the processes simulated. This could lead to varying results (Gabrielle et al., 2002).

2.5.2 Modelling solute transport in sludge-amended media

Not only have models been used to estimate release of nutrients and elements from sludge, but mathematical modelling has also been used to estimate the rate at which elements from substances applied to porous media move down the profile. Prediction of movement of solutes within porous media has been propelled by the concern that pollutants such as metals and nitrates pose to groundwater.

Transport of solutes is governed by a complex interaction between several processes (Seuntjens, 2000):

i. The movement of water through the medium by convection
ii. Displacement of solutes due to a concentration gradient (molecular diffusion) and to the irregular flow paths causing small-scale variations in pore water velocity (dispersion)
iii. Chemical reaction of the dissolved solute with the solid phase of the medium (retardation or immobilization) or distribution of the solute between solution and gas-phase (volatilization) and/or
iv. Degradation of a degradable compound or decay of a radio-active element.

The advection-dispersion equation is the most commonly used to describe contaminant movement in porous media. Many existing transport models have been poor in predicting solute transport because they do not consider interactions among elements in solution, speciation effects and implications of soil surface properties such as cation exchange capacity. On the other hand, many geochemical models while taking these chemical interactions into account, are weak in predicting movement of solutes except when coupled with a transport model. Dissolution/precipitation and adsorption/desorption are the most important processes affecting solute interaction with porous media. Dissolution/precipitation is more likely to be the key process where chemical non-equilibrium exists while adsorption/desorption is likely to be key where chemical equilibrium exists (Dawood, 2007).

2.7 Conclusions

Proper disposal of sludge could become one of the greatest problems facing municipalities in modern times. This, coupled with the increasing prices of commercial fertilizer has given impetus to the use of the material as a cost effective soil amendment for agricultural soils. Its chemical properties have also made it a useful product in land rehabilitation. However, caution has to be exercised with land application of sludge so that constituent elements do not become a risk to the environment. For this purpose, accurate mathematical modelling of nutrient release and transport is valuable.

Before evaluating nitrogen dynamics in sludge-amended coal gasification ash, it is useful to determine maximum application rates above which environmental risks due to trace elements are most likely. This was done using column leaching techniques and is the focus of the next chapter.

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Chapter 3: Establishing a realistic sludge application rate based on trace element solubility in sludge-amended coal gasification ash

Abstract

Use of sludge or fine ash to amend coarse coal gasification ash dumps may aid plant establishment and subsequent rehabilitation. However, an investigation of changes in the solubility of potentially toxic elements is critical to determine the safety of such a management option. In this study the solubility of elements was evaluated in a column experiment after coal gasification ash was amended with 0, 10, 20, 30, 40 and 50% organic industrial sludge or fine ash (wet mass/wet mass) and treatments were made to undergo ten leaching cycles equivalent to 1270 mm of rainfall over a period of 12 months. Total elemental release showed that amendment of coarse ash with sludge may reduce leachate amount of Al, Cr and Pb. However, As, Cd, Fe, Ni and Se may be elevated, with As, Cd and Se being of major concern due to their environmental toxicity and observed concentrations. Increases in the solubility of certain elements with increasing sludge percent is attributed to phenomena such as pH reduction or ligand promoted dissolution; while decreases may result from metal retention by functional groups associated with organic matter, or precipitation of these elements in mineral phases. Amendment of coarse ash with fine ash did not reduce leachate amounts of any of the elements studied. They either increased as with Al, Cr and Pb, or remained largely unaffected. The study found that with respect to trace element release, up to 30% (wet mass/wet mass, equivalent to 5%) sludge addition may be safe for amending coarse coal gasification ash.

Key words: *coal gasification ash, fine ash, heavy metals, PHREEQC, rehabilitation, sludge*

3.1 Introduction

Safe disposal of coal gasification ash generated by the process of producing synthetic fuel from low grade coal, has been a huge challenge to industry for many years. Worldwide, there are about 160 modern gasification plants in operation that produce syngas, oxy-chemicals, methanol, hydrogen, and electricity (Minchener, 2005). The coal gasification process produces synthesis gas (a mixture of carbon monoxide and hydrogen) from low-grade, medium rank C (bituminous) coal and extraneous rock fragments, usually carbonaceous shale, siltstone, sandstone and mudstone (Matjie et al., 2005). The process which takes place in gasifiers at elevated temperatures greater than 1350 ºC and pressures exceeding 2 MPa, generates a co-product called gasification ash, also known as coarse ash. This waste comprises of particles varying from fine materials to irregularly shaped aggregates ranging from 4 mm to 75 mm in size (Matjie and van Alphen, 2008).

Although coarse ash has found usage mostly in the making of cement bricks, its use has been hampered by transport and handling costs. Consequently, most of the coarse ash generated is dumped in the vicinity of gasification plants. Rehabilitation of these coarse ash dumps has become imperative considering the toxic elements that with time, could leach down and pose a threat to groundwater. Moreover, small particles from ash dumps can be carried by wind, constituting a health hazard and degrading surface water bodies (Van Rensburg et al., 1998).

Use of topsoil to cap ash dumps has been suggested, but the depletion of the donor land's topsoil and the costs of transporting topsoil to coal ash sites are drawbacks to this management option. Recently, use of sludge to rehabilitate coal ash dumps has been proposed to help sustain vegetation on ash dumps by supplying needed plant nutrients and improving the water-holding capacity of the porous medium. The practice could also be a much safer sludge utilization option than the usual practice of sludge disposal through incineration.

The possibilities of mixing organic matter and coal ash have previously been explored. Van Rensburg et al. (1998) in an endeavour to revegetate a coal fine ash dump using organic and inorganic amendments reported that the addition of organic material resulted in better plant growth than inorganic fertilizer treatment alone. That positive effect may have been due to improved water infiltration, improved water holding capacity, increased macropore space, addition of nutrients and stimulation of microbial populations. A reduction of pH due to organic matter addition to the alkaline ash dump may also make for a more conducive medium for plant growth and survival (Van Rensburg et al., 1998).

These trials showed that mixtures of coal ash and sludge can indeed support vegetation, nevertheless, there is need to determine the effect these combinations have on the availability of the elements which are usual environmental problems associated with coal ash and sludge. Such investigation is critical in assessing the environmental implications of such a proposed management option.

Observations from researchers with respect to heavy metal solubility after amendment of metal-rich media with sludge have varied. Studies such as that by Urasa and Macha (1999) and Basta et al. (2001) have shown that sludge has a high affinity for heavy metals, and could reduce their extractability and bioavailability in metal rich media such as coal ash. Organic matter has a high affinity for metal cations due to the presence of ligands or functional groups such as carboxyl, phenolic, hydroxyl, and carbonyl groups. As pH increases, H^+ dissociates from these functional groups thereby increasing their affinity for metal cations (Park et al., 2011). Sludge may also remove metals by means of precipitation/co-precipitation of these metals as hydroxides, carbonates and sulfides (Andrés and Francisco, 2008). Other researchers such as Al-Webel et al. (2002) and Clemente et al. (2006) have reported greater mobilization of metals after addition of organic wastes to soils or mine tailings, and have suggested greater mobility of these elements as organo-metal complexes. The effect of sludge on element solubility might also be element and medium specific. For example, Andrés and Francisco (2008) observed the retention of Cu, Pb, Fe and Mn and the mobilization of Ni and Zn after sludge addition to mine tailings.

This study investigates changes in metal solubility as a result of amending coarse coal gasification ash with organic industrial sludge. Results are mirrored against metal solubility changes resulting from amending coarse coal gasification ash with fine ash, another byproduct of coal gasification. Co-disposal of coarse ash with fine ash has been suggested as holding promise with respect to retention of water in coarse ash dumps since the finer texture of fine ash and its cementing properties may retard the movement of leachate down the ash dump (de Jager et al., 2013).

In this study, these phenomena are investigated for coal gasification ash using a column set up. Column leaching experiments are a common way of investigating in the laboratory, movement of materials down the profile of soil or any growth medium and have also been applied to studies involving coal ash (Singh and Paul, 2001; Wang et al., 2008). Reemtsma and Mehrtens (1997) noted that compared to static batch tests, column leaching procedures appear to be closer to natural conditions. Moreover, Wang et al. (2008) observed that column leaching strips the most mobile elements initially, which does not leave these in solution for continued interaction with other elements as is observed in batch leaching. Column experiments have been known to simulate field conditions more precisely than the USEPA toxicity characteristic leaching procedure (TCLP) (Navarro et al., 2011; Chotpantarat et al., 2011).

Column leaching experiments were performed under controlled laboratory conditions, the aim of which was to determine the effect of co-disposing coarse ash with sludge or fine ash on the solubility of select trace elements. Special attention was paid to those elements which from literature are considered to be either of major concern (As, Cd, Pb, and Se) or of moderate concern (Cr, Ni) with regards to pollution from coal combustion by-products (Yunusa et al., 2006). Aluminium and Fe have also been discussed. It is hypothesized that up to a certain sludge rate will reduce concentrations of trace elements in leachates from coal gasification ash. Above this sludge rate increases in trace element solubility might be observed. The overarching goal is to find this sludge limit in order to make recommendations with respect to co-disposal of coal gasification ash and sludge.

3.2 Materials and methods

3.2.1 Origin and characterization of materials

Coarse coal ash and fine ash were collected from freshly dumped sites while fresh sludge was collected from a wastewater treatment plant in close proximity to the ash sites. The sludge is an aerobically activated sludge originating from industrial coal gasification waste streams. Gravimetric water content of these materials was 15.5% for coarse ash, 36.3% for fine ash and 89.8% for sludge. Characterization and concentrations of some elements in these wastes determined after microwave digestion and inductively coupled plasma mass spectrometry (ICP-MS) analyses are listed in Table 3.1. The particle size distribution of coarse and fly ash has been reported by Sukati (2012) using the sieve method (Non-affiliated Soil Analysis Working Committee, 1990), and is shown in Appendix 1.

Table 3.1 Characterization of coarse ash, fine ash and sludge

Parameter	**Coarse Ash**	**Fine ash**	**Sludge**
pH	10.8	> 12	6.8
Volatile Solids (%)	4.6	16.9	82.4
Total N (%)	< 0.04	0.04	7.9
Total C (%)	5.7	2.67	56.3
C/N Ratio	-	66.8	7.1
Ca (%)	7.22	5.36	0.58
Mg (%)	1.51	1.42	0.26
P (%)	0.33	0.33	0.46
K (%)	0.02	0.02	0.1
Na (%)	0.34	0.39	0.09
Fe (%)	2.88	12.0	0.6
Al (%)	12.1	10.5	0.31
As (mg kg^{-1})	10.7	8.7	29.7
B (mg kg^{-1})	202	117	34
Cd (mg kg^{-1})	0.41	0.31	0.22
Co (mg kg^{-1})	33	135	2.2
Cr (mg kg^{-1})	135	266	55
Cu (mg kg^{-1})	58.3	51.7	18.2
Mn (mg kg^{-1})	280	814	90
Mo (mg kg^{-1})	4.3	4.2	5.36
Ni (mg kg^{-1})	25.7	36.8	10
Pb (mg kg^{-1})	26.7	20.1	5.09
Se (mg kg^{-1})	<0.1	<0.1	536
V (mg kg^{-1})	117	118	143
Zn (mg kg^{-1})	12.3	25.8	146

3.2.2 Preparation of treatments and column set up

Combination of waste materials was done on a wet mass basis. This approach was followed mainly because practically, it might be unrealistic to dry waste materials on site before co-disposing them. The mixtures were made on a percent basis. Coarse ash was amended with 0, 10, 20, 30, 40, and 50% sludge or fine ash (wet mass/wet mass). The treatments were mixed thoroughly in a concrete mixer and packed in columns at a uniform wet bulk density of 1200 kg m^{-3}. This density was an approximation of the density of actual coarse ash dumps.

The column set up consisted of 300 mm long transparent polyethylene columns, with an internal diameter of 105 mm and a wall thickness of 3 mm. The transparency of the columns allowed visual examination of the progress of the wetting front and the detection of any preferential flow channels along the walls of the column (Andrés and Francisco, 2008). The column diameter was at least 30 times the maximum particle size of the waste materials in order to minimize the problem of channeling in the columns (Relyea, 1982; Andrés and Francisco, 2008). A series of filters consisting of five layers of filter material was placed at the base of the column in order of decreasing pore size. The first layer directly in contact with the mixture was a 2 mm polypropylene mesh. This was followed by three nylon meshes with pore sizes of 25, 10 and 5 µm. The last mesh at the outflow boundary was again, a 2 mm polypropylene mesh. A Schott Duran glass bottle that can screw in at the bottom of the column base was used to collect leachates. The columns were fitted with suction valves connected to a vacuum system to aid downward movement of leachates. The entire structure was mounted on workbenches (Fig 3.1).

Fig 3.1 The leaching column set up

3.2.3 Leaching and analysis of leachates

Amount of water to leach with was based on the calculated porosity of the media. For all the mixtures a pore volume of about 1100 cm^3 was calculated. Ten wetting and drying cycles over a period of 12 months were simulated. In each case, an amount of distilled water equivalent to one pore volume was passed through the columns. This amount of water translates to about 127 mm of rainfall per leaching cycle and a total of 1270 mm for the ten leaching cycles.

The free drained leachates were collected after 24 hours and remaining water was sucked out at about -10 kPa using a vacuum pump. All samples were subjected to membrane filtration

(0.45 µm) to minimize colloidal interference. EC and pH of leachates were determined and leachates were stored below 4 ºC until analyzed. Treatments were left to air-dry before the subsequent wetting cycle.

Concentration of elements in leachates from each wetting cycle was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The accuracy of results for ICP problematic elements such as As and Se was verified in spiked solutions of known concentrations of these elements.

The cumulative total elemental release (mg kg^{-1}) over the ten leaching events was calculated, and concentrations of the elements (mg ℓ^{-1}) from each leaching cycle were compared with international drinking water standards.

Hydrogeochemical analyses of the first leachates were done to determine the speciation of dissolved constituents and calculate the saturation indices of anticipated mineral phases. This was carried out with the geochemical model PHREEQC (Parkhurst and Appelo, 1999) using the Minteq.v4 database.

3.3 Results and discussion

The release of metals from ash dumps is a concern when potential utilization or disposal may impact surface water or groundwater. Groundwater serves as drinking water for billions of people worldwide (Hashim et al., 2011). Although the column leachate is not a substitute for potable water, drinking water standards are frequently applied to categorize potential hazards (Appelo and Postma, 2005; Kim, 2009), and these standards have been used in this study as well.

3.3.1 Aluminium, Arsenic, Cadmium and Chromium

Fig 3.2 shows the effect of coarse ash amendment with sludge or fine ash on total Al, As, Cd and Cr release per mass of mixture over ten leaching cycles; while Fig 3.3 shows the concentration of these elements in leachates from each of the ten leaching cycles.

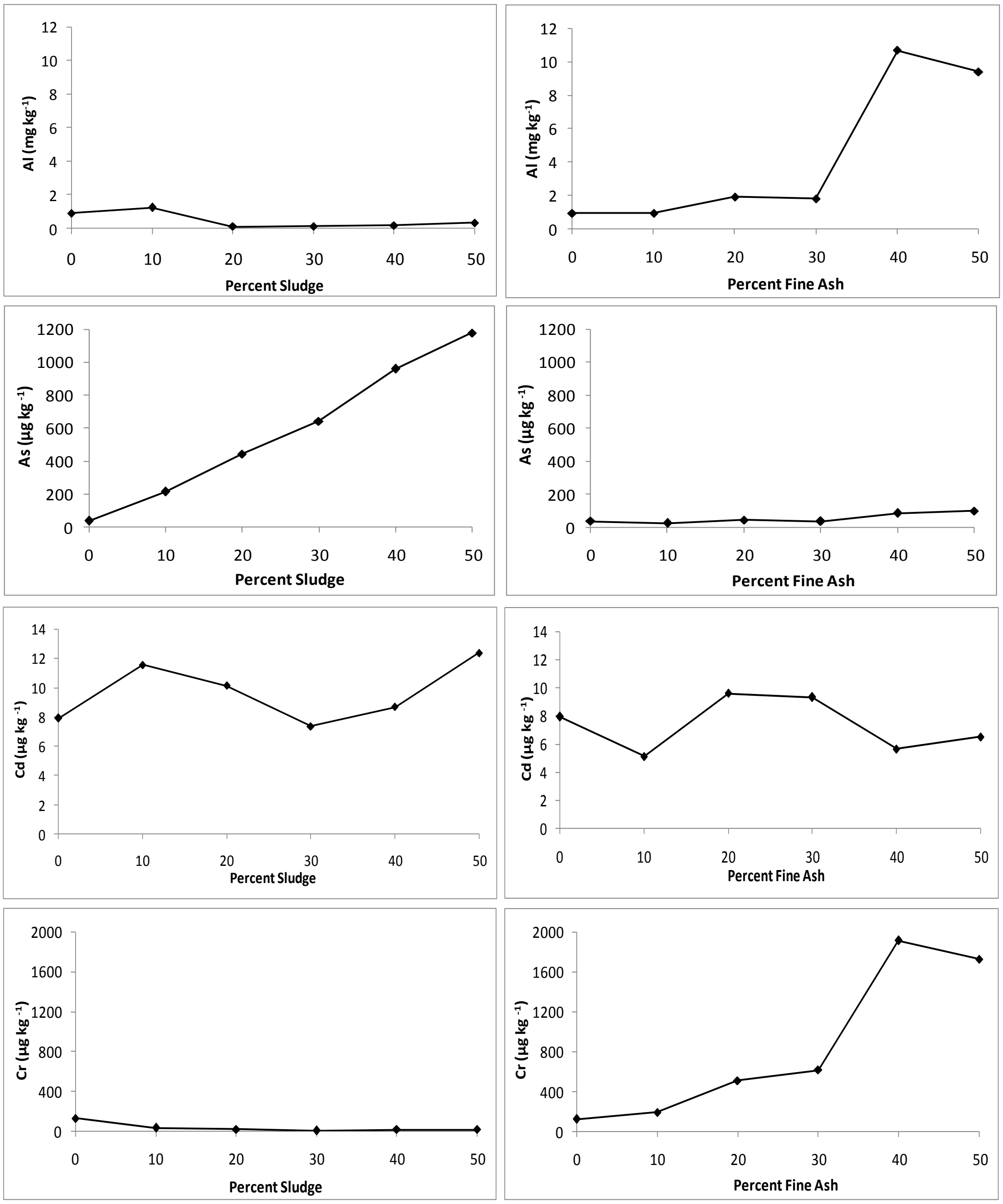

Fig 3.2 Effect of coarse ash amendment with sludge or fine ash on total Al, As, Cd and Cr release per mass of mixture over ten leaching cycles

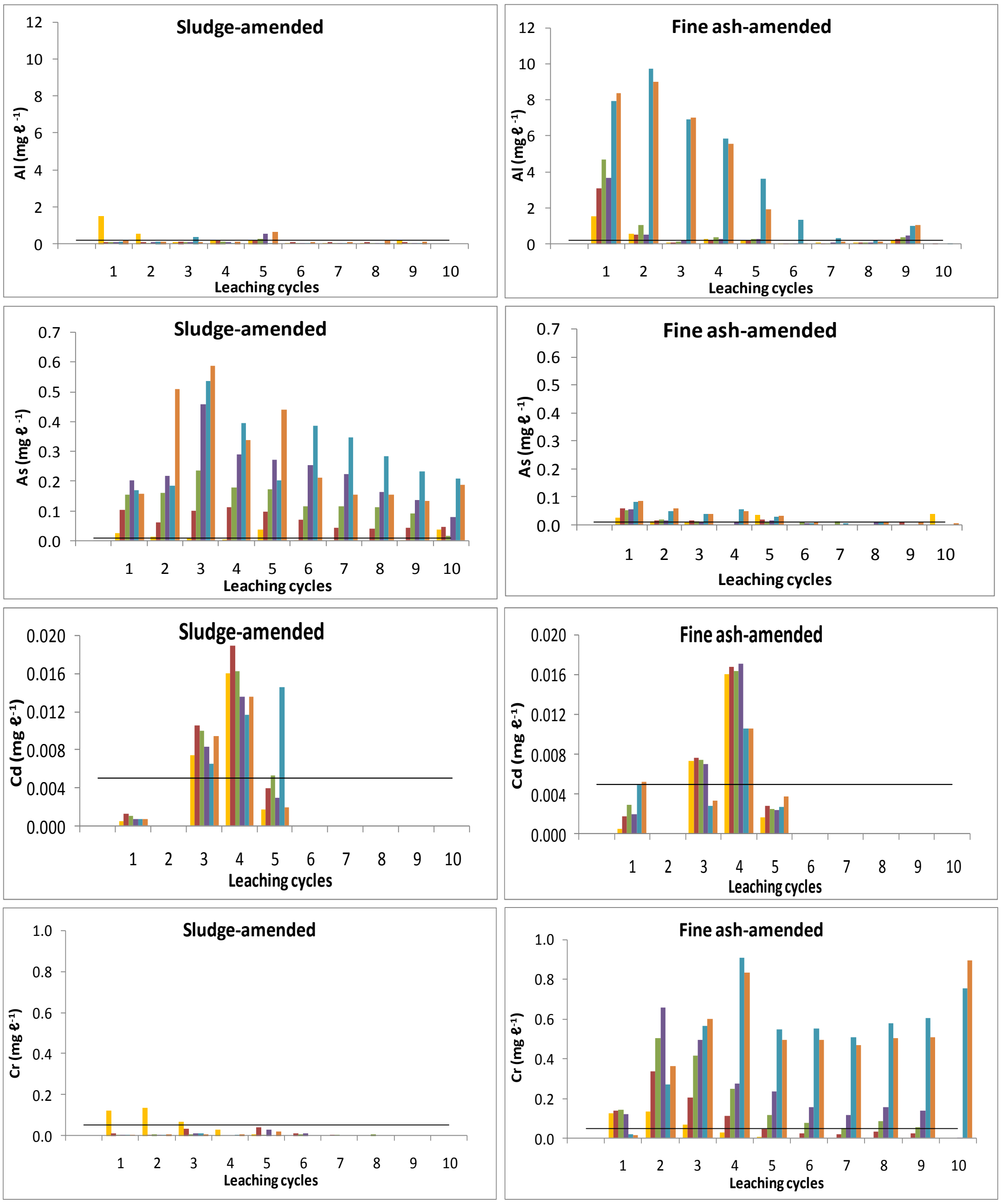

Fig 3.3 Concentration of Al, As, Cd and Cr in leachates after amendment of coarse ash with sludge or fine ash.
🟨 = unamended coarse ash; 🟥 = 10% amendment; 🟩 = 20% amendment; 🟪 = 30% amendment; 🟦 = 40% amendment; 🟧 = 50% amendment. Horizontal line indicates international allowable maximum concentrations for drinking water.

Aluminium showed a slight decline with increase in percent sludge, and a rapid increase with increasing fine ash percent (Fig 3.2). Fine ash may have contained appreciable quantities of leachable Al. Moreover, since Al solid phases such as Al_2O_3 or $Al(OH)_3$ are amphoteric, their solubility will increase at high as well as at low pH, exhibiting the lowest solubility at a neutral pH. The pH of treatments for the first and last leaching cycles is shown in Fig 3.4. Amendment with fine ash kept the system highly alkaline. The increase in pH resulting from addition of the more alkaline fine ash, therefore, may have contributed to the liberation of Al. A maximum of 10.7 mg kg $^{-1}$ was recorded for 40% fine ash.

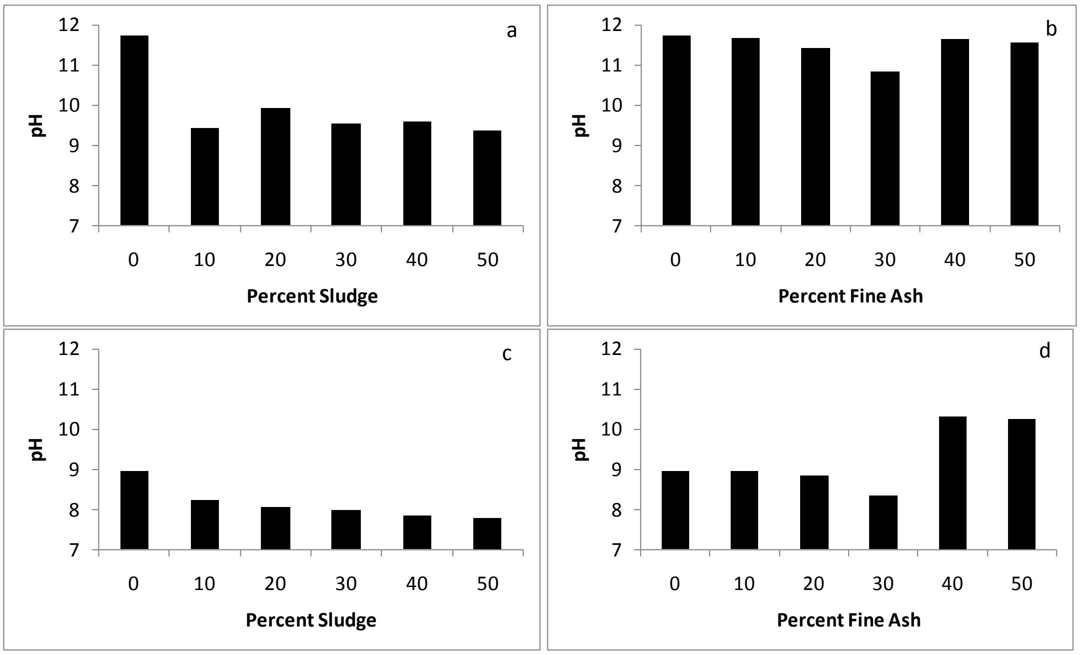

Fig 3.4 pH trend for sludge and fine ash-amended coarse ash for the 1st leaching cycle (a and b) and the 10th leaching cycle (c and d)

Amendment of coarse ash with sludge reduced Al solubility. This decrease may have resulted from a reduction of pH with increasing sludge percent (Fig 3.4) or as a result of complexation reactions with functional groups in organic matter. Decrease in Al solubility in the presence of organic matter has been reported (Wesselink et al., 1996). Yagasaki et al. (2006) suggested that the low dissolution of Al minerals may be as a result of the alteration of the physico-chemical characteristics of their surfaces, caused by complexation with organic matter.

Reduction of Al with sludge amendment may also be a result of precipitation of Al in mineral phases, probably diaspore. Saturation indices of mineral phases in the first leachates calculated with PHREEQC show increases in saturation index of certain Al mineral phases with increase in sludge amendment (Fig 3.5).

Saturation index (SI) is defined as

$\mathrm{SI} = \log\frac{\mathrm{IAP}}{\mathrm{Ksp}}$……………………………………Eq 3.1

Where IAP is the free ionic activities product and K_{sp} is the thermodynamic solubility product constant. If SI > 0, then the solution is supersaturated for that mineral and the mineral is expected to precipitate out of solution.

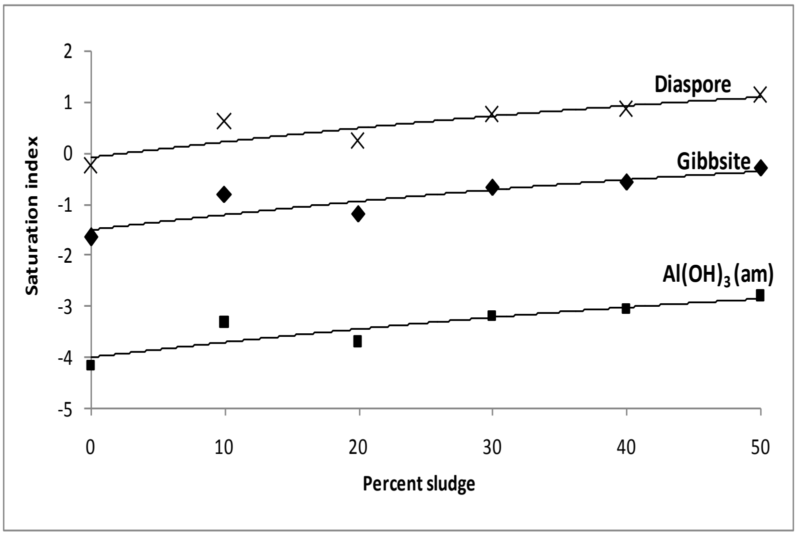

Fig 3.5 Change in saturation index of Al minerals with increase in percent sludge for first leaching cycle

Certain health problems such as neurological disorders have been linked to Al toxicity in drinking water (Wang et al., 2010). Guidelines stipulate a maximum of 0.2 mg ℓ $^{-1}$ in drinking water (Ikem et al., 2002) which was not exceeded by most sludge-amended treatments (Fig 3.3).

Arsenic levels in leachates were relatively unaffected by increments of fine ash except for 40 and 50% fine ash where there were slight increases (Fig 3.2). Arsenic, however, showed a consistent rise with increasing percent sludge from 36.87 µg kg $^{-1}$ at 0% sludge to 1178.93 µg kg $^{-1}$ at 50% sludge. Arsenic content of sludge (Table 3.1) was higher than As in coarse ash or fine ash. Therefore, the increase in As content in sludge-amended samples may have been due to the inherently high As content of sludge. It is important to note, however, that As leached even at the highest sludge percent was only a small fraction of the As content of the wastes (Table 3.1).

Increase in As solubility with increasing sludge may also result from dissolution related to functional groups in organic matter. At high pH, these functional groups are dissociated and become negatively charged with a more open configuration. Organic acids such as humic acids and fulvic acids may compete strongly with As(III) and As(V) for active adsorption sites on mineral surfaces. Moreover, the formation of soluble As complexes with organic matter may enhance As solubility. In general, organic matter may enhance the release of As through competition for available adsorption sites, forming aqueous complexes, and changing the redox chemistry of site surfaces and arsenic species (Wang and Mulligan, 2006). There is evidence that As release may be enhanced by the redox reactions between organic matter, As and substrates, leading to the reduction of As(V) to the more mobile As(III) (Redman et al., 2002).

Arsenic is probably the element that causes the most concern with respect to contamination of groundwater sources. At very minute concentrations serious health problems could be triggered, forcing authorities to stipulate a maximum limit of 0.01 mg ℓ^{-1} in drinking water (Tamasi and Cini, 2004). The metalloid has been linked to cancer of the skin, lung, bladder, kidney and liver (Smith et al., 1992).

Arsenic concentration in leachates was higher with sludge amendment than with fine ash for all leaching cycles (Fig 3.3). Concentration of As remained below 0.1 mg ℓ^{-1} for the treatments with fine ash. All the treatments including coarse ash alone, yielded As concentrations higher than the international maximum limit.

Toxicity of arsenic is dependent on its chemical form. Therefore, knowledge of its total concentration alone is not sufficient to assess its environmental impact. Arsenic can exist in the pentavalent state as arsenate or in the trivalent state as arsenite. Under oxidizing conditions in aerobic environments, arsenates are the more stable species. Arsenite is the more toxic, more soluble and mobile species (Wang and Mulligan, 2006), therefore, keeping the system under aerobic conditions may reduce As toxicity.

Cadmium was not affected by percentage sludge or fine ash in any distinct increasing or decreasing trend (Fig 3.2). Nevertheless, sludge-amended treatments had higher Cd levels in leachates. The highest amount of Cd leached was 12.4 µg kg $^{-1}$ recorded for 50% sludge amendment. Cadmium adsorption onto mineral surfaces can be substantially decreased by dissolved organic matter, especially at high pH (Robert, 1996).

Cadmium levels in leachates were initially low, then increased with the third leaching, and were finally undetectable after the fifth leaching (Fig 3.3). In the third and fourth leaching cycles, many of the treatments yielded Cd concentrations higher than the maximum level of 0.005 mg ℓ^{-1} (Yao et al., 2009).

Chromium concentration reduced slightly from 124.9 µg kg^{-1} with no sludge to a minimum of 3.5 µg kg^{-1} at 30% sludge (Fig 3.2). Metal uptake by sludge has been attributed to chemisorption processes involving organic ligands such as hydroxyl, carboxyl, and substituted aromatic functional groups found in natural organic matter; and to phosphate minerals e.g. apatite in sludge (Urasa and Macha, 1999). Cr concentrations, however, increased with increase in fine ash addition from 124.9 µg kg^{-1} with no fine ash to a maximum of 1918 µg kg $^{-1}$ at 40% fine ash.

Saturation index PHREEQC calculations of the first leachates show increases in Cr mineral phases with increasing sludge, and suggest that Cr_2O_3 and $Cr(OH)_3$ (am) may control the solubility of Cr in sludge-amended coarse ash (Fig 3.6). Under alkaline to slightly acidic conditions, Cr has been known to precipitate as $Cr(OH)_3$ (Banks et al., 2006).

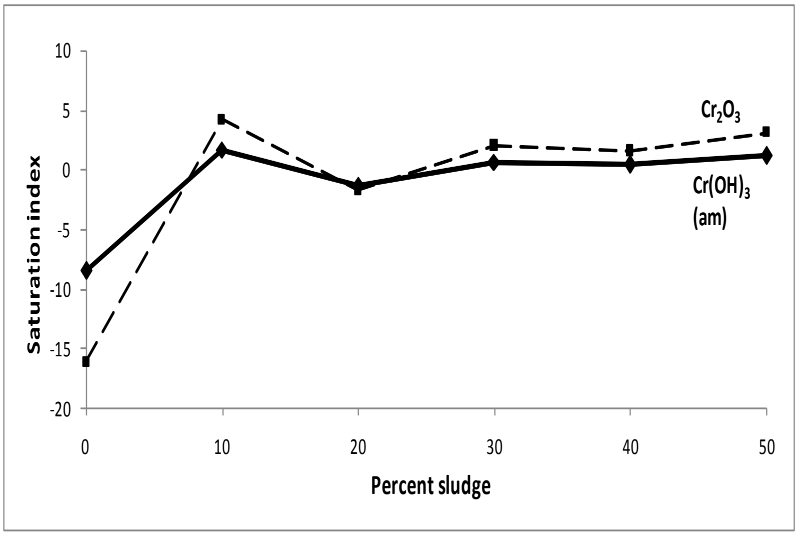

Fig 3.6 Change in saturation index of Cr mineral phases with increase in percent sludge for first leaching cycle

Cr exists in the +6 and +3 oxidation states with Cr(VI) being the dominant form of the element in alkaline media (Hashim et al., 2011). The trivalent cation has a strong affinity for negatively-charged ions and colloids and is therefore less mobile and less toxic (Yao et al., 2009). Organic matter has been observed to reduce Cr(VI) (Banks et al., 2006). In the sludge-amended treatments, where organic matter is abundant, there is expected to be a reduction of Cr(VI) and Cr will most likely be present as the less mobile Cr(III) (Bolan and Duraisamy, 2003).

Apart from the first leaching, there seemed to be an increase in Cr with increase in percentage fine ash (Fig 3.3), suggesting that fine ash does contain appreciable quantities of leachable Cr. The critical limit for total chromium is 0.1 mg ℓ^{-1} (Kim, 2009), and concentrations were lower than this for most sludge treatments. Chromium has been reported to be carcinogenic and exposure to Cr(VI) can lead to various point mutations in DNA and to chromosomal damage (Dayan and Paine, 2001).

3.3.2 Iron, Lead, Nickel and Selenium

Fig 3.7 shows the effect of coarse ash amendment with sludge or fine ash on total Fe, Pb, Ni, and Se release per mass of mixture over ten leaching cycles; while Fig 3.8 shows the concentration of these elements in leachates from each of the ten leaching cycles.

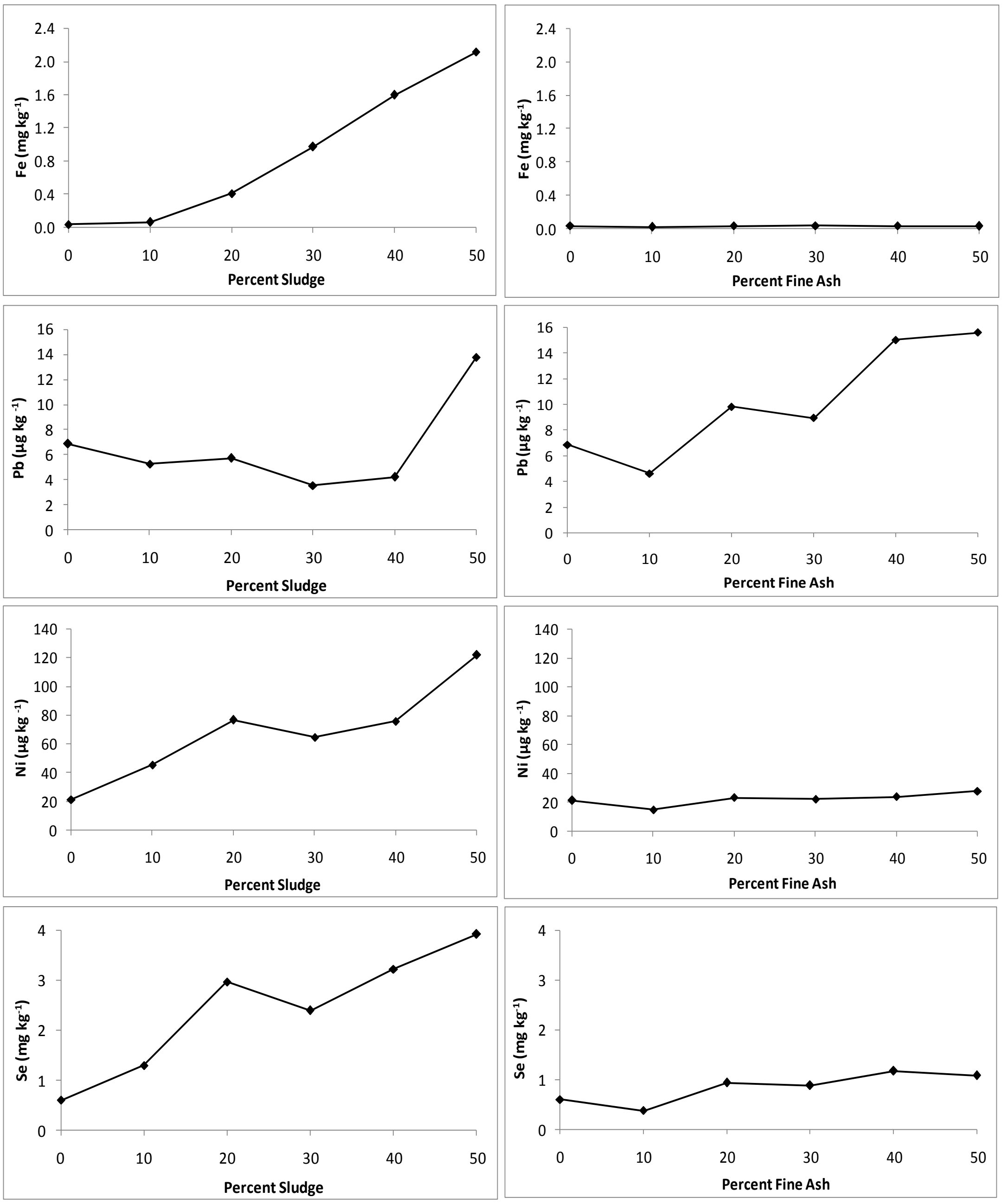

Fig 3.7 Effect of coarse ash amendment with sludge or fine ash on total Fe, Pb, Ni and Se release per mass of mixture over ten leaching cycles.

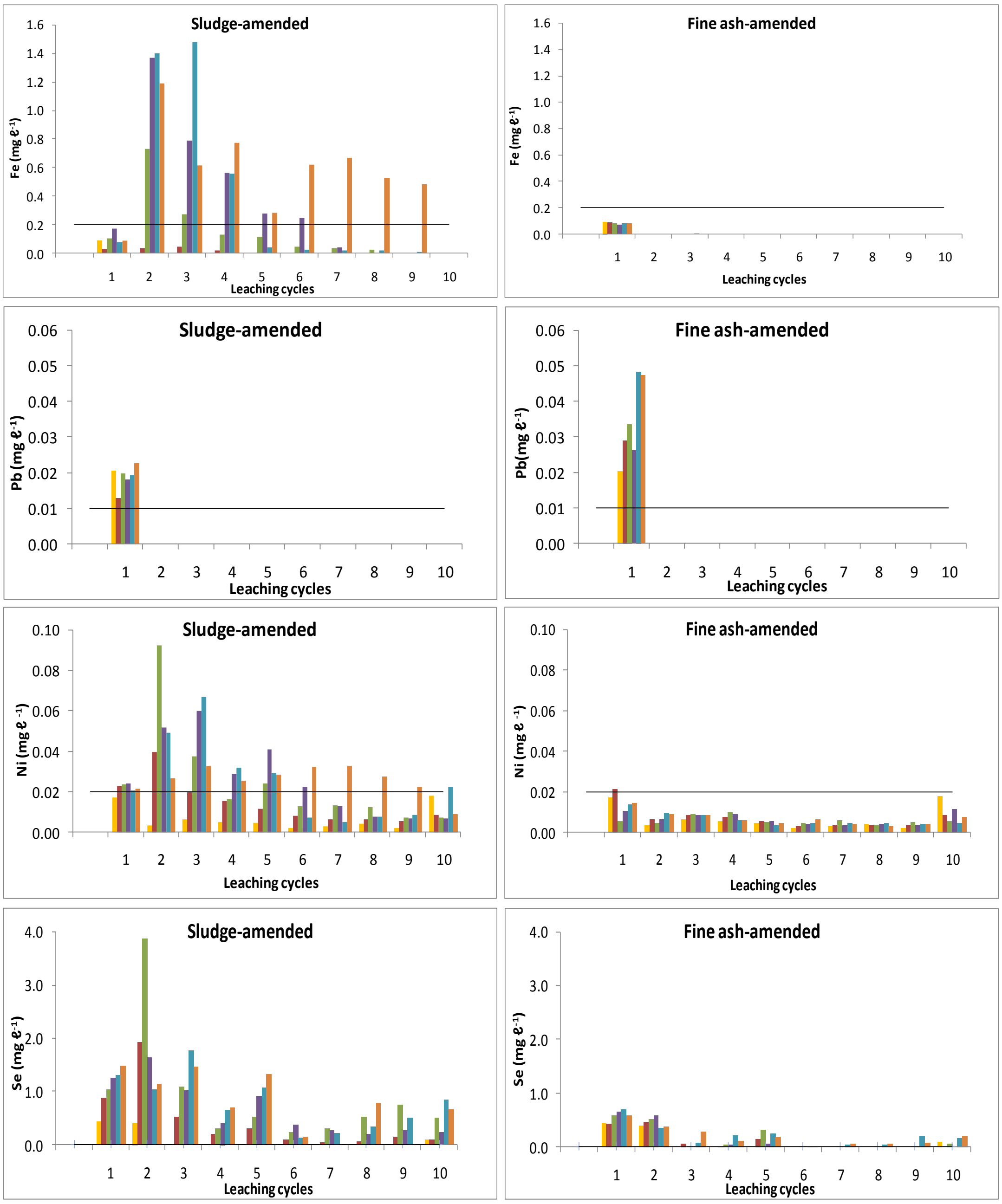

Fig 3.8 Concentration of Fe, Pb, Ni and Se in leachates after amendment of coarse ash with sludge or fine ash.

🟨 = unamended coarse ash; 🟥 = 10% amendment; 🟩 = 20% amendment; 🟪 = 30% amendment; 🟦 = 40% amendment; 🟧 = 50% amendment. Horizontal line indicates international allowable maximum concentrations for drinking water.

Concentration of Fe in leachates increased substantially with increase in percent sludge but remained largely unchanged with increase in fine ash (Fig 3.7). Leachate from unamended coarse ash had a concentration of 0.03 mg kg^{-1} Fe, and at 50% sludge the total amount of Fe in leachates reached a maximum of 2.12 mg kg^{-1}. Ferric iron is an important electron acceptor and therefore a redox sensitive element. It is hypothesised that the increase in iron release was caused by redox promoted dissolution of ferric (oxy) hydroxide solid phases present in the ash upon the addition of sludge. The reduced carbon in the sludge is a source of electrons and acts as an electron donor (reducing agent). When the mediums are saturated, oxygen diffusion is limited. When coupled with microbial respiration, pe values can potentially be suppressed to below 2. Under these conditions, ferric iron will be reduced to ferrous iron and this subsequently increases the solubility of ferric-containing minerals. The maximum allowable concentration of Fe in drinking water is 0.2 mg ℓ^{-1} (Tamasi and Cini, 2004). Leachates from fine ash amended treatments remained below this level (Fig 3.8).

Amendment of coarse ash with sludge initially decreased Pb in leachates, although only slightly (Fig 3.7). The total amount of Pb released from the mixtures decreased from 6.86 µg kg^{-1} in unamended coarse ash, to 3.51 µg kg^{-1} at 30% sludge (Fig 3.7). This is in agreement with results obtained by Andrès and Francisco (2008), when they observed that sludge has a high affinity for Pb in leachates from mine tailings. Urasa and Macha (1999) also reported that the metal uptake of composted sludge was particularly pronounced for Pb and attributed this behaviour to several mechanisms including ion exchange involving apatite ($Ca_{10}(PO_4)_6(OH)_2$) present in the sludge, in which case Pb is exchanged with Ca, forming very low solubility orthophosphate and resulting in the release of an equivalent amount of Ca in leachates. Lead forms sparingly soluble precipitates with phosphate and in the presence of aluminium and phosphate, highly insoluble solid phases, for example, plumbogummite ($PbAl_3(PO_4)_2(OH)_5 \cdot H_2O$) can form (Essington, 2004). Furthermore, Pb also exhibits an affinity for organic material, and complexes readily with functional groups associated with organic matter.

In a P-abundant environment, Pb mobility may be reduced by ionic exchange and precipitation of pyromorphite-type minerals (Park et al., 2011). In a low P environment, Andrès and Francisco (2008) suggested, after geochemical modelling, that Pb may be removed from solution due to the formation of stable phase minerals such as $Pb(OH)_2$ and PbS (under reduced conditions). It is expected that acidification will mobilize Pb because both $Pb(OH)_2$ and lead phosphate minerals are amphoteric and their solubility will increase at both high and low pH. This may have been the cause of the sharp increase in Pb at 50% sludge. The optimum pH range for Pb precipitation has been found to be about pH 10 (Navarro et al., 2011). PHREEQC saturation index calculations of the first leachates suggest that a reduction in Pb with increasing sludge may be due to precipitation of Pb as $Pb(OH)_2$ (Fig 3.9).

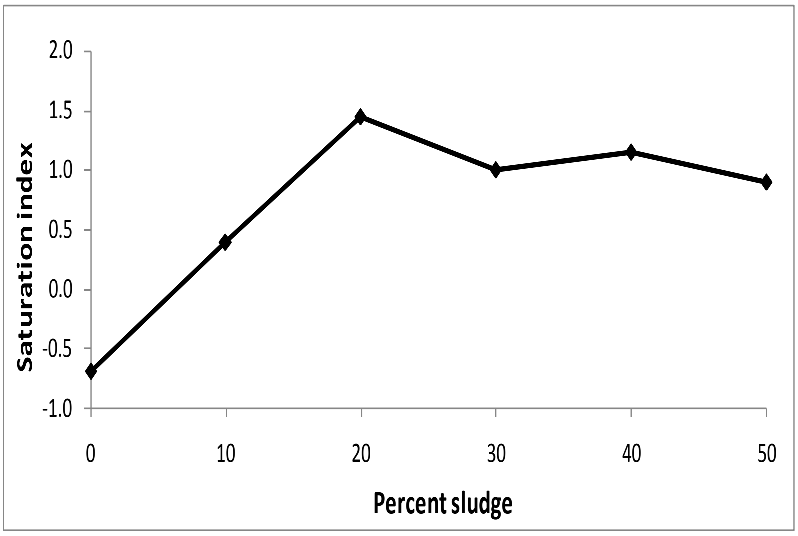

Fig 3.9 Change in saturation index of $Pb(OH)_2$ with increase in percent sludge for first leaching cycle

The pH of the treatments without sludge was highly alkaline (pH > 11 for the first leachate) (Fig 3.4) and the amphoteric character of the above mentioned solid phases could be responsible for the increase in Pb in leachates from fine ash amended treatments. An increase was recorded from 6.86 µg kg^{-1} with coarse ash alone up to a maximum of 15.6 µg kg^{-1} at 50% fine ash.

Pb concentration was below detection limits after the first leaching (Fig 3.8). All the treatments yielded concentrations higher than the critical level of 0.01 mg ℓ^{-1} proposed for drinking water (Yao et al., 2009). From an environmental toxicology point of view, Pb poisoning has raised serious health concerns around the world, and has been identified as the culprit of disorders of the peripheral and central nervous systems, especially in children (Cheng and Hu, 2010).

Nickel was relatively unaffected by increase in fine ash application, but showed a consistent rise with percentage sludge up to a maximum of 122 µg kg^{-1} at 50% sludge (Fig 3.7) in spite of the fact that sludge contained less Ni than coarse ash or fine ash (Table 3.1). A similar observation has been made by Andrés and Francisco (2008) when they reported the effect of sewage sludge on heavy metal leaching from mine tailings. They attributed the mobilization of Ni to migration of Ni as organic complexes. Most of the treatments with fine ash yielded Ni concentrations lower than the maximum critical value (Yao et al., 2009) of 0.02 mg ℓ^{-1} (Fig 3.8).

Selenium generally increased with sludge percentage, and only increased slightly with percentage fine ash (Fig 3.7). A maximum of 3.9 mg kg^{-1} over ten leaching cycles was observed at 50% sludge. Sewage sludge has long been recognized as a source of environmental selenium (Cappon, 1991), much more so if a significant contribution to the sludge is industrial wastewater. Selenium content of the sludge as shown in Table 3.1 is indeed high. International standards stipulate a maximum of 0.05 mg ℓ^{-1} in drinking water (EPA, 2006). Generally, leachates from all treatments exceeded this limit.

3.4 Conclusions

Coarse coal gasification ash dumps constitute a potential risk with regards to the movement of toxic elements down into the groundwater. In the quest to establish vegetation on coarse ash dumps, co-disposal with sewage sludge may increase the availability of both beneficial plant elements and potentially toxic ones, either by increasing their solubility due to a reduction in pH, or by the high concentrations of these elements in sludge. From literature, ligand promoted dissolution and redox reactions may be other pathways for increased solubility of elements. Amendment with sludge may also reduce the solubility and mobility of certain elements through phenomena such as metal retention by the organic and inorganic functional groups associated with natural organic matter or by the process of precipitation in mineral phases.

The following deductions can be made from this study:

1. The tested hypothesis was only true for Pb, Al and Cr. Co-disposal of coarse ash with sludge may reduce the amounts of these elements in leachates. However, the amounts

of Fe, Cd, As, Se and Ni in leachates may be elevated. Among these elements, As, Se and Cd can be delineated as elements of major concern and Fe and Ni as moderate concern based on their environmental toxicity and levels observed in leachates.

2. Keeping sludge percentage at or below 30% (wet mass sludge to wet mass coarse ash) may keep the increase of As, Se and the other elements of concern within manageable limits. This translates to amending dry coarse ash with about 5% dry sludge or amending coarse ash dumps with 90 tons/ha sludge assuming a bulk density of 1200 kg m^{-3} and a mixing depth of 15 cm. Sludge application above this level is not recommended. Moreover, keeping the system continuously in an aerobic oxidized state may reduce the environmental toxicity of arsenic by reducing the abundance of the more toxic form of the element.
3. Co-disposal of coarse ash with fine ash did not lead to a reduction in the leached amount of any of the studied elements. The elements were either increased as with Pb, Al and Cr, or remained largely unaffected with increase in percent fine ash. Therefore co-disposal of coarse ash with fine ash may only hold promise with respect to the ability of the fine material to store water necessary for establishment of vegetation on coarse ash dumps; however, this has to be assessed against the backdrop of the highly cementing nature of fine ash.
4. Co-disposal of coarse ash with fine ash may be safe if fine ash is kept at or below 30% (wet mass to wet mass). Above 30%, Pb, Al and Cr may become a risk to groundwater.
5. In most cases, leachate element concentrations exceeded international critical limits for drinking water.

Looking ahead, it is a reasonable assumption that mobility of metals will be altered from what was observed in this experiment if vegetation is established on a growth medium of sludge/fine ash and coarse ash. Studies with this inclusion should be pursued and because of the increase in solubility/availability of many metals in sludge-amended coarse ash systems, it might be helpful to consider plants with high phytoremediation properties when establishing vegetation on these media. Furthermore, although the results from this study show changes in the solubility of selected elements, it is yet to be determined if and when these elements will leach through the ash pile and pose a risk to groundwater. One factor controlling cation leaching is the anion level of the solution (McColle and Cole, 1968). Water leach analysis of anions in the coal gasification ash indicate that sulphates are the most dominant anions (Appendix 3), arising from the use of the ash dump as a salt sink (Van den Berg, 2004). Studies on the effect of anion species on metal transport will be useful in the management of metal leaching in sludge-amended ash.

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Chapter 4: Nitrogen mineralization from sludge in an alkaline, saline coal gasification ash environment*

Abstract

Rehabilitating coal gasification ash dumps by amendment with waste activated sludge has been shown to improve the physical and chemical properties of ash and facilitate the establishment of vegetation. However, mineralization of organic nitrogen from sludge in such an alkaline and saline medium, and the effect that ash weathering has on the process are poorly understood and need to be ascertained in order to make decisions regarding the suitability of this rehabilitation option. This study was aimed at investigating the rate and pattern of nitrogen mineralization from sludge in a coal gasification ash medium, determining the prevalent inorganic nitrogen form in the system and assessing the effect of ash weathering on N mineralization. An incubation experiment was carried out in which fresh ash, weathered ash and soil were amended with the equivalent of 90 Mg ha^{-1} sludge and nitrogen mineralization was evaluated over 63 days. More N (24%) was mineralized in fresh ash than in weathered ash and in soil, both of which mineralized 15% of the initial organic N in sludge. More nitrification occurred in soil while most of the N mineralized in ash was in the form of ammonium, indicating an inhibition of nitrifying organisms in the ash medium and suggesting that at least initially, plants used for rehabilitation of coal gasification ash dumps will take up N mostly as ammonium.

Keywords: *coal gasification ash, nitrogen mineralization, rehabilitation, sludge*

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4.1 Introduction

Gasification of coal to produce fuel may reduce the dependence on crude oil reserves, but the process leaves behind millions of tons of coal gasification ash (CGA). Gasification is the reaction of solid fuels with air, oxygen, steam, carbon dioxide, or a mixture of these gases at temperatures greater than 700 °C, to yield a gaseous product used as a source of energy or as a raw material for the synthesis of chemicals and fuels **(**Collot, 2006). There are about 160 modern gasification plants in operation worldwide that produce syngas, oxy-chemicals, methanol, hydrogen, and electricity (Minchener, 2005). South African Coal and Oil (*Suid Afrikaanse Steenkool en Olie*, Sasol) operates one of such plants and in its Lurgi coal gasification process, produces synthesis gas (a mixture of carbon monoxide and hydrogen) from low-grade, medium rank C (bituminous) coal and extraneous rock fragments, usually carbonaceous shale, siltstone, sandstone and mudstone (Matjie et al., 2008). The process which takes place in gasifiers at elevated temperatures greater than 1350 ºC and pressures of more than 20 bar generates the waste coal gasification ash. Matjie et al. (2005) estimates that at its Secunda plant, approximately 28 million tons of coal is consumed by the gasification process annually while 7 million tons of CGA is produced. Gasification ash is a combination of red and white to grey fused clinkers with heterogeneous texture varying from fine material to large irregularly shaped aggregates of sizes ranging from 4 mm to 75 mm; and is composed predominantly of quartz, mullite, anorthite, diopside, hematite, cristobalite and anhydrite (Matjie et al., 2005).

The fact that ash reuse for purposes such as brick-making has not kept up with the rate at which the waste is generated, makes stockpiling of ash inevitable. The pollution risks associated with coal ash wastes have been well documented, for example Jala and Goyal

(2006). Acid rain characteristic of many industrial areas, falling on these dumps could strip ash particles of salts and toxic elements and facilitate their transport. Moreover, dust carried by wind from these ash dumps could constitute major health hazards as well as degrade surface water bodies. It has thus, become imperative to rehabilitate these ash dump sites.

Use of topsoil to cap ash dumps has been suggested (van Rensburg et al., 1998), however, the consequent loss of arable topsoil and the costs of transporting soil to ash sites are major drawbacks with this rehabilitation option. One of the more recently proposed management options is the amendment of coal ash with sludge, both to aid rehabilitation of ash dump sites, and as a viable sludge disposal system (Annandale et al., 2004). Use of sludge in rehabilitation efforts has been based on the premise that sludge would add necessary nutrients, improve physical attributes such as water holding capacity, and bind metals, thereby reducing their bioavailability and toxicity, thus allowing vegetation to be established (Scholl and Pase, 1984; Basta et al., 2001). The established vegetation subsequently reduces the spread of pollution by wind or water erosion, and reduces water ingress and accompanying salt and metal leaching (Tandy et al., 2009).

Various studies such as van Rensburg et al. (1998) and Haynes (2009) have noted that amendment of coal ash with organic materials such as sludge, improved the physical and chemical properties of the medium, making it more able to sustain vegetation. More importantly, sludge could supply a range of essential plant nutrients, mainly nitrogen and phosphorus.

Most of the nitrogen in sludge, however, is bound in organic forms which have to be mineralized by microorganisms into plant-usable nitrogen species. Nitrogen release from sludge has been shown to be affected by the properties of the medium in which it is applied (Hernández et al., 2002). The usefulness of amending CGA with sludge can only be realized if sufficient nitrogen is able to be mineralized from sludge in this highly alkaline and saline ash medium.

The effect of salinity and alkalinity on nitrogen mineralization from organic materials has been previously reported. Pathak and Rao (1998) observed a decrease in net nitrogen mineralization with increasing pH or salinity. They also found that ammonification continued to take place at EC levels that inhibited nitrification, confirming earlier studies that ammonifiers are more tolerant of salinity than nitrifiers (McClung and Frankenberger, 1985). While most of the studies on N mineralization from organic materials have been done on soil, studies dealing with N mineralization in non-soil media such as coal ash have indeed been rare. Fang et al. (1999) reported nitrogen dynamics after co-composting sewage sludge and coal fly ash. Apart from the high temperature conditions of the co-composting process, it is not clear whether the same observations can be detected in ash from coal gasification processes under temperature conditions expected in actual ash dumps. Ginster and Matjie (2005) have noted that coal gasification ash differs from coal fly ash from power stations in chemical and mineralogical characteristics.

At present, it is unclear to what extent mineralization of organic N is attainable in a CGA medium where a high pH is compounded by a high electrical conductivity. It is imperative to understand the rate at which inorganic nitrogen is released from sludge applied on gasification ash dumps in order to ensure that sufficient nitrogen is available for vegetation while excessive generation of nitrates is avoided.

It is also critical to determine which inorganic nitrogen forms are prevalent in such a system if indeed mineralization of organic N does take place. Microbial species involved in nitrification are especially sensitive to high pH, suggesting that in these alkaline media ammonium might be abundant. Moreover, since nitrite oxidizers are inhibited by free ammonia to a greater extent than ammonium oxidizers (Smith et al., 1997), excess ammonium could lead to an accumulation of nitrite.

Furthermore, the effect of ash weathering on N mineralization would be an important consideration to make in deciding when to apply sludge to CGA dumps. Weathered ash may have more negatively charged surfaces than fresh ash with implications for ammonium attenuation. On the other hand, the ameliorating effect of salt leaching during weathering may create a more hospitable medium for nitrifying bacteria.

The objectives of this study, therefore, were to determine the rate and pattern of nitrogen mineralization from sludge in a coal gasification ash medium; to determine the prevalent inorganic nitrogen form in the system; and to assess the effect of ash weathering on N mineralization. The following hypotheses were tested:

(1). There would be less N mineralization in sludge-amended ash than in sludge-amended soil due to the high pH and high salinity of the ash medium.

(2). Ammonium will dominate in sludge-amended ash because nitrifying bacteria are sensitive to high pH.

(3). More N mineralization will occur in sludge-amended weathered ash than in sludge-amended fresh ash due to the ameliorating effect that weathering has on salinity.

4.2 Materials and methods

Estimates of organic nitrogen mineralization rates from sludge usually rely on incubation studies (field or laboratory), crop N uptake studies (field or greenhouse), average mineralization rates of biosolid treatment (processing/stabilization) methods, and regression equations based on biosolid organic nitrogen content (Henry et al., 1999). In this study mineralization rates and patterns were evaluated using incubation procedures.

4.2.1 Preparation of materials

Coal gasification ash was collected from Sasol Synfuels in Secunda, South Africa. Gasification ash delineated as 'fresh ash' was collected from a freshly dumped ash heap. Gasification ash delineated as 'weathered ash' is fresh ash that had undergone ten laboratory leaching and drying cycles over a period of one year. Total amount of water used during the column leaching process was equivalent to 1270 mm of rainfall corresponding to the amount of rainfall received in Secunda in about 2 years (Jovanovic et al., 2004). Details of the column leaching set up can be found in de Jager et al. (2013). The sludge used for this study was obtained from Sasol's activated sludge treatment plant. The sludge originated from the activated treatment of industrial wastewater and has a C/N ratio of 7.1. Topsoil (0-15 cm) of a loamy sand was collected from an experimental farm of the University of Pretoria near

Cullinan, Gauteng Province, South Africa where sludge has not previously been applied. The inclusion of soil in this experiment was to compare sludge N mineralization in ash with N mineralization in a more common sludge application medium. Nitrogen speciation, and some chemical characteristics of coal gasification ash, soil and sludge determined in a 1:5 sample:water mixture are shown in Table 4.1.

Table 4.1. Some chemical characteristics of experimental materials†

	Fresh ash	Weathered ash	Soil	Sludge
pH(H_2O)	8.71 (0.08)	9.46 (0.04)	5.58 (0.035)	5.8 (0.03)
EC(dS m^{-1})	2.02 (0.02)	0.53 (0.005)	0.096 (0.0016)	0.65 (0.07)
Total N (%)	0.0095 (0.0028)	0.00925 (0.001)	0.024 (0.00014)	7.91 (0.006)
NH_4-N (mg kg^{-1})	1.25 (0.036)	1.21 (0.012)	20.9 (0.88)	7104 (356.2)
NO_3-N (mg kg^{-1})	7.2 (0.65)	2.33 (0.11)	22.1 (1.32)	167 (6.7)
NO_2-N (mg kg^{-1})	1.34 (0.1)	0.54 (0.019)	0.75 (0.39)	8.71 (0.79)
Organic N (mg kg^{-1})	85 (29.05)	88 (10.49)	196 (5.01)	71820 (336.9)
Ca (mg kg^{-1})	1517 (53)	462 (7.9)	17.8 (3.1)	394 (2.1)
Mg (mg kg^{-1})	94.8 (2.5)	7.4 (0.4)	8.7 (1.2)	299 (2.8)
K (mg kg^{-1})	158 (4.7)	18.6 (0.53)	12.2 (1.7)	851 (18.9)
Na (mg kg^{-1})	480 (14.7)	35 (2.0)	5.8 (1.9)	371 (8.7)
Fe (mg kg^{-1})	0.035 (0.0095)	0.026 (0.0075)	42.19 (1.33)	8.98 (0.14)
Al (mg kg^{-1})	0.653 (0.03)	2.68 (0.05)	126.97 (29.5)	10.13 (0.08)
Cu (mg kg^{-1})	0.016 (0.003)	0.012 (0.0025)	0.128 (0.026)	0.235 (0.03)
Mn (mg kg^{-1})	0.0189 (0.0027)	0.0039 (0.001)	2.705 (0.54)	5.38 (0.025)
Zn (mg kg^{-1})	0.162 (0.014)	0.0068 (0.00076)	0.83 (0.03)	2.69 (0.29)

†Values represent the mean followed by the standard deviation in parentheses

Soil and gasification ash were air-dried and passed through a 2 mm sieve. Sludge was air-dried and milled. Water retention characteristics of CGA and soil were generated based on the relationship between water potential and water content using a Dew Point Potentiometer (WP4, Decagon Devices, Pullman WA, USA). Due to the high water absorption capability of gasification ash and in order to use a uniform water potential for both ash and soil, water contents corresponding to -70 kPa were chosen for both soil and gasification ash.

4.2.2 Incubation and chemical analysis

Ten grams of soil or fresh or weathered ash were weighed into 100 ml containers and amended with 5% dry sludge. The choice of 5% sludge was made based on heavy metal release studies conducted earlier, which showed that amending CGA with more than 5% dry Sasol sludge may increase the solubility of certain metals to levels of environmental concern (Chapter 3; de Jager et al., 2013). Assuming a bulk density of 1200 kg m^{-3} and a depth of 15 cm, rate of sludge amendment was equivalent to 90 Mg of dry sludge per hectare. The containers used for incubation had airtight lids in order to maintain constant water contents. A headspace was left above the mixtures to aid aeration.

Treatments were wet to the predetermined water content at -70 kPa. N mineralization from unamended soil and ash served as controls in order to subtract this from mineralization observed from amended samples and determine the actual mineralization from sludge. Although this approach downplays the phenomenon of a ‘priming effect’, it is widely accepted for estimating mineralization rates from organic materials (Agehara and Warncke, 2005). Priming is a phenomenon that is observed when fresh substrates used for soil amendment accelerate N mineralization in such a way that the amount of N mineralized is greater than the amount of N mineralized from the substrates added and the amount of N mineralized from unamended soil.

Triplicate treatments were made for sampling days 0, 7, 21, 28, 35, 56 and 63. For each sampling day, unamended soil, fresh ash and weathered ash served as control. Treatments were placed at a temperature of 25 ± 3 °C and aerated weekly by opening the container lids for about 5 minutes in order to keep the system oxidized. Water loss was checked by weighing, in order to keep the treatments at the required water content.

On the sampling days, 50 cm^3 of distilled water was added to the samples which were then shaken in a reciprocating shaker at 200 oscillations per minute, for 60 minutes. pH was measured with a glass electrode (Consort C830, Belgium) and electrical conductivity (EC) measurements were taken thereafter (Consort C861, Belgium). Samples were filtered through a Whatman number one filter paper and stored below 4 °C prior to analysis. Inorganic N was determined in a segmented Technicon (SEAL Analytical) flow autoanalyzer system (Bremner, 1965). Total N was determined after acid digestion (Bremner, 1996). Organic N was taken as the difference between Total N and inorganic N.

The cumulative N mineralized (N_{min}) from unamended soil or ash at time t, (N_{min})control was calculated by:

$(N_{min})\text{control} = \text{Inorganic N(control)}_t - \text{Inorganic N(control)}_{t=0}$ ……………Equation 4.1.

N mineralized from sludge was given as the sum of the inorganic forms of the N in sludge-amended soil/ash adjusted for mineralization of soil/ash N and the initial inorganic N added with the sludge. The cumulative amount of N mineralized from sludge at time t was therefore calculated by:

(N_{min})sludge = (Inorganic N of sludge-amended treatment)$_t$ – (Inorganic N of control)$_t$ – (Inorganic N added with sludge)…………………………………………. .Equation 4.2.

Percent organic N mineralized was estimated as:

% organic N_{min} = (N mineralized/organic N added) x 100 …………………..Equation 4.3.

4.2.3 Statistical analysis

Data were analysed by Analyses of Variance (ANOVA) in a completely randomized design using the General Linear Model (GLM) procedures of Windows SAS version 9.0 (SAS Institute, 2002). When treatment effects were found to be significant, separation of means was carried out using the Tukey test.

The rate of N mineralization from sludge was estimated using the model proposed by Smith et al. (1980):

$N_{min} = N_0 [1 – \exp(-kt)]$……………………………………………………Equation 4.4.

Where N_{min} is the amount of N mineralized from sludge at a specific time (t); N_0 is the potentially mineralizable organic nitrogen; k is the first-order rate constant; and t is the time of incubation.

4.3 Results and discussion

4.3.1 pH and electrical conductivity

Weathered unamended ash had a higher pH than fresh ash (Fig. 4.1). The exposure of ash to air (CO_2) and water during the process of leaching and weathering is capable of liberating the more alkaline compounds of ash. During that process, calcium oxide is converted to the more alkaline calcium hydroxide, and in the end to $CaCO_3$. In unamended ash samples, pH remained fairly constant over the 63 day period, while it showed a decline in unamended soil. pH of soil declined from 5.58 at the start of the incubation to 4.59 on day 63. This decline is attributed to the acidifying effects of the process of nitrification (Brady and Weil, 1999).

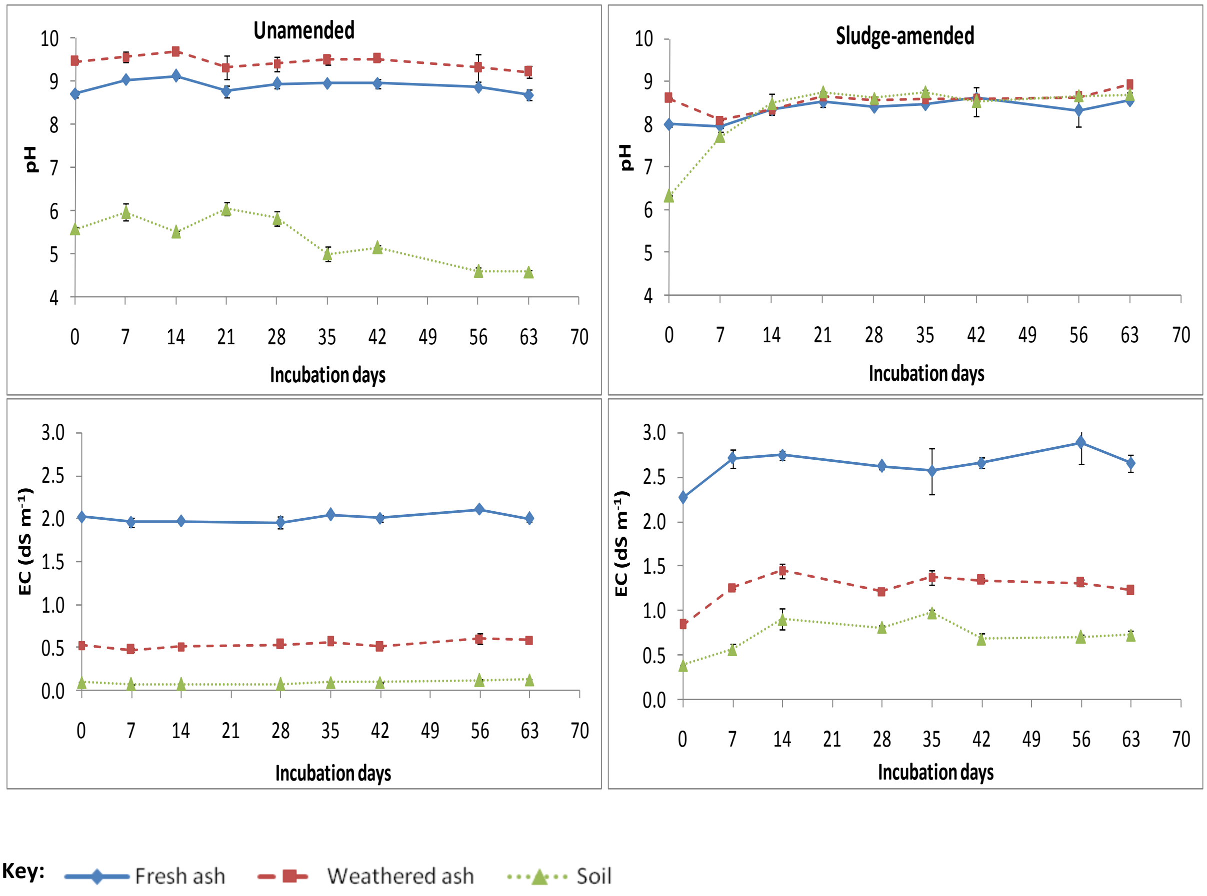

Fig 4.1. pH and electrical conductivity of unamended and sludge-amended fresh ash, weathered ash and soil during a 63 day incubation. Error bars show standard deviation of three replicates.

Addition of sludge significantly (α = 0.05) reduced the pH of fresh ash from 8.7 to 8.0 and of weathered ash from 9.5 to 8.6 at the start of incubation. pH was further reduced at day 7 to 7.95 for fresh ash and 8.09 for weathered ash, and remained near these values throughout the incubation period. This reduction of pH is linked to the net effect of the mineralization process, and to carbonation, a situation where carbon dioxide released during the breakdown of sludge forms carbonic acid. A reduction of pH is one of the benefits accruable from amending ash with sludge, as nutrient deficiencies are common in high alkaline conditions.

The pH of sludge-amended soil increased at the start of the incubation and with time up to day 21. At day 0, sludge-amended soil had a pH of 6.32 and at day 21, pH was 8.75 after which pH remained fairly constant and similar to sludge-amended ash. This increase in pH can be attributed to the hydrolysis of urea in sludge to unstable carbamic acid which subsequently decomposes rapidly to form ammonia and carbon dioxide. Reaction of ammonia with water results in the formation of ammonium and the hydroxide ion which consequently increases the local microsite pH (Coyne, 1999).

Fresh ash had significantly (α = 0.05) higher electrical conductivity (EC) than weathered ash and soil. At the Sasol Synfuels plant, brines are used for ash transport in a wet ash/slurry transport system, and the high-salt containing effluents from the tubular reverse osmosis process obtained during the treatment of Clear Ash Effluent are deposited on the ash heap in a bid to limit salt mobility; for example, SO_4 was found to be retained in a stable phase in the ash (van den Berg, 2004). During ash weathering, exposure of ash to leaching removes soluble salts from ash (Haynes, 2009). For unamended treatments, EC was 2.02 dS m^{-1} for fresh ash, 0.53 dS m^{-1} for weathered ash, and 0.1 dS m^{-1} for soil at day 0, and did not change considerably throughout the incubation period.

The EC of the three materials increased significantly ($\alpha = 0.05$) upon addition of sludge. At day 0, EC of sludge-amended samples were 2.27 dS m^{-1} for fresh ash, 0.83 dS m^{-1} for weathered ash, and 0.39 dS m^{-1} for soil. Increase of EC after sludge amendment has been widely reported (for example Tsadilas et al., 1995; Tesfamariam et al., 2009) and is attributed to the soluble salts in sludge, and to ligand promoted dissolution which is capable of liberating salts from sludge-amended media. Amending ash with sludge for revegetation purposes will therefore have to take into account the high EC resulting from sludge addition, and salinity-tolerant plant species may have to be considered. Annandale et al. (2004) and Van Rensburg et al. (1998) found that *Cynodon dactylon* adapted well to conditions in sludge-amended coal ash. Khan et al. (1999) and Hameed and Ashraf (2008) have also cited the salt-tolerance of *Cynodon dactylon*.

4.3.2 Ammonium, nitrite and nitrate

Ammonium in unamended samples increased slightly from 1.25 to 12 mg kg^{-1} for fresh ash, 1.21 to 9.4 mg kg^{-1} for weathered ash, and 20.9 to 29.3 mg kg^{-1} for soil during the incubation period (Fig. 4.2). Upon addition of sludge, ammonium increased to approximately 200 mg kg^{-1} for all treatments at the start of the experiment. For sludge-amended samples, ammonium steadily increased reaching a maximum on day 35, of 1240 mg kg^{-1} for fresh ash, 886 mg kg^{-1} for weathered ash, and 936 mg kg^{-1} for soil. The decrease of ammonium after day 35 is attributed to both volatilization due to a high pH, and conversion of ammonium to nitrite and nitrates.

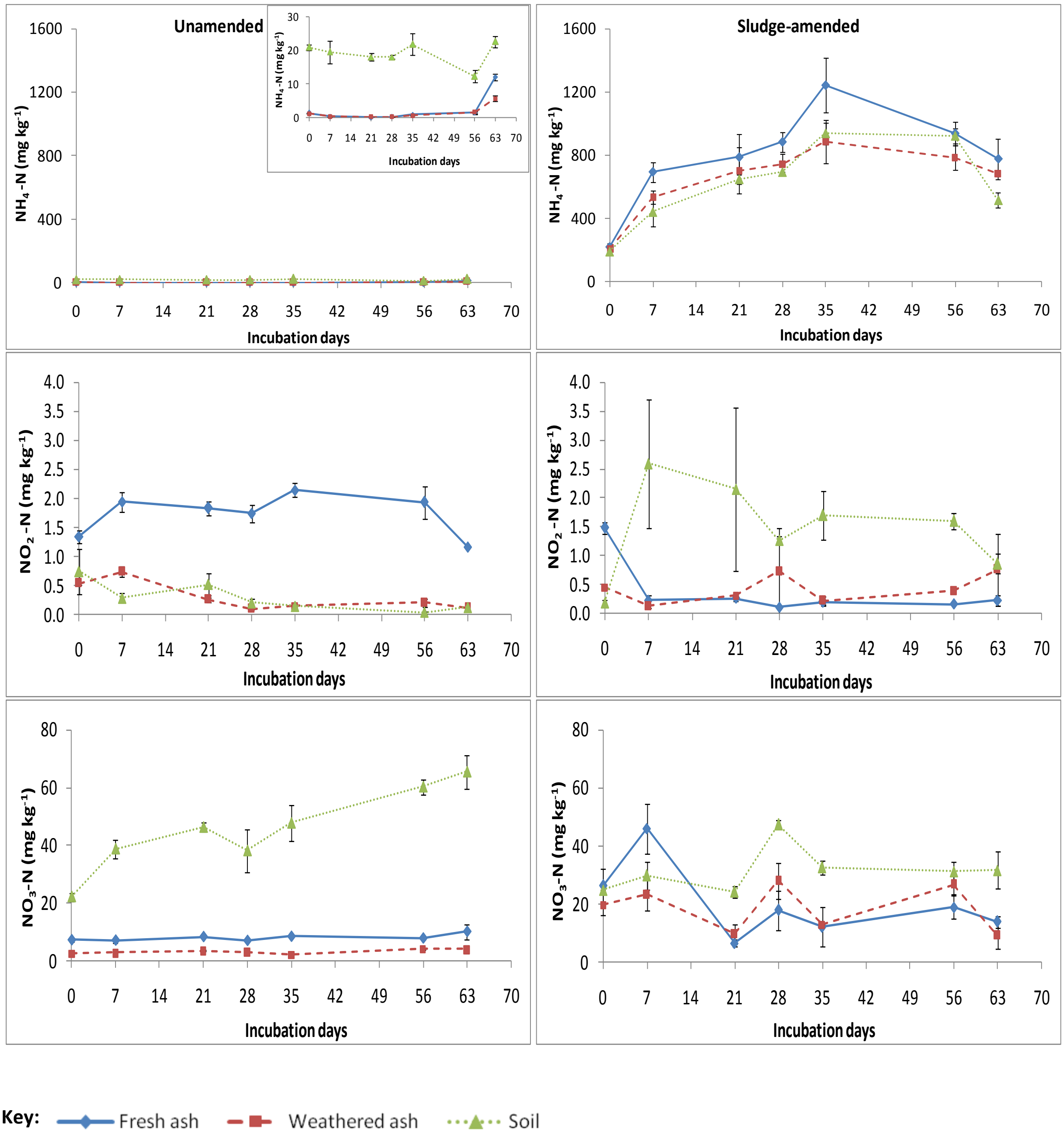

Fig 4.2. Ammonium, nitrite and nitrate concentrations of unamended and sludge-amended fresh ash, weathered ash and soil during a 63 day incubation. Error bars show standard deviation of three replicates.

Ammonium levels were higher for fresh ash than for weathered ash and soil over the incubation period. Since ash weathering leads to the formation of clay minerals, it is suggested that the lower ammonium levels in weathered ash and soil is due to clay protection of organic matter from mineralization or due to clay adsorption of ammonium. Zevenbergen et al. (1999) noted that over time, weathering causes a transformation of the ash components converting alumino-silicate glass into non-crystalline clay minerals. Binding of proteins (such as urease) to clays may hide the specific peptide bonds that extracellular proteases require to decompose the proteins. Proteins may also be protected in micropores that are too small for microorganisms to enter (Coyne, 1999).

In soil little attention has been paid to nitrite because of analytical difficulties (Isobe et al., 2012) and because under favourable conditions, transformation of nitrites to nitrates is rapid and accumulation of nitrite is negligible (Nishio and Fujimoto, 1990). However, in an alkaline medium with high inputs of ammonium, nitrite dynamics may be different and this warrants investigation.

Unamended fresh ash had a higher content of nitrites than unamended weathered ash or soil. During gasification of coal, NH_3 is introduced into the electrostatic precipitator to enhance the removal of fly ash. Under conditions of high alkalinity and salinity, oxidation of the introduced NH_3 may only yield nitrite. Leaching of ash during ash weathering would have resulted in removal of nitrite in the leachates.

For unamended soil, nitrite decreased progressively during the incubation period as a result of oxidation to nitrates. It decreased from 0.75 mg kg^{-1} on day 0, to a minimum of 0.04 mg kg^{-1} on day 56. Nitrite levels increased rapidly when soil was amended with sludge, and then decreased as incubation progressed. This initial increase can be attributed to the oxidation of ammonium to nitrites. Under favourable conditions, this process should proceed rapidly and nitrite should not accumulate. However, because of the build up of ammonium, nitrite may accumulate. Smith et al. (1997) suggested that nitrite oxidizers can be inhibited by free ammonia to a greater extent than ammonium oxidizers. The build-up of nitrite (NO_2-) and hydroxylamine (NH_2OH) which in turn, are toxic to nitrifying bacteria further inhibits nitrification.

Amending fresh ash with sludge reduced the concentration of nitrite. This reduction of nitrite in sludge-amended ash may be as a result of nitrite fixation and volatilization in the presence of organic matter. Bremner and Führ (1966) were among the first to point out the fixation of nitrite by soil organic matter. Moreover, volatilization of nitrite has been found to increase with increase in soil organic matter (Nelson and Bremner, 1969). Nelson and Bremner (1970) reported that after soils were treated with nitrite under aerobic conditions, nitrite decomposition led to the formation of substantial amounts of the gases NO_2 and N_2 and small amounts of N_2O, with the largest amount of N_2 formed in the soil with the highest organic matter content. In soil where conditions are more conducive for nitrification, the intensity of the nitrite generating process may have exceeded processes that deplete nitrite.

Nitrite was the nitrogen form with the lowest concentration among the three inorganic nitrogen forms investigated. The reduction of nitrite upon addition of sludge to fresh ash is a benefit with respect to environmental mitigation and will aid in plant establishment. Plants affected by nitrite toxicity are small, chlorotic and prone to wilting. Nitrite toxicity is pH dependent. At pH 7 plants can tolerate up to 200 mg NO_2-N kg^{-1} whereas at pH 4 a nitrite concentration of only 2 mg NO_2-N kg^{-1} is toxic. As little as 15 mg NO_2-N kg^{-1} is toxic to lettuce while 5 mg NO_2-N kg^{-1} is toxic to tobacco in soils with pH of about 5.5 (Cleemput and Samater, 1995).

Nitrate was increasingly generated in unamended soil, beginning from 22 mg kg^{-1} at the start of incubation to 65 mg kg^{-1} on day 63. Soil NO_3-N concentration of between 21 and 25 mg kg^{-1} has been found to be sufficient for optimum yield of corn (Fox et al., 1989). Sludge-amended soil, however, resulted in relatively lower levels of NO_3-N. This can be attributed to the higher pH and EC of sludge-amended soil as well as to the inhibitory effects of excess ammonium on the activities of nitrifying organisms. Nishio and Fujimoto (1990) found that nitrification was inhibited at ammonium concentrations >300 mg kg^{-1}. High ammonium input to alkaline soils has been found to inhibit oxidation of nitrite to nitrate (Shen et al., 2003).

Nitrate formation occurred in sludge-amended ash howbeit less than in soil. The organisms involved in converting ammonium to nitrates may have been inhibited by the higher pH and EC of ash. Fang et al. (1999) in co-composting sewage sludge and coal fly ash also observed that ash inhibited nitrification.

Ammonium was the more dominant inorganic nitrogen species in sludge-amended ash. If plants are established on ash dumps, this has important implications on the ionic balance of the rhizosphere. Plants take up nitrogen from the soil solution mainly as NO_3^- and NH_4^+ ions. The relative amounts of these ions taken up by plant roots affect the pH of the soil solution in close proximity to plant roots. Nitrate anions exchange with HCO_3^- or OH^- at the root surface thereby causing an increase in the pH of the soil solution around plant roots. When ammonium cations are absorbed, they exchange with hydrogen ions thereby lowering the pH of the solution around the rhizosphere (Brady and Weil, 1999). With time this may ameliorate the high pH of coal ash dumps.

4.3.3 Total inorganic N and N mineralized from sludge

Some studies calculate rate of mineralization by the decrease in organic N. Others follow the approach of calculating the increase in inorganic N. Ideally, both approaches should give the same results. In this study, the increase in inorganic N is used to determine rate of mineralization. Nitrogen losses by volatilization of ammonia were not evaluated, thus this approach may underestimate mineralized N. Nevertheless, with regard to the environment and plant establishment, ammonium, nitrites and nitrates are the more relevant species.

Mineralization proceeded rapidly up to the 35th day of incubation (Fig. 4.3). Hernández et al. (2002) also found that mineralization from sludge was rapid in the early stages of incubation. This increase in rate within the early periods of incubation is attributed to the mineralization of the easily mineralizable organic N pool. Sludge has been shown to contain different pools of organic N with differing rates of mineralization (Rowell et al., 2001; Gil et al., 2011). Unstabilized sludge such as the one used in this study, characterized by a high content of volatile solids, has been reported to contain more of the easily mineralizable organic nitrogen pool than those with a higher stability (Henry et al., 1999; Nobela, 2011). As this disappears leaving the more recalcitrant pool, mineralization rate decreases. Moreover, at the beginning of the incubation, N mineralized exceeds the N needs of the microbial population leading to a net increase in inorganic N.

The decrease in inorganic N after day 35 may be as a result of gaseous losses of N due to ammonia volatilization (Martines et al., 2010). Denitrification is not a likely process due to the aerobic nature of the experiment and the low levels of nitrate observed (Wu et al., 2013). Rise in pH may lead to increased loss of nitrogen through volatilization. Dendooven et al. (2010) observed that amending ash with sludge may give rise to large losses of ammonium due to ammonia volatilization, but that this may be reduced by incorporating sludge into the ash.

Nitrogen mineralized from sludge-amended ash was more than sufficient and even exceeded the nitrogen requirements of many pasture crops (Mears, 1970). This has to be taken into consideration so that while applying sludge to ash aids in sludge disposal, excess ammonium generated does not become an environmental problem. Lower rates of sludge application will be adequate to meet plant nitrogen needs.

Contrary to the hypothesis, more nitrogen was mineralized from fresh ash than from weathered ash, and soil. The greater attenuation of organic matter in weathered ash and soil due to the presence of more clay minerals is put forward as a possible explanation. On day 35, the difference in N mineralized was significant ($\alpha = 0.05$) between fresh ash and weathered ash. There was no significant difference ($\alpha = 0.05$) between N mineralized in weathered ash and N mineralized in soil. In fresh ash 24% of organic N was mineralized, while 15% was mineralized in both weathered ash and soil.

Nitrogen mineralization was low in soil. Having already a substantial amount of ammonium, the addition of sludge may have resulted in an impediment of the relevant microorganisms in soil by the build-up of ammonium. Moreover, the coarser texture of gasification ash may have aided mineralization. Hernández et al. (2002) found more mineralization of N in a sandy-loam than in a clayey-loam and attributed this to better aeration in the light textured soil which accelerated sludge-organic N decomposition.

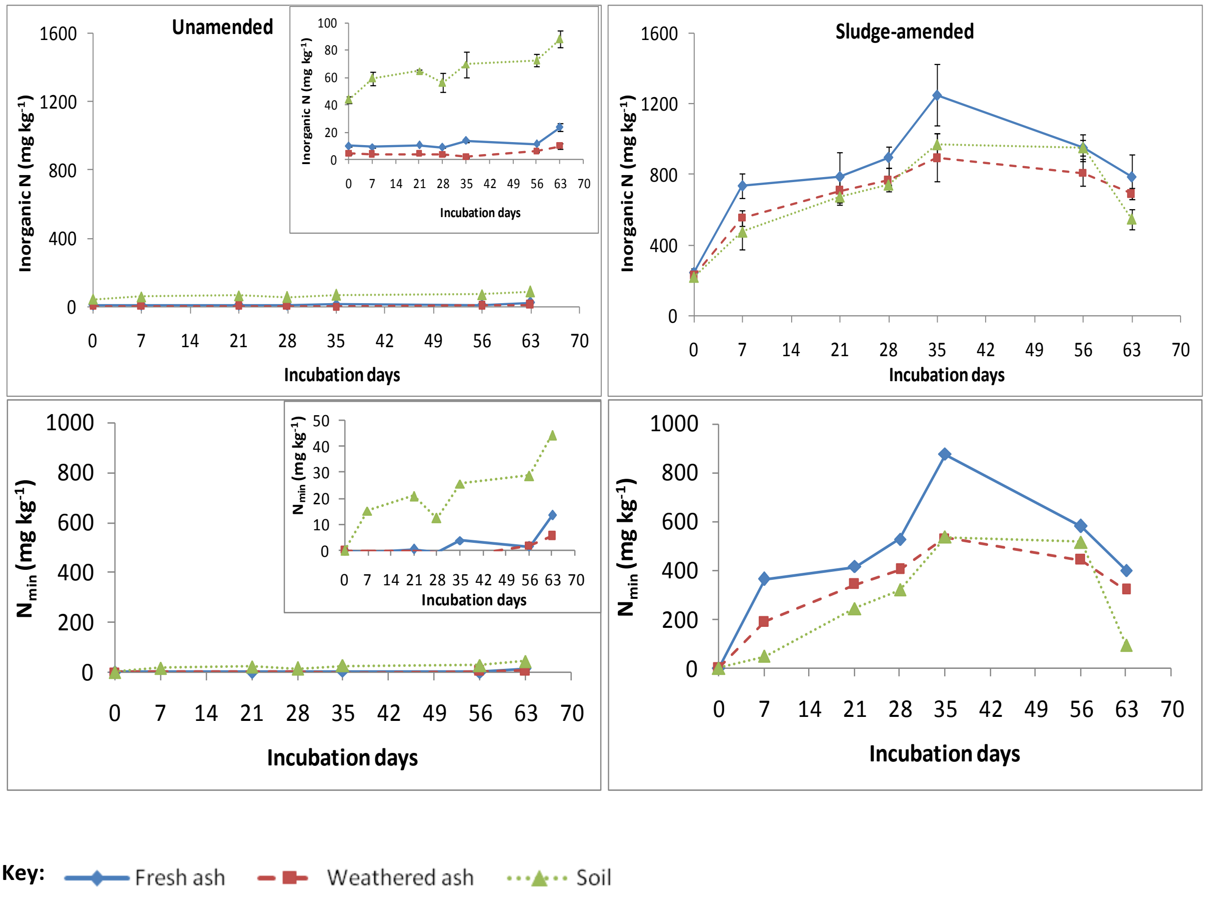

Fig 4.3. Total inorganic N and N mineralized in unamended and sludge-amended fresh ash, weathered ash and soil during a 63 day incubation. Error bars show standard deviation of three replicates.

Mineralization of organic N from sludge over the first 35 days was well approximated using first order kinetics, with resulting high R^2 values. Fig. 4.4 shows the rate constants calculated using the model proposed by Smith et al. (1980) (Equation 4). When $\ln(1-(N_{min}/N_0))$ is plotted against incubation days, the slope of the graph gives the rate constant per day.

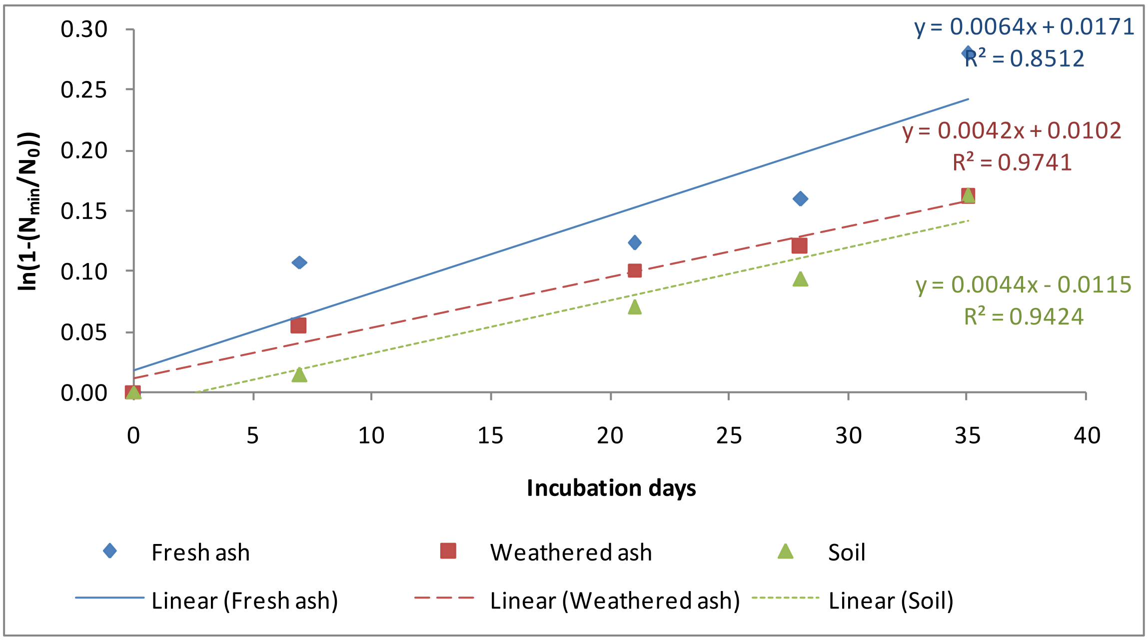

Fig 4.4. N mineralization rate constants for sludge-amended fresh ash, weathered ash and soil in the first 35 days of incubation.

Rate constants were 0.0064 day^{-1} for fresh ash, 0.0042 day^{-1} for weathered ash, and 0.0044 day^{-1} for soil. These values are smaller than the value of 0.013 day^{-1} found by Nobela (2011) using the Sasol synfuels sludge on soil at a rate of 10 Mg ha^{-1} at similar water and temperature conditions. The inhospitality of the ash medium and the higher sludge rate and consequent ammonium toxicity are put forward as reasons for the lower mineralization rate in this study. In Nobela's study, sludge obtained from the Sasol Synfuels facility had the highest mineralization rate compared to the municipal sludges used in that experiment, attributable to Sasol sludge having the highest total N and volatile solid content.

It has to be noted that in actual coal gasification ash heaps particles larger than the 2 mm maximum size used in this experiment are common. However, in this laboratory study, for proper comparism with soil, a uniform maximum particle size had to be used. Rates of N mineralization in sludge-amended ash heaps might therefore differ slightly from those calculated in this study, nevertheless, these results give an indication of the trends expected.

4.4 Conclusions

Organic nitrogen from sludge was mineralized in a coal gasification ash medium. More nitrogen was mineralized in fresh ash than in weathered ash and in soil, and the dominant inorganic nitrogen form in sludge-amended ash was ammonium; therefore, only hypothesis (2) (ammonium will dominate in sludge-amended ash) is accepted. The low nitrification observed in sludge-amended ash implies that at least initially, plants grown on these amended dumps will take up nitrogen mostly as ammonium. Moreover, potential for nitrate leaching is low. It is recommended that for rehabilitation purposes, management should aim to balance the nitrogen needs of vegetation with rates of N mineralization calculated under the prevailing conditions.

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Chapter 5: Ammonium sorption in coal gasification ash

Abstract

Amendment of a coal gasification ash dump with wastewater sludge may aid in rehabilitation and establishment of vegetation, however, studies show that because of the inhospitality of the ash medium to nitrifying bacteria, there might be a build-up of ammonium in this environment. The risks of ammonium leaching from the ash dump necessitate an investigation into the ammonium sorption capacity of coal gasification ash. Batch experiments were performed reacting fresh and weathered coal gasification ash with ammonium concentrations in the range of common sludge materials (7, 11, 15, 30, and 59 mg ℓ^{-1} of NH_4^+). Results showed high ammonium sorption in ash with more ammonium sorption occurring in weathered ash than in fresh ash. For an initial ammonium concentration of 59 mg ℓ^{-1}, 80.5% was sorbed by fresh ash while 96.7% was sorbed by weathered ash. The amount of sorbed ammonium increased with increasing concentration of dissolved ammonium and the Freundlich isotherm was adequate in describing the sorption process. A Freundlich sorption coefficient of 11.32 ($mg^{1-1/n}\ \ell^{1/n}\ kg^{-1}$) was found for fresh ash, and 91.62 ($mg^{1-1/n}\ \ell^{1/n}\ kg^{-1}$) for weathered ash. These observations suggest that ammonium leaching from sludge-amended coal gasification ash will be minimal.

Keywords: *ammonium, coal gasification ash, isotherms, sorption*

5.1 Introduction

Gasification of coal for fuel production has become a growing alternative to depletion of crude oil reserves, but the process leaves behind millions of tons of waste ash annually. The fact that ash reuse for purposes such as brick making has not kept up with the rate at which the waste is generated, has resulted in stockpiling of coal gasification ash (CGA) around the vicinity of gasification plants. The hazards posed by coal ash dumps, especially with regard to leaching of toxic elements down to groundwater, have been widely reported (Reynolds et al., 2002; Jala and Goyal, 2006). It has thus become imperative to rehabilitate these ash dumps on site.

Sludge amendment of CGA in a rehabilitation endeavour has been shown to aid the establishment of vegetation and reduce infiltration into the heap, by improving the nutrient status of the ash medium and supplying necessary plant nutrients, especially nitrogen and phosphorus (van Rensburg et al., 1998). Nitrogen is by far the most important element in plant nutrition, and its significance is magnified by the environmental implications of its inorganic species. Under favourable conditions, organic nitrogen in sludge is converted first to ammonium, then to nitrite, and finally to nitrate, by microorganisms in a process influenced by a range of environmental factors. Some of the ammonium produced can be adsorbed onto clay particles by ion exchange reactions or by organic ligands, making ammonium initially unavailable for the process of nitrification. Plants are only able to utilize ammonium and nitrate, and the conversion from nitrites to nitrates is usually so rapid under favourable conditions, that nitrite does not accumulate in the system (Nishio and Fujimoto, 1990). A previous study showed that because of the unfavourable conditions in coal ash, namely a high pH and high salinity, nitrifying bacteria may have been inhibited, limiting the conversion of ammonium to nitrites and nitrate and resulting in a large build-up of ammonium in sludge-amended CGA (Mbakwe et al., 2013, Chapter 4).

While plants can take up nitrogen as ammonium, in the face of excess ammonium, there are risks of NH_4 leaching if the ash medium cannot retain this nitrogen form. Under steady-state conditions, occupation of sorption sites with ammonium is in equilibrium with the concentration in the solvent phase, but any disturbance of steady-state conditions activates the sorption surfaces as a source or sink for ammonium ions (Raaphorst and Malschaert, 1996). If ammonium is held by ash, the medium can act as a nitrogen reservoir, and ammonium will be nitrified at a later period when conditions in the ash heap become more favourable for nitrifying organisms. If ammonium is not held sufficiently by ash, there are possibilities that it could easily be washed away into other ecosystems where it can be nitrified and cause various health and environmental problems (Korentajer, 1991). Moreover, high concentrations of ammonium could decrease dissolved oxygen (as ammonium is oxidized), and become toxic to aquatic organisms at an ammonium concentration range of 0.2 – 0.5 mg ℓ^{-1} (Zhu et al., 2011).

Sorption is a surface phenomenon by which a solute is attracted to a solid adsorbent and forms attachments via physical or chemical bonds, and is often described using isotherms. A sorption isotherm is a curve describing the phenomenon governing the retention or mobility of a substance from an aqueous medium to a solid-phase at a particular temperature and pH (Foo and Hameed, 2010). Ammonium sorption in soils has been well investigated (Blackmer and Thompson, 1992; Matschonat and Matzner, 1996; Yu et al., 2011). The process has also been studied in fly ash from coal-fired power stations (Zhang et al., 2011; Juan et al. 2009).

At present, it is not certain how much ammonium will be sorbed by coal gasification ash and if ash weathering has any influence on this phenomenon. There is a need to determine sorption coefficient values of ammonium for coal gasification ash and designate the sorption isotherm that can best describe the process, especially because these are essential in predicting ammonium transport in ash dumps using mathematical modelling.

The aims of this study were to estimate sorption capacities for ammonium by fresh and weathered coal gasification ash using batch experiments, and to assign an appropriate isotherm to the sorption process. The tested hypothesis is that ammonium sorption will be higher in weathered ash than in fresh ash due to the creation of more surfaces for ion exchange reactions and ammonium retention through ash weathering.

5.2 Materials and methods

5.2.1 Experimental set-up and analysis

Fresh ash was collected from a freshly dumped CGA heap. Weathered ash was fresh ash that had been made to undergo ten leaching and drying cycles over a period of 12 months with volume of water used for leaching equivalent to 1270 mm of rainfall. Details of the column leaching set-up can be found in Chapter 3 and in de Jager et al. (2013). Nitrogen speciation, and some chemical characteristics of fresh and weathered CGA determined in a 1:5 sample:water mixture are shown in Table 5.1.

Table 5.1. Some chemical characteristics of fresh and weathered coal gasification ash†

	Fresh ash	**Weathered ash**
pH(H_2O)	8.71 (0.08)	9.46 (0.04)
EC(mS m^{-1})	202 (2)	53 (0.5)
Total N (%)	0.0095 (0.0028)	0.0093 (0.001)
NH_4-N (mg kg^{-1})	1.25 (0.036)	1.21 (0.012)
NO_3-N (mg kg^{-1})	7.2 (0.65)	2.33 (0.11)
NO_2-N (mg kg^{-1})	1.34 (0.1)	0.54 (0.019)
Organic N (mg kg^{-1})	85 (29.05)	88 (10.49)
Ca (mg kg^{-1})	1517 (53)	462 (7.9)
Mg (mg kg^{-1})	94.8 (2.5)	7.4 (0.4)
K (mg kg^{-1})	158 (4.7)	18.6 (0.53)
Na (mg kg^{-1})	480 (14.7)	35 (2.0)
Fe (mg kg^{-1})	0.035 (0.0095)	0.026 (0.0075)
Al (mg kg^{-1})	0.66 (0.03)	2.68 (0.05)
Cu (mg kg^{-1})	0.016 (0.003)	0.012 (0.0025)
Mn (mg kg^{-1})	0.019 (0.0027)	0.0039 (0.001)
Zn (mg kg^{-1})	0.16 (0.014)	0.0068 (0.00076)

†Values represent the mean followed by the standard deviation of replicates

Batch sorption experiments were performed using the method described by Papiernik and Yates (2002). Ash was passed through a 2 mm sieve and 5 g was placed in 50 ml centrifuge tubes. A 20 ml solution containing different concentrations of NH_4^+ was added. The concentrations used were: (0, 7, 11, 15, 30, and 59 mg ℓ^{-1} of NH_4^+). These were equivalent to 0, 27, 43, 60, 118, and 236 mg kg^{-1} ammonium. These ammonium concentrations were within the ranges normally found in sludge. Two drops of chloroform were added to each tube to inhibit microbial activity. Tubes were shaken end-over-end on a shaker for 24 h at 25 ºC at a speed of 190 oscillations per minute. The mixtures were then centrifuged at 2500 rotations per minute for 10 minutes and the supernatants were analyzed for ammonium (Bremner, 1965) using a SEAL autoanalyzer (SEAL Analytical, Mequon, WI). Triplicate samples were made for each treatment. All chemicals used in the experiment were analytical grade reagents, and all solutions were made using distilled water.

5.2.2 Calculations

The amount of ammonium sorbed was given by:

$$S = \frac{(C_i - C_e)V}{m} \quad \text{……………………………………………..Eq 5.1.}$$

Where S = ammonium sorbed per unit mass of ash

C_i = initial ammonium concentration

C_e = equilibrium concentration of ammonium in solution

V = volume of solution used for equilibration

m = mass of ash used

Percentage of ammonium sorbed was given by:

$$\frac{C_i - C_e}{C_i} \times 100 \quad \text{…………………………………………….Eq 5.2.}$$

The ammonium sorption isotherms were prepared by plotting mass of ammonium sorbed per mass of ash as a function of residual concentration of ammonium at equilibrium. The mean values of triplicates of each concentration were plotted and fitted to three common models (Linear, Freundlich and Langmuir).

The linear model has the general formula

$S = a + K(C_e)$ ……………………………………………….Eq 5.3

Linear regression is used to find the slope (K) and the intercept (a).

The Freundlich isotherm has the general formula

$S = K_f\, C_e^{\,1/n}$……………………………………………….Eq 5.4

where the Freundlich parameters K_f and n are empirically determined. A plot of log S *vs.* log C_e allows for a determination of these parameters.

The Langmuir isotherm is used when sorption increases to a maximum value with C_e, and has the general formula

$$S = \frac{bK_LC_e}{1+K_LC_e}$$ ……………………………………………….Eq 5.5

Where b is the maximal substance amount of sorbate per unit mass of the adsorbent and K_L is the sorption constant. A plot of $\frac{C_e}{S}$ *vs* C_e allows for determination of b and K_L.

5.3 Results and discussion

5.3.1 Ammonium sorption

Ammonium sorption by fresh and weathered ash is shown in Fig 5.1. Sorption increased with increase in initial ammonium concentration. Ammonium sorption was higher for weathered than for fresh ash with the differences becoming more apparent with increase in initial ammonium concentration. For an initial ammonium concentration of 59 mg ℓ^{-1} (equivalent to

236 mg kg^{-1}), 190 mg kg^{-1} NH_4^+ representing 80.5% of the initial ammonium concentration was sorbed by fresh ash, while weathered ash sorbed 229 mg kg^{-1} NH_4^+ representing 97% of the initial concentration. The ammonium sorption capacity of coal fly ash has been widely reported, and zeolites synthesized from coal fly ash have been effective in ammonium removal from wastewater (for example Zhang et al., 2011). Juan et al. (2009) observed that powdered zeolitic materials obtained from coal fly ash reduced about 80% of ammonium from wastewater while granulated ones achieved a 70% ammonium reduction.

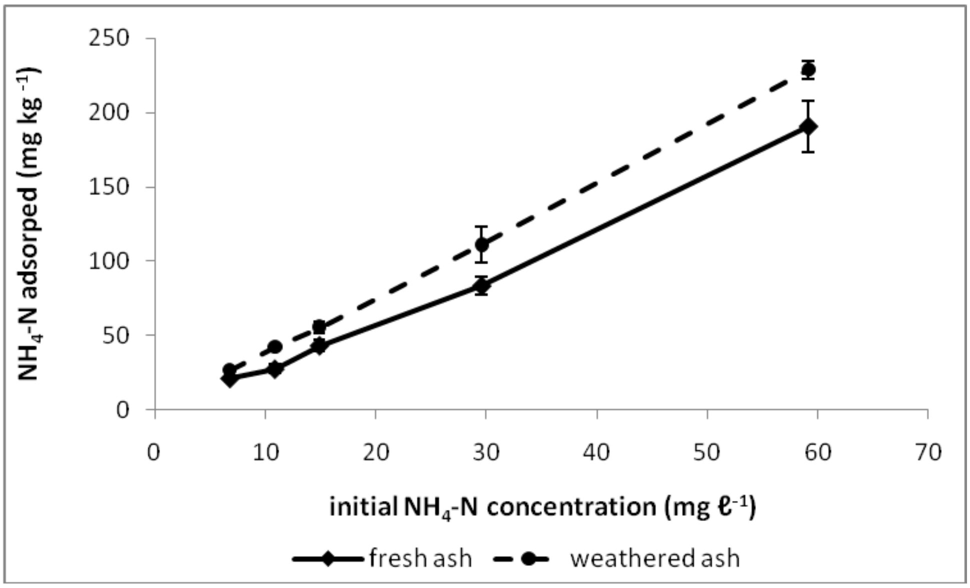

Fig 5.1. Ammonium sorption in fresh and weathered coal gasification ash. Error bars show standard deviation of the mean of three replicates.

It is hypothesized that a greater sorption of ammonium will be observed in ash heaps that have weathered considerably. It has been reported that over time, weathering can cause a transformation of coal ash components converting alumino-silicate glass into non-crystalline clay minerals (Zevenbergen et al., 1999; Donahoe, 2004; Haynes, 2009). This would in turn, imbue weathered ash with more negatively charged surfaces for ammonium sorption.

In actual sludge-amended coal gasification ash dumps, it is probable that struvite ($NH_4MgPO_4 \cdot 6H_2O$) formation may be another mechanism for ammonium retention in ash heaps, especially because of the alkalinity of the ash medium, and the high phosphorus content of sludges. The solubility of struvite decreases with increasing pH up to a pH of about 9 after which its solubility increases (Doyle and Parsons, 2002). As the alkalinity of the medium is neutralized by acid-generating processes, ammonium bound in struvite will be slowly released for nitrification and plant uptake. For practical purposes, retention of ammonium in complexes such as struvite is more desirable than if ammonium is only adsorbed on the ash surface. If ammonium is only held on the ash surface, simple management practices such as fertilization of the media with a competing cation like potassium could trigger a sudden flush of ammonium.

Whatever the retention mechanism, sorbed ammonium can become available for exchange at prolonged periods of low ammonium concentrations, making the ash medium a potential reservoir for inorganic nitrogen. It is expected that due to the high ammonium sorption capacity of CGA, there would be little loss of ammonium by leaching or by volatilization as ammonia gas and this reduces the environmental risks associated with nitrogen when amending CGA with sludge. These risks are further reduced for older ash heaps that have undergone a considerable degree of weathering. Consequently, to limit ammonium leaching losses in a rehabilitation scenario involving sludge, older ash heaps should be preferred.

5.3.2 Ammonium sorption isotherms

Plots of the three isotherms fitted to the experimental data are shown in Fig 5.2. Although the linear isotherm model had a higher coefficient of determination (R^2) for fresh ash than the Freundlich isotherm, there is a greater spread of data points around the line. The R^2 value for the Freundlich isotherm was close to that of the linear model and the plotted points show a better fit. The linear model may be suitable for sorbates at low concentrations, however, many substances follow a sorption behaviour in which there is increasing sorption with increasing concentration, but as sorption sites become saturated, the incremental amount of solute sorbed decreases (Minasny and Perfect, 2004). Therefore the Freundlich isotherm model is suitable here to describe the sorption behaviour of ammonium in both fresh and weathered CGA.

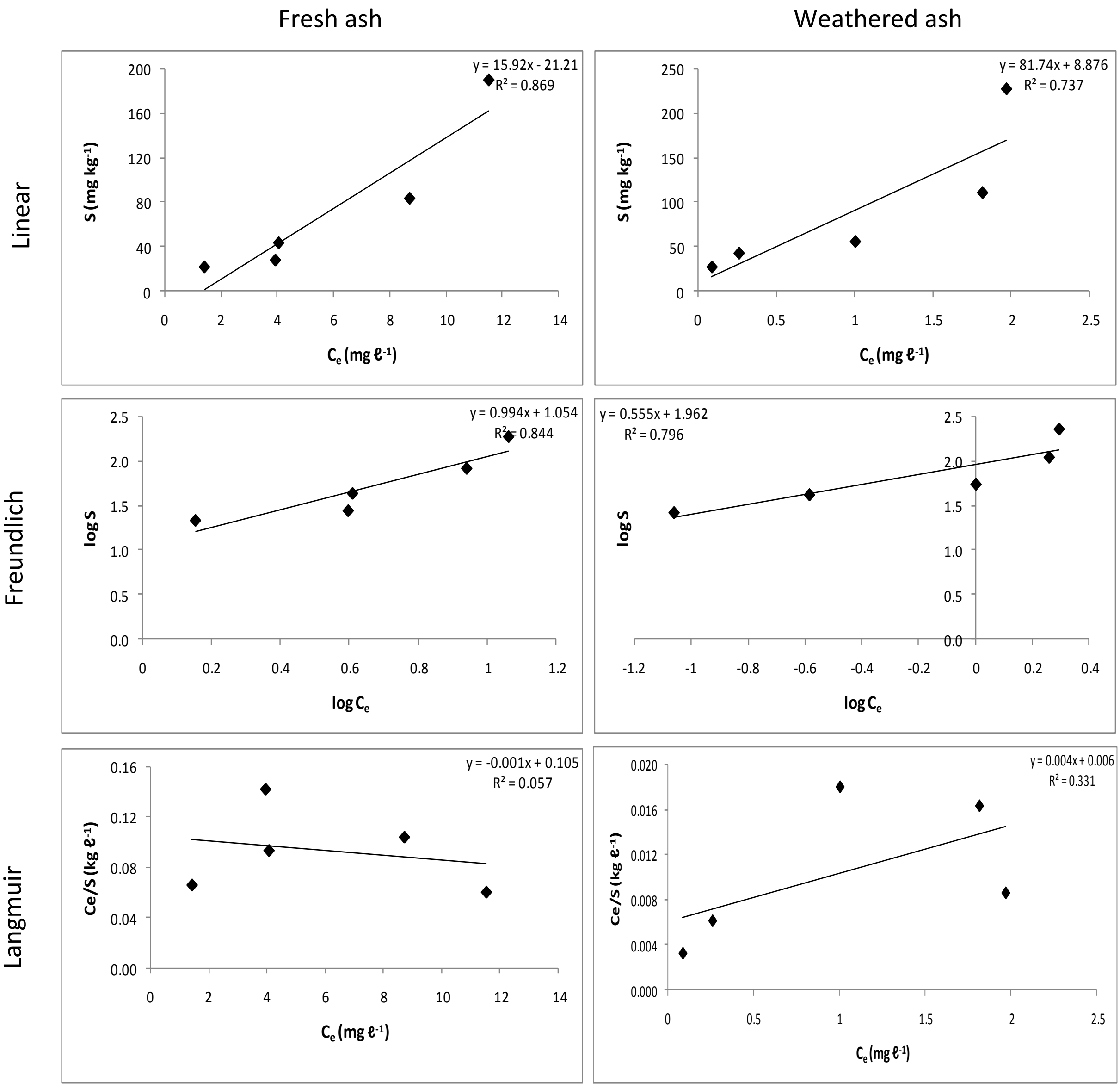

Fig 5.2 Isotherm plots for sorption of ammonium by fresh and weathered coal gasification ash

Table 5.2 gives a summary of the parameters derived from the Freundlich plots in Fig 5.2. The 1/*n* constant for the Freundlich isotherm ranges from 0 to 1 and is a measure of exchange intensity. A value of 1/*n* smaller than 1 describes favourable removal conditions (Malekian et al., 2011). Therefore, results show that conditions for ammonium sorption are more favourable in weathered ash.

Table 5.2 Calculated Freundlich isotherm parameters for ammonium sorption by fresh and weathered coal gasification ash

Parameter	**Fresh ash**	**Weathered ash**
R^2	0.844	0.796
K_f ($mg^{1-1/n}$ $\ell^{1/n}$ kg^{-1})	11.32	91.62
n	1.0	1.8

5.4 Conclusions

The potential risks associated with excess ammonium as a result of sludge-amendment of coal gasification ash gave rise to this study. Results show that ammonium can be retained sufficiently by ash, with ammonium sorption being higher in weathered ash than in fresh ash. Leaching losses of ammonium from amended ash dumps are likely to be minimal, therefore risks for nitrogen pollution of nearby water sources are greatly reduced. The Freundlich isotherm was adequate to predict sorption behaviour of ammonium in coal gasification ash, and the parameters generated will be helpful input in modelling ammonium transport in a sludge-amended coal gasification ash dump under similar conditions.

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Chapter 6: Modelling ammonium retention in sludge-amended coal gasification ash by chemical precipitation

Abstract

Amending waste coal gasification ash (CGA) with sludge has been shown to be a potential site rehabilitation option because sludge will supply nitrogen required by plants which will enhance the revegetation of ash dump sites. The CGA environment has also been shown to be inhibitory to nitrification processes, resulting in an accumulation of ammonium in sludge-amended CGA. The potential for excess ammonium to leach out from amended ash dumps gave rise to an investigation into the possible mechanisms for ammonium retention in this medium. Conditions in sludge-amended CGA, namely a high pH and sufficient supply of ammonium, P, and Mg, suggest that ammonium might be retained as struvite (magnesium ammonium phosphate hexahydrate, $MgNH_4PO_4.6H_2O$) and be slowly released with time. The aim of this study was to evaluate struvite formation in sludge-amended CGA and to assess factors likely to be limiting to its formation. CGA amended with 5% sludge (on a dry mass basis) and packed in a column was made to undergo nine leaching and drying cycles simulating natural weathering conditions. Leachates were analysed and the geochemical model PHREEQC was used to estimate the saturation index of struvite. Mineral saturation indices indicate that struvite can form initially, but the mineral will be solubilised as pH and ammonium decrease due to nitrification, and as P is reduced by calcium phosphate precipitation. Results show that in this medium, pH, nitrification and concentration of Ca may play the biggest role in the possibility for struvite formation.

Keywords: *ammonium, coal gasification ash, PHREEQC, sludge, struvite*

6.1 Introduction

Disposal of waste ash generated during the process of gasification of coal for production of fuel has been a challenge to industry for many years. Unlike waste fly ash from power stations which finds usage in cement industries (Torrey, 1978) and more recently, in agriculture (Singh et al., 2011), beneficial use of gasification ash has been hampered by the material’s coarse nature and costs related to transport and grinding of the material for brick making purposes. Consequently, millions of tons of coal gasification ash (CGA) is landfilled or piled up in dumps in the vicinity of gasification plants. The environmental implications of such dumps have been well documented, with leaching of toxic elements being of major concern (Jala and Goyal, 2006).

Rehabilitation of gasification ash dumps through amendment with sludge has been suggested as having the potential to facilitate growth of vegetation on these dumps thereby reducing infiltration into this medium (Annandale et al., 2004). The ameliorating effect of sludge on this highly alkaline material, coupled with a rich supply of plant nutrients and an improvement to physical properties, make sludge-amending coal gasification ash a potential recourse to the environmental footprints left by these dumps. Because CGA is mostly devoid of nitrogen, sludge could supply this very important plant nutrient.

Previous studies have shown that because of the inhospitality of coal ash, nitrification is inhibited and ammonium will be the dominant nitrogen species in a sludge-amended ash dump (Mbakwe et al., 2013; Chapter 4). Although plants may take up ammonium, excess ammonium may be lost from the ash heap and transported into other ecosystems where ammonium can be oxidized to nitrites and nitrates causing significant environmental degradation.

Batch experiments using CGA and chemical ammonium reagent have shown that ammonium can be adsorbed sufficiently by the ash particles (Chapter 5). Chemical principles also suggest that in a CGA-sludge medium, ammonium can also be retained by the formation of struvite (magnesium ammonium phosphate hexahydrate, $MgNH_4PO_4.6H_2O$) since CGA contains appreciable quantities of magnesium and sludge can supply phosphates and ammonium. The precipitation of struvite can be represented by Eq 6.1.

$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \leftrightarrows MgNH_4PO_4.6H_2O$……………………………….. (Eq 6.1)

Struvite can serve as a slow release source of nitrogen because it is sparingly soluble in water and under neutral and alkaline conditions, but becomes soluble as the environment becomes more acidic (Zhang et al., 2011). This mechanism of ammonium retention in the ash heap is more desirable than if ammonium is only electrostatically adsorbed. This is because if ammonium is only adsorbed on the ash particles fertilization with for example potassium might trigger a flush of ammonium as the introduced cation displaces it from the exchange sites.

At present it is unclear whether conditions in sludge-amended CGA will be conducive for struvite formation over a period of time if ash heaps are exposed to leaching and weathering conditions. Struvite precipitation is influenced by factors such as pH, concentrations of Mg^{2+}, $PO4^{3-}$ and NH_4^+, as well as the presence of other interfering ions, such as calcium (Ca^{2+}) (Liu, 2009).

The aim of this study is to evaluate struvite formation in sludge-amended CGA exposed to several leaching and drying cycles simulating natural weathering conditions and to assess which factors are likely to be limiting to its formation. The hypothesis tested is that struvite will form in a CGA-sludge medium, but will dissolve with time as factors conducive to its stability become limiting.

6.2 Materials and methods

6.2.1 Column leaching

Coal gasification ash amended with 5% sludge was packed in a transparent column at a wet bulk density of 1200 kg m^{-3} and leached nine times with an amount of water equal to one pore volume for each leaching cycle. Leachates sucked out after 24 hours using a vacuum pump set at 10 kPa suction were used for chemical analyses. These leachates were deemed to be closer to equilibrium than freely drained ones. Treatments were allowed to dry before the subsequent wetting cycle. Details of the column design and leaching process have been described in Chapter 3 and in de Jager et al. (2013). Some chemical properties of CGA and sludge are shown in Table 6.1. Concentration of elements in leachates from each leaching cycle was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Inorganic nitrogen was determined by Kjeldahl distillation (Bremner and Keeney, 1965). Leachate composition is shown in Table 6.2.

Table 6.1 Some chemical properties of coal gasification ash and sludge

Parameter	CGA	Sludge
pH	10.8	6.8
Volatile Solids (%)	4.6	82.4
Total N (%)	< 0.04	7.9
Total C (%)	5.7	56.3
C/N Ratio	Nil	7.1
Ca (%)	7.22	0.58
Mg (%)	1.51	0.26
P (%)	0.33	0.46
K (%)	0.017	0.1
Na (%)	0.34	0.087
Fe (%)	2.88	0.6
Al (%)	12.13	0.31
As (mg kg^{-1})	10.7	29.7
B (mg kg^{-1})	202	34
Cd (mg kg^{-1})	0.41	0.22
Co (mg kg^{-1})	33	2.2
Cr (mg kg^{-1})	135	55
Cu (mg kg^{-1})	58.3	18.2
Mn (mg kg^{-1})	280	90
Mo (mg kg^{-1})	4.3	5.36
Ni (mg kg^{-1})	25.67	10
Pb (mg kg^{-1})	26.7	5.09
Se (mg kg^{-1})	<0.1	535.7
V (mg kg^{-1})	117	143
Zn (mg kg^{-1})	12.33	146.67

Table 6.2 Analyses of leachates from sludge-amended coal gasification ash during nine leaching cycles†

Cycle	pH	Ca	Mg	K	Na	Al	Cd	Cr	Cu	Fe	Mn	Ni
1	9.54	1192.1	21.6	175.2	222.3	0.0965	0.00070	0.0025	0.0079	0.172	0.117	0.0241
2	8.35	374.8	745.8	166.7	184.1	0.0852	0.00000	0.0045	0.0000	1.366	0.236	0.0521
3	8.86	54.2	551.6	126.5	141.3	0.0961	0.00827	0.0093	0.0122	0.788	0.095	0.0602
4	8.82	84.4	321.6	63.7	72.0	0.0520	0.01350	0.0000	0.0265	0.564	0.104	0.0292
5	8.79	42.6	339.8	74.3	101.2	0.5531	0.00297	0.0303	0.0665	0.279	0.064	0.0413
6	8.5	66.0	364.3	62.7	95.0	0.0325	0.00000	0.0130	0.0144	0.247	0.019	0.0224
7	8.33	232.8	573.5	39.0	74.2	0.0378	0.00000	0.0000	0.0012	0.044	0.024	0.0128
8	7.52	535.9	684.7	3.8	41.1	0.0250	0.00000	0.0000	0.0000	0.000	0.070	0.0078
9	7.72	407.1	453.7	3.9	32.0	0.0231	0.00000	0.0000	0.0000	0.000	0.045	0.0069

Cycle	Se	Zn	V	Co	Pb	B	Mo	As	Hg	P	S	Cl	NH_4
1	1.268	0.079	0.165	0.0054	0.0181	2.17	0.42	0.201	0.0422	1.31	512	477	45
2	1.639	0.065	0.034	0.0106	0.0000	14.69	1.01	0.218	0.0212	27.39	1742	341	55
3	1.014	0.105	0.333	0.0085	0.0000	14.71	1.15	0.460	0.0012	9.01	1570	292	77
4	0.405	0.053	0.226	0.0014	0.0000	10.60	1.04	0.289	0.0262	3.57	799	594	60
5	0.927	0.052	0.132	0.0061	0.0000	22.21	1.17	0.273	0.0284	3.31	1101	371	63
6	0.375	0.040	0.313	0.0014	0.0016	10.51	0.72	0.254	0.0118	2.48	857	82	50
7	0.278	0.027	0.257	0.0000	0.0000	10.17	0.47	0.223	0.0022	2.67	580	59	37
8	0.193	0.014	0.173	0.0000	0.0000	9.06	0.30	0.163	0.0031	5.12	371	42	28
9	0.273	0.011	0.178	0.0000	0.0000	7.46	0.23	0.135	0.0066	3.81	350	30	21

†Element concentrations are in mg ℓ^{-1}

6.2.2 Thermodynamic modelling

Thermodynamic modelling of struvite formation was done with the geochemical model PHREEQC (Parkhurst and Appelo, 1999) using the Minteq.v4 database.

The saturation index (SI) of struvite formation was calculated. SI is defined as

$$\mathrm{SI} = \log \frac{\mathrm{IAP}}{\mathrm{Ksp}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Eq 6.2}$$

Where IAP is the free ionic activities product and K_{sp} is the thermodynamic solubility product constant. If SI > 0, then the solution is supersaturated for struvite and this mineral is expected to form. In other words, struvite will precipitate when the ionic activity product of the components of struvite exceeds its solubility product.

Because struvite is not found in the original databases that came with PHREEQC, struvite was defined as a new phase. Struvite solubility product values were estimated from literature. This study used a pK_{sp} of 12.6 which is the most commonly used value in engineering (Snoeyink and Jenkins, 1980; Rahaman et al., 2006).

The dissolution of struvite was defined as (Roncal-Herrero et al., 2011)

$$MgNH_4PO_4.6H_2O \rightarrow Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Eq 6.3}$$

Using the leachate composition (Table 6.2) as input in PHREEQC, the model's output was used to estimate the minerals that can be formed.

6.3 Results and Discussion

Changes in the saturation index of struvite over the course of the leaching cycles are shown in Fig. 6.1. The SI of struvite increased and struvite was slightly supersaturated by the 3rd leaching after which SI declined.

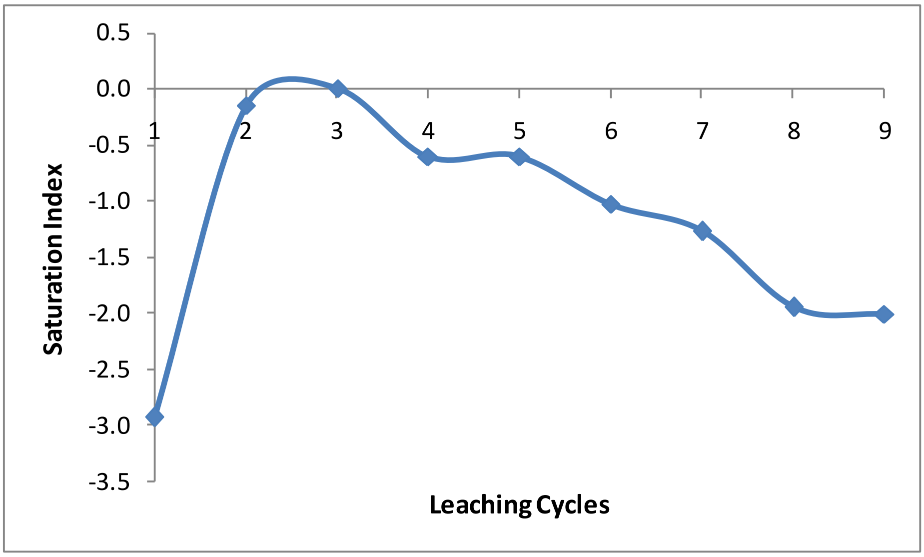

Fig.6.1. Saturation index of struvite in leachates from sludge-amended coal gasification ash during nine leaching cycles

This decline in the SI of struvite can be linked to a drop in pH. pH levels over the leaching period are shown in Fig. 6.2. Song et al. (2007) found that pH is the most important controlling factor for struvite crystallization and that optimum pH was in the range of 9.5 – 10.5. Liu (2009) found an optimum pH of struvite precipitation in the range of pH 8 - 9. pH dependency of struvite is linked to the effect that pH has on the activities of both NH_4^+ and PO_4^{3-}. pH affects the solubility of PO_4^{3-} and determines whether N will remain in solution as NH_4^+ (Liu, 2009). At high pH, NH_4^+ may be easily converted to free NH_3 (Song et al., 2007). At very high pH of above 11, struvite precipitation might also be inhibited because the formation of brucite ($Mg(OH)_2$) will reduce the Mg^{2+} available for struvite formation.

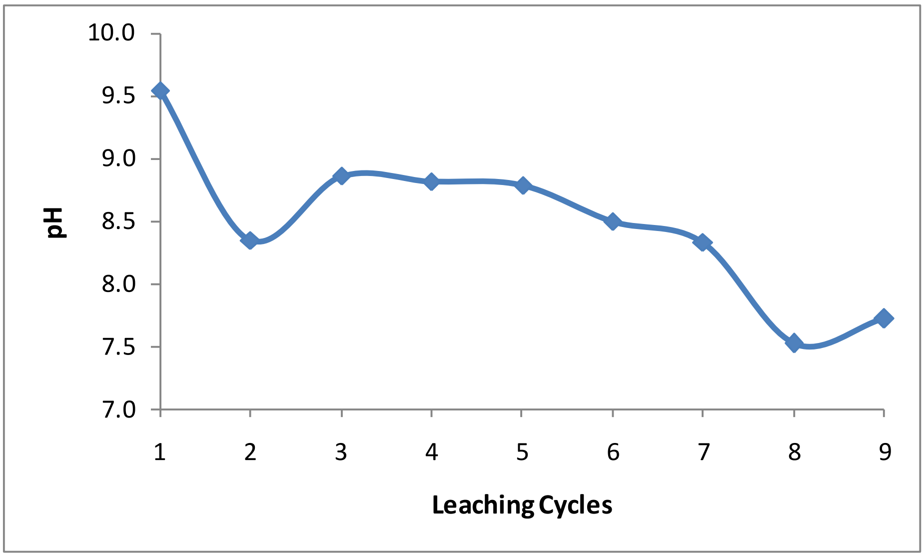

Fig.6.2. pH of leachates from sludge-amended coal gasification ash during nine leaching cycles

The drop in pH can be attributed to two phenomena. First, when CGA is amended with sludge, carbonation, a situation where carbon dioxide released during the breakdown of sludge forms carbonic acid, may produce a drop in pH. Secondly, although nitrification is inhibited in this CGA-sludge medium, it is not completely prevented. Therefore as nitrification progresses (Fig. 6.3.), extra acidity is generated (Brady and Weil, 1999).

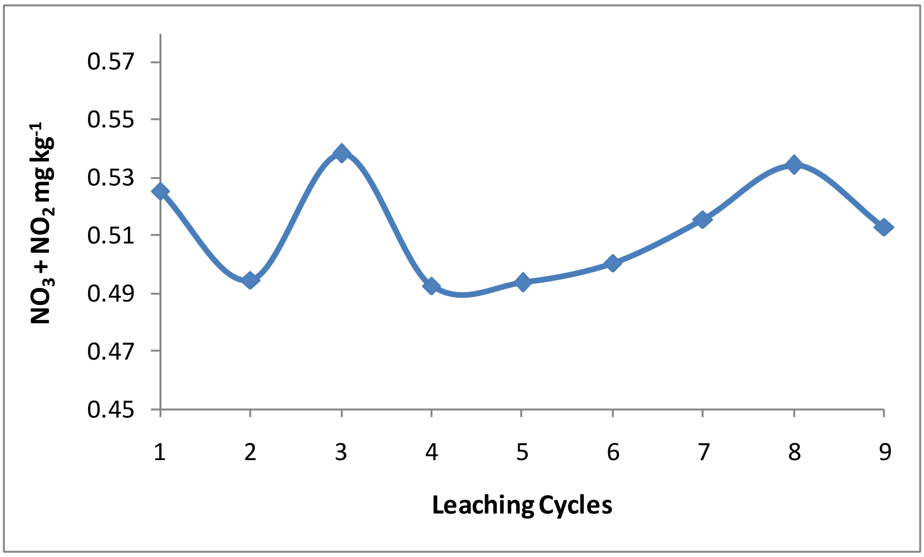

Fig.6.3. Concentration of nitrites and nitrates in leachates from sludge-amended coal gasification ash during nine leaching cycles

Another controlling factor for struvite precipitation is the concentrations of the constituent elements – ammonium, phosphates and magnesium. Fig 6.4 shows the changes in the concentrations of these elements over the leaching cycles.

Ammonium increased up to the 3rd leaching due to mineralization of organic N in sludge, and then declined. The depletion of ammonium may have been due to nitrification or ammonium loss through volatilization as ammonia. The high pH of CGA suggests that there might be substantial N losses through ammonia volatilization (Zia et al., 1999), although the high ammonium sorption capacity of coal ash can limit gaseous losses (Zhang et al., 2011; Juan et al., 2009; Salazar et al., 2012).

Results show that unlike Mg that may be generated with time through ligand promoted dissolution (Zhang and Bloom, 1999), P may over time, be a limiting factor for struvite formation in sludge-amended CGA. Leaching of P from media amended with organic materials has been observed and can be linked to the competitive adsorption of dissolved organic carbon (DOC) against P on anion exchange sites (Kang et al., 2011).

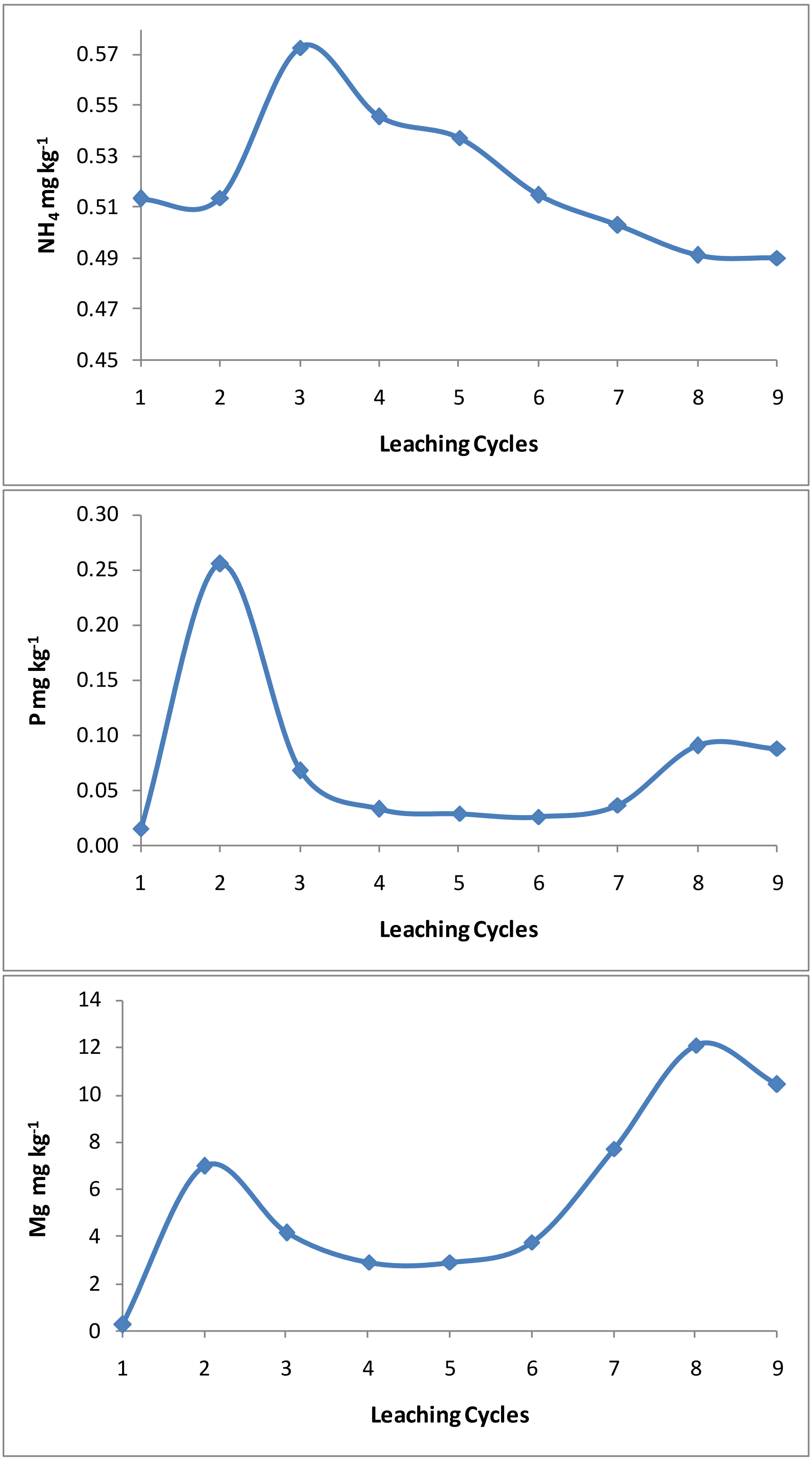

Fig.6.4. Concentration of ammonium, Mg, and P in leachates from sludge-amended coal gasification ash during nine leaching cycles

The highest leachate concentration of P was about 27 mg ℓ^{-1} (Table 6.2). Assuming that there was no P leaching or that P fertilization was done to keep P constantly at this level, model simulations for the saturation index of struvite were run. Results show that the possibility for struvite precipitation is increased (Fig 6.5). Nevertheless, when pH drops to 8.33 at the 7th leaching, struvite is again solubilized.

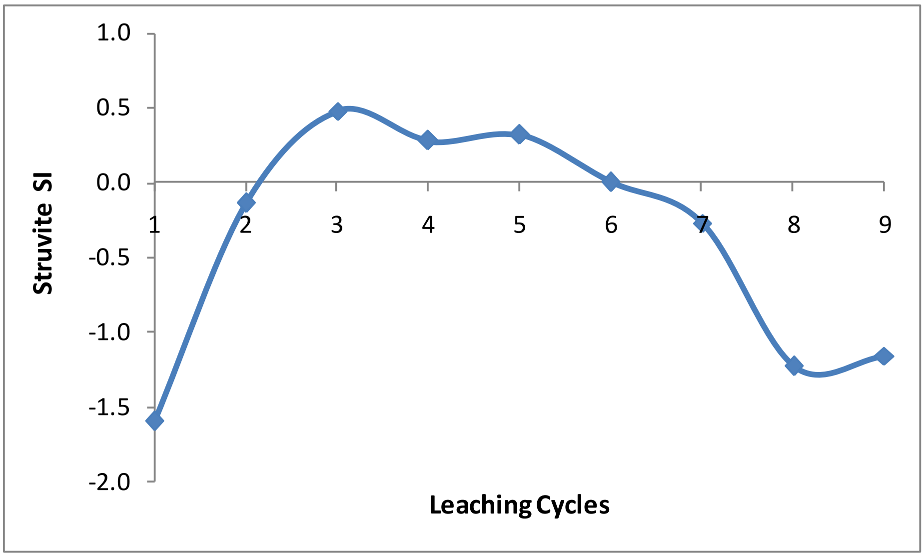

Fig.6.5. PHREEQC modelling output of saturation index of struvite when concentration of P in leachates from sludge-amended coal gasification ash is kept constant at 27 mg ℓ^{-1}.

P may also be rendered unavailable for struvite formation due to the precipitation of calcium phosphate (Song et al., 2007; Zhang et al., 2011). Therefore the concentration of Ca^{2+} is an indirect factor affecting struvite formation. Calcium concentration in leachates is shown in Fig 6.6.

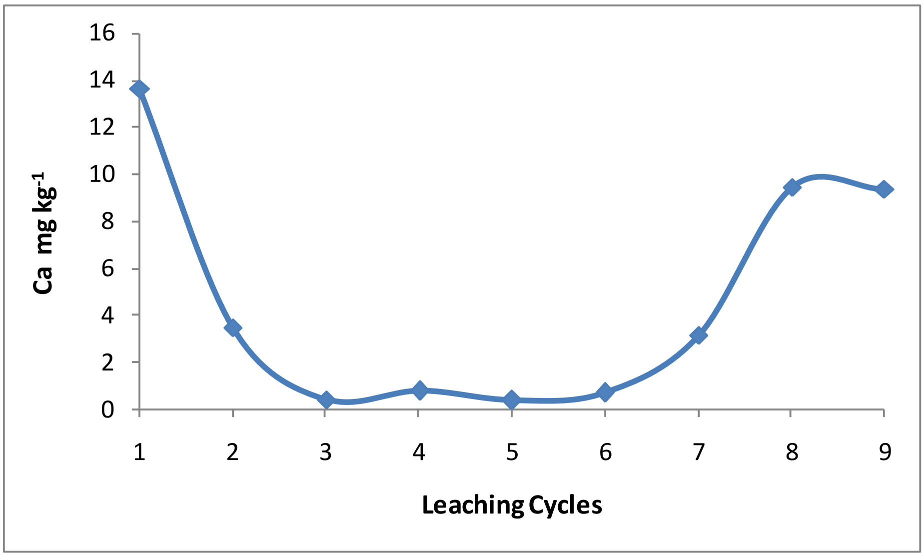

Fig 6.6 Concentration of calcium in leachates from sludge-amended coal gasification ash during nine leaching cycles

The initial high Ca concentrations, especially relative to Mg and P (Fig 6.4) suggest that struvite formation will be inhibited by Ca^{2+}. Several authors such as Song et al. (2007) and Wang et al. (2005) found that a high Ca/Mg or Ca/P ratio inhibited struvite formation because of precipitation of calcium phosphate.

Among the different kinds of calcium phosphates that can precipitate in saturated solutions such as $Ca_5(PO_4)_3OH$ (hydroxyapatite), $CaHPO_4.2H_2O$ (dicalcium phosphate dihydrate), $Ca_4H(PO_4)_3.2.5H_2O$ (octacalcium phosphate), and $Ca_3(PO_4)_2$ (tricalcium phosphate), hydroxyapatite is thermodynamically the most stable (Koutsoukos et al., 1980; Song et al., 2002). The saturation index for hydroxyapatite calculated by PHREEQC is shown in Fig 6.7. Results show that leachates are supersaturated with hydroxyapatite, so calcium phosphate is expected to form and precipitation of calcium phosphate will therefore reduce the P available for struvite formation.

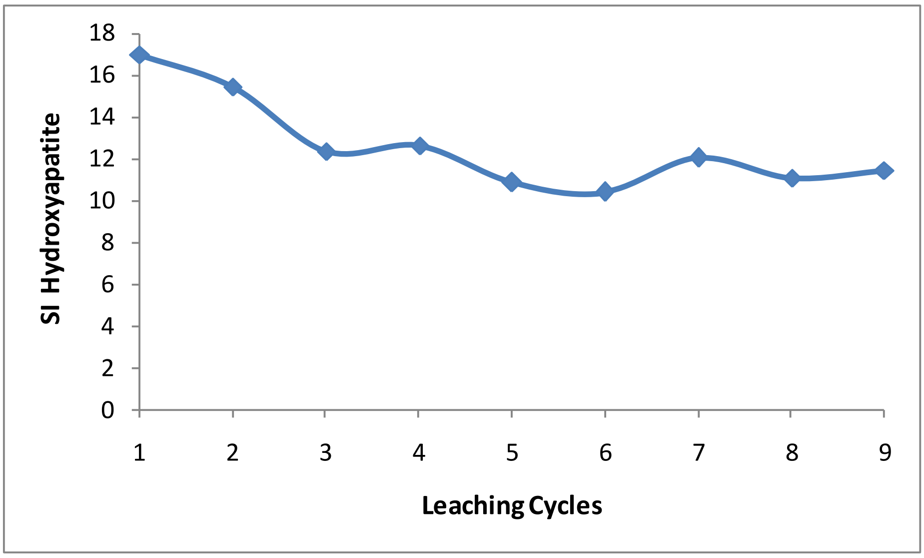

Fig.6.7. Saturation index of hydroxyapatite in leachates from sludge-amended coal gasification ash during nine leaching cycles

6.4 Conclusions

In a sludge-amended coal gasification ash medium, ammonium retention in struvite is desirable because this will ensure slow release of nitrogen for plants used for revegetation of dump sites so that excess ammonium will not be leached easily from the ash heap. Results from PHREEQC modelling of column leachates indicate that in sludge-amended CGA, struvite can form initially, but the mineral will be solubilised as pH and ammonium decrease due to nitrification, and as P is reduced due to precipitation of calcium phosphate. pH, nitrification and concentration of calcium will therefore, play the biggest role in the possibility for struvite formation. Fertilizing sludge-amended ash heaps with P may be the most feasible solution to enhancing struvite formation in sludge-amended CGA.

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Chapter 7: Ammonia volatilization from sludge-amended coal gasification ash

Abstract

Amendment of coal gasification ash (CGA) dumps with sludge has been shown to aid in site rehabilitation by improving the nutrient status of the dump and transforming the ash heap into a medium that can support plant growth. The conversion of organic nitrogen in sludge into plant usable nitrogen forms, though attainable in CGA, favours a build-up of ammonium. The increased ammonium and the alkaline conditions of the ash medium suggest that ammonia volatilization may be substantial, warranting investigation. This study was carried out to estimate ammonia loss in sludge-amended CGA. Fresh and weathered CGA were amended with the equivalent of 90 tons ha^{-1} activated sludge and ammonia volatilization monitored in a laboratory set-up over a period of 14 days. A soil treatment was included for comparison. Results showed that ammonia volatilization was greater and more rapid in soil (1.36% of initial total N) than in CGA, and that less nitrogen was volatilized in weathered ash (1.08% of initial total N) than in fresh ash (1.34% of initial total N). The low ammonia volatilization from ash is attributed to the high ammonium sorption capacity of CGA which is enhanced by ash weathering.

Keywords: a*mmonia, coal gasification ash, sludge, volatilization*

7.1 Introduction

Use of sludge to amend coal gasification ash (CGA) for rehabilitation purposes will improve the physical and chemical properties of ash, and add necessary plant nutrients, especially nitrogen and phosphorus. A previous study showed that because of the inhospitality of the ash medium to nitrifying organisms, ammonium may accumulate in the ash profile (Mbakwe et al., 2013). The high pH of CGA suggests that there might be substantial N losses through ammonia volatilization (Zia et al., 1999). Moreover, the inhibition of nitrification in CGA may increase the availability of ammonium for ammonia volatilization (He et al., 1999; Soares et al., 2012). Ammonia volatilization has also been shown to be enhanced by salinity (McClung and Frankenberger, 1985), suggesting that losses of N through ammonia volatilization in this alkaline and saline coal gasification ash environment may be substantial.

An estimate of losses of nitrogen by volatilization is necessary because volatilization reduces plant-available nitrogen, and contributes to adverse environmental effects. Although nitrogen gaseous losses may be either as ammonia (NH_3), nitrogen oxides (NO_x), nitrous oxide (N_2O) or dinitrogen (N_2), losses through ammonia have been known to account for approximately 98% of gaseous N losses (Beck Friis et al., 2001). Nitrogen losses by ammonia volatilization, apart from its economic significance in farming, can cause soil acidification upon returning to the ground, may act as a secondary source of N_2O production, and enhance eutrophication of water bodies (Soares et al., 2012). The aim of this study was to estimate ammonia losses in sludge-amended coal gasification ash. The hypotheses tested are:

1. ammonia volatilization will be higher in CGA than in soil due to the high pH of CGA.
2. ammonia volatilization will be higher in fresh CGA than in weathered CGA due to the higher salinity of fresh CGA and the greater sorption of ammonium by weathered ash.

7.2 Materials and methods

7.2.1 Sample characteristics

Fresh coal gasification ash was collected from a freshly dumped coal gasification ash heap. “Weathered ash” was fresh ash that had undergone ten leaching and drying cycles over a period of 12 months, with the volume of water used for leaching equivalent to 1270 mm of rainfall. Details of the column leaching set-up can be found in Chapter 3 and in de Jager et al. (2013). The sludge used for this experiment was obtained from an activated sludge treatment plant. The sludge originated from the activated treatment of industrial wastewater and has a C/N ratio of 7.1. Topsoil (0-15 cm) of a loamy sand was collected from an experimental farm of the University of Pretoria near Cullinan, Gauteng Province, South Africa where sludge has not previously been applied. The inclusion of soil in this experiment was to compare ammonia volatilization in ash with ammonia volatilization in a more common sludge application medium. Nitrogen speciation, and some chemical characteristics of coal gasification ash, soil and sludge determined in a 1:5 sample:water mixture are shown in Table 7.1.

Table 7.1. Some chemical characteristics of experimental materials†

	Fresh ash	Weathered ash	Soil	Sludge
pH(H_2O)	8.71 (0.08)	9.46 (0.04)	5.58 (0.035)	5.8 (0.03)
EC(dS m^{-1})	2.02 (0.02)	0.53 (0.005)	0.096 (0.0016)	0.65 (0.07)
Total N (%)	0.0095 (0.0028)	0.00925 (0.001)	0.024 (0.00014)	7.91 (0.006)
NH_4-N (mg kg^{-1})	1.25 (0.036)	1.21 (0.012)	20.9 (0.88)	7104 (356.2)
NO_3-N (mg kg^{-1})	7.2 (0.65)	2.33 (0.11)	22.1 (1.32)	167 (6.7)
NO_2-N (mg kg^{-1})	1.34 (0.1)	0.54 (0.019)	0.75 (0.39)	8.71 (0.79)
Organic N (mg kg^{-1})	85 (29.05)	88 (10.49)	196 (5.01)	71820 (336.9)
Ca (mg kg^{-1})	1517 (53)	462 (7.9)	17.8 (3.1)	394 (2.1)
Mg (mg kg^{-1})	94.8 (2.5)	7.4 (0.4)	8.7 (1.2)	299 (2.8)
K (mg kg^{-1})	158 (4.7)	18.6 (0.53)	12.2 (1.7)	851 (18.9)
Na (mg kg^{-1})	480 (14.7)	35 (2.0)	5.8 (1.9)	371 (8.7)
Fe (mg kg^{-1})	0.035 (0.0095)	0.026 (0.0075)	42.19 (1.33)	8.98 (0.14)
Al (mg kg^{-1})	0.653 (0.03)	2.68 (0.05)	126.97 (29.5)	10.13 (0.08)
Cu (mg kg^{-1})	0.016 (0.003)	0.012 (0.0025)	0.128 (0.026)	0.235 (0.03)
Mn (mg kg^{-1})	0.0189 (0.0027)	0.0039 (0.001)	2.705 (0.54)	5.38 (0.025)
Zn (mg kg^{-1})	0.162 (0.014)	0.0068 (0.00076)	0.83 (0.03)	2.69 (0.29)

†Values represent the mean followed by the standard deviation in parentheses

7.2.2 Sample preparation and experimental set up

Samples (100 g) of fresh and weathered CGA passed through a 2 mm sieve were moistened to -70 kPa water tension (40% gravimetric water content). These were incubated for 31 days at 25 ± 3 °C in order to obtain a relatively steady rate of microbial activity (Quemada and Cabrera, 1997). After incubation, sludge was mixed thoroughly with ash at the rate of 90 tons ha^{-1} (5 g of sludge per sample, assuming a bulk density of 1200 kg m^{-3} and a depth of 15 cm) and the samples were brought back to water content at -70 kPa. Samples were placed in volatilization vessels under controlled laboratory conditions at a temperature of 25 ± 3 °C. Treatments were replicated thrice and completely randomized. Soil (100 g) amended with the same sludge rate and kept under the same water and temperature conditions was also included in order to compare ammonia volatilization in a more common sludge application medium.

The volatilization set-up has been described by Botha and Pretorius (1987, 1988) and is shown in Fig 7.1. The volatilization vessels were 0.5 kg screw-cap jars with a base area of 36.3 cm^2. The jars had tight-sealing lids the centre of which was fitted with two tubes, one to introduce constant airflow via a compressor set at 250 kPa pressure, and the other to conduct ammonia from the jar into a volumetric flask containing 100 ml of a 20 g ℓ^{-1} boric acid solution with mixed indicator (bromocresol green and methyl red). An empty jar was included to estimate the ammonia content of the introduced air. The boric acid was replaced when a colour change indicated ammonia volatilization (Fig 7.2). Ammonium nitrogen in boric acid was determined by titration of excess acid using 0.1 N H_2SO_4 and the amount of ammonia evolved was calculated as percentage of initial total N. Total ammonia volatilized was calculated as the cumulative ammonia after 14 days. Studies such as Velasco Velasco et al. (2011) and Jiang et al. (2012) have shown that ammonia volatilization can be well estimated within this period. Water content was maintained by weighing samples in order to estimate evaporated water.

Fig 7.1 Volatilization chamber showing jars, volumetric flasks containing boric acid solution with mixed indicator (bromocresol green and methyl red) and airflow compressor.

A separate set of sludge-amended samples incubated under the same conditions were used to determine changes in pH, electrical conductivity and ammonium concentrations over the 14 day period. Ammonium was determined following the method of Bremner and Keeney (1965).

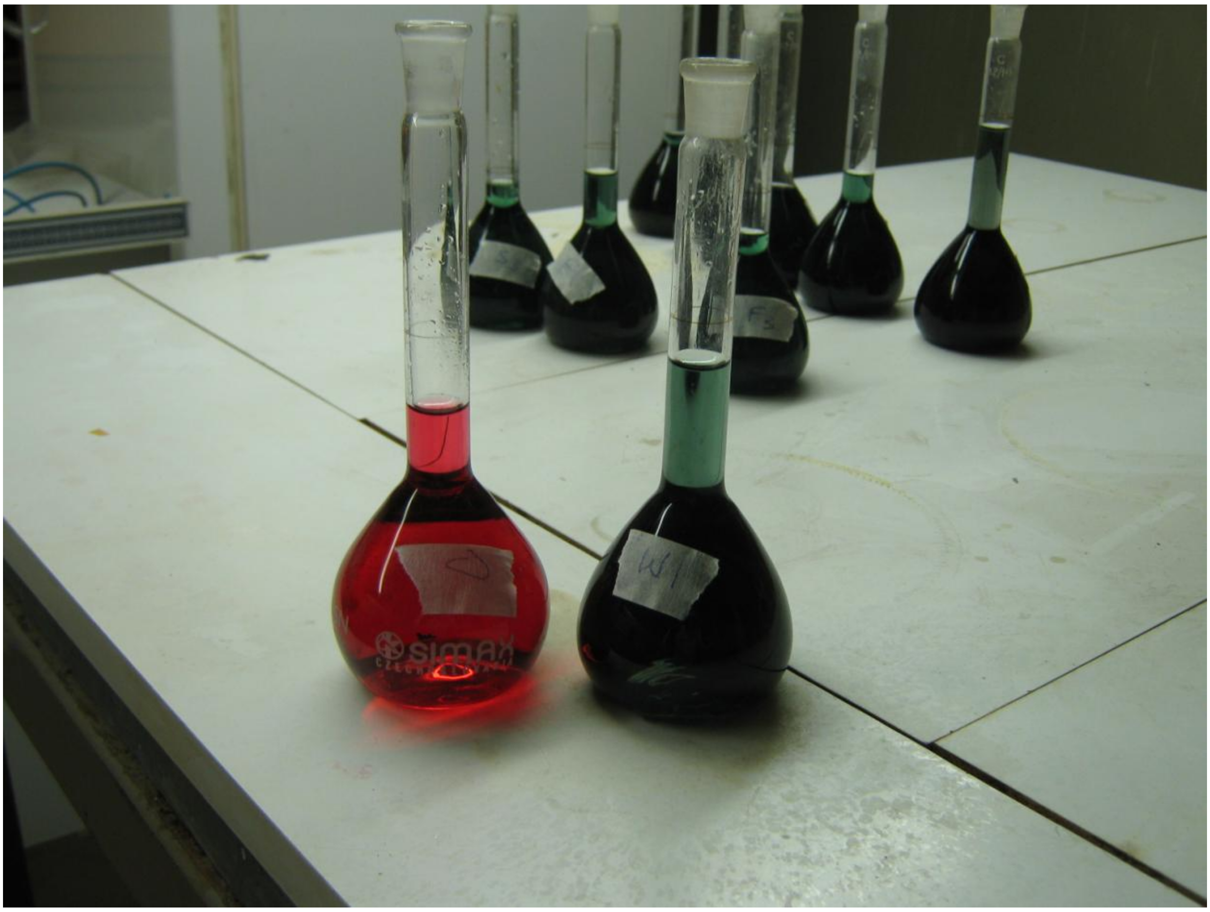

Fig 7.2 Volumetric flasks showing dark green colour change indicative of ammonia volatilization. In contrast is one volumetric flask from an empty jar used to estimate the ammonia content of the introduced air.

7.3 Results and discussion

Ammonia volatilization was first detected on day 5 for soil, peaking on day 8, but it appeared later on day 8 for both fresh and weathered ash and peaked on day 11 after which it declined. This is in agreement with Jiang et al. (2012) who found that ammonia volatilization from urea amended soils peaked from day 5 to day 9 and then declined. Velasco-Velasco et al. (2011) found that most ammonia volatilization occurred during the first 15 days of composting sheep manure. Soares et al. (2012) observed that because urea hydrolyses quickly, the majority of ammonia losses occur during the first week after application.

Percent of initial Total N in ash and soil volatilized as ammonia is shown in Fig 7.3. For soil 1.36% (0.0058 g) of initial Total N was volatilized, for fresh ash 1.34% (0.0055 g) was volatilized, and for weathered ash 1.08% (0.0044 g) was volatilized as ammonia. From ANOVA, these did not differ significantly from each other at α = 0.05.

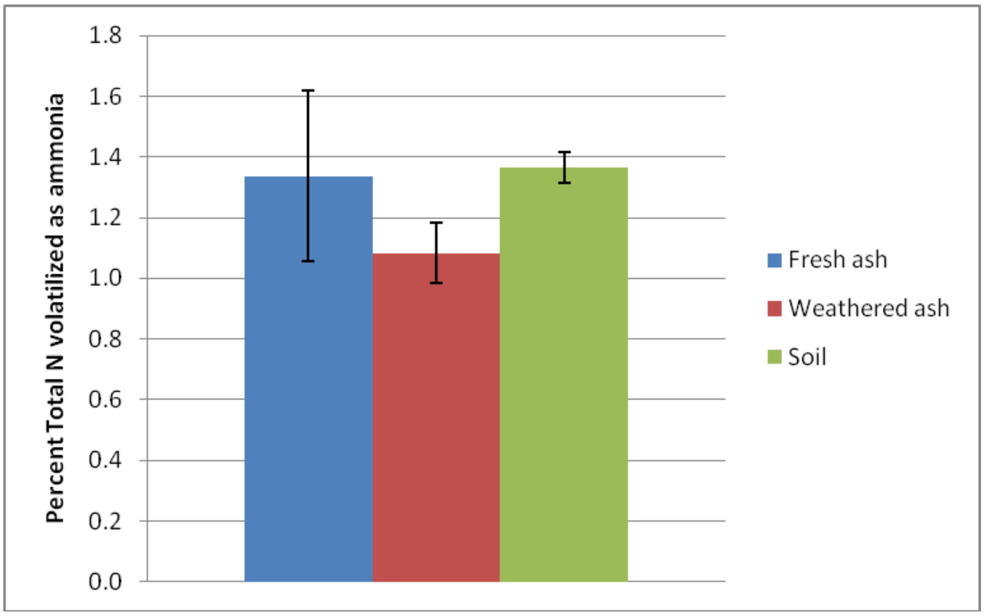

Fig 7.3 Percent of initial Total N volatilized from sludge-amended coal gasification ash and soil. Error bars show standard deviation of the mean of three replicates

Average ammonia losses worldwide is estimated to be about 14% of the N fertilizers used and can even be as high as 60%, especially in warmer climates (Soares et al., 2012). But this high percentage is because N in these fertilizers is often inorganic ammonium and more susceptible to volatilization whereas most of the N in sludge is organic and is transformed gradually to inorganic forms. This demonstrates yet another advantage of sludge as a slow release N source. Studies such as those of van Niekerk (2004) have already pointed out that nitrate leaching is minimized in sludge-amended soils compared to soils amended with inorganic N fertilizer because inorganic nitrogen in sludge is released slowly, and when synchronized with plant uptake, risks of nitrate leaching are greatly reduced.

On average, ammonia volatilized from soil was slightly higher than that from ash. Addition of sludge increased soil pH rapidly from 6.3 on day 0 to 8.5 on day 14 (Fig 7.4). This increase in pH can be attributed to the hydrolysis of urea in sludge to unstable carbamic acid which subsequently decomposes rapidly to form ammonia and carbon dioxide (Eq 7.1).

$(NH_2)_2CO + H_2O \rightarrow NH_3 + H_2NCOOH \rightarrow 2NH_{3(gas)} + CO_{2\ (gas)}$…………… (Eq 7.1)

Reaction of ammonia with water results in the formation of ammonium and the hydroxide ion (Eq 7.2) which consequently increases the local microsite pH (Coyne, 1999; Soares et al., 2012).

$NH_{3(gas)} + H_2O \rightarrow NH_4^+ + OH^-$……………………………………………….(Eq 7.2)

At this high pH, ammonia emission is expected to increase because a high pH favours ammonia in the ammonia/ammonium equilibrium in solution (Freney et al., 1983). Since ash already had a high pH, addition of sludge caused only a slight change in pH (Fig 7.4).

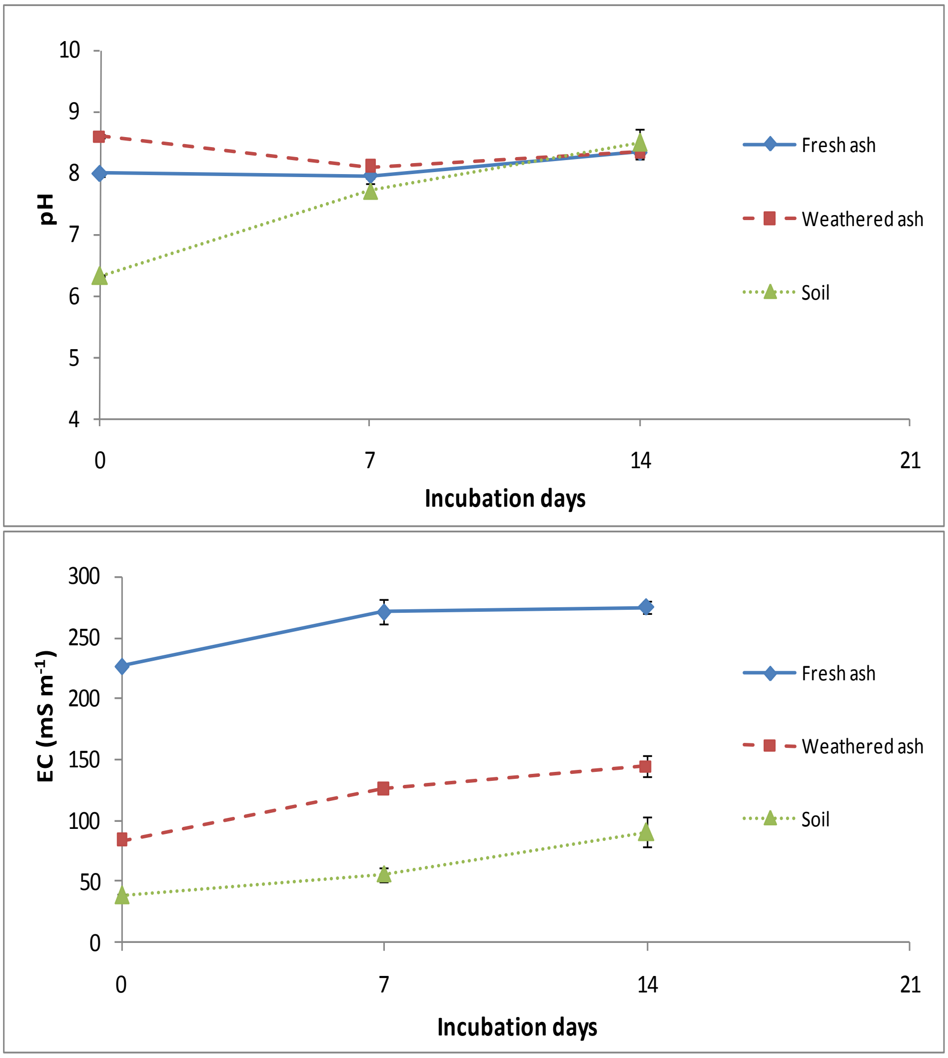

Fig 7.4 pH and electrical conductivity of sludge-amended coal gasification ash and soil during 14 days of incubation. Error bars show standard deviation of the mean of three replicates

Ammonium concentrations of incubated samples are shown in Fig 7.5. It is noteworthy that although more ammonium was observed for weathered ash, it volatilized less ammonia. As a percentage of ammonium formed after 14 days of incubation, ammonia volatilized was 6.3% for fresh ash, 3.2% for weathered ash, and 6.2% for soil. Ammonia volatilized from weathered ash was least and from analysis of variance, differed significantly ($\alpha = 0.05$) from that volatilized by fresh ash.

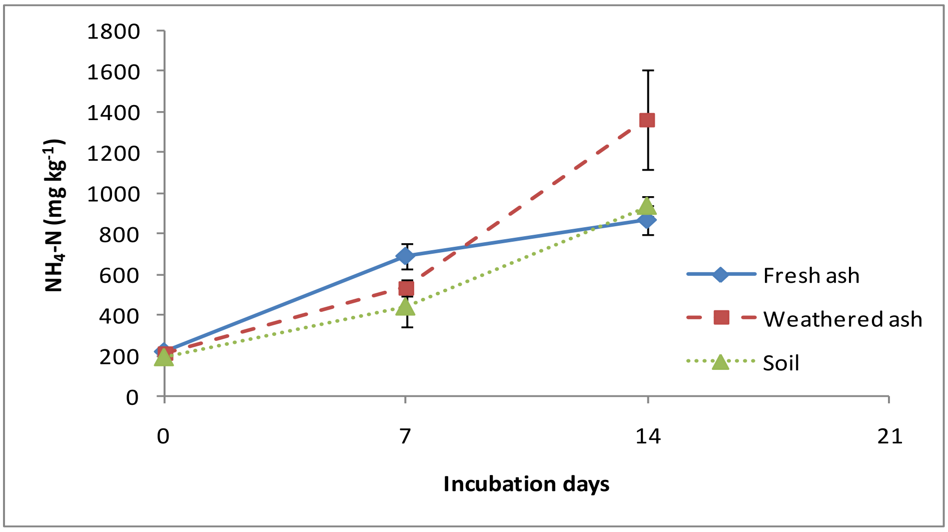

Fig 7.5 Ammonium concentrations of sludge-amended coal ash and soil during 14 days of incubation. Error bars show standard deviation of the mean of three replicates

The very low ammonia volatilization in sludge-amended ash can be attributed to the high ammonium sorption capacity of coal ash (Zhang et al., 2011; Juan et al., 2009) which may prevent ammonium losses by leaching and gaseous emissions (Salazar et al., 2012). Weathered ash has also been shown to have a higher ammonium adsorption capacity than fresh unweathered ash due to the presence of clay minerals caused by ash weathering, a process which can convert alumino-silicate glass in coal into non-crystalline clay minerals with more negatively charged surfaces for ammonium sorption (Zevenbergen et al. 1999). The higher ammonia volatilization observed for fresh ash may be linked to its higher salinity (Fig 7.4). It has long been reported that salinity favours ammonia loss (Gandhi and Paliwal, 1976; McClung and Frankenberger, 1985). Bacteria responsible for nitrification are sensitive to saline conditions, and this may cause ammonium to accumulate, with a greater potential to be lost as ammonia.

Ammonia volatilization has been shown to increase with increase in water content, air temperature and wind speed (Søgaard et al., 2002). Therefore in actual coal gasification ash dumps amended with sludge, ammonia volatilization will be influenced by these variables, and coupled with covering of sludge with a layer of ash, strategies to reduce wind speed and air temperature such as use of wind barriers and tall trees will reduce loss of nitrogen through ammonia volatilization.

7.4 Conclusions

Losses of nitrogen through ammonia volatilization in sludge-amended CGA are minimal. Ammonia volatilization is further reduced for weathered ash, therefore only the second hypothesis (ammonia volatilization will be higher in fresh CGA than in weathered CGA) is accepted. To achieve even lower ammonia volatilization lower sludge rates may be used. It is envisaged that as pH drops due to nitrogen mineralization, ammonia emission will decrease even further because a low pH favours ammonium in the ammonia/ammonium equilibrium in solution.

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Chapter 8: General discussions and conclusions

As industrialization expands and new technologies emerge to serve a growing population, management of the resulting wastes ought to be at the forefront of research and development activities. In South Africa, where power generation is mainly from coal combustion and where over 40% of liquid fuel comes from coal gasification, disposal of coal ash wastes will continue to be one of the most challenging problems for government and industry executives for many years to come. Although capping of ash dumps with topsoil can be a viable rehabilitation option, the inevitable degradation of the donor land and the costs involved in transporting soil make this a less favourable alternative. As a result, use of other amendments has been sought. Sludge amendment of coal ash dumps is enticing not only because it could aid rehabilitation, but also as a possible solution to disposal of sludge which regulatory limits and societal aversion cause to accumulate at wastewater treatment plants.

This study was initiated to determine the possible outcomes of amending coal gasification ash (CGA) with sludge with respect to nitrogen dynamics. It adds to previous work by Annandale et al. (2004), Sukati (2012) and de Jager et al. (2013) who carried out studies of CGA-sludge mixtures generally to determine the ability of the medium to support plant growth. This study, however, delved deeper into nutrient dynamics, evaluating the risks and benefits of CGA-sludge mixtures, determining the rate and pattern of nitrogen mineralization from sludge in a CGA medium so as to assess the potential of such media to release plant-usable nitrogen species, and enhancing the understanding of nitrogen dynamics in alkaline, saline environments.

The first undertaking was to determine the elements which pose the greater concern in order to delineate limits for sludge application to ash. Column leaching experiments indicate that at high sludge doses, As, Cd, Se, and Pb could pose a threat to the environment. The study also noted that applications of 5% or less sludge and keeping the medium well aerated could reduce the risks associated with these elements.

Next, the question of the ability of the ash medium to mineralize nitrogen from sludge was addressed. To determine the prevalent inorganic nitrogen form is critical in order to find out if sufficient nitrogen can be mineralized to support vegetation and if generation of nitrates and nitrites could be excessive and pose further risks to the environment. It was also important to know if and how ash weathering affects nitrogen mineralization from sludge. Results from that study showed that organic nitrogen from sludge can be mineralized in a CGA medium and that mineralization was faster in fresh ash than in weathered ash. That study also noted that the dominant nitrogen form in the sludge-amended ash medium was ammonium and that nitrification was inhibited, implying that the risks for nitrate leaching will be low and suggesting that in a rehabilitation scenario, plants will, at least initially, take up nitrogen mainly as ammonium. At the start of rehabilitation, the plant species that may thrive in the sludge-amended ash medium will likely be those that can take up ammonium without adverse effects. Therefore, plants grown on this medium should be screened for this capability. A review by Britto and Kronzucker (2002) on ammonium toxicity in higher plants provides helpful information on plants that are adapted to ammonium as a nitrogen source such as the heather *Calluna vulgaris* and the sedge *Carex*. However, any selected ammonium-adaptable plants should also thrive under alkaline and saline environments, and be suited to the prevailing climatic conditions. *Cynodon dactylon* has been found to adapt well to conditions in sludge-amended coal ash (Annandale et al., 2004; Van Rensburg et al., 1998).

The resulting effect that ammonium uptake by plants will have on the ash heap will also help transform the heap into a more suitable medium for plant growth. When ammonium ions are absorbed, they exchange with hydrogen ions which are then released into solution, lowering pH. With time this can reduce the alkalinity of the ash medium and create a more favourable condition for nitrification to proceed, so that eventually, plants less tolerant of ammonium as nitrogen source can also thrive in the medium.

Furthermore, it is advisable that when amending CGA with sludge, fresh, newly deposited ash heaps should be considered differently from old, weathered ones. Because sludge N mineralization is faster in fresh heaps, these may need to receive less sludge than heaps that have been considerably weathered.

Due to the substantial build-up of ammonium, the ability of the ash exchange complex to sorb ammonium had to be investigated. If ash has a low ammonium sorption capacity, ammonium may not be retained by the medium and may be washed away to ecosystems where it can be nitrified and pose a threat to human health and the environment. On the other hand, if ash has substantial ammonium sorption capacity, ammonium can be retained in the profile and form a reservoir for nitrogen and for acid-generating processes. In the long run, this will be beneficial to the alkaline medium we are trying to rehabilitate, as pH will likely be pushed lower to levels that most plants can thrive at. Batch experiment results showed high ammonium sorption by CGA, with sorption being higher in weathered than in fresh ash, hypothetically as a result of more surfaces for ion exchange created by ash weathering. Therefore, risks for ammonium leaching from sludge-amended ash is low and is further reduced for weathered ash heaps. Sorption isotherms were plotted for the observed data, and the Freundlich isotherm proved suitable to describe the sorption process. The sorption coefficients calculated are helpful input data for computer modelling of ammonium transport in CGA dumps.

Next, chemical precipitation of struvite was investigated as a possible additional mechanism for ammonium retention in sludge-amended CGA. PHREEQC modelling results showed that struvite can be formed in the CGA-sludge medium but the mineral will be dissolved with time as pH and ammonium levels drop due to nitrification, and as P is reduced due to precipitation of calcium phosphate. Modelling also showed that struvite formation in this medium will be enhanced by P fertilization. It is therefore highly likely that most of the ammonium retained in CGA may be adsorbed on the ash particles. Consequently, care should be taken when fertilizing sludge-amended CGA with a fertilizer such as K, so that the introduced cation does not displace ammonium from the ash exchange sites and cause a sudden flush of this nitrogen form.

Lastly, the possibilities for nitrogen loss through ammonia emissions from sludge-amended ash were investigated. Results showed that ammonia volatilization was low in CGA, and even lower in weathered ash, attributable to the high ammonium sorption capacity of CGA which is enhanced by ash weathering. Gaseous losses of nitrogen will therefore be minimal. This has positive implications for nitrogen conservation and environmental protection.

In conclusion, amending coal gasification ash with sludge is capable of generating inorganic nitrogen needed for plant establishment, and under good management practices, will result in minimal environmental risks with respect to nitrogen species. Because of differing nitrogen contents of sludge with time, regular sludge characterization is important in order to generate accurate parameters necessary to manage nitrogen and predict its dynamics in sludge-amended coal gasification ash using mathematical models. It is recommended that the relationship between nitrogen mineralization and metal solubility be investigated. There is a possibility that as nitrogen is mineralized metal cations associated with amine groups will be released into solution. This has implications for metal risks in the long term. Moreover, vegetated ash dumps should be studied in order to quantify water and nutrient dynamics, as these will differ from studies involving ash and sludge alone. Furthermore, there is a need to study mineral formation over time in sludge-amended CGA in order to gain a better understanding of the transformation of the ash medium into a more 'soil-like' material.

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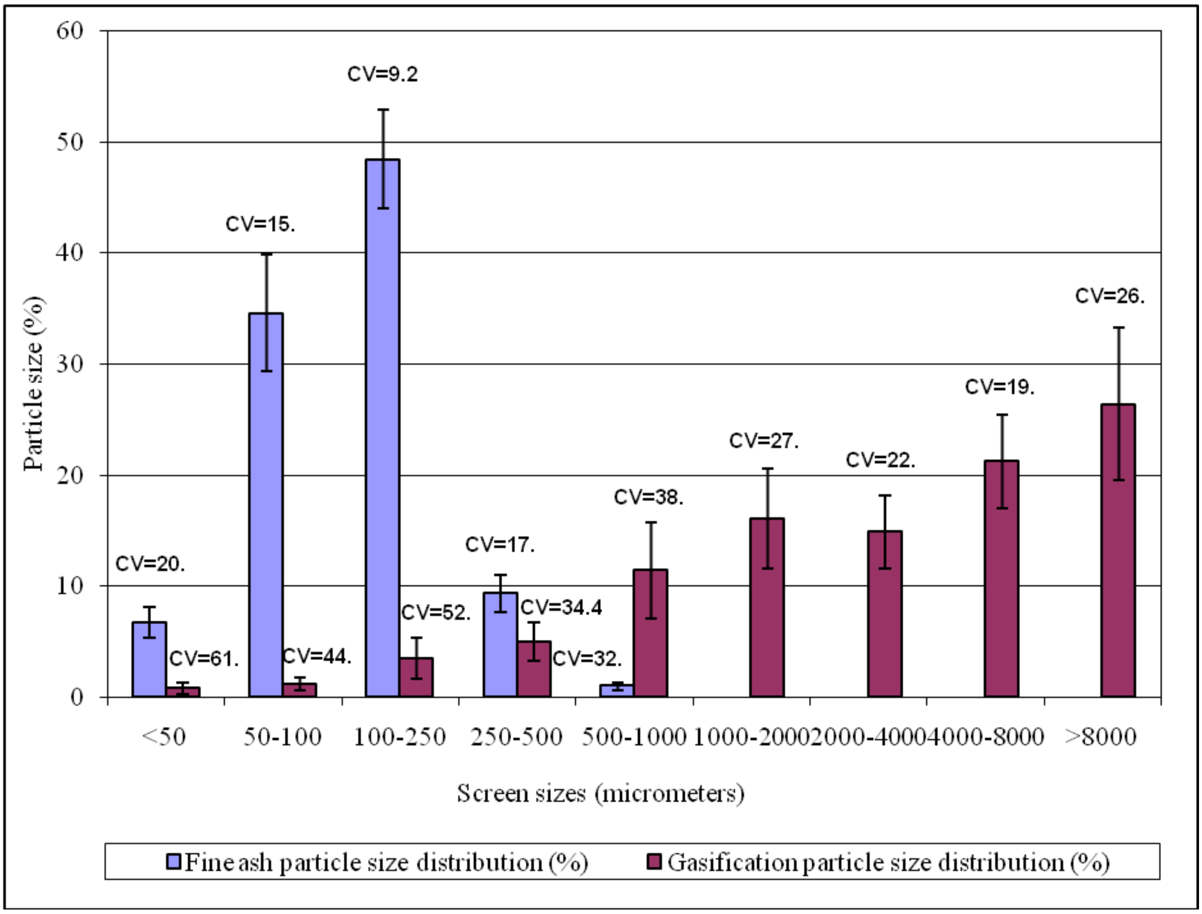
Appendix 1: Particle size distribution of coarse coal gasification ash and fine ash used in the column leaching experiment of Chapter 3



Particle size distribution of fine and gasification ash. The error bars are standard deviations. The values above the bars are the coefficient of variance (n = 30) (Sukati, 2012).

Reference

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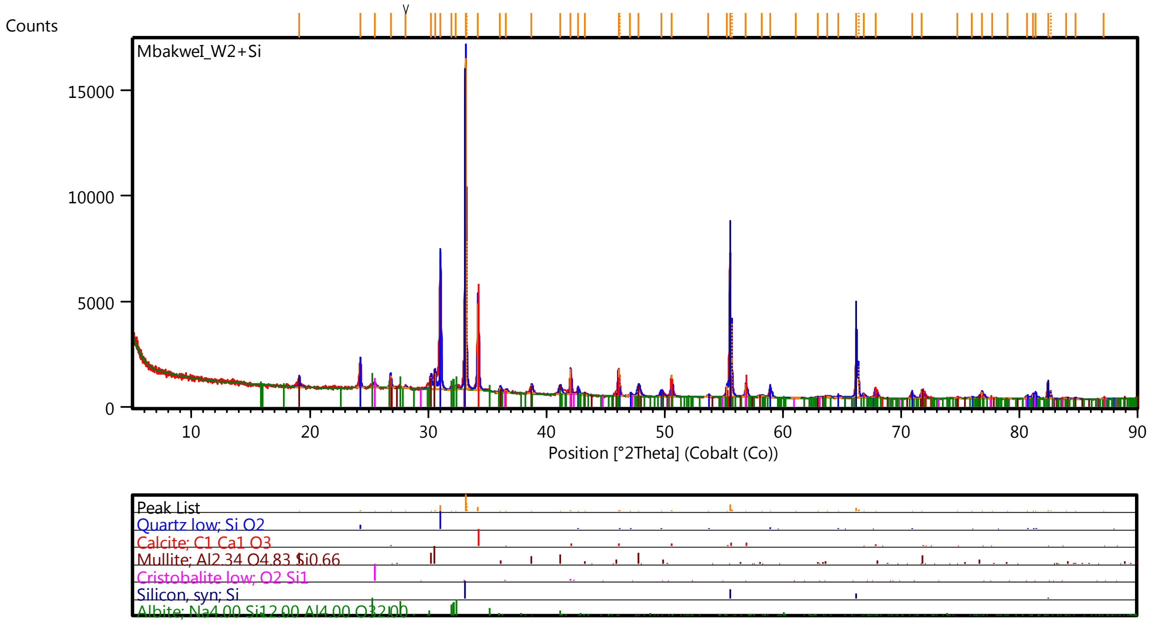
Appendix 2: Qualitative and quantitative XRD analysis of coal gasification ash and soil used in this study

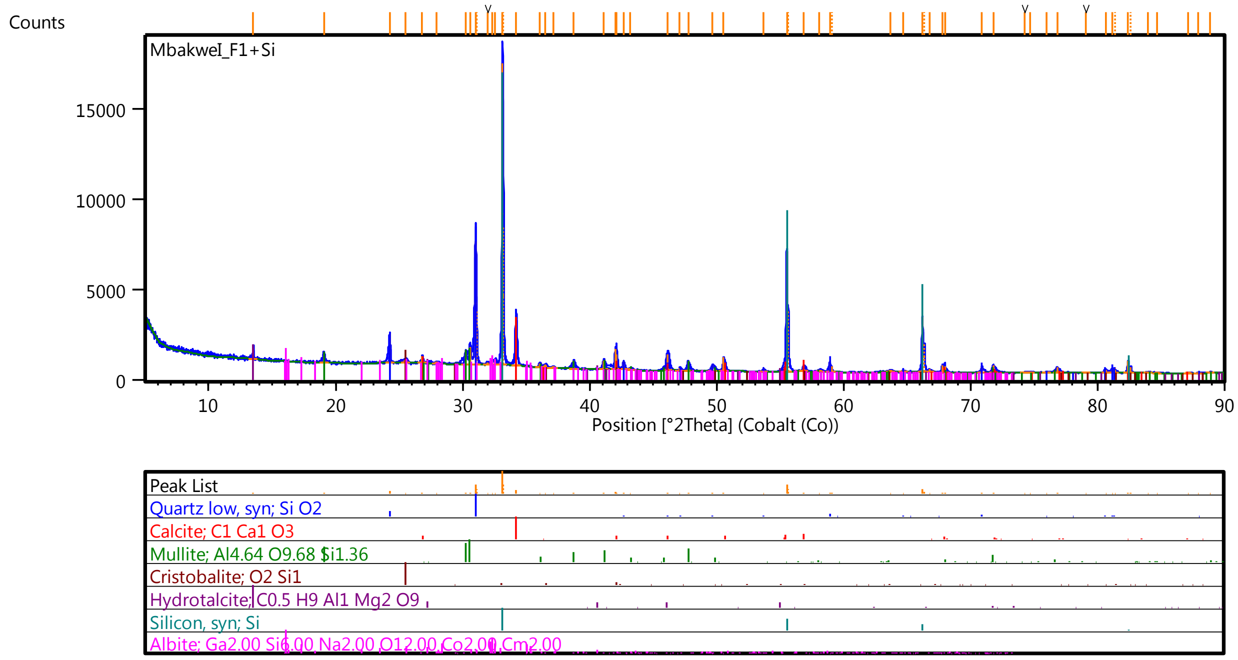
Method: After addition of 20% Si (Aldrich 99% pure) for determination of amorphous content and milling in a McCrone micronizing mill, the samples were prepared for XRD analysis using a back loading preparation method.

They were analyzed using a PANalyticalX'Pert Pro powder diffractometerin θ–θ configurationwith an X'Celerator detectorand variable divergence- and fixed receiving slits with Fe filtered Co-Kα radiation(λ=1.789Å). The phases were identified using X'PertHighscore plus software.

The relative phase amounts (weight%) were estimated using the Rietveld method (Autoquan Program). Errors are on the 3 sigma level in the column to the right of the amount.

Graphical representations of the qualitative results are shown below.

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Mbakwel_F1+Si
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10000
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0
10
20
30
40
50
60
70
80
90
Position [°2Theta] (Cobalt (Co))
Peak List
Quartz low, syn; Si O2
Calcite; C1 Ca1 O3
Mullite; Al4.64 O9.68 Si1.36
Cristobalite; O2 Si1
Hydrotalcite; C0.5 H9 Al1 Mg2 O9
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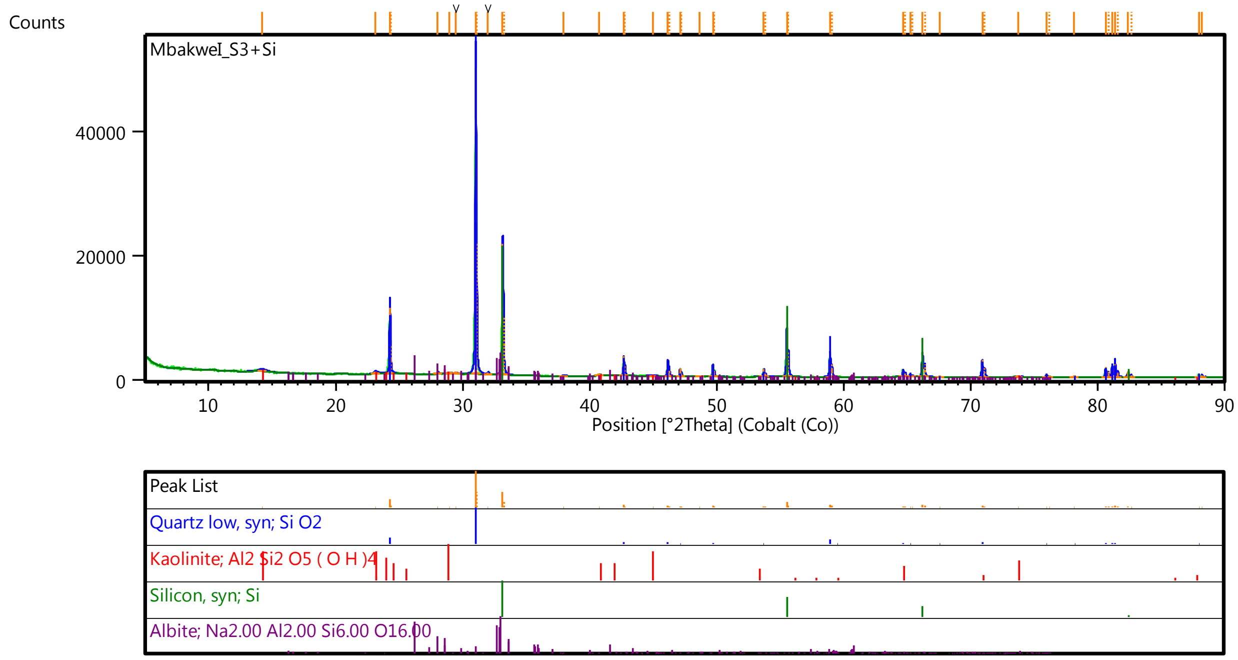
Albite; Ga2.00 Si6.00 Na2.00 O12.00 Co2.00 Cm2.00


Counts
Mbakwel_S3+Si
40000
20000
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10
20
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50
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70
80
90
Position [°2Theta] (Cobalt (Co))
Peak List
Quartz low, syn; Si O2
Kaolinite; Al2 Si2 O5 (O H)4
Silicon, syn; Si
Albite; Na2.00 Al2.00 Si6.00 O16.00

Quantitative Results:

Fresh ash			**Soil**			**Weathered ash**		
	weight%	3 σ error		weight%	3 σ error		weight%	3 σ error
Amorphous	31.61	1.5	Amorphous	15.34	1.56	Amorphous	39.32	1.29
Calcite	17.97	0.48	Kaolinite	12.72	0.57	Calcite	20.06	0.45
Cristobalite	3.5	0.45	Plagioclase	1.85	0.48	Cristobalite	2.54	0.25
Hydrotalcite	1.24	0.29	Quartz	70.09	1.2	Mullite	20.59	0.9
Mullite	24.08	0.99				Plagioclase	3.19	0.51
Plagioclase	3.61	0.57				Quartz	14.3	0.39
Quartz	17.99	0.45						

Appendix 3: Major anions extracted by the Water Leaching Procedure from coarse ash and fine ash (de Jager et al. 2013).

Ash	F	NO_3	Cl	SO_4	PO_4	NO_2	B
				µmol l^{-1}			
coarse ash	85.3	33.1	1808	2029	b.d.	194	161
fine ash	36.9	4.68	244	743	b.d.	b.d.	19.4
				mmol kg^{-1} ash			
coarse ash	1.71	0.66	36.2	40.6	b.d.	3.89	3.22
fly ash	0.74	0.09	4.87	14.87	b.d.	b.d.	0.39

b.d = Below detection

Reference

De Jager P.C., Annandale, J.G., Mbakwe, I., Sukati, B.H., 2013. The potential of sludge amended combustion coal ash residues as soil media: A laboratory column study to assess the influence of weathering on the elemental release. Water Research Commission Report No 1724/2/12. Pretoria, South Africa.