SUSTAINABLE SLUDGE LAND APPLICATION AND CO-DISPOSAL STRATEGIES

The potential of sludge amended combustion coal ash residues as artificial plant growth media: A laboratory column study to assess the influence of weathering on the elemental release

Report to the
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by

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This report forms part of a series of two reports. The other report in the series is *Sustainable Agricultural use of Municipal Wastewater Sludge: Matching Nutrient Supply and Demand* (WRC Report No.1724/1/12).

PREFACE

Management of sludge from both industrial and domestic origins is an ever growing challenge. The beneficial utilization of sludge is no doubt a better long-term waste management strategy than disposal. Municipal sludge is a source of essential nutrients and it is believed that its agricultural use will play an ever increasing role in future strategies. On the other hand, petro-chemically derived biological sludge emanating from Sasol Secunda also has favourable properties that can aid in the vegetation of the large gasification ash dumps at the Sasol Petrochemical Plant. The beneficial utlilization of sludge in both an agricultural and environmental context was therefore the main impetus behind this project titled “Sustainable Sludge Land Application and Co-disposal Strategies”. Over the course of three years two focuses evolved: 1) Strategies for sustainable agricultural use of municipal sewage sludge as a source of nutrients, and; 2) The potential of sludge amended combustion coal ash residues as plant growth media.

As a result, the findings of this study are also compiled in two separate reports. The report “Sustainable Agricultural Use of Municipal Wastewater Sludge: Matching Nutrient Supply and Demand” details the quantification of responsible sludge application rates in an attempt to match nutrient supply from sludge to actual crop uptake for sustainable agricultural use. It also reports on the development of a mechanistic crop water balance model (SWB) to which N routines were added to provide a reasoning support tool to this end. The P fertilizer value of several sludges, and N mineralisation as influenced by sludge stability and water potential, are also investigated and reported on.

The second report focuses on the potential use of a petro-chemically derived sludge for reclamation of a coarse ash dump and is entitled “The potential of sludge amended combustion coal ash residues as artificial plant growth media: A laboratory column study to assess the influence of weathering on elemental release”. It includes a laboratory column study in which weathering, elemental release and water holding characteristics of co-disposed industrial sludge, fine and gasification mixtures are investigated to assess chemical and physical suitability as potential growing media for plants. The report highlights the benefits and risks of mixing various waste streams in certain ratios, as well as the expected end products as these mixes weather over time.

EXECUTIVE SUMMARY

The management of coal gasification ash in order to minimise its environmental impact has been a challenge to industry for many years. A potential management option is the establishment of vegetation on the growing gasification ash heaps at Secunda. Co-disposal with industrial sludge may aid in creating a more hospitable environment for plants because it is a source of essential nutrients which the ash is poor in. However, the medium created will be a challenging environment in many respects for plants (for example high alkalinity and salinity) and the addition of sludge also introduces elements potentially harmful to the environment and further creates a very complex chemical environment. It is therefore important to ascertain the feasibility of this co-disposal strategy from both a plant growth medium and environmental point of view.

A laboratory scale low tension column set-up was developed and mixtures of a wide compositional range of industrial sludge, fine and gasification ash were subjected to conditions of sequential wetting and drying for 12 months. The purpose of this baseline study was to gain a better understanding of the chemical environment created when combining these waste streams and the changes that occur when subjected to weathering. With this fundamental understanding established, it would be possible to delineate combinations showing the most promise as growth media based on the release and availability of both essential nutrients and elements of concern. The set-up also made it possible to obtain some insights in the water holding characteristics of the various mixtures.

The chemical picture that developed for the gasification ash suggested that initially unweathered ash on its own will be an inhospitable environment for plants. Based on elemental release, various nutritional imbalances existed: sodium was the dominant cation and the solubility of magnesium (Mg), potassium (K) and phosphorus (P) was low. It is also expected that high salinity and alkalinity will further contribute in making it a challenging environment.

Sludge addition accelerated ash weathering and the breakdown products of the sludge proved to be powerful weathering agents and liberated elements like calcium (Ca), magnesium, potassium and phosphorus from the ash. The alkaline ash environment created conditions conducive to the oxidative breakdown of sludge. From a growth medium point of view these ligands can increase mineral solubility and increase the plant availability of macro and micro nutrients that would

otherwise have been locked up in the ash. The promising result from this study was that sludge addition did rectify the potential nutritional imbalances of the ash media to some extent.

However, the data suggested that it will be a more prudent approach to delineate the best combination of gasification ash, fine ash and sludge based on environmental considerations. Sludge is a source of trace elements of environmental concern like selenium (Se), arsenic (As) and boron (B). Based on elemental release, sludge content should be kept at or below 30% on a wet mass basis to keep the loading of these elements to the mixtures low. Both As and Se are redox sensitive elements and the reduced forms are of more concern. Keeping the system continuously in an aerobic state will further reduce their environmental toxicity.

It is not expected that the application of 3 and 6% sludge, on a wet mass basis, as currently investigated by Sasol, will result in substantial elemental mobilisation from the gasification ash. The data, however, also suggested that from a growth medium point of view these application rates are too low to have any substantial beneficial effect in terms of nutrient release. If the end purpose is the vegetation of the heaps, it is expected that the additional application of nutrients like nitrogen, phosphorus and potassium will be needed for some time to meet plant demand and ensure successful vegetation establishment.

High amendment levels of fine ash (> 30%, on a wet mass basis) did not show any benefits. Application levels > 30% resulted in the elevated elemental release of aluminium (Al) and chromium (Cr) and to a lesser extent vanadium (V). More leaching cycles were also necessary to lower the pH of mixtures with high fine ash content. The data suggested that it is not necessary to apply high levels of fine ash to appreciably increase water holding capacity. The positive effect of fine ash amendment on water retention was evident even at relatively low fine ash levels (< 20%, on a wet mass basis). Amendment of gasification ash with fine ash therefore holds promise as a strategy to retain water necessary for the establishment of vegetation on coarse ash dumps. However, potentially fine ash weathered down to smaller particles, or colloidal particles that derived from the ash, will be prone to colloidal movement and migration in the heaps.

Modelling of solute movement in coarse ash dumps using the HP1 model (a coupling of the geochemical model PHREEQC and the transport model HYDRUS 1D) may help predict future outcomes of amending coarse ash dumps with sludge. Although in its nascent stages, modelling shows that downward movement of solutes could be rapid in these dumps. The peculiar movement pattern of nitrates implies that all or almost all of the nitrates are leached out completely from

different depths with time. Consequently, as a growth medium, addition of sludge to coarse ash heaps should be done when plants can take up maximum amounts of nitrates. Future modelling endeavours will need to be validated with actual measurements, and must consider various scenarios, including nutrient uptake by vegetation.

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CHAPTER 1: BACKGROUND AND MOTIVATION

1.1. Introduction

Combustion of coal (bituminous, sub-bituminous, anthracite and lignite) for the generation of energy produces significant amounts of wastes/combustion residues (CCRs) such as fine ash and gasification ash (Wang & Wang, 1992, Reijnders, 2004 and Haynes, 2009). Three sizable waste streams are generated by SASOL Synfuels at Secunda; fine and gasification ash, by-products of coal gasification, as well as a biological sludge. Proper disposal of especially coal gasification ash (also called coarse ash) generated by the process of producing synthesis fuel from low grade coal, has been a huge challenge to industry for many years. In South Africa, about 7 million tons of coal gasification ash is generated annually at SASOL's Secunda plant as waste from gasifying 28 million tons of low-grade, high ash coal (Ginster and Matjie, 2005). These materials comprise 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, use of coarse ash from Secunda has been hampered by its geographical location which makes it difficult to transport to the Vaal Triangle area where between 2 to 3 million coarse ash-containing bricks are made per day using mostly ash from SASOL's Sasolburg site (Ginster and Matjie, 2005). Consequently, most of the coarse ash produced in Secunda is landfilled.

Currently, excess biological sludge, produced from the aerobic activated biosolid treatment process, is incinerated, an energy intensive waste disposal strategy. Furthermore, the combustion of the sludge does not only generate carbon dioxide (CO_2), a greenhouse gas, but also possibly a myriad of flue gases and toxic residues (Moldes *et al.,* 2007). Globally, governments are under increasing pressure to reduce especially CO_2 emissions. The transfer of soluble pollutants from the gasification ash dumps to surface and ground water is also a cause for concern in the long term. Current legislation in South Africa, for which the Department of Minerals and Energy is responsible, states that future closure of these sites, necessitates capping to prevent water infiltration and the mobilisation of solutes into the environment.

These waste streams can be combined, as part of a more integrated waste disposal strategy, to transform the outer layers of the coarse ash dump at Secunda into a more suitable growth medium for plants with the aim to vegetate the coarse ash dump. This is proposed as a possible alternative to importing valuable topsoil as a growth medium and capping material from elsewhere. It is envisaged

that a well-established vegetative cap, consisting of deep and shallow rooted plants, will be able to access water from different strata's of the ash dump, acting as biological pumps and controlling water and solute movement through evapotranspiration. A vegetative cap will therefore help to minimise pollutant transfer to the environment and also increasing the water transfer efficiency to the atmosphere.

These waste products have many attributes making them potentially suitable to engineer a growth medium for plants. The fine and gasification ash have many attributes essential for a functional growth medium. The macro porosity of the gasification ash will provide much needed aeration necessary for root respiration, water uptake and many microbially mediated processes, essential for a functioning growth medium, e.g. mineralisation and nitrification. It will also ensure rapid infiltration and minimise run-off from the ash dumps. Fine ash will contribute to the micro porosity and will increase the ability of mediums to retain water. The increased unsaturated hydraulic conductivity will also increase capillary rise resulting in more sustained transfer of water to the atmosphere and greater cumulative evaporation.

Ash may be rich in essential plant nutrients such as Ca, Mg, K, P and B (Jankowski *et al.,* 2006). It also contains the basic building blocks (aluminium and silicon) necessary for the formation of clay minerals (phyllosilicates) and other hydrated minerals, for example, layered double hydroxides (Zevenbergen *et al.,* 1999, Dermatas & Meng, 2003). From basic soil chemistry it is known that the chemical reactivity and fertility of soils resides in the colloidal fraction (<2 µm).The weathering of ash to secondary minerals, and the subsequent increase in reactive surface area will play an important role in the development of cation exchange capacity (CEC) and anion exchange capacity (AEC) and the attenuation of elements.

The sludge, on the other hand, is a source of organic material and plant nutrients, especially nitrogen. Humified / stabilised sludge will also promote the establishment of soil micro-flora and -fauna, increase water holding capacity and contribute to cation exchange capacity. Therefore, stabilised sludge will generally increase the fertility of the medium.

It is vital to strike the right balance between the different waste streams. Coal ash is alkaline and can have pH values exceeding 12. High pH values such as those of ash induce deficiencies of essential nutrients such as phosphorus (P) and trace elements such as iron (Fe), manganese (Mn), zinc (Zn), and copper (Cu) and can also cause increased accumulation of some non-essential trace elements in plants such as arsenic (As), selenium (Se), and vanadium (V). Unweathered ash deposits can also

have high levels of soluble salts. High salinity will induce osmotic stress in plants and microorganisms, making it difficult for them to take up water, an important factor that will limit the suitability of any medium to support life. Biologically, ash exhibits a low organic matter content and a very wide C:N ratio(>30:1) and such a ratio suggests a net immobilization of nitrogen (Brady & Weil, 2008, Haynes, 2009).

Mixtures should be sufficiently aerobic to ensure it success as a growth medium. Many important biological processes are linked to the soil or porous medium's ability to facilitate sufficient oxygen diffusion and ensure that consumption by root and microbial respiration does not exceed the rate it is supplemented by the atmosphere. Insufficient oxygen supply will inhibit many important aerobic processes, e.g. mineralisation, nitrification and humification. Anaerobic conditions can also set in motion processes potentially detrimental to the environment and plant growth, e.g. anaerobic decomposition of organic material which can result in acetogenesis and methanogenesis, the volatilisation of carbon in the form of methane (CH_4) instead of CO_2. The effect of CH_4 on global warming is far greater than that of CO_2 (Langenkamp and Marmo, 2000). Denitrification will also occur under anaerobic conditions and can result in the volatilisation of nitrogen. Gaseous exchange is facilitated by the macro pores in the medium.

A medium that is too macro porous, on the other hand, will have a low water holding capacity and will not be able to provide enough water for shallow rooting plants, making plant establishment difficult limiting options for vegetative caps. The amount of leaching past the root zone of a vegetated cap is also likely to be significant on a medium of poor water holding capacity. On the other hand aeration, water infiltration and root growth will be negatively influenced if the mixture contains too much fine ash. Physically, too much fine ash can restrict root growth due to the natural compaction of fine ash particles and/or formation of impermeable cemented layers due to the pozzalanic nature of ash (Haynes, 2009).

To conclude, it is evident that the physical and chemical behaviour of mixtures of these three waste streams must be elucidated and quantified in order to gain predictive capability on the most suitable porous growth medium combinations.

1.2. Aim

The purpose of this baseline study was to gain a better understanding of the chemical and physical environment created when combining these waste streams and the changes that occur when subjected to weathering. With this fundamental understanding established, it would be possible to delineate combinations showing the most promise as functional porous plant growth media based on the release and availability of both essential nutrients and elements of concern.

The is arguably a more concise aim than the aim originally state at the first reference group meeting, however, the essence of it did not change: “To characterise coarse ash, fine ash and sludge mixtures in order to establish and gain predictive capability on the contributions these components will make to a hospitable growth medium”.

1.3. Hypotheses

Various hypotheses can be formulated in this pursuit to elucidate functional growth media:

- The individual waste products (sludge, fine and gasification ash) to have varying quantities of both total macro and micronutrients;
- Extreme environments will gradually be moderated by universal soil forming processes. Especially leaching (leaching) will remove delerious soluble elements from the root zone making the porous medium more hospitable to plant growth;
- It is expected that sludge will moderate ash mixtures by reducing the pH to tolerable levels and increase mineral solubility making essential elements like Ca and Mg more plant available. It is expected that with time oxides of calcium and magnesium in the ash, will gradually be carbonated. With time the pH will stabilise in the range of 7-8, generally the range for calcareous soils;
- Total elemental analysis with XRF showed that more than 80% of the elemental ensemble of ash is silicon and aluminium (on a mole basis), the basic building blocks of clay minerals. With the onset of soil forming processes, phyllosilicate clay mineral formation is inevitable.

CHAPTER 2: THE DEVELOPMENT OF THE COLUMN SYSTEM

A low tension column set-up was developed in order to investigate the interaction of gasification ash, fine ash and sludge mixtures and the resulting elemental release in an aerobic environment under alternating wetting and drying conditions. Low tension refers to the fact that the columns were connected to a vacuum system and a static vacuum of approximately -10 kPa can be applied at the base of the columns to encourage drainage.

2.1. Advantages of a Low Tension Approach over Free Draining Columns

Low tension systems are arguably a better approach compared to free draining systems to simulating release and sequestering dynamics of ***unsaturated*** porous systems:

1) Firstly, in free draining lysimeters, columns or pots, water perching or ponding occurs at the outflow boundary, resulting in artificially wetter conditions at best, and potentially anaerobic conditions at worst, compared to unconfined porous media;
2) Applying tension at the base of the columns helps to minimise these boundary conditions and ensure that they drain better ensuring conditions closer to that of unconfined porous media;
3) The ability to apply vacuum allows better control of the water content and aeration of the columns:
    - Different tensions can be applied to simulate different aeration scenarios if needed;
    - Wetting and drying cycles under laboratory conditions can be accelerated through vacuum drying / force aeration of the columns.
4) Pore solution chemistry can be investigated directly and residence time can be controlled. In free draining systems the only means to gain any insight into pore solution chemistry are through the analysis of the drainage collected. Little control over the residence time of solution in free draining steady state flow systems exists. In order to interpret data in context, the assumption must be made that the chemistry of the free drainage system more or less mirrors pore solution chemistry. A better approach is to approximate the closeness of the residence time to “equilibrium” or more correctly steady state conditions. This is done by using, for example, the Damköhler number (D_a) = R• K• L• V^{-1}, where R is the retardation coefficient of the element of interest, L the column length, V the pore velocity (ms^{-1}) and K kinetic constant based on the rate of elution (Andrés & Francisco, 2008). Preferential flow paths can develop in any artificially packed system. This will decrease

tortuosity resulting in shorter residence times and less contact of the percolating solution with the total surface area of the medium. This will also influence pore velocity calculations. All conclusions made and recommendation forwarded about nearness to equilibrium, solution composition, ion concentration and ion activities are, therefore, transport and pathway dependant. The advantage of a low tension system is that entrained pore solutions, in pores that can retain water against gravity, can be sampled directly after they were allowed to equilibrate for a specific time. The intricacies of relating the chemistry of the free drainage to pore solution chemistry and the nearness to equilibrium are circumvented. This allows the comparison of pore solution chemistry of different residence times to that of free drainage.

2.2. Limitations of Column Systems

The representivity of the porous continuum of artificially confined porous media has always been contentious. Especially when attempting to derive transport parameters for field scale modelling, for example, the hydraulic conductivity of a medium or diffusion coefficients of ions.

The purpose of this baseline column study was to gain a basic understanding of the chemical behaviour of the different mixtures and their water holding properties. We have not yet reached the level of understanding to investigate or quantify the workings of transient transport processes in these mediums.

2.3. Column Specifications and Set-up

The column ensemble consisted of the following:

1) A column base cut from polypropylene with an internal diameter of 110 mm (outer rim with a 10 mm thickness). The depth of the base is 45 mm (Fig 2.1a-d);
2) An O-ring about 4 mm diameter (Fig 2.1c) was fitted in the column bases to ensure vacuum tight seal with the column;
3) The 300 mm long transparent polyethylene column, with an outer diameter of 110 mm (Fig 2.1a),
4) A “depth filter” placed at the base of the column consisting of five layers of filtering material (Fig 2.2b and c). The filtering materials were placed in an order of decreasing pore size: The first layer directly in contact with the mixture was a 2 mm polypropylene mesh followed by three nylon meshes with a decreasing pore size of 25, 10 and 5 µm. The last mesh at the outflow boundary was again a 2 mm polypropylene mesh;
5) Schott Duran glass bottle that can screw in at the bottom of the column base (Fig 2.2 d)

The column bases were connected to the vacuum system as illustrated in Fig 2.2d. A main vacuum line, connected to a vacuum regulator on the bench, serviced eight columns. In total, two rows of 24 columns were mounted back-to-back on one bench (Fig 2.3).The column laboratory had a capacity for 96 columns.


(a)

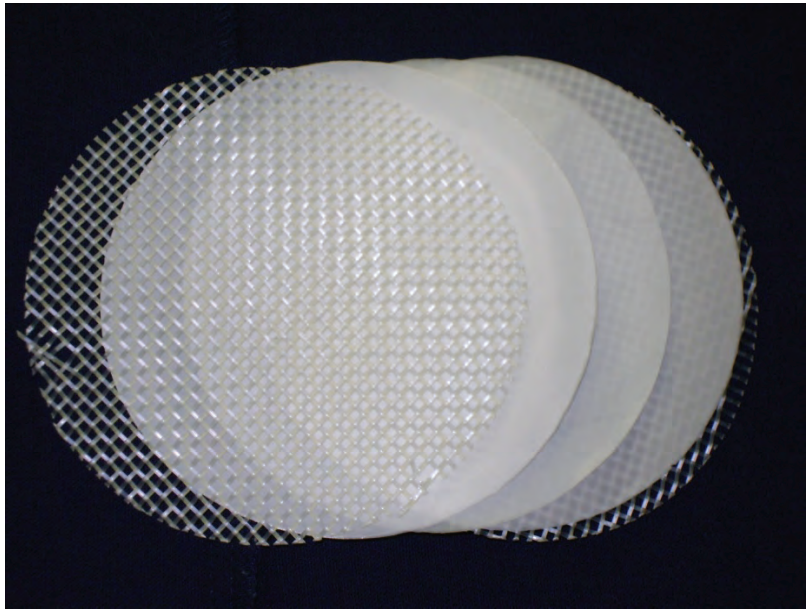

(b)

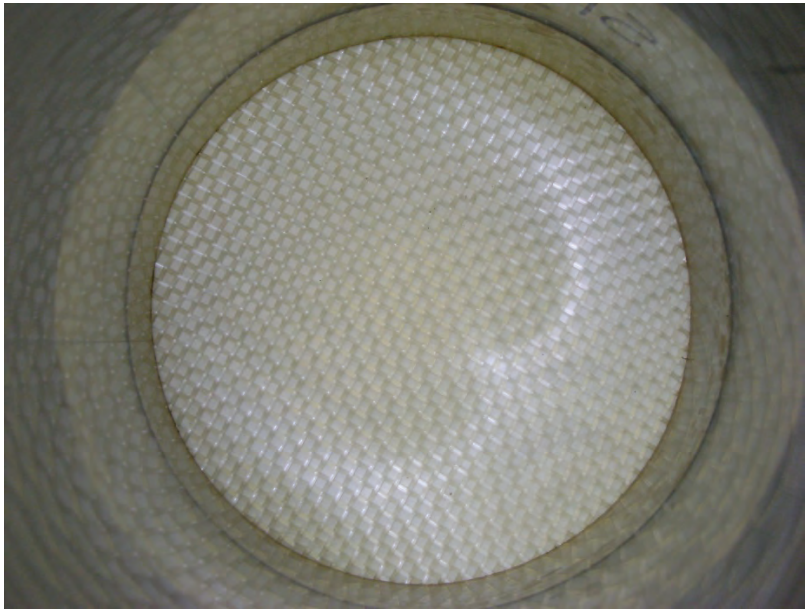

(c)


(d)

Figure 2.1 The column base. a) Side view showing opening to which vacuum is connected, b) Top view showing grooved “floor” and drainage outlet, c) Side view showing the imbedded O-ring to ensure a vacuum tight seal between column and base, d) Bottom view showing drainage outlet and threaded opening to which a Schott Duran glass bottle can be connected


(a)


(b)


(c)

(d)

Figure 2.2 a) The transparent polyethylene column (length: 300 mm, internal diameter: 110 mm), b) The five layered mesh placed at the outflow boundary of the column, c) The securing of the mesh by the column in the column base, d) The column ensemble consisting of the transparent column, the column base and the Schott bottle collection flask connected to the vacuum system (blue pipe from column connected to the red main vacuum line)

Figure 2.3: The low tension column battery on each bench

CHAPTER 3: MIXTURE FORMULATION, LEACHING CYCLES AND LEACHATE ANALYSIS

3.1. Mixture Formulations

In total 51 different mixtures were formulated containing varying amounts of gasification ash, fine ash and sludge. The mixtures were divided in 6 groups based on sludge content (Fig 3.1). Group 1 (mixtures 1-11) represented treatments that received no sludge while fine ash content was decreased and gasification ash content was increased (with increasing mixture numbers). Group 2 (mixtures 12-21) represented treatments that received 10% sludge (wet mass of sludge as a percentage of the total wet mass) while fine ash content was increased and gasification ash content was decreased. Group 3 (mixtures 22-30), group 4 (31-38), group 5 (39-45) and group 6 (46-51) received 20, 30, 40 and 50% sludge respectively while the fine ash decreased and gasification ash increased. The varying fine ash and gasification ash content is illustrated in Figs 3.2 & 3.3.

Fresh gasification ash, fine ash and sludge were collected from SASOL plant in Secunda. Gravimetric water content of these materials was 15.5%, 36.3% and 89.8% for coarse ash, fine ash and sludge respectively. Combination of waste materials was done on 'as is' basis. This approach was followed mainly because practically, it will be unrealistic to dry waste materials on site before co-disposing them. Moreover, a previous approach to base sludge applications on dry matter content proved impractical because the high liquid content of the sludge resulted in final mixture volumes in excess of the volume capacity of the columns.

3.2. Calculations Involving the Packing of the Columns and Water Addition

The columns were packed at an initial wet bulk density ($\rho_b^{'} = M_{total}/V_{total}$) of approximately 1200 kg m^{-3}. In order to leave adequate space for the addition of water in the mixture only 25 cm of the column height was considered for total volume calculation. Based on this, the mass of mixture that must be added to each column was calculated:

$$\text{Volume} = \Pi r^2 h \qquad \text{(a)}$$

Where r is the radius and h is the height.

Column volume (cm^3) = Π x $(5.25\ cm)^2$ x 25 cm

= 2164.75 cm^3

Total mass of mixture = wet bulk density x volume (b)

= 1.2 g/cm^3 x 2164.75 cm^3

= 2598 g

The porosity and pore volume were estimated based on the following calculations:

Total porosity = $1 - \rho_b / \rho_s$ (c)

Where:

ρ_b = dry bulk density = M_{solids}/ V_{total} (e)

ρ_s = particle density = M_{solids}/ V_{solids}

Pore volume = total porosity x V_{total} (d)

(Lal & Shukla, 2004)

To calculate the porosity and pore volume, the equivalent dry bulk density or more specifically the dry mass of the mixtures was needed. The dry mass was obtained by weighing off 100 g sub samples of the mixtures (in duplicate) in pre-weighed beakers followed by oven drying at 105^oC for 24 hours. The beakers with their content were then cooled in a desiccator, and afterwards the dry mass of each treatment was determined. The particle density was taken as 2650 kg m^{-3} or 2.65 g cm^{-3}.for porosity calculations. This estimation of the pore space was just a first estimation that was used as a point of departure for the amount of water to be added.

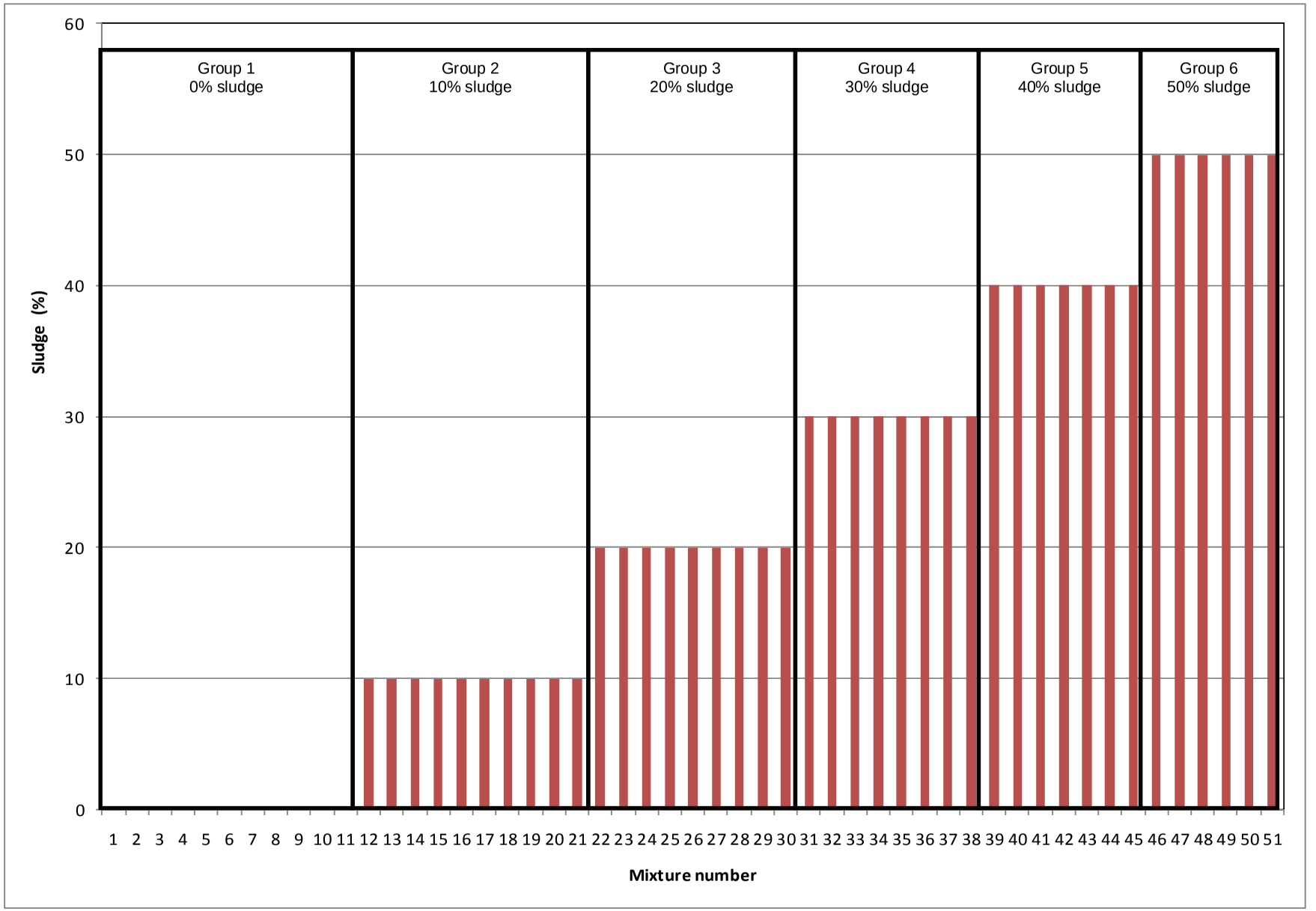


Figure 3.1 Sludge content of mixtures (wet mass of sludge as a percentage of the total wet mass)

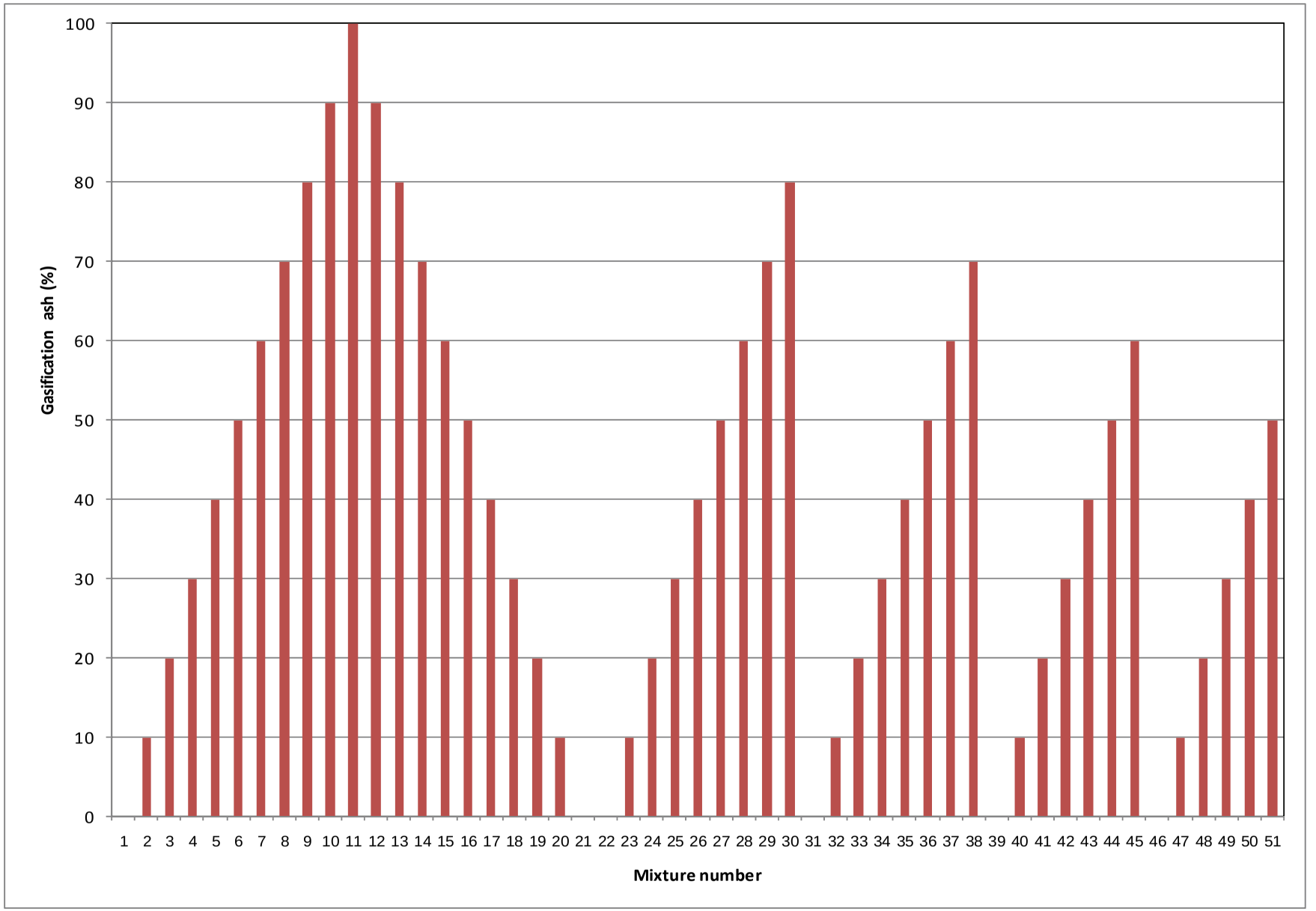


Figure 3.2 Gasification ash content of mixtures (wet mass of gasification ash as a percentage of the total wet mass)

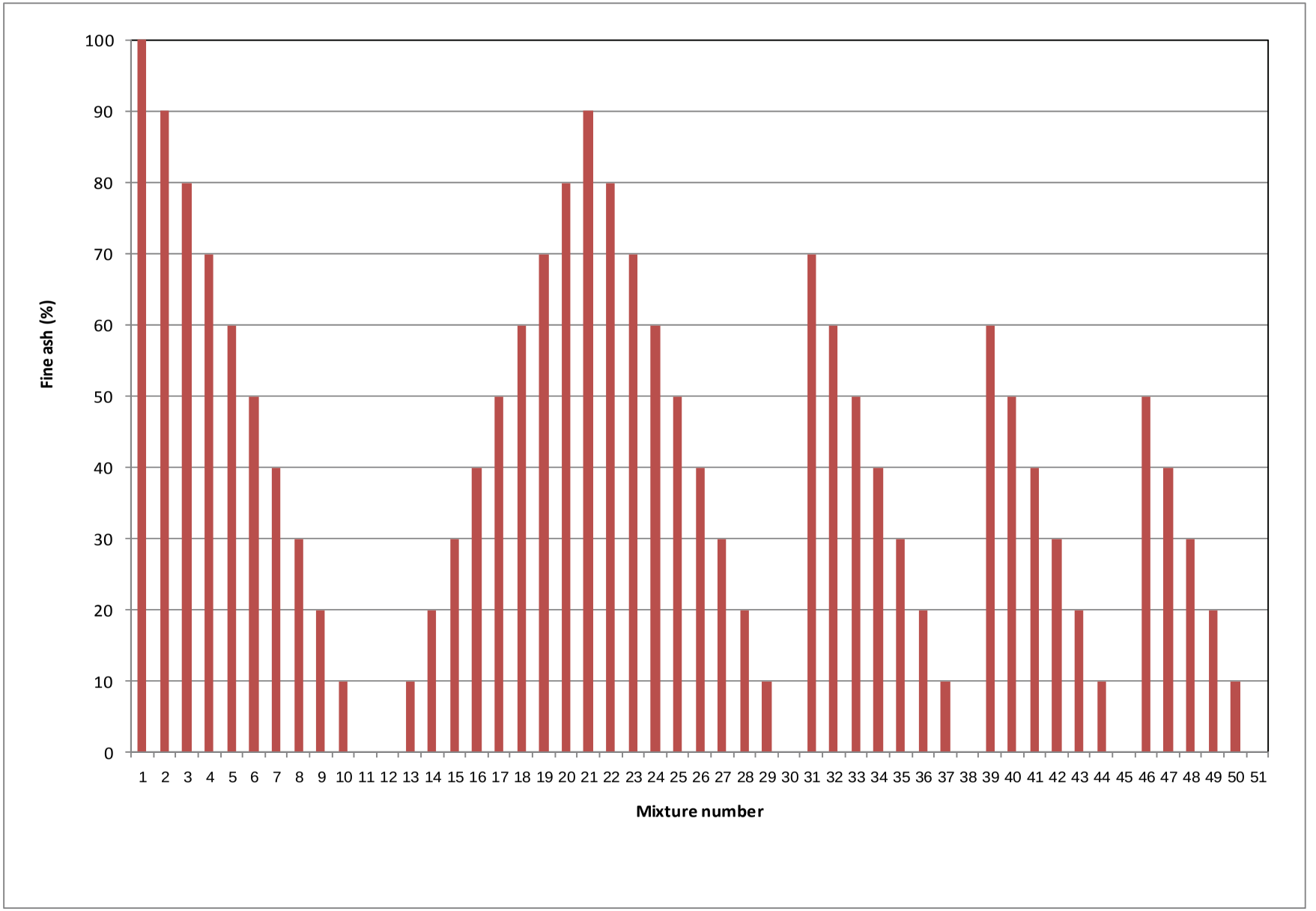


Figure 3.3 Fine ash content of mixtures (wet mass of fine ash as a percentage of the total wet mass)

3.3. Leaching of Columns and Leachate Analyses

The approached followed was to simulate wetting and drying cycles. The study started in January 2010 and ended in December 2010 and a total of nine wetting and drying cycles were simulated. The initial amount of water to be added to the columns was based on the initial porosity estimation calculated porosity and pore volume of the media. In each case, an amount of distilled water equivalent to approximately one pore volume was passed through the columns. The free drained leachates that collected in Schott bottles, shown in Fig 2.3, were removed after 24 hours and stored below 4ºC until analyzed. Clean Schott bottles were then connected to the column bases and a vacuum of -10 kPa was applied in order to collect the pore solution. The volumes, as well as the mass of the collected solutions, were determined for mass balance purposes. The pH and EC of both the free drained and pore solutions were also determined. Twenty millilitres of each solution was transferred to 30 ml polyethylene tubes. These samples, including 12 blanks, were analysed on an axially viewed Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) for K, P, Mg and Ca. Other elements determined included Mn, Fe, Zn, Mo, Al, Cd, Cr, Cu, Na, Ni, S, Se, V, Co, Pb and As.

CHAPTER 4: ELEMENTAL RELEASE, pH AND SALINITY

4.1. pH

pH is viewed as the master variable controlling the rate of redox reactions, microbial activity, solution speciation of elements, surface charge characteristics as well as mineral precipitation and dissolution. Under extreme acid conditions Ca, Mg, P, B, and Mo can become deficient, while Fe and more specifically Al and Mn may reach bio-toxic levels. Similarly, the availability of Cu, Fe, Zn and Mn are reduced under alkaline conditions. Another parameter also controlled by pH is anion and cation exchange and attenuation. The net negative charge of secondary minerals with pH dependent charge increases with increasing pH. The consequence of this is that cation retention becomes more pronounced at pH values greater than the point of zero charge (pzc). When solution pH is lower than the pzc, the surface will exhibit a net positive charge and the surface affinity for anions increases (Prasad and Power, 1997, Essington, 2004, Brady and Weil, 2008).

Initial characterisation of the unweathered gasification and fine ash showed it to be a challenging environment for plants when viewing it as a growth medium (Appendix A). The salinity, alkalinity as well as sodicity were in ranges generally considered unsuitable for most plants.

The pH of the pore solution, extracted under vacuum after 24 hour equilibration, was close to or above 11 for the treatments that did not receive sludge (Fig 4.1). This is indicative of hydroxide alkalinity. Both fine ash and gasification ash are products of coal combustion and during combustion, carbonates and sulphides decompose to form oxides (Merrick, 1984). The wetting of the columns resulted in hydrolysis and the transformation of the oxides to hydroxides. These hydration and hydrolysis reactions are associated with volume increase and swelling was observed initially for all treatments. Some of these hydroxides, for example, $MgOH_2$ and $CaOH_2$, are quite soluble in water, and the dissociation in solution will release hydroxyls. The influence of fine ash on the pH of the mixtures was only visible for the first leaching cycle (Fig 4.6a). The columns that were amended with 40 and 50% fine ash maintained a pH above 11 up to the fifth leaching. The fine ash was not necessarily more alkaline, it is expected that the finer particles size and greater surface area just makes it more reactive and soluble. Subjecting the columns to more leaching progressively decreased the pH with time. This is attributed to the removal of soluble hydroxide alkalinity and also the gradual carbonation takes place as water in equilibrium with atmospheric CO_2 successively leaches through the columns.

The effect of sludge amendment was also visible after the first leaching cycle. There was an abrupt transition from the treatments that received no sludge (Treatments 1-11) to the treatments that received varying amounts of sludge (12 to 51) (Fig 4.1). Sludge amendment lowered the pH and the frequency distribution (Fig 4.2) also showed two distinct populations that developed. The pH of the sludge treatments settled in a narrow pH window (9.64 ± 0.38, coefficient of variance = 3.99%). Doubling the sludge content (from 10% to 20% and 20% to 40%) did not result in a further drastic pH decrease indicating that buffering around this pH occurred. The treatments that received the most sludge maintained the pH of the pore solution close to 9 up to the ninth leaching cycle (Fig 4.6b). The pH range was close to the pKa of NH_4^+ / NH_3 equation (i) and it is possible that the transformation of ammonium to ammonia and the resultant releasing of protons in solution possibly played a role in buffering the pH in this range for the sludge amended treatments.

$$NH_4^+ = NH_3 + H^+ \qquad pKa = 9.2 \qquad \text{(i)}$$

Various other reactions most likely took place resulting in the release of protons and buffering of the solution. The tan colour of solutions collected from the sludge amended treatments, for instance, is attributed to dissolved organic carbon (DOC) and visual evidence that the ash created an environment conducive for the oxidative breakdown of the sludge (Figs 4.3 & 4.4). The increase in DOC showed that the decomposition products of sludge were polar and therefore water soluble to some extent. The molecular nature of the DOC can only be speculated about at this point in time and should be a focus of future research. However, it is reasonable to expect that fulvic acid would be present in the DOC. This deduction is based on the fact that fulvic acid is often isolated from sludge amended soils (Sposito *et al.,* 1978). In soil analytical chemistry, fulvic acid is isolated from organic material by performing alkaline extractions (KOH or NaOH) after pre-treatment with a strong electron acceptor. Fulvic acid has a myriad of functional groups including carboxylic groups (-COOH, pKa = 4-6). The greater solubility under alkaline conditions is caused by the deprotonation and ionisation of the various functional groups at pH conditions greater than their respective pKa values. This makes the organic molecule more polar and thus water soluble. Carboxylic groups, for example, will be completely ionised (-COOH → $-COO^-$ + H^+) at the pH measured for the various treatments (Kleber & Johnson, 2010). The ionisation / deprotonation of these functional groups will obviously also contribute to the increase in proton activity in solution.

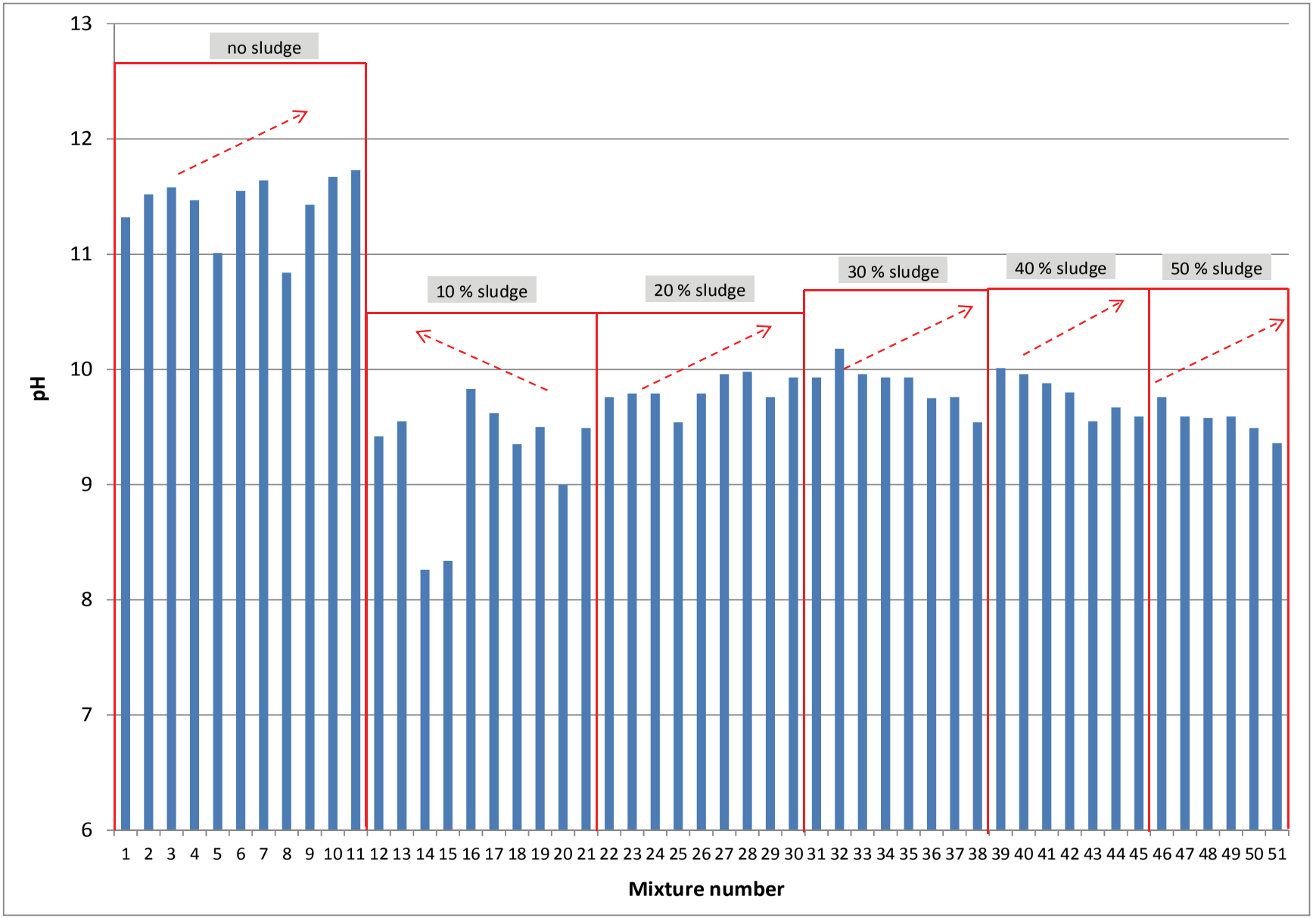


Figure 4.1 The pH of the pore solution upon sludge addition for the first leaching cycle

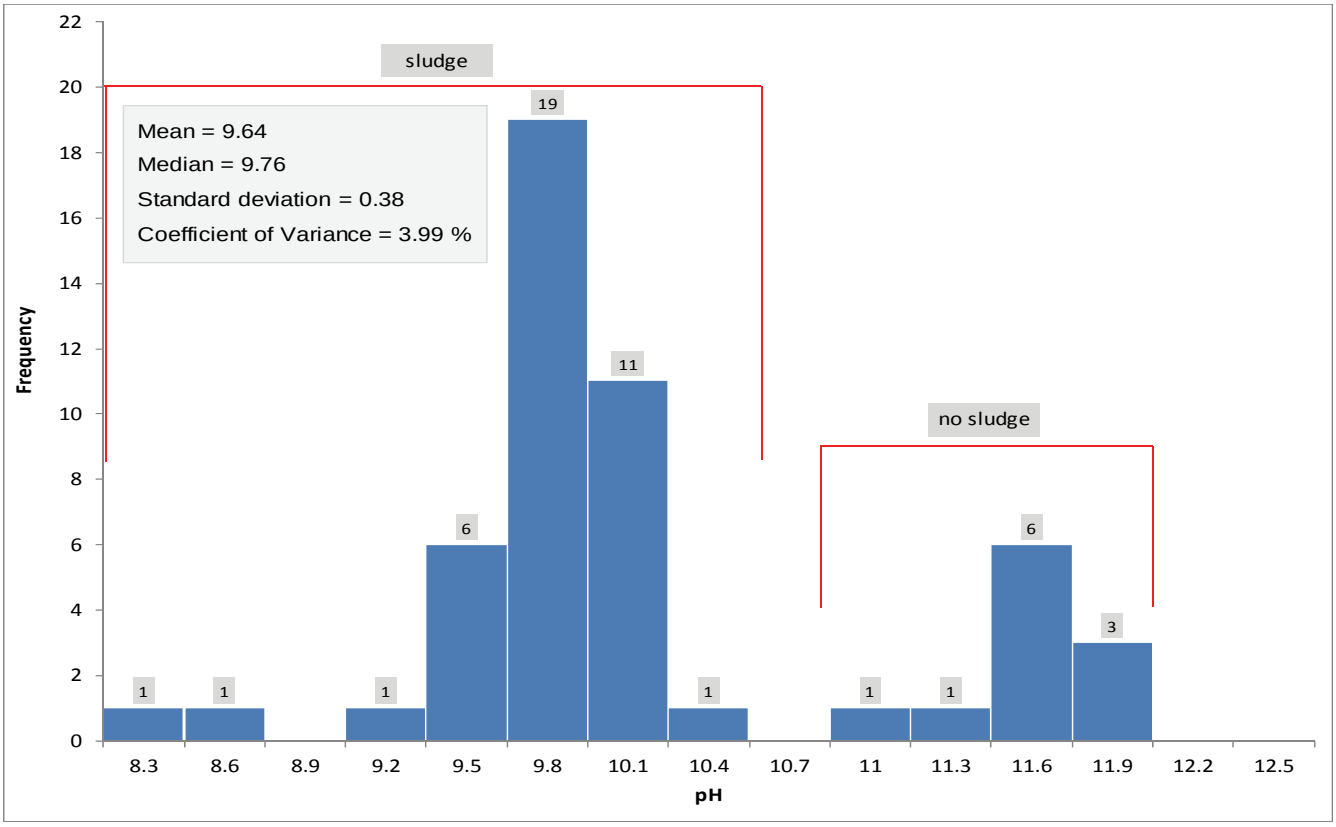


Figure 4.2 The frequency distribution of the pore solution pH for the first leaching cycle. The x axis depicts the upper boundaries of the respective frequency groups, for example, 9.8 includes all values $9.5 < x < 9.8$

Although the experimental setup was not designed to assess CO_2 fluxes, it was expected that, as a result of the oxidative breakdown of organic material, the sludge treated columns will generate more CO_2 compared to columns that did not receive sludge. The subsequent carbonation of the solution (the solvation of CO_2 and formation of carbonic acid) and deprotonation to form HCO_3^- and CO_3^{2-} will increase the aqueous proton concentration and activity. After nine leaching cycles the pH of all the treatments merged into one population (Fig 4.5) exhibiting a mean of 7.8 with a CV = 4%. PHREEQC modelling showed that this is close to the range typically expected of a $CaCO_3 – CO_2 – H_2O$ system. (Table 4.1).

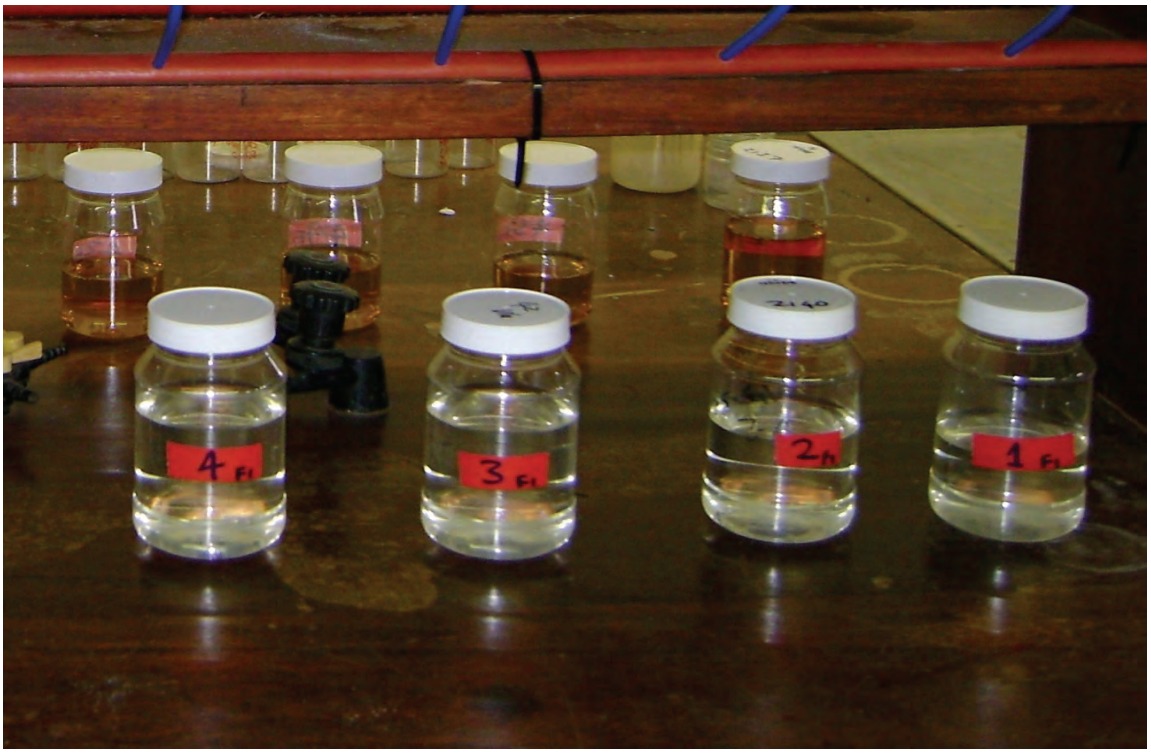


Figure 4.3 Free drained solution of mixtures 1-4 which received no sludge

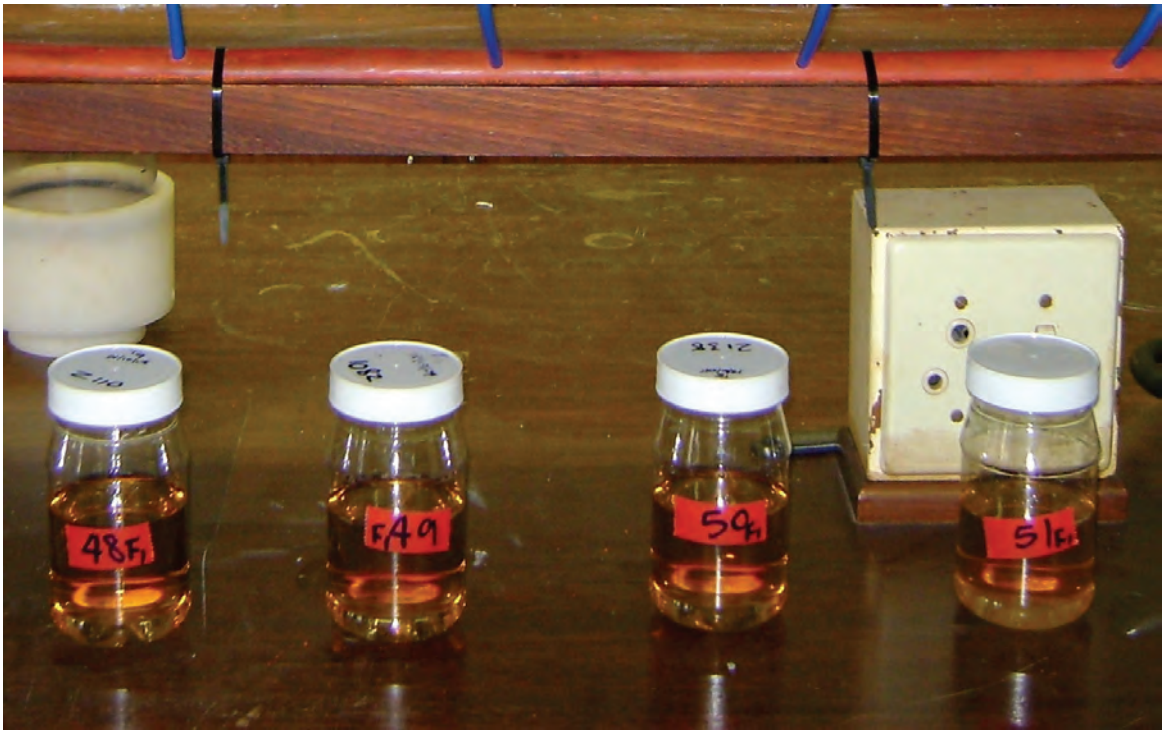


Figure 4.4 Free drained solution of mixtures 48-51 which received 50% sludge

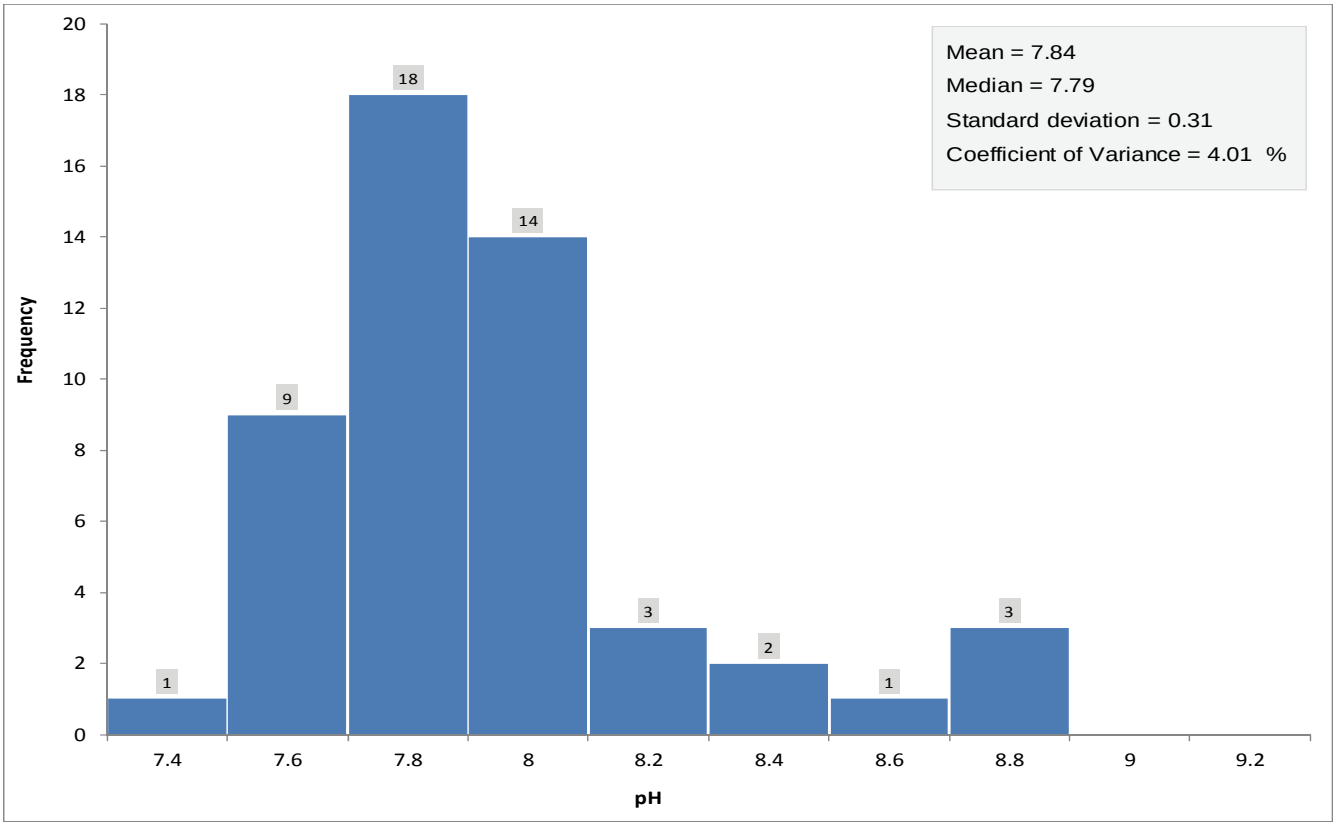


Figure 4.5 The frequency distribution of the pore solution pH for the ninth leaching cycle

Table 4.1 PHREEQC predicted pH of the $CaCO_3$ – CO_2 – H_2O system considering various forms of $CaCO_3$ and partial CO_2 pressures of $10^{-1.8}$, $10^{-2.5}$ and $10^{-3.5}$ atm.

Phase	Log K_{sp}	Equilibrium pH at various CO_2 pressures atm		
		$10^{-1.8}$	**$10^{-2.5}$**	**$10^{-3.5}$**
$CaCO_3$(am)	-6.40	7.83	8.27	8.91
Ikiate	-6.62	7.37	7.82	8.47
Vaterite	-7.91	7.35	7.81	8.46
SWB-$CaCO_3$	-7.95	7.21	7.67	8.32
Calcite (a)	-8.35	7.20	7.65	8.31
Calcite (b)	-8.40	7.18	7.64	8.29
Calcite (c)	-8.44	7.19	7.64	8.30
Calcite (d)	-8.42	7.17	7.62	8.28

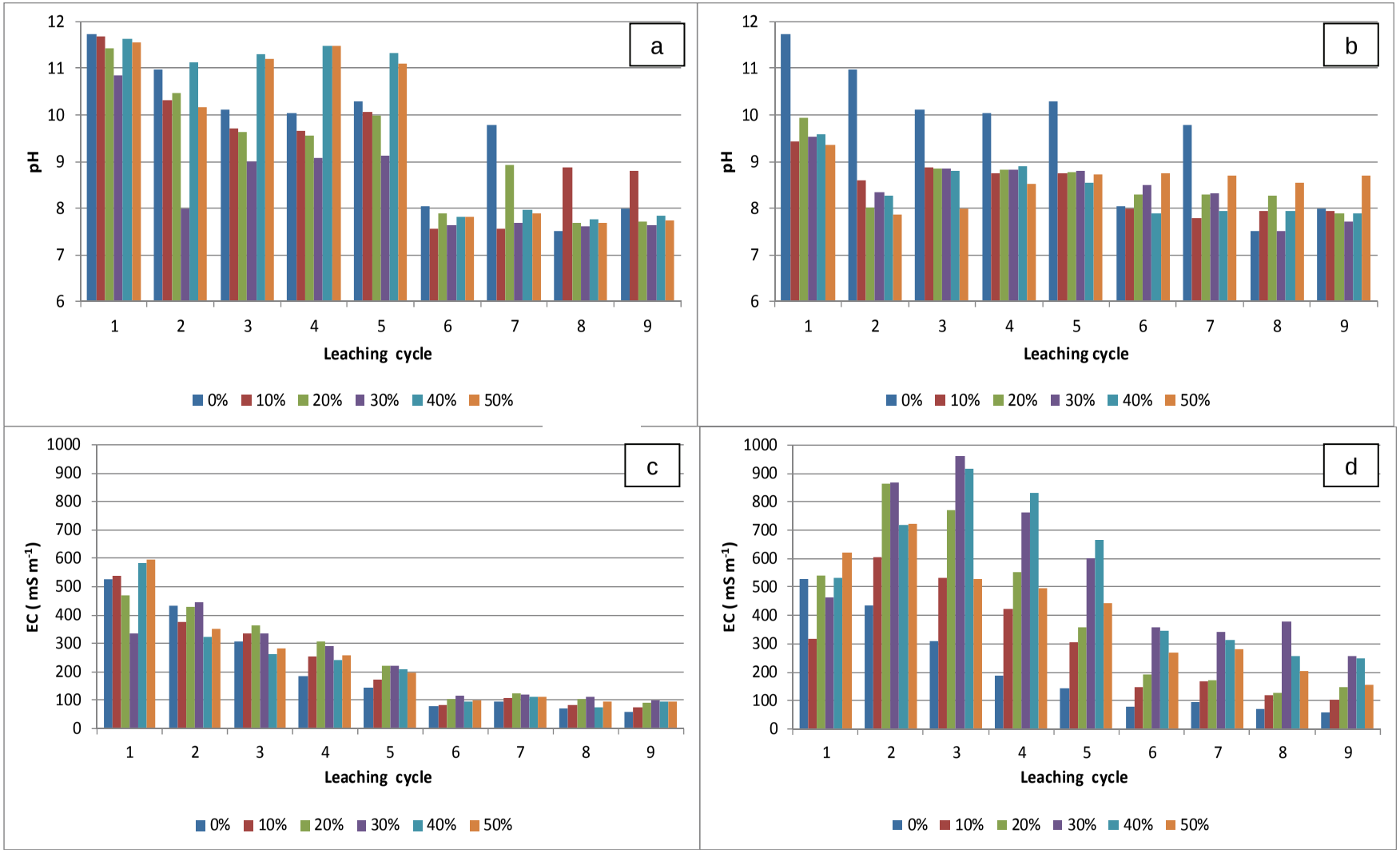


Figure 4.6 Isolating the effect of fine ash amendment of gasification ash on the pH (a) and EC (c) (fine ash content given at bottom of the graphs), as well as sludge amendment on pH (b) and EC (d) (sludge content given at bottom of the graphs).

4.2. Electrical Conductivity (EC)

Salinity is another factor that can initially limit the chemical suitability of the mediums to support plant growth and survival. The high salinity is the result of the large mass of soluble elements that were left in the ash after the gasification process. Ca to S molar ratios of over 2.5 in the feedstock results in the ash containing not only $CaSO_4$ but also CaO (Anthony *et al.*, 2003). According to Tsai, (1982) the constituents of coal ash can be classified into acidic (silica, alumina and titania) and basic (iron, calcium, magnesium and alkaline oxides). However, the high pH environment most likely also played a role in increasing the solubility of the various solid phases in the ash.

The amendment with sludge caused a substantial release of salts from the ash and the 30% to 40% sludge treatments peaked above 900 mS m^{-1} for the third leaching cycle (Fig 4.6c). For the fine ash treatments, most salts were released initially, with the 50% fine ash treatment releasing the most salts (595 mS m^{-1}). This rapid initial release of salts is attributed to soluble salts with fast dissolution kinetics, residing in the ash. The EC in general increased with an increase in sludge content up to 30 to 40% sludge. The highest sludge treatments, however, yielded lower salinity and this can be attributed to a dilution effect. The ionised fraction of the DOC most likely contributed to the greater electrical conductivity. However, DOC is a strong complexing and reducing agent and the increased EC is attributed to ligand and proton promoted dissolution which increased the solubility of the various solid phases present in the ash. The peaking of EC at a later stage for the sludge treatments is attributed to the liberation of elements by means of ligand and redox promoted dissolution, from less soluble solid phases. These dissolution reactions were kinetically slower than those of soluble solid phases. With time EC decreased appreciably, especially for the fine ash amended treatments which decreased below 100 m S m^{-1} (Fig 4.6 c). The sludge amended treatments sustained a greater salt release up to the ninth leaching cycle (Fig 4.6 d).

The greatest contributors to salinity were S, Mg, Ca and Na. The impact of sludge amendment on the release of various elements will be discussed in the following sections.

4.3. Calcium and Magnesium

After sulphur, more magnesium was cumulatively released from the sludge amended treatments after 9 leaching cycles than any other element (Fig 4.7), closely followed by calcium (Fig 4.8). The total Ca content of the mixtures was appreciably higher than that of Mg (Fig 4.9 *versus* Fig 4.10) and the most

abundant element after silicon and aluminium (Appendix A, Table A1). The calculated total Ca content varied in a narrow range with a mean of 5.2%, with the changing sludge, gasification and fine ash content resulted in a standard deviation of only 0.3%. The mean total Mg content was more than 5 times lower at 0.93%. The greater cumulative release of Mg, despite the lower total content, showed that the solid phases Mg resided in, were more soluble than calcium containing solid phases. The addition of sludge resulting in the cumulative liberation of more Ca and Mg than treatments without sludge (Figs 4.7 & 4.8). The 10 and 20% sludge treatments showed an increasing Mg release with an increase in gasification content, however, at higher sludge content this trend disappeared.

The amendment with sludge had a profound impact on the release pattern of both Ca and Mg (Fig 4.11a, b, c, d) and the data suggests that the amendment with sludge resulted in the preferential removal of Mg. The impact of sludge amendment on increasing the solubility of Mg containing solid phases in the ash was also well illustrated by the molar ratios of Ca and Mg in the mixtures (Fig 4.12). For the 10% sludge addition, the ratio predominantly favoured Ca, however, greater sludge amendment change the ratio in favour of Mg. However, it is expected that because of the greater solubility of Mg in the ash it will decrease faster than Ca and the ratio will change in favour of Ca again. Mg containing solid phases in the ash unamended with sludge exhibited a lower solubility than that of Ca containing solid phases (Fig 4.11 a & c) and the molar ratio therefore favoured Ca.

Sludge amendment resulted in changing the release pattern of calcium. The first leaching cycle was the dominant contributor to Ca release for the treatment that received sludge. The first leaching cycle for the 50% sludge treatment, for example, represented 53.5% of the total Ca released compared to 0.6% for the gasification ash only. In the case of Mg, it was the opposite, with the first eluvation contributing the least to total Mg release.

Calcium will arguably play a pivotal role in the chemistry of these weathering mixtures. Saturation index calculations with PHREEQC, as well as the pH of the leachate and pore solution data, suggests that these systems are gradually being carbonated and driven towards systems in equilibrium with $CaCO_3$.The significance of this is that the pH and alkalinity of these systems will be controlled by $CaCO_3$. Ca will also play a role in controlling P and As attenuation.

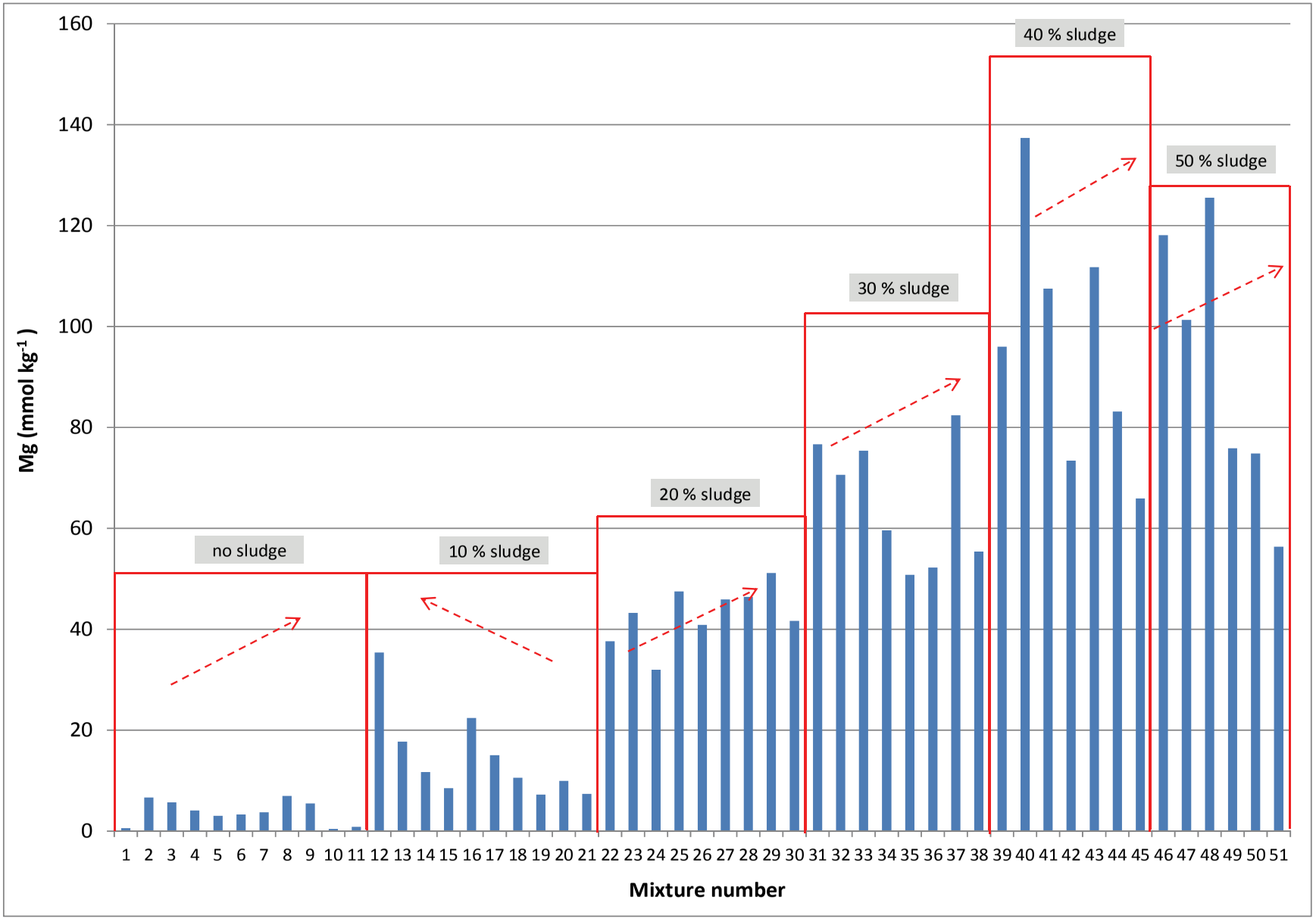


Figure 4.7 Cumulative Mg release after 9 leaching cycles. The arrows indicate the direction of increasing gasification ash content of each sludge treatment group

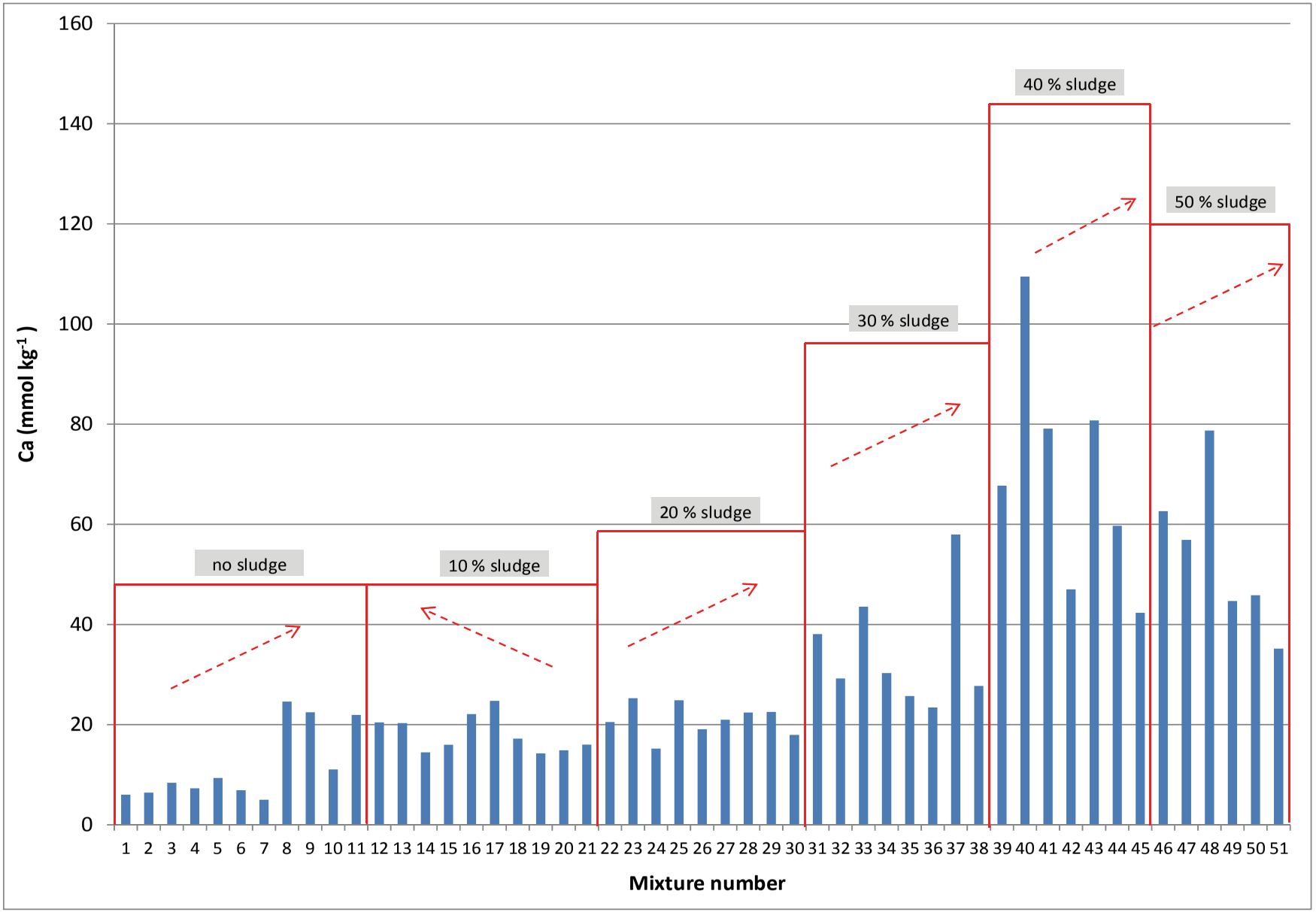


Figure 4.8 Cumulative Ca release after 9 leaching cycles. The arrows indicate the direction of increasing gasification ash content of each sludge treatment group

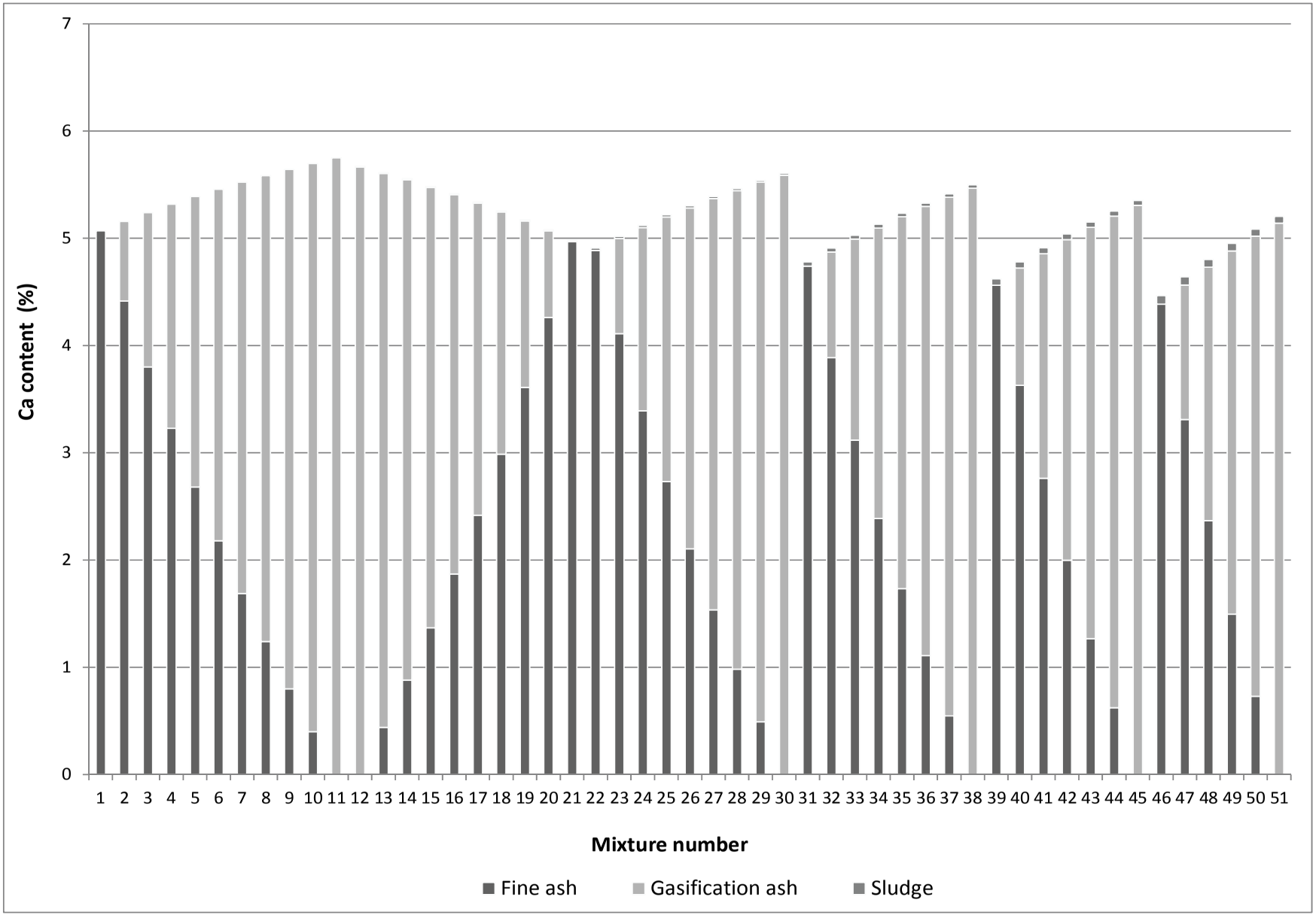


Figure 4.9 Contribution of gasification ash, fine ash and sludge to the Ca content of the various mixtures

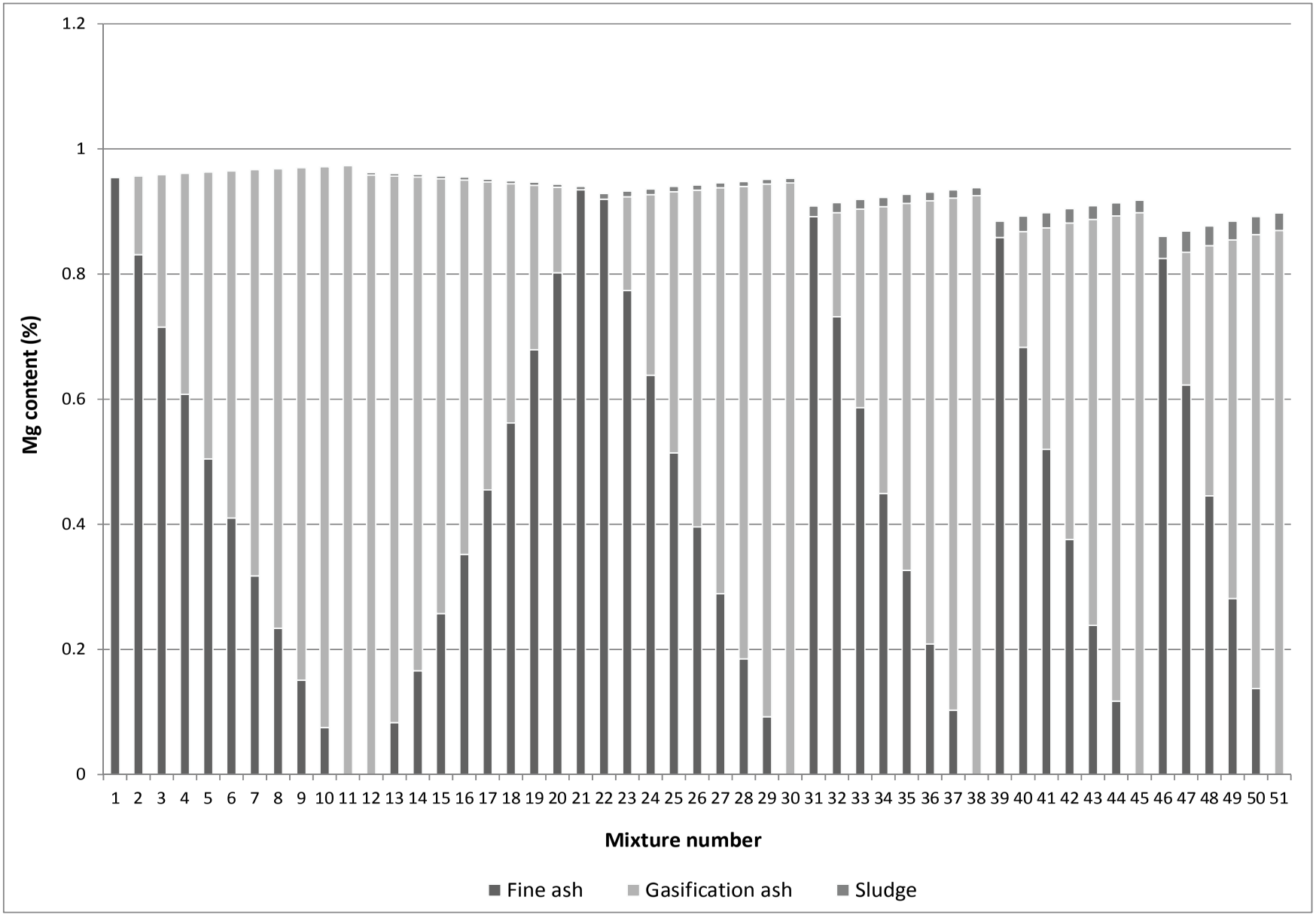


Figure 4.10 Contribution of gasification ash, fine ash and sludge to the Mg content of the various mixtures

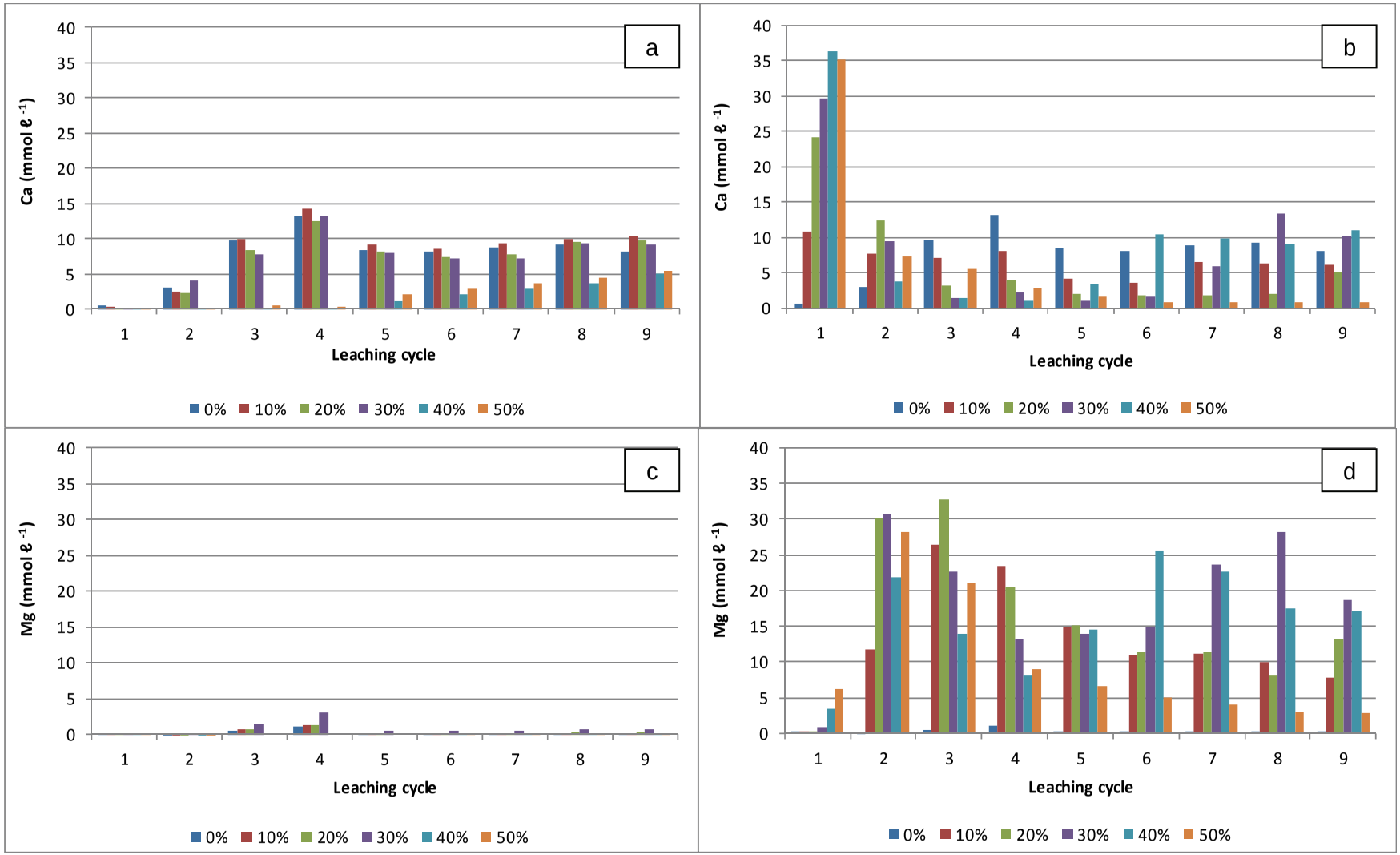


Figure 4.11 Isolating the effect of fine ash and sludge amendment on Ca and Mg release from gasification ash: The temporal change in the pore solution concentration of Ca and Mg as influenced by fine ash amendment (a & c) (fine ash content given at bottom of the graphs) and sludge amendment (b & d) (sludge content given at bottom of the graphs)

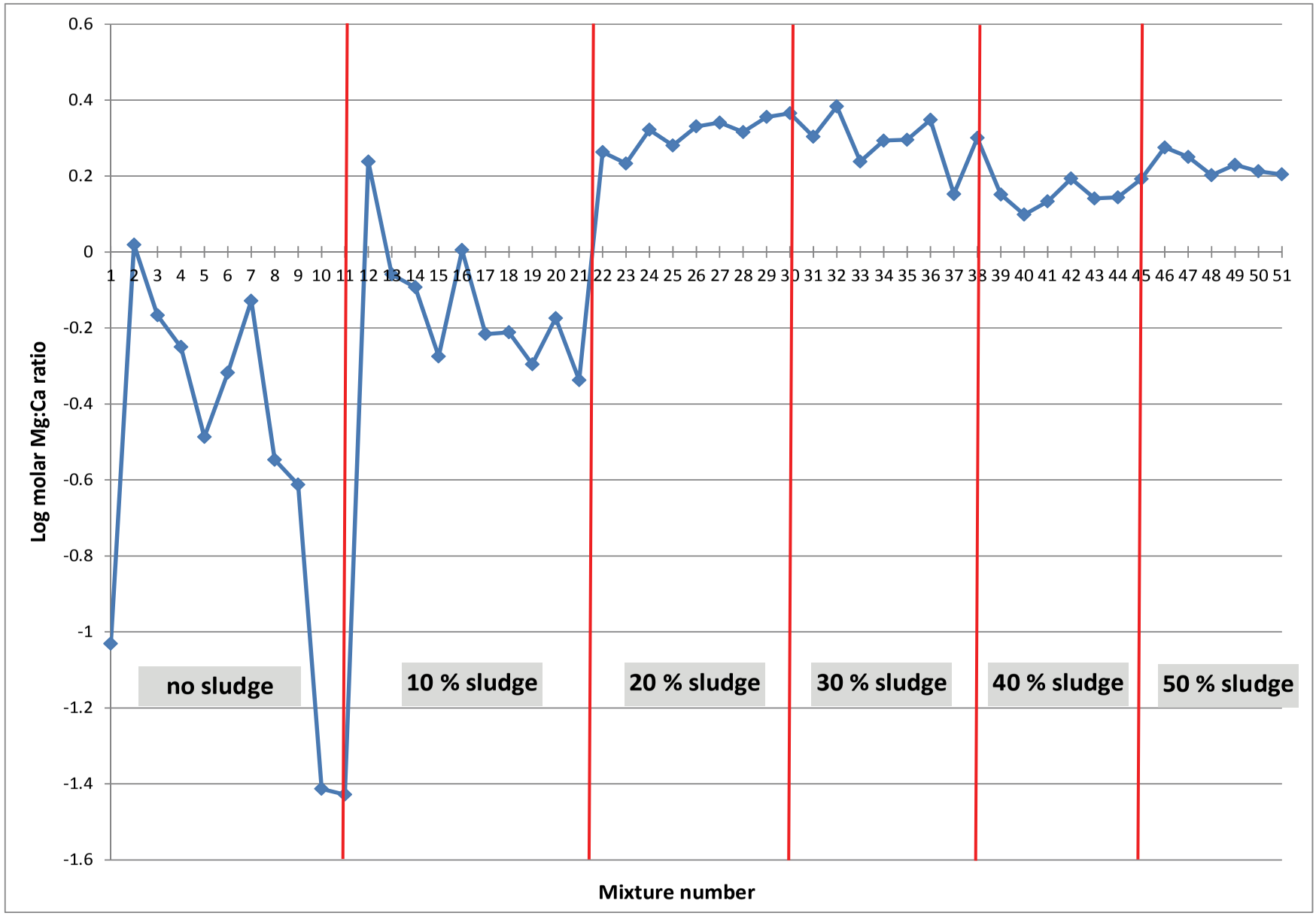


Figure 4.12 Log molar Mg:Ca ratio based on the cumulative calcium and magnesium released after nine leaching cycles

4.4. Potassium and Sodium

When comparing the cumulative elemental release of the four dominant cations (Mg, Ca, Na and K), Na was by far the most dominant cation in solution for treatments that did not contain sludge (Fig 4.13 Treatment 1-11 *versus* Figs 4.7, 4.8 & 4.14). This further underlines the inhospitable nature of the gasification and fine ash when evaluating it as a growth medium. A medium where Na is the dominant aqueous cation is not a desirable situation. Firstly, sodium is phytotoxic and secondly it will suppress the uptake of other essential cations like Mg, Ca, K and cationic trace elements, for example, Zn and Cu. The sodicity was markedly decreased with the addition of sludge and, as showed previously indicated, the release of especially Mg and Ca was drastically increased with increasing sludge amendment. Although the same trend was observed for Na and K upon sludge addition, the effect was less pronounced. The addition of sludge rectified the nutrient imbalance, and for the highest sludge treatments, Mg and Ca, were the dominant cations in solution. Ca should preferably be the dominant soluble cation and this is often the condition that is aimed for from a soil fertility point of view when considering the four major cations. Na concentration should preferably be the lowest of the four major cations.

Gasification and fine ash contained similar amounts of Ca and the same was observed for Mg. In the case of Na and K, the gasification ash seemed to be more enriched with both these elements. This was the reason for the variable total content of Na and K for the various treatments (Figs 4.15 & 4.16) compared to Ca and Mg (Figs 4.9 & 4.10), which stayed fairly constant.

Interestingly, the Na and K content were similar on a molar basis for sludge (74.2 mmol kg^{-1} for K *versus* 69.6 mmol kg^{-1} for Na) and fine ash (67 mmol kg^{-1} for K and 62.2 mmol kg^{-1} for Na). Only the gasification ash differed somewhat (231.2 mmol kg^{-1} for K *versus* 166.6 mmol kg^{-1} for Na).

Na in the mixtures proved to be more leachable / soluble than K (Fig 4.17) and the data suggested that fine ash was the source of soluble Na. The 40 and 50% fine ash treatments elevated the Na concentration of the pore solution of the first leaching cycle (Fig 4.17a). A strong positive correlation also existed between cumulative Na released and fine ash contents of 30% and more (Fig 4.18).In the absence of fine ash, increasing sludge amendment decreased Na pore solution concentration. The cumulative release from the gasification ash amended with sludge only treatments (Mixture numbers 30, 38, 45 and 51) was also the lowest. A combination of the highest sludge and highest fine ash amendment resulted in the greatest cumulative Na released (Fig 4.13).

Potassium solubility was less affected than Na by sludge and fine ash amendment (Fig 4.17 c & d) and it seemed that the gasification ash was a more important source of K than in the case of Na. At higher sludge levels a weak relation with fine content manifested.

K solubility was relatively low compared to the other major cations, and decreased even more substantially with time. Sludge did not liberate appreciable amounts of K from the ash as in the case of Ca and Mg. Sludge is evidently also not a particular rich source of potassium either and the addition of sludge resembles a dilution effect. This means that K can potentially become a limiting macro nutrient in the long run if not supplemented. An aqueous molar Na:K ratio favouring Na will definitely worsen the situation, however, increasing sludge amendment did change this in favour of K (Fig 4.19). Sodium is quite soluble and will be removed with time, however, a management strategy to keep Na the lowest of the four major cations would be to keep the fine ash content low. The lower dependency of potassium solubility on fine ash content means that sodium levels can be decreased without unnecessarily lowering the K availability.

Apart from trace element analysis in the parts per million range and parts per billion range, XRF is commonly employed for total elemental analyses. In this study XRF analysis of both the gasification ash and fine ash for Ca, K, Na, and K consistently yielded lower concentrations than wet chemical extraction (an acid digestion followed by an ICP-MS analysis). Calculations for mass balance purposes, for example, calculated elemental content of mixtures were therefore not based on XRF analyses.

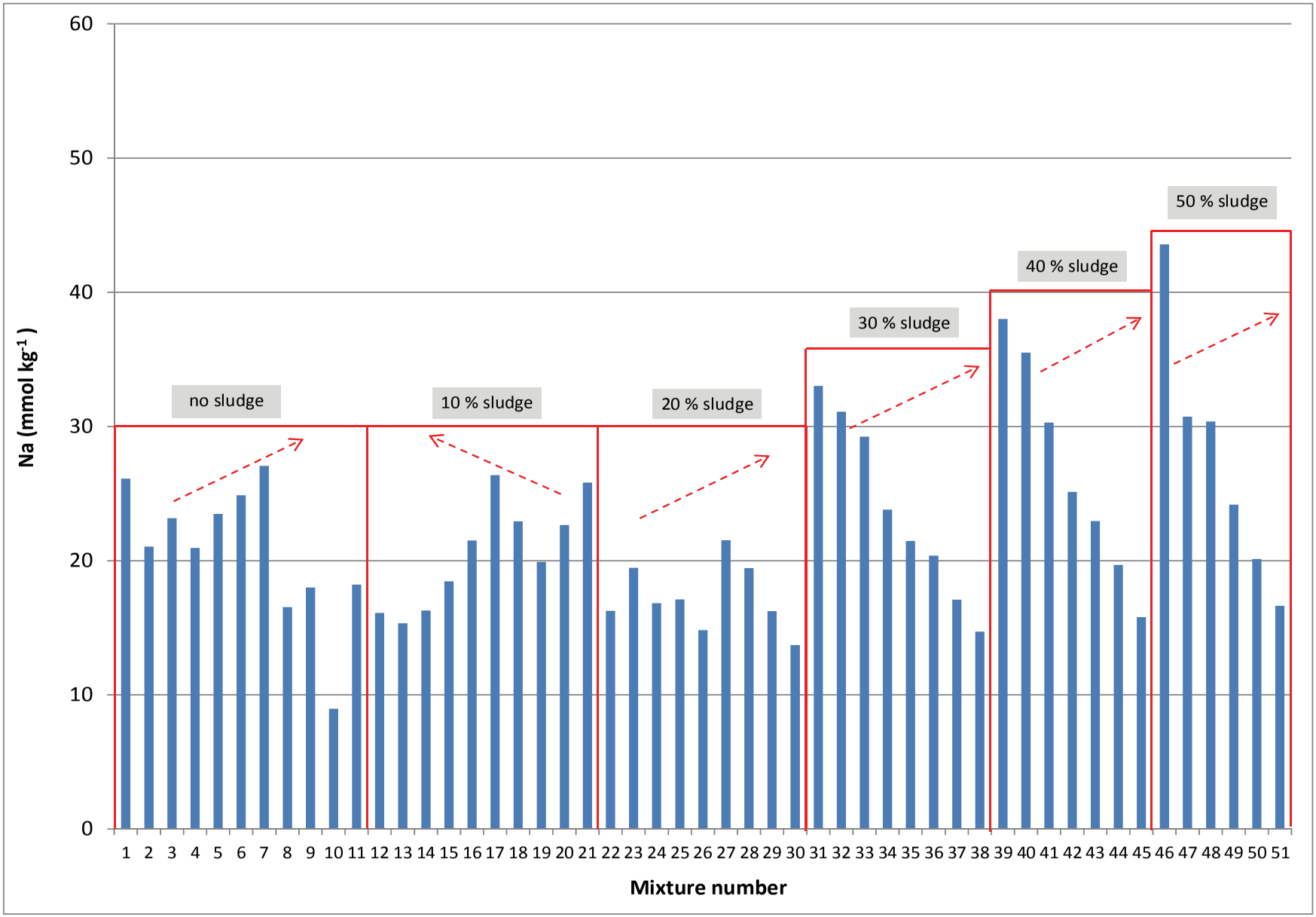


Figure 4.13 Cumulative Na release after 9 leaching cycles. The arrows indicate the direction of increasing gasification ash content each for each sludge treatment group

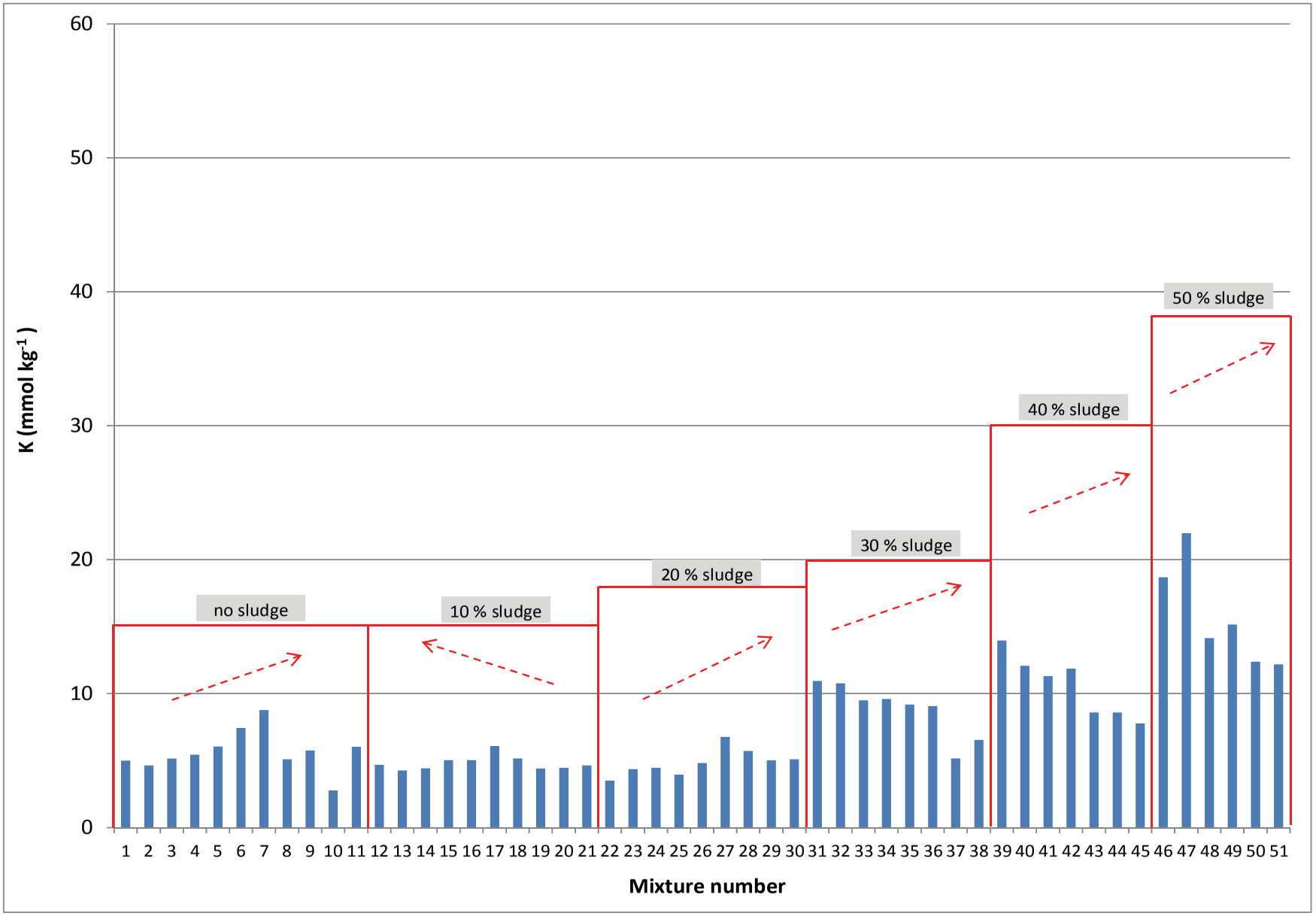


Figure 4.14 Cumulative K release after 9 leaching cycles. The arrows indicate the direction of increasing gasification ash content each for each sludge treatment group

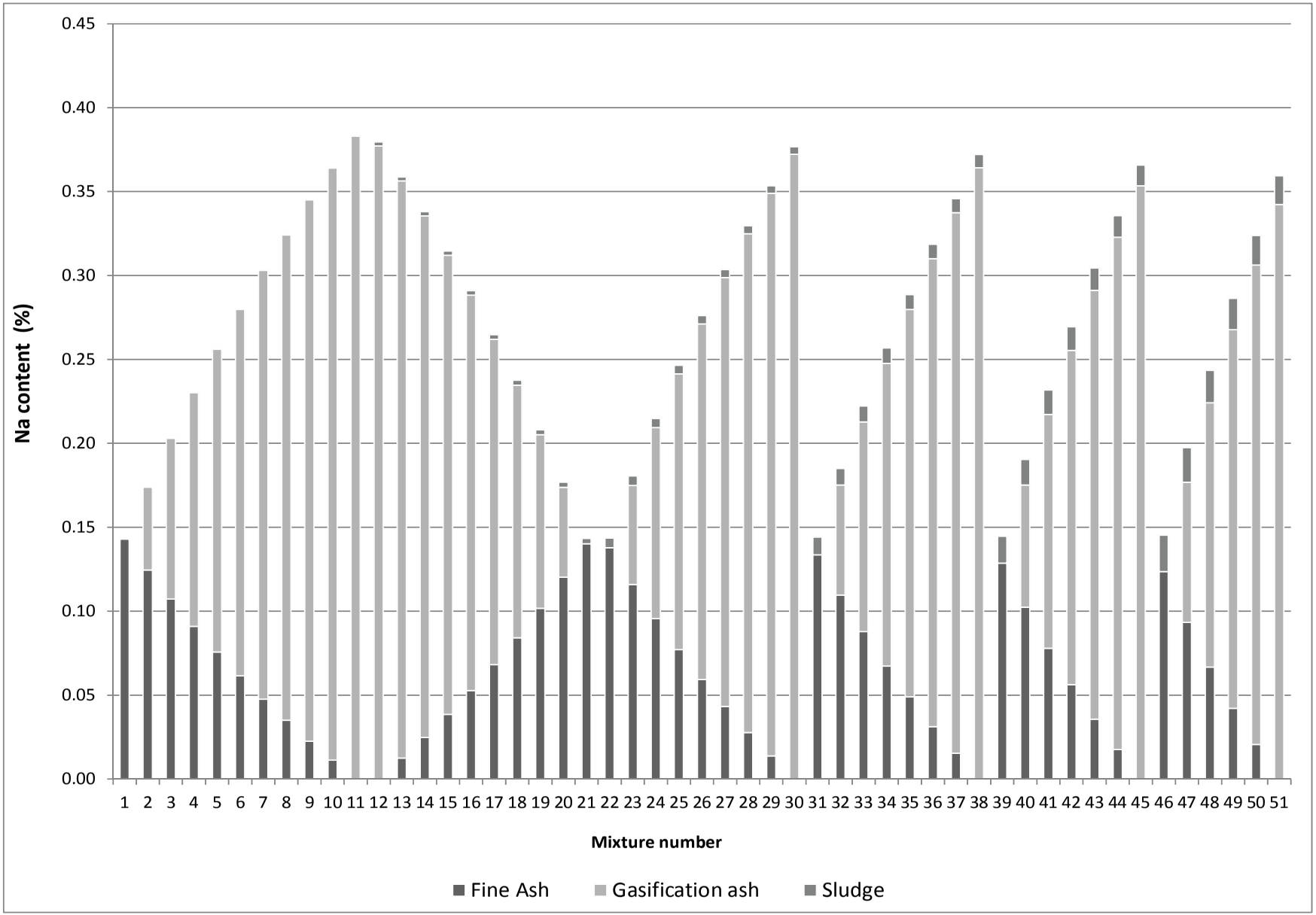


Figure 4.15 Contribution of gasification ash, fine ash and sludge to the Na content of the various mixtures

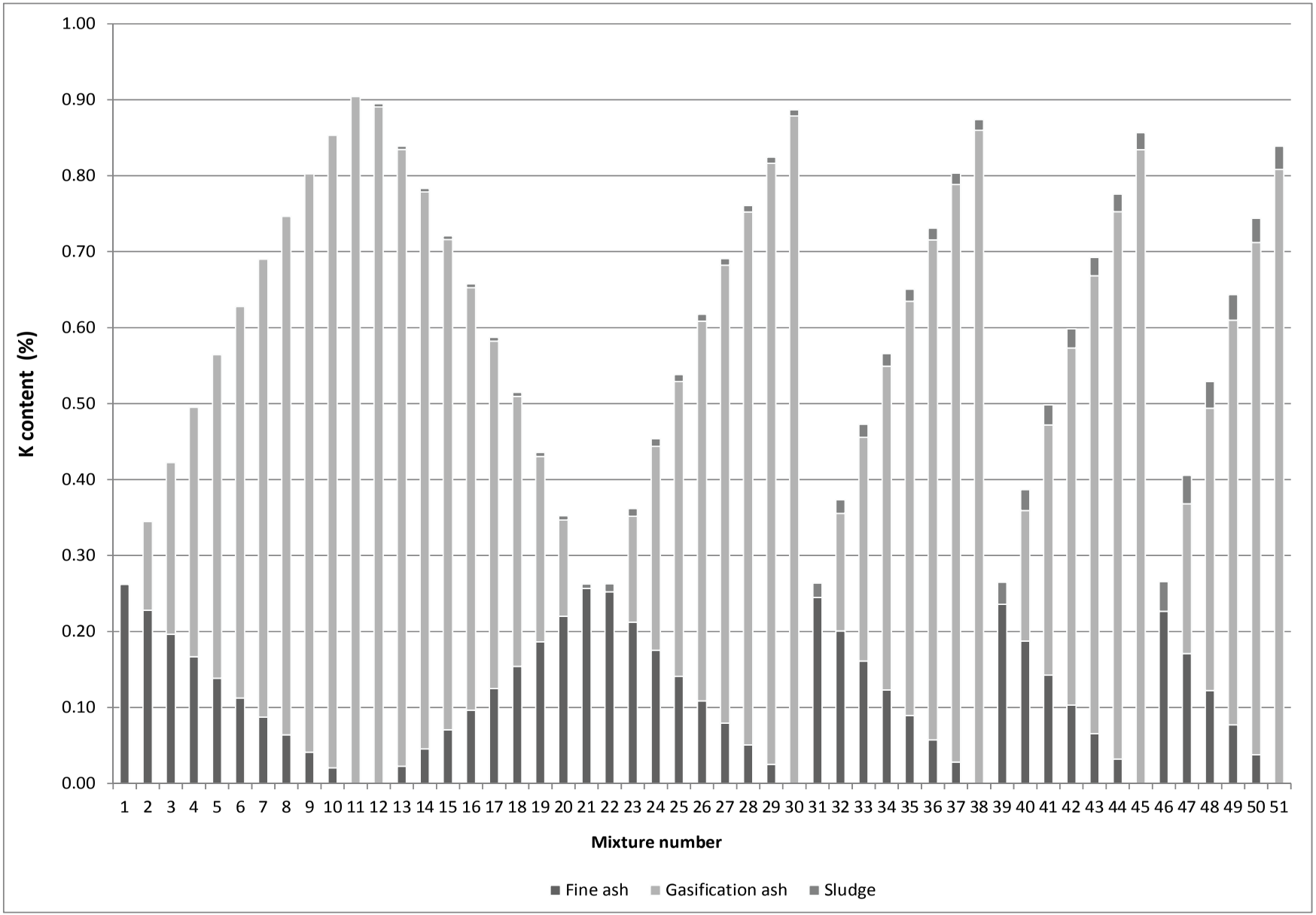


Figure 4.16 Contribution of gasification ash, fine ash and sludge to the K content of the various mixtures

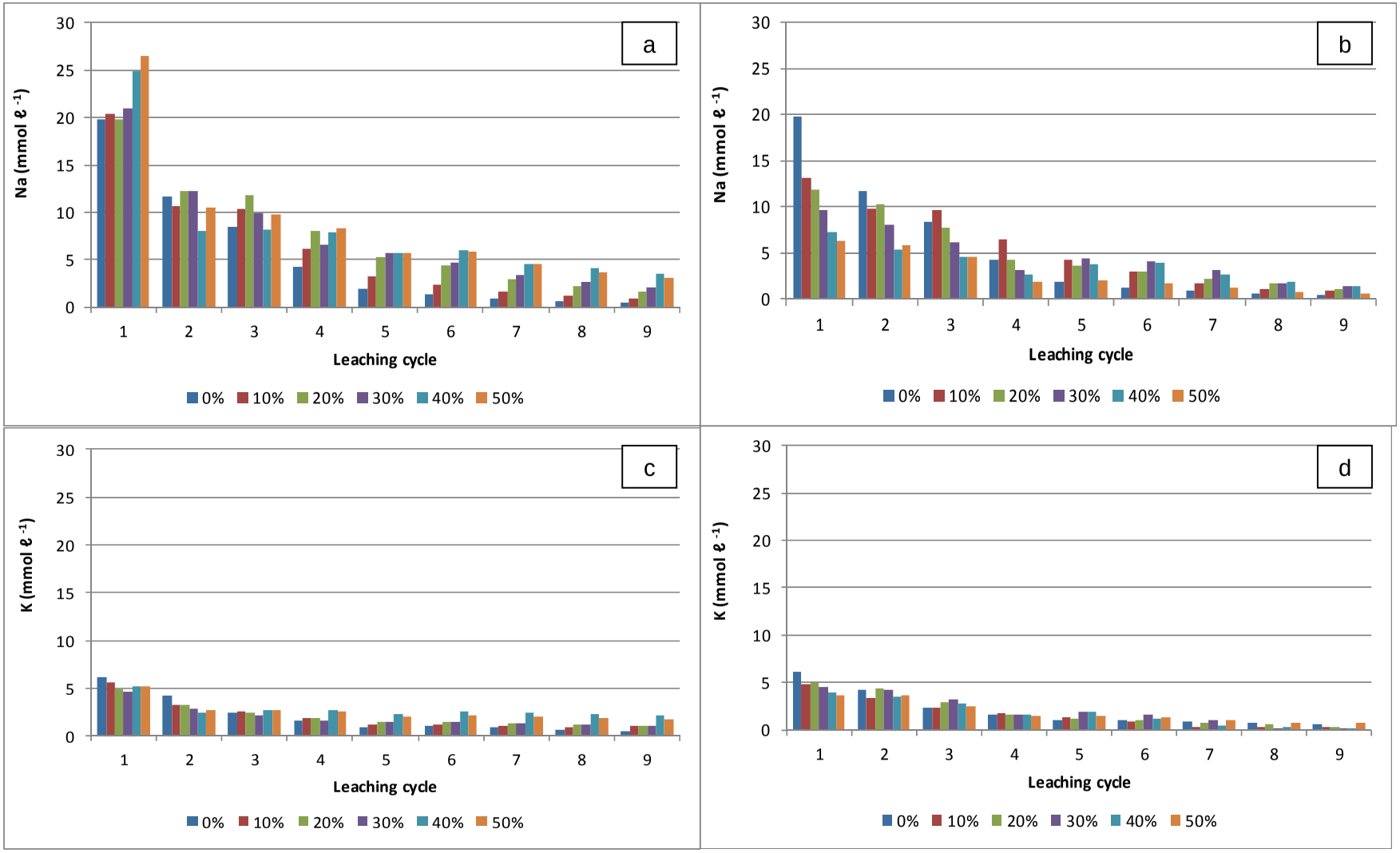


Figure 4.17 Isolating the effect of fine ash and sludge amendment on Na and K release from gasification ash: The temporal change in pore solution concentration of Na and K as influenced by fine ash amendment (a & c) (fine ash content given at bottom of the graphs) and sludge amendment (b & d) (sludge content given at bottom of the graphs)

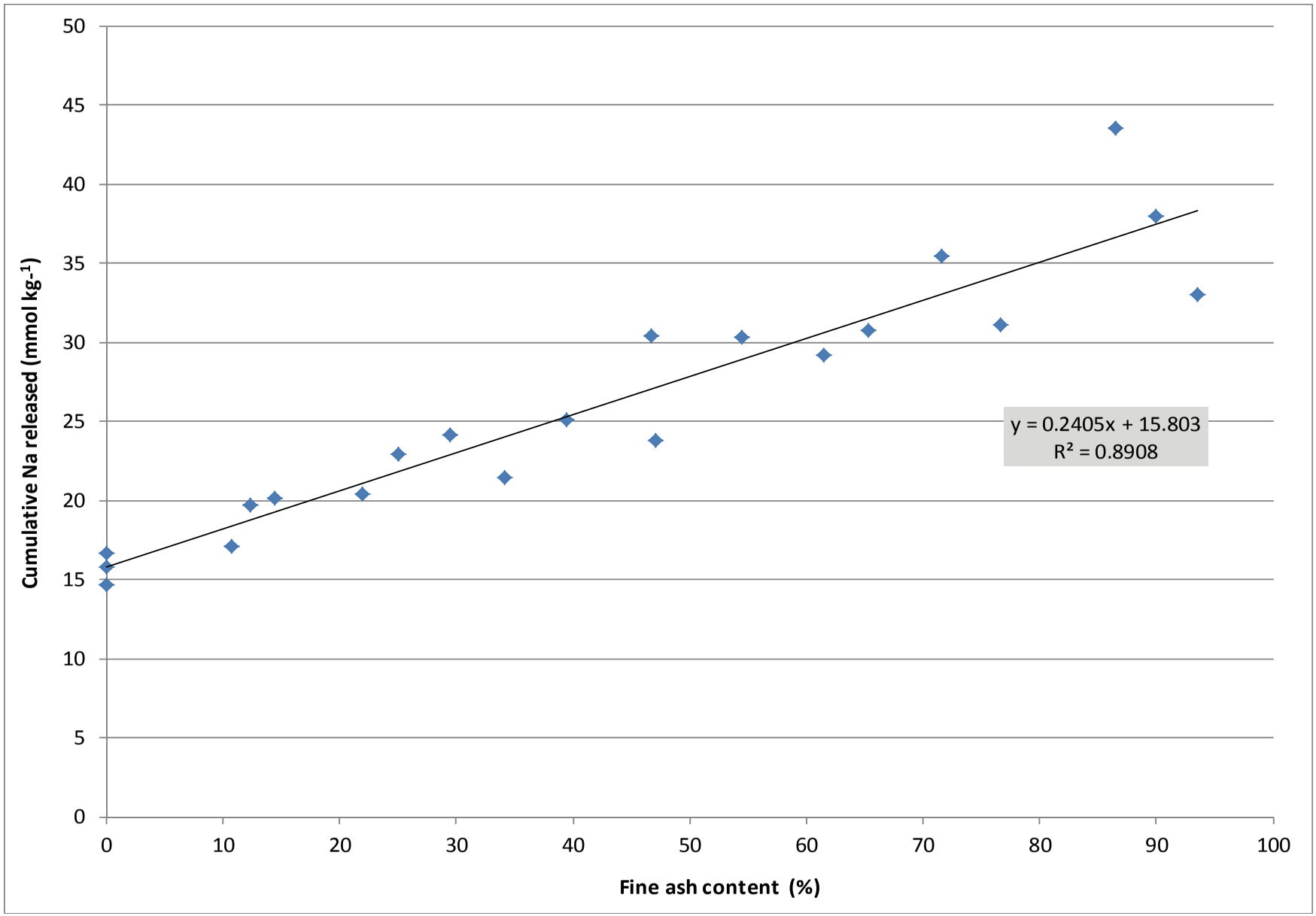


Figure 4.18 Relationship between cumulative Na released and fine ash content of the 30, 40 and 50% sludge treatments

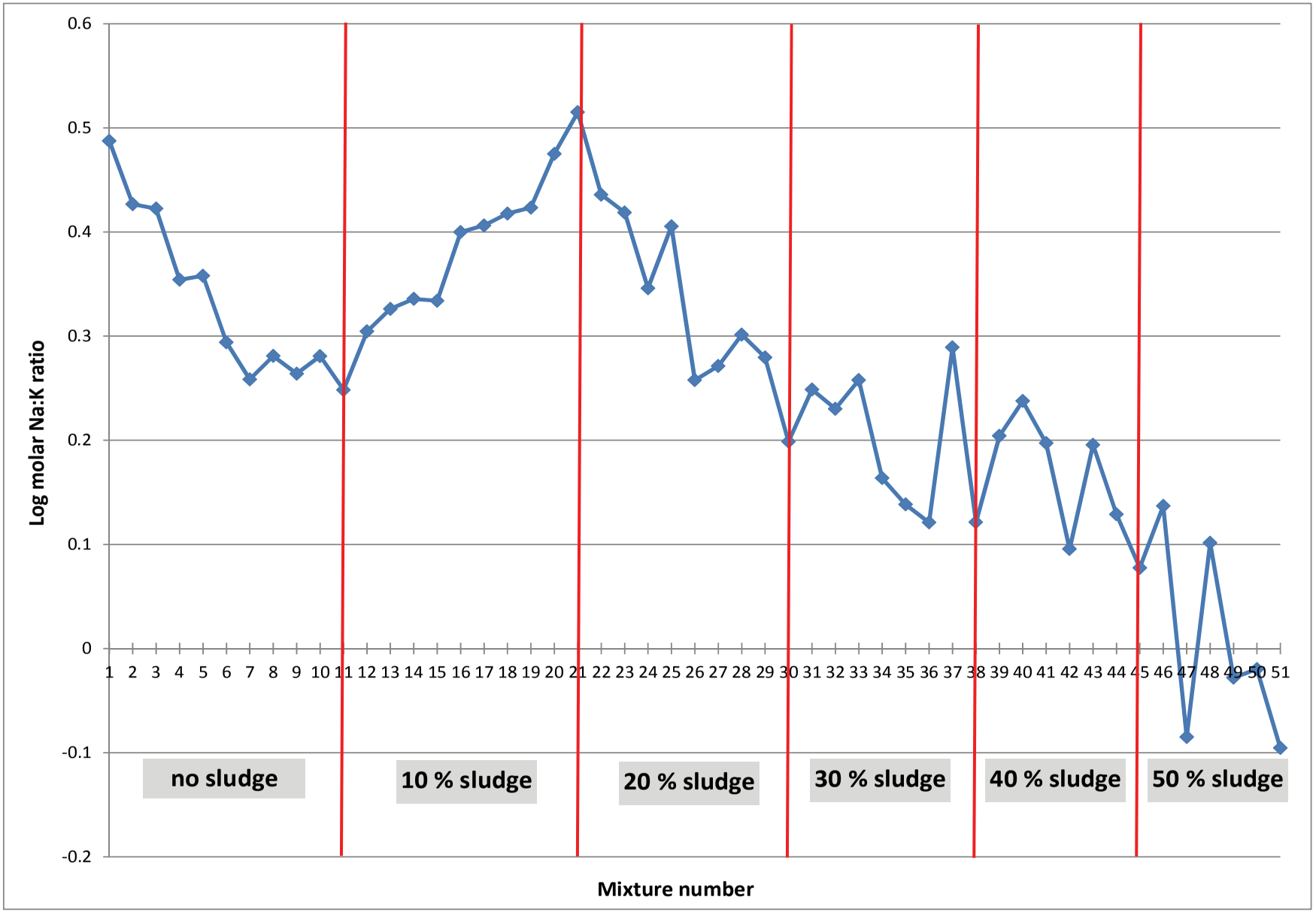


Figure 4.19 Log molar Na:K ratio based on the cumulative Na and K released after nine leaching cycles

4.5. Arsenic and Selenium

Arsenic and selenium, along with mercury and chromate, are trace elements of significant environmental concern because of their acute toxicity to living organisms even at low parts per billion (ppb) concentrations. Analytical technology, for example, the lowering of ICP–MS, ICP-AES (or OES) and Ion Chromatograph system detection limits, as well as advances in chemical purification, have improved in the last 20 years. The net result is the constant improvement of detection limits for trace elements and authorities are constantly lowering stipulated maximum limits in drinking water as research increasingly find that exposure to minute concentrations causes health problems. In 2004 the USEPA lowered the upper limit for As in drinking water from 40 $\mu g\ \ell^{-1}$ (0.53 $\mu mol\ \ell^{-1}$) to 10 $\mu g\ \ell^{-1}$ (0.13 $\mu mol\ell^{-1}$), which was quite a substantial lowering for a parts per billion ranged element (Tamasi and Cini, 2004, EPA, 2006). Arsenic is perceived to be more toxic, based on the USEPA upper limit for Se set at 50 $\mu g\ \ell^{-1}$ (0.63 $\mu mol\ \ell^{-1}$) for drinking water. Solutions emanating from the mixture made in this study were not considered potable by any stretch of the imagination, however, the figures quoted do give a conservative point of reference.

Globally, arsenic has been a focus of research for many decades and causes the most concern with respect to contamination of groundwater sources. This metalloid has been linked to cancer of the skin, lung, bladder kidney and liver (Smith et al., 1992). One of the dangers resides in the fact that, along with mercury, Se and As are susceptible to methylation making it lipophilic and easily assimilated by living organisms (Stumm & Morgan, 1996). Jackson & Miller, (1999), investigated Se and As speciation in soils amended with sludge and sludge-fine ash mixtures using an ion chromatography coupled to an inductively coupled plasma mass spectrometer(IC-ICP-MS). In this study only low levels of monomethylarsonicacid, $CH_3AsO(OH)_2$ (MMA) was found, and dimethylarsinic acid, $(CH3)_2AsO(OH)$ (DMA) was not detected.

In terms of cumulative release, increased sludge amendment did increase Se and As release substantially (Figs 4.20 & 4.21). Mixtures not amended with sludge released little Se and As after 9 leaching cycles. This trend was similar to that of Ca and Mg. However, in the case of Se, it seems that sludge amendment also increased the calculated Se content of the mixtures (Figs 4.22). The Se content of the gasification ash and fine ash were relatively low (89.9 $\mu mol\ kg^{-1}$ for the gasification ash and 71.6 $\mu mol\ kg^{-1}$ for fine ash) compared to the sludge (478 $\mu mol\ kg^{-1}$). In this study municipal sludge was not analysed for Se for comparison, however, the weighted mean for Se reported by Snyman

et al. (2004) was 10 mg kg^{-1} (0.13 mmol kg^{-1}). As content is also expected to increase with increasing sludge content (Figs 4.23).

A comparison of pore solution concentration of the treatments amendment with sludge with that amended with fine ash underlined the increase in Se brought about by sludge amendment (Figs 4.24a & b). Fine ash amendment did increase soluble Se of the mixtures, however, the soluble fraction was largely removed after two leaching cycles (Figs 4.24a). The pore solution concentration of As was low for the fine ash treatments compared to the sludge amended treatments (Figs 4.24c & d), and reflected the low solubility of As in ash. Based on Se and As release, it would be prudent to keep sludge content below 30%, on a wet mass basis, in order to keep the release of these elements form the mixtures low.

Toxicity of both arsenic and selenium are dependent on their chemical form. Therefore, knowledge of its total concentrations alone especially of As is not sufficient to assess 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 stable specie. There is a strong analogue between the chemistry of arsenate (AsO_4^{3-}) and phosphate (PO_4^{3-}). Similar to phosphate, arsenate is strongly sorbed by ferric (oxy) hydroxides in a low pH environment and associate with Ca to form Calcium arsenates, for example, pharmacolite ($CaHAsO_4$. $2H_2O$).Under anoxic conditions (pe + pH < 9, or pe< 2 at pH 7) arsenite predominates. Arsenite is the more toxic, more soluble and mobile specie, therefore keeping the pe + pH of the system above 9 will be important in keeping it in the arsenate form managing the toxicity of arsenic in these mixtures. As mentioned above, the interplay between pH and pe is important. Based on equilibrium redox chemistry, the stability field of arsenate is extended well into anoxic conditions at pH levels greater than 7. Therefore the reduction of arsenate can be inhibited under anoxic conditions if the environment is kept alkaline (Essington, 2004).

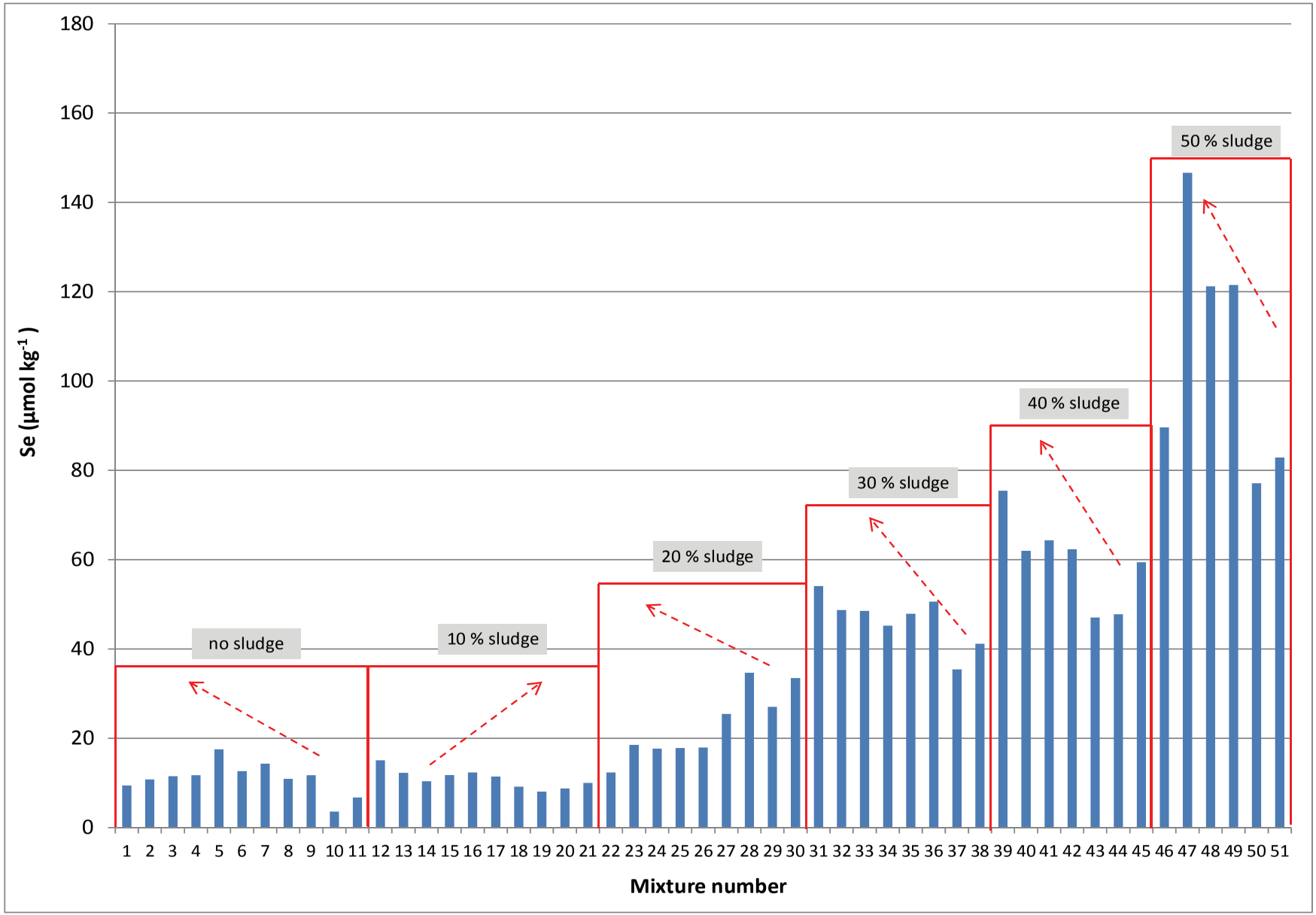


Figure 4.20 Cumulative Se release after 9 leaching cycles. The arrows indicate the direction of increasing fine ash content of the various sludge treatment groups

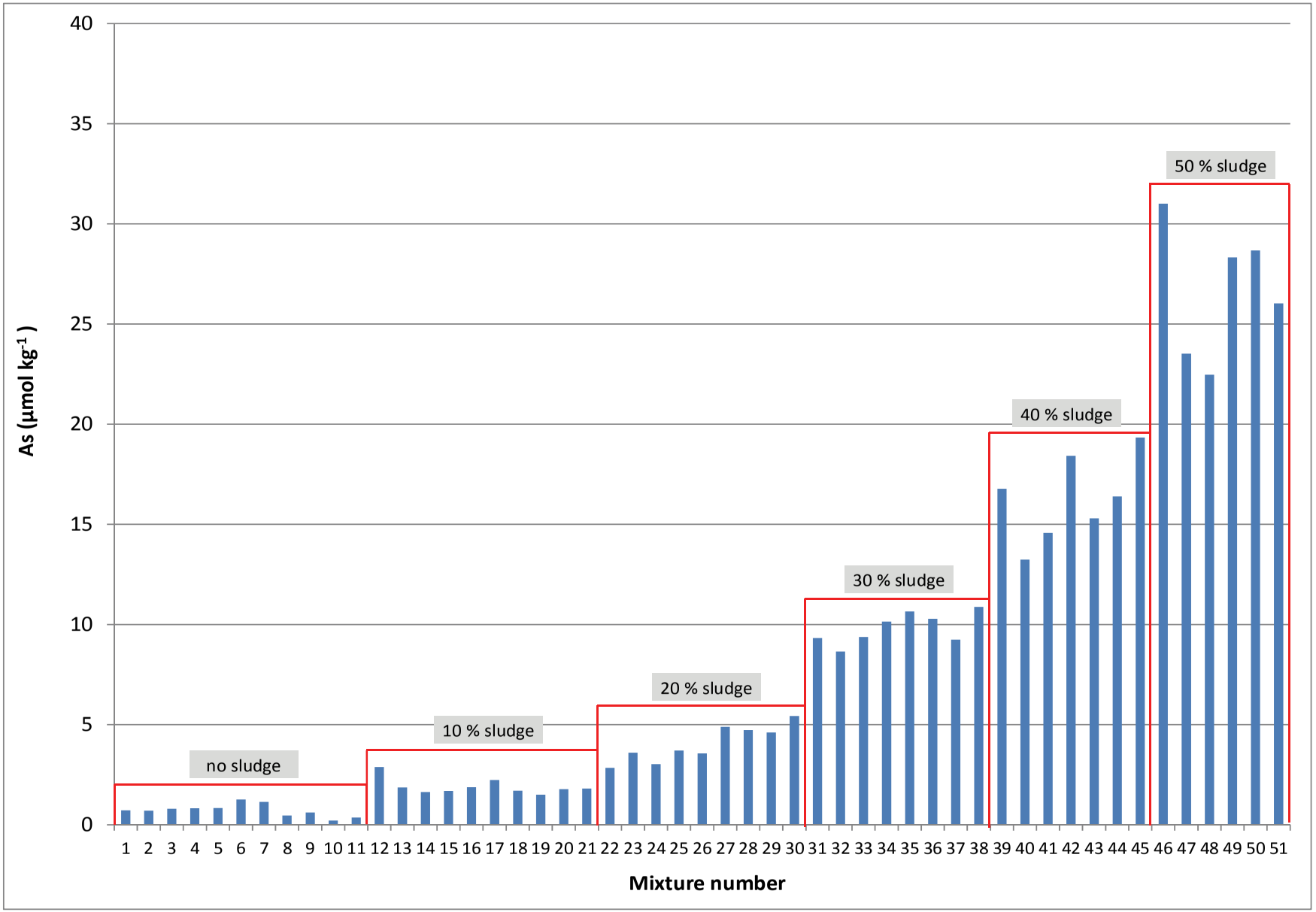


Figure 4.21 Cumulative As release after 9 leaching cycles

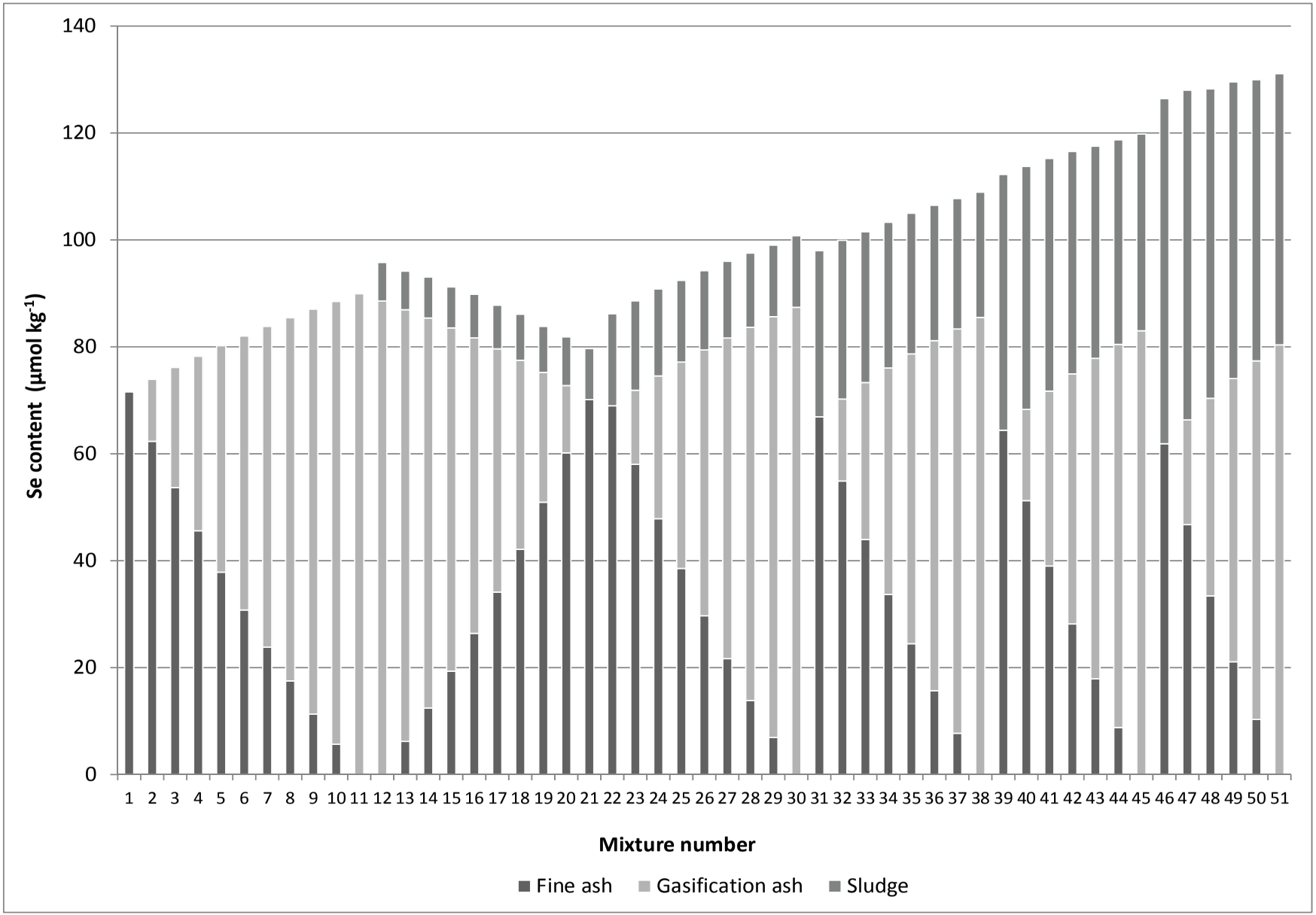


Figure 4.22 Contribution of gasification ash, fine ash and sludge to the Se content of the various mixtures

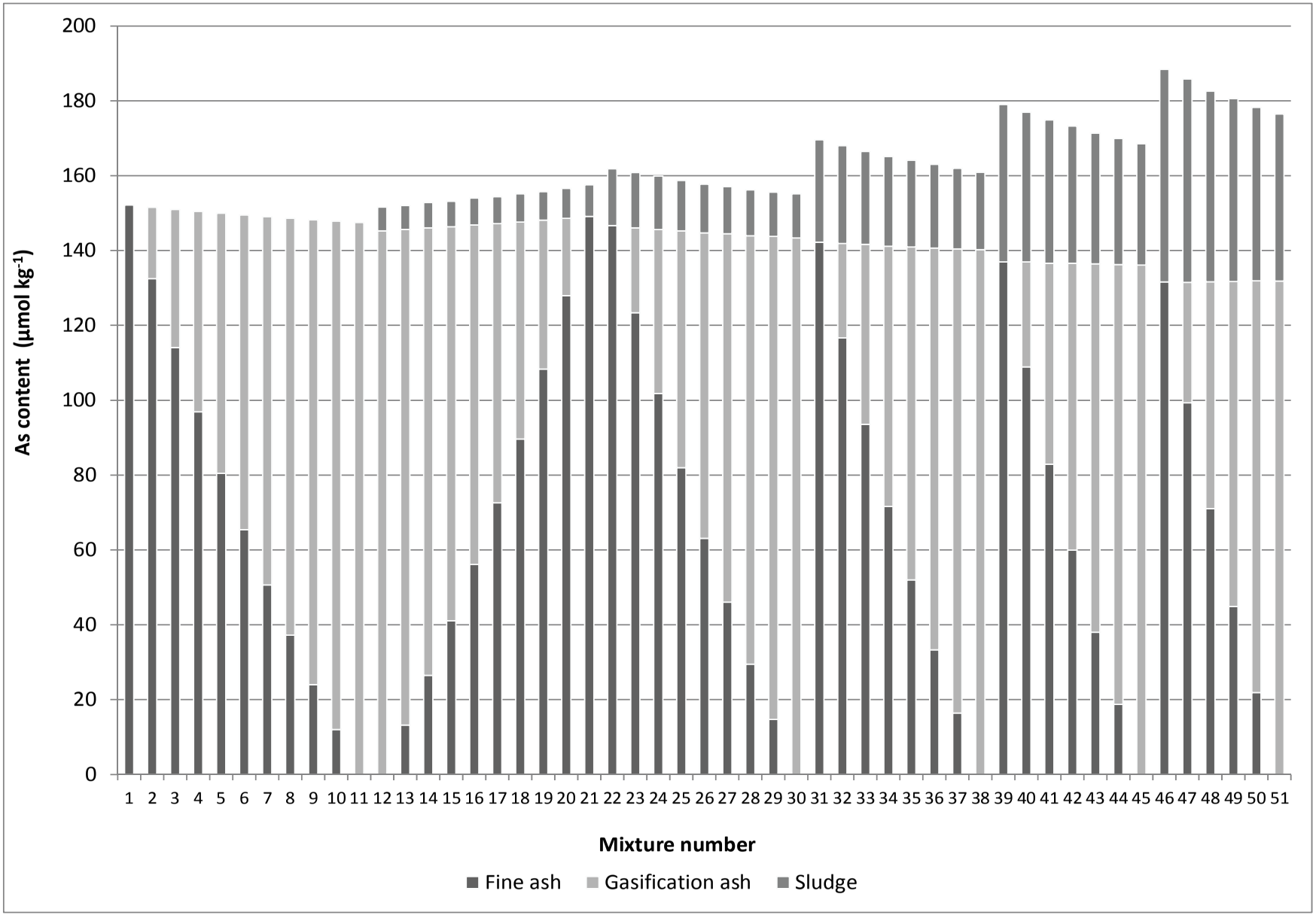


Figure 4.23 Contribution of gasification ash, fine ash and sludge to the As content of the various mixtures

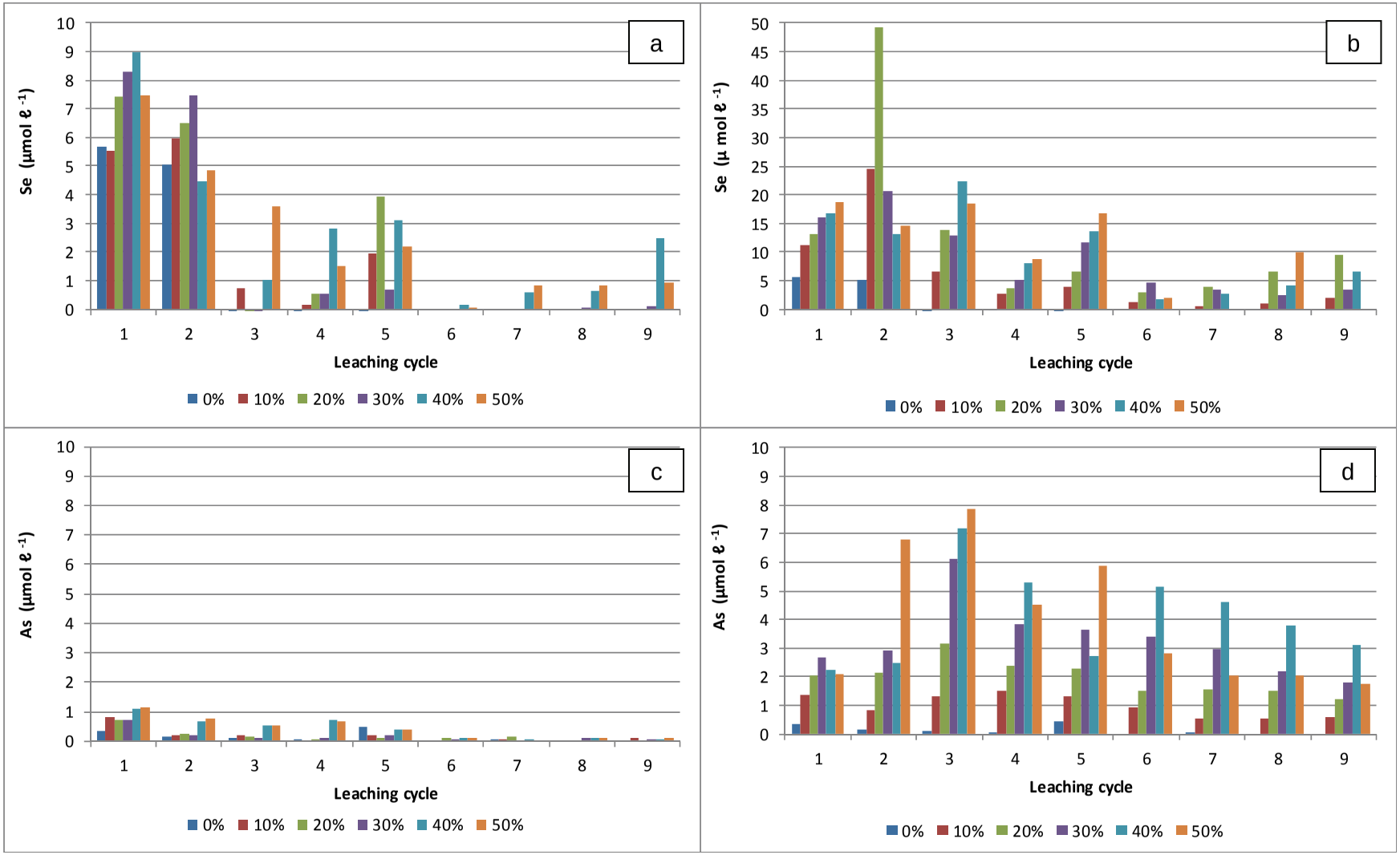


Figure 4.24 Isolating the effect of fine ash and sludge amendment on Se and As release from gasification ash: The temporal change in pore solution concentration of Se and As as influenced by fine ash amendment (a & c) (fine ash content given at bottom of the graphs) and sludge amendment (b & d) (sludge content given at bottom of the graphs)

4.6. Aluminium and Iron

After silicon, aluminium is the second most abundant element in both the fine and the gasification ashes. The gasification ash had the highest Al content of 6.75% (2503 mmol kg^{-1}). Fine ash Al content was 2.03% (752 mmol kg^{-1}) and sludge was a minor contributor to the mixtures with 0.23% (84.5 mmol kg^{-1}) (Fig 4.30).Based on the principles of weathering it is expected that Al will play an important part in the transformation of the mixtures and will be an important constituent of the fabric (or mineralogy) of the weathered end products. In order to gain predictive capability on possible thermodynamic end points of these systems, it is important to elucidate potential mineralogical / solubility controls of Al.

The pore solution Al concentration of leaching cycles 8 and 9 were situated between the solubility limits of amorphous $Al(OH)_3$ and gibbsite, the crystalline, less soluble gibbsite form of $Al(OH)_3$ (Fig 4.25). Initially the systems were further removed from equilibrium with known $Al(OH)_3$ solid phases. The pore solution concentration of cycle 1 was mostly outside the solubility boundary of gibbsite. For leaching cycle 5, mixtures without sludge fell outside the boundary of gibbsite and with sludge fell inside the boundary. The data therefore suggested that these systems were moving closer to systems in equilibrium with $Al(OH)_3$ solid phases. Gibbsite is thermodynamically the more stable $Al(OH)_3$ and it is reasonable to expect that this is the equilibrium end point. However, gibbsite is known to form solid solutions with varying contents of Fe(III), Cr(III), Al(III) and Mn(III) in octahedral positions. It is unlikely that in heterogeneous systems like these standard state gibbsite (pure and crystalline) will form. Using the available standard state databases in chemical models will therefore not give the complete picture. These systems could in fact already be in equilibrium with non-standard state gibbsite, with Fe(III), Cr(III), Al(III) and Mn(III) occupying some octahedral positions which altered its solubility relative to pure gibbsite.

The gibbsite and amorphous $Al(OH)_3$saturation indices for leaching 9 showed that for the treatments without sludge, but dominated with fine ash, the pore solutions were almost in equilibrium with amorphous $Al(OH)_3$ (Fig 4.26). However increasing sludge content resulted in solutions becoming increasing undersaturated with amorphous $Al(OH)_3$. On the other hand, the oversaturation with respect to gibbsite decreased with increasing sludge content.

No clear mineralogical control could be established with the data collected so far. However, Al solid phases in the mixtures showed an amphoteric character similar to Al hydroxides found in soil, which is a decrease in solubility as the pH increase to a circum-neutral range and increase in solubility at a pH

greater than 7. Beyond pH 7 the predicted aqueous Al concentration in equilibrium with gibbsite increases logarithmic with increase in pH. Thermodynamic modelling with PHREEQC showed that one log unit increase in pH significantly increases the solubility of gibbsite. At pH 10, for example, the predicted concentration is 40 µmo $l\ell^{-1}$ and increases to 413 µmol ℓ^{-1} at pH 11. In the absence of sludge, the pore solution pH of the 40 & 50% fine ash treatments were greater than 11 up to the fifth leaching and also had the highest Al pore solution concentrations(Fig 4.27 a). The 20% fine ash treatment exhibited a pore solution concentration of 11.3 µmol $\ell^{-1}$and a pH of 9.98 for the fifth leaching cycle while the 40% fine ash treatment exhibited a pH of 11.38 and an Al concentration of 133.8 µmol ℓ^{-1}. Mixtures that maintained a higher pH (treatments without sludge) also released cumulatively the most Al after nine leaching cycles (Fig 4.28). On the other end of the spectrum, sludge amendment in the absence of fine ash suppressed Al pore solution concentration (Fig 4.27 a & b).

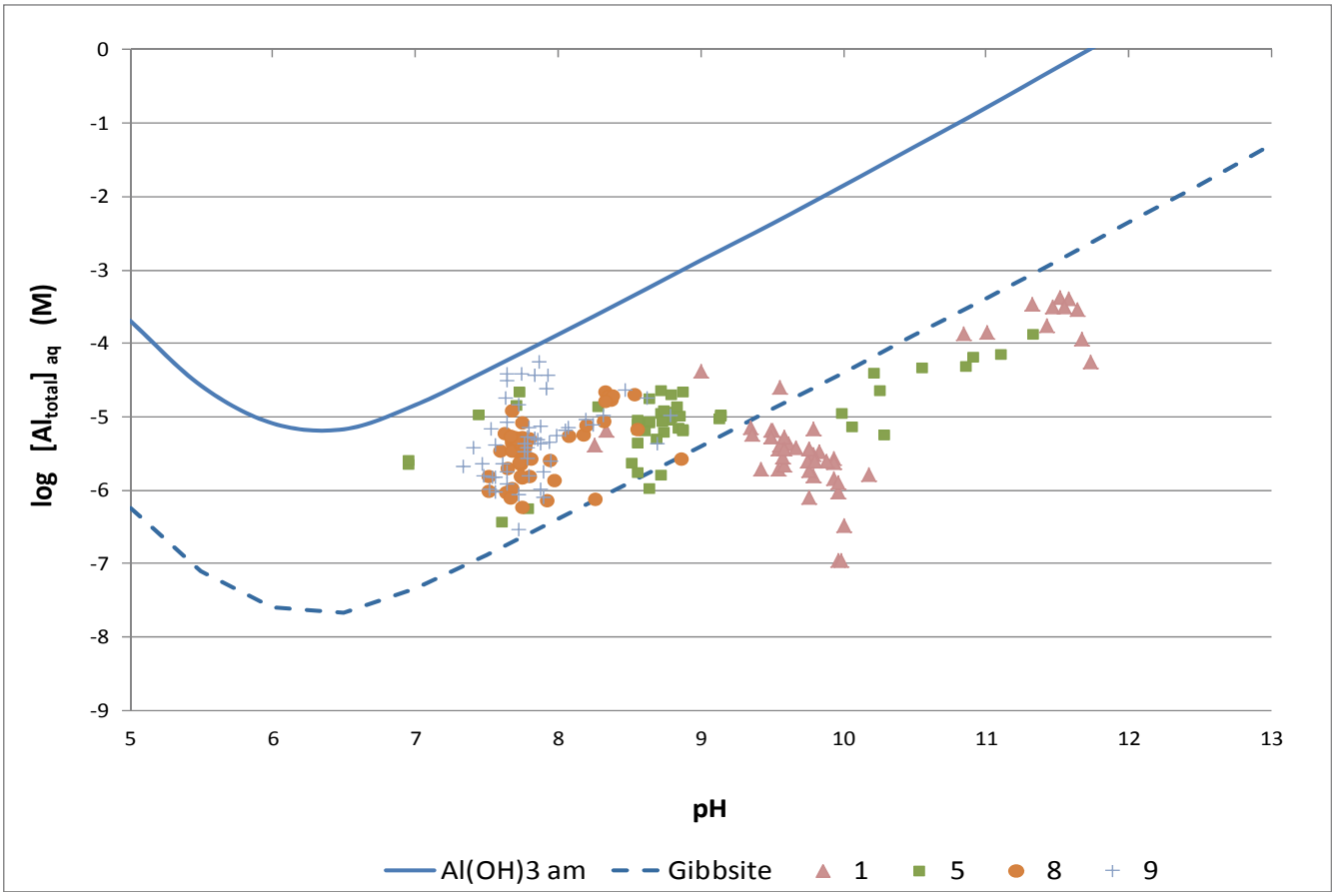


Figure 4.25 Comparing measured Al pore concentration of leaching cycles 1, 5, 8 and 9 with predicted solubility limits of gibbsite and amorphous $Al(OH)_3$, given by the predicted equilibrium Al concentration obtained with PHREEQC simulations

Figure 4.26 Gibbsite and amorphous $Al(OH)_3$ saturation indices of the various mixtures for the ninth leaching cycle. Log IAP/ K_{sp} = 0 means solution is saturated with respect to a specific mineral, example, Gibbsite and this mineral can possibly control Al activity and availability

Fe showed an opposite trend to Al, and cumulative Fe release increased with increasing sludge amendment (Figs 4.28 & 4.29). Both aluminium and ferric iron are hard Lewis acids and exhibit similar chemical behaviour in many respects. However, ferric iron is an important electron acceptor in the environment 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 labile electrons and acts as an electron donor (reducing agent). When the mediums are saturated with water, 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.

It is unlikely that the increased Fe released with sludge amendment was due to high Fe content of the sludge, because the contribution of sludge to the total Fe content of the mixtures was low (Fig 4.31) The pore solution Fe concentration was similar for the first leaching cycle when comparing the sludge effect on Fe pore solution concentration with that of fine ash (Figs 4.27c & d). However, the sludge amended mixtures showed an increase in Fe solubility onwards for leaching cycles 2 and 3, while in the absence of sludge, Fe exhibited a very low solubility.

Iron is an essential trace element for plants. Based on the low solubility in the absence of sludge, plant availability would be limited if the pH is not lowered or if the gasification ash is not amended with organic material to increase Fe solubility.

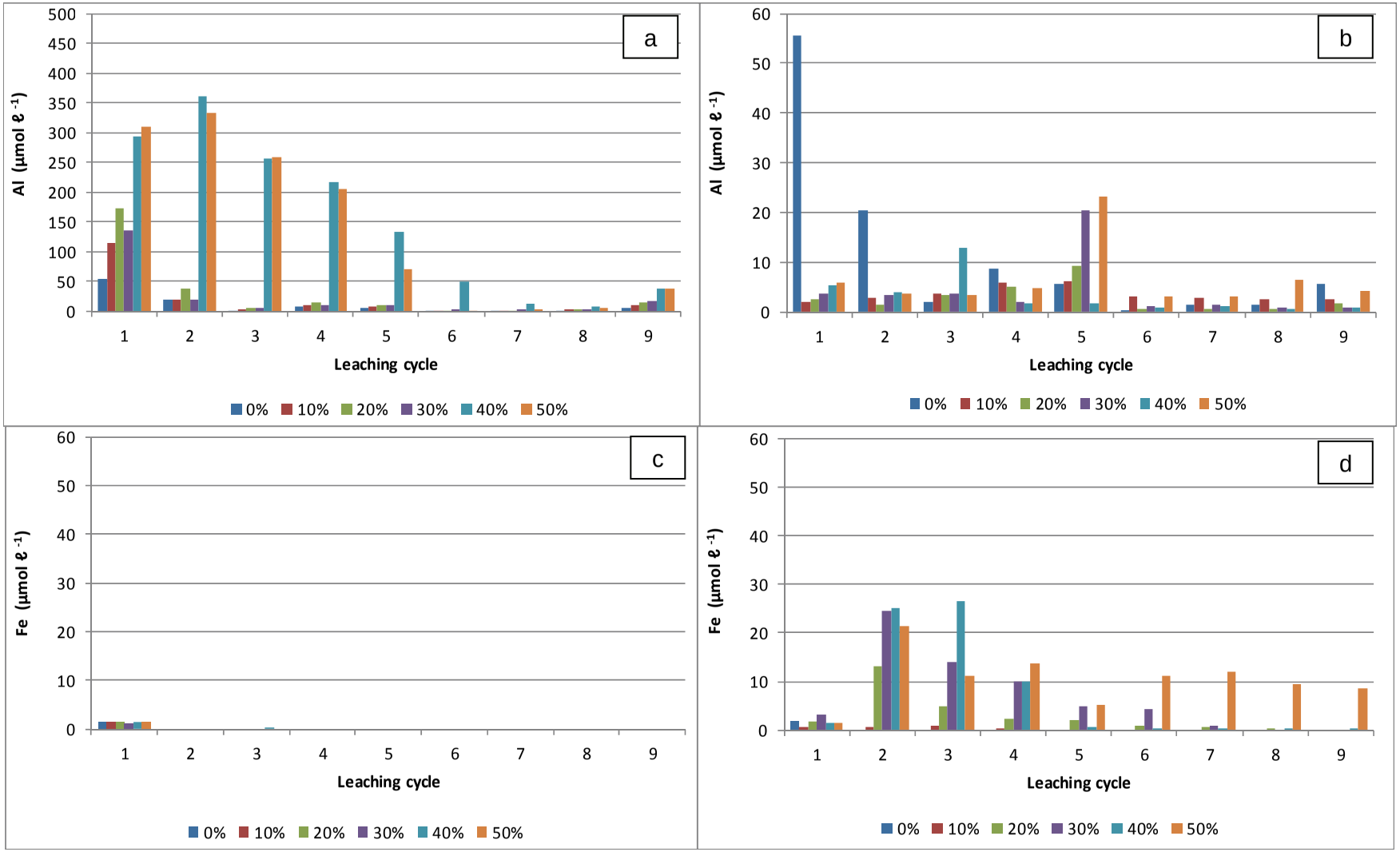


Figure 4.27 Isolating the effect of fine ash and sludge amendment on Al and Fe release from gasification ash: The temporal change in pore solution concentration of Al and Fe as influenced by fine ash amendment (a & c) (fine ash content given at bottom of the graphs) and sludge amendment (b & d) (sludge content given at bottom of the graphs)

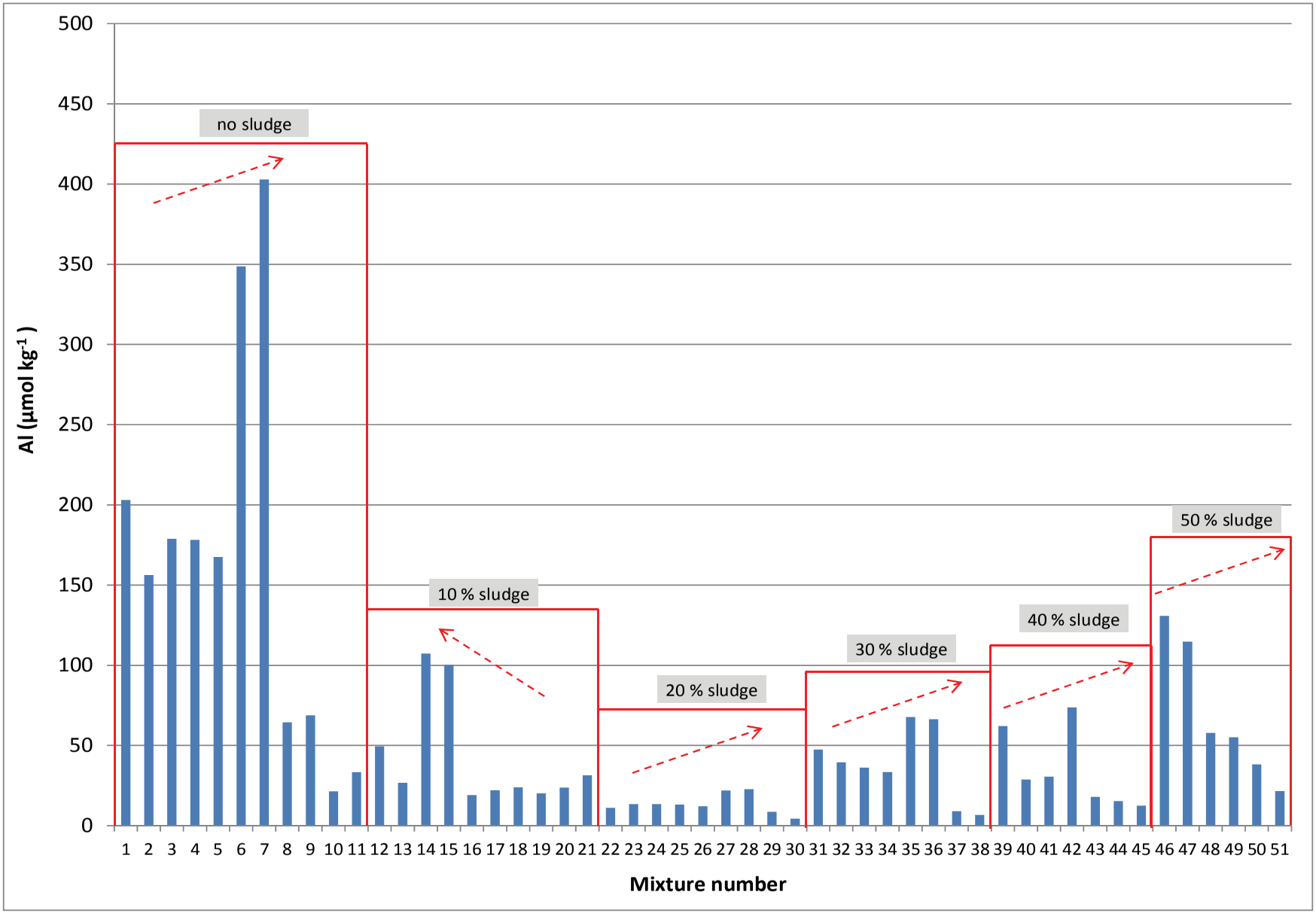


Figure 4.28 Cumulative Al release after 9 leaching cycles. The arrows indicate the direction of increasing gasification ash content of the various sludge treatment groups

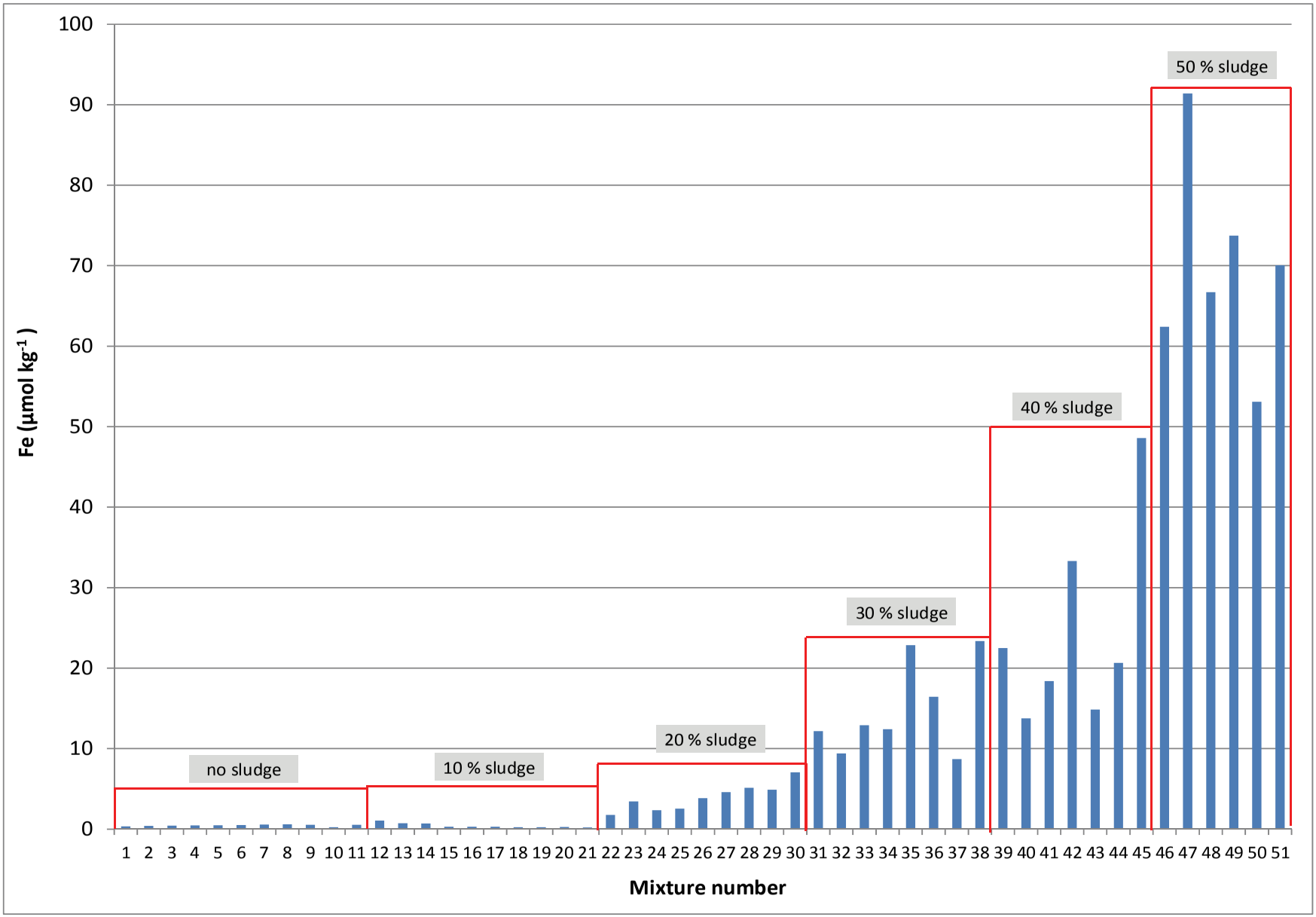


Figure 4.29 Cumulative Fe release after 9 leaching cycles

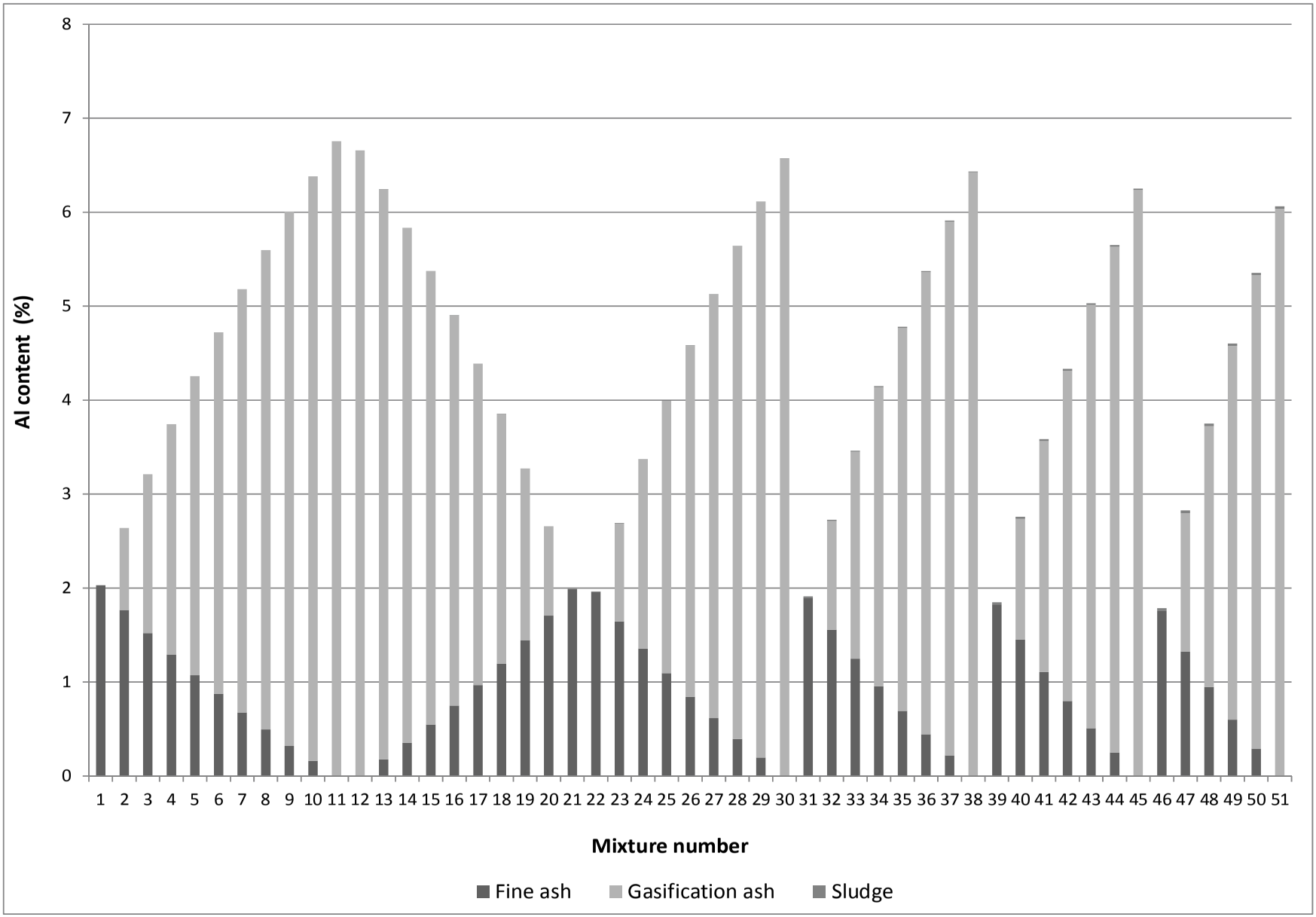


Figure 4.30 Contribution of gasification ash, fine ash and sludge to the Al content of the various mixtures

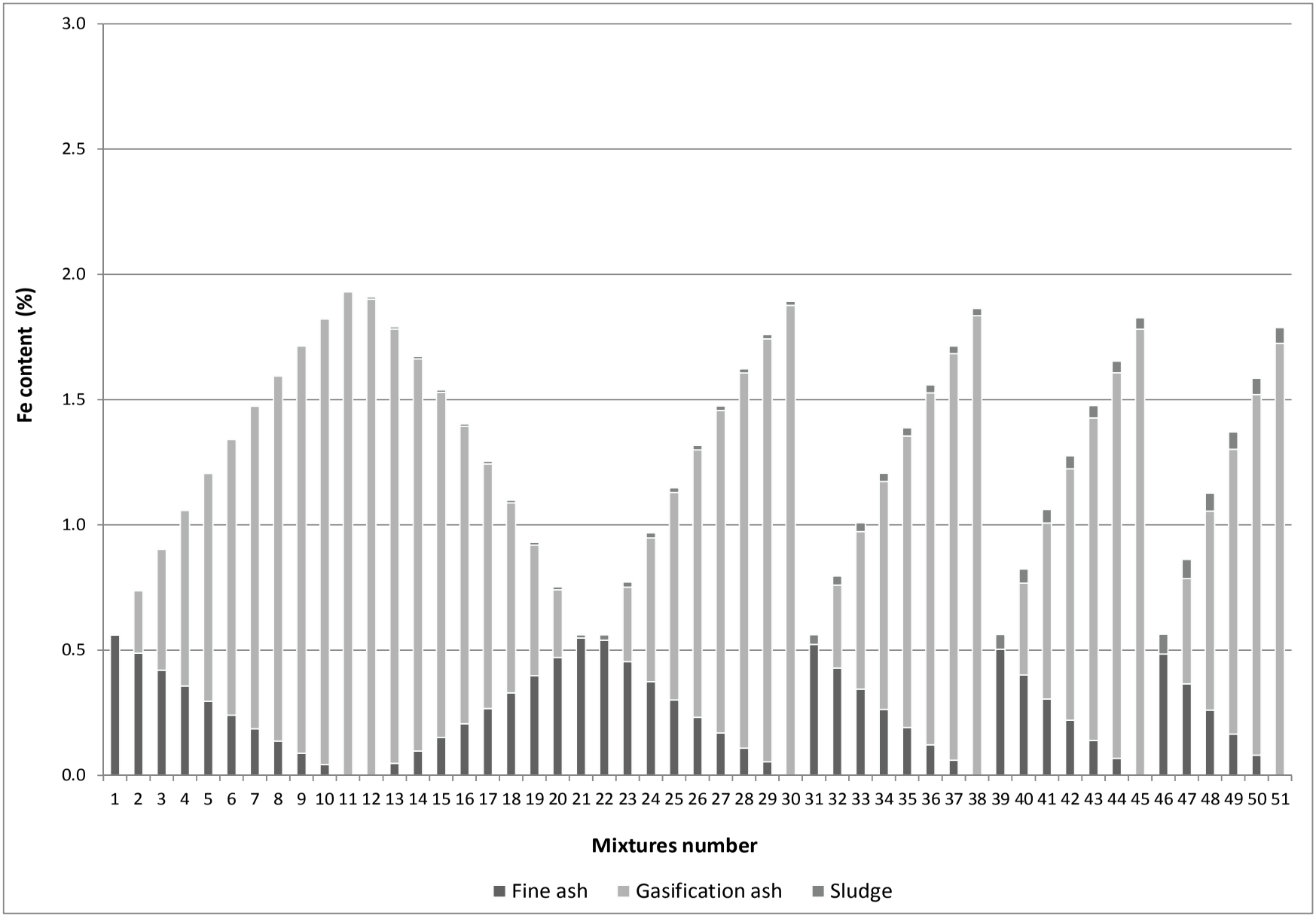


Figure 4.31 Contribution of gasification ash, fine ash and sludge to the Fe content of the various mixtures

4.7. Trends for other Elements

4.7.1. Chromium and Vanadium

Cumulative chromium release was similar to Al. Mixtures that maintained a higher pH (treatments without sludge) also released cumulatively the most Cr after nine leaching cycles (Fig 4.32). On the other end of the spectrum, sludge amendment suppressed Cr mobility. Chromium oxide and hydroxide minerals will show a similar amphoteric character as aluminium. However, the suppression of Cr release when sludge content become appreciable, could also arise due to a reduction of chromate to less soluble Cr(III) because the reduced carbon in the sludge is a strong electron donor. In the absence of strong electron donors and in alkaline environments Cr(VI) can prevail. Vanadium showed high solubility in the absence of sludge, and at the highest sludge amendment (Fig 4.33).

4.7.2. Phosphorus, Boron and Sulphur

Phosphorus, boron and sulphur showed similar cumulative elemental release trends, which were that sludge amendment increased the cumulative amount of elemental released. Boron release was about an order of a magnitude greater than P, and also showed a strong positive relationship with fine ash content. The higher the ash and sludge content the greater the boron released (Fig 4.35). P solubility did not show this relation with fine ash content of the mixtures (Fig 4.34). More sulphur was released than any other element (Fig 4.36). Boron and sulphur showed a similar trend, normally that the highest sludge and fine ash treatment combinations resulted in the greatest cumulative release. Addition of sludge resulted in much higher S pore solution concentrations (data not shown). Pore solution S concentrations peaked for all sludge treatments with the second and third leaching cycle at concentrations between 40 and 60 mmol ℓ^{-1} and then steadily decreased to values similar to the treatments without sludge of around 10 mmol ℓ^{-1}. This indicated that a solubility control existed for S after some time. The barium content of the gasification ash was 15.5 mmol kg^{-1} (2127 mg kg^{-1}) and that of the fine ash was 13.5 mmol kg^{-1} (1850 mg kg^{-1}). PHREEQC assessments suggest barite ($BaSO_4$. $2H_2O$) could possibly be a sink for S, guarded these systems are aerobic (pe + pH > 9) and all sulphur is oxidised to sulphate. With the pH decreasing to below 9 over time it is unlikely that ettringite ($Ca_6Al_2(SO4)_3(OH)_{12}$.26 H_2O) will play a long term role as a sink for S.(Myneni et al., 1998). Sludge was not a significant source of S and B, and the increase in the amount of S and B released was attributed to the ability of the sludge (or its breakdown products) to mobilise these elements from the ash.

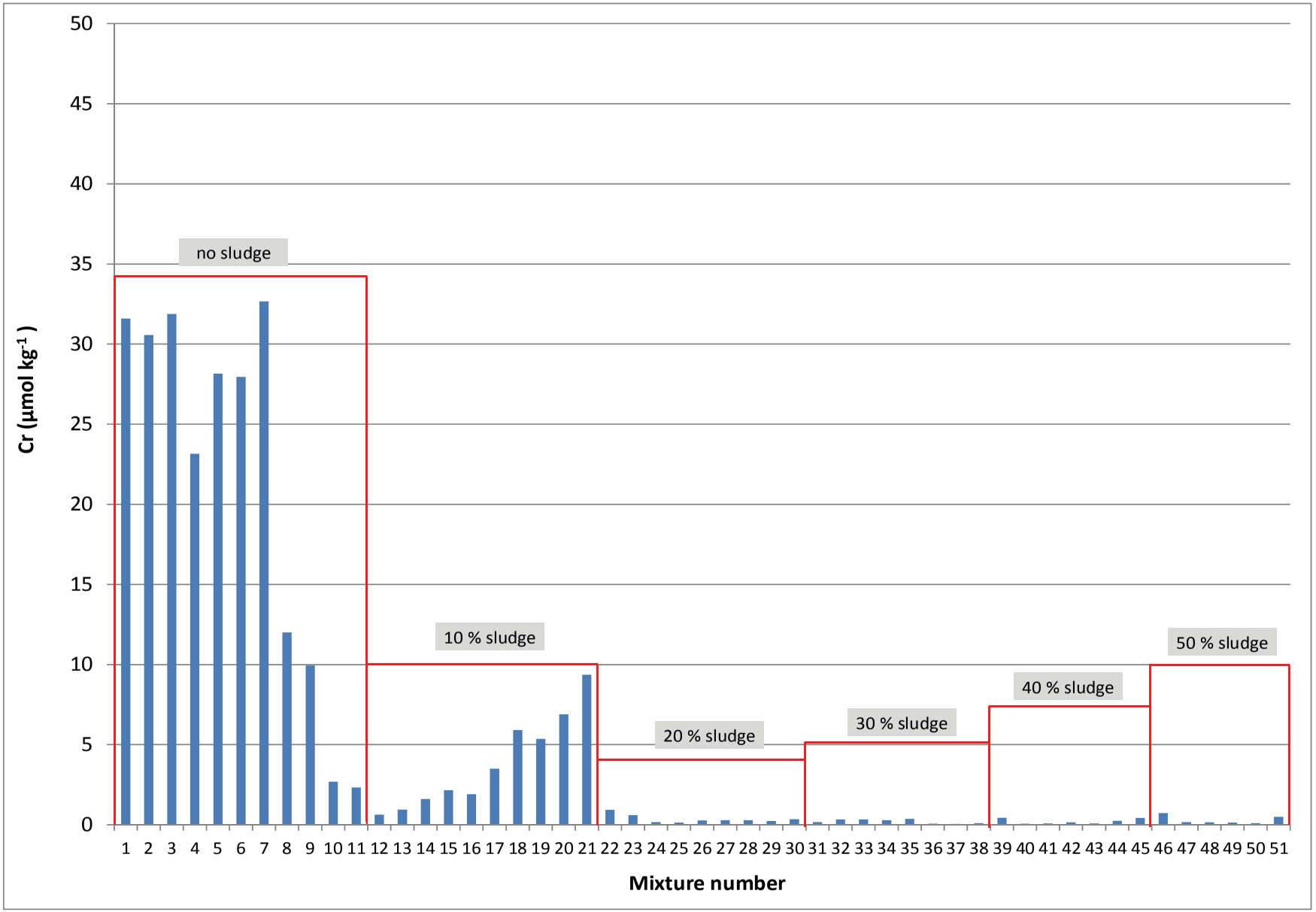


Figure 4.32 Cumulative Cr release after 9 leaching cycles

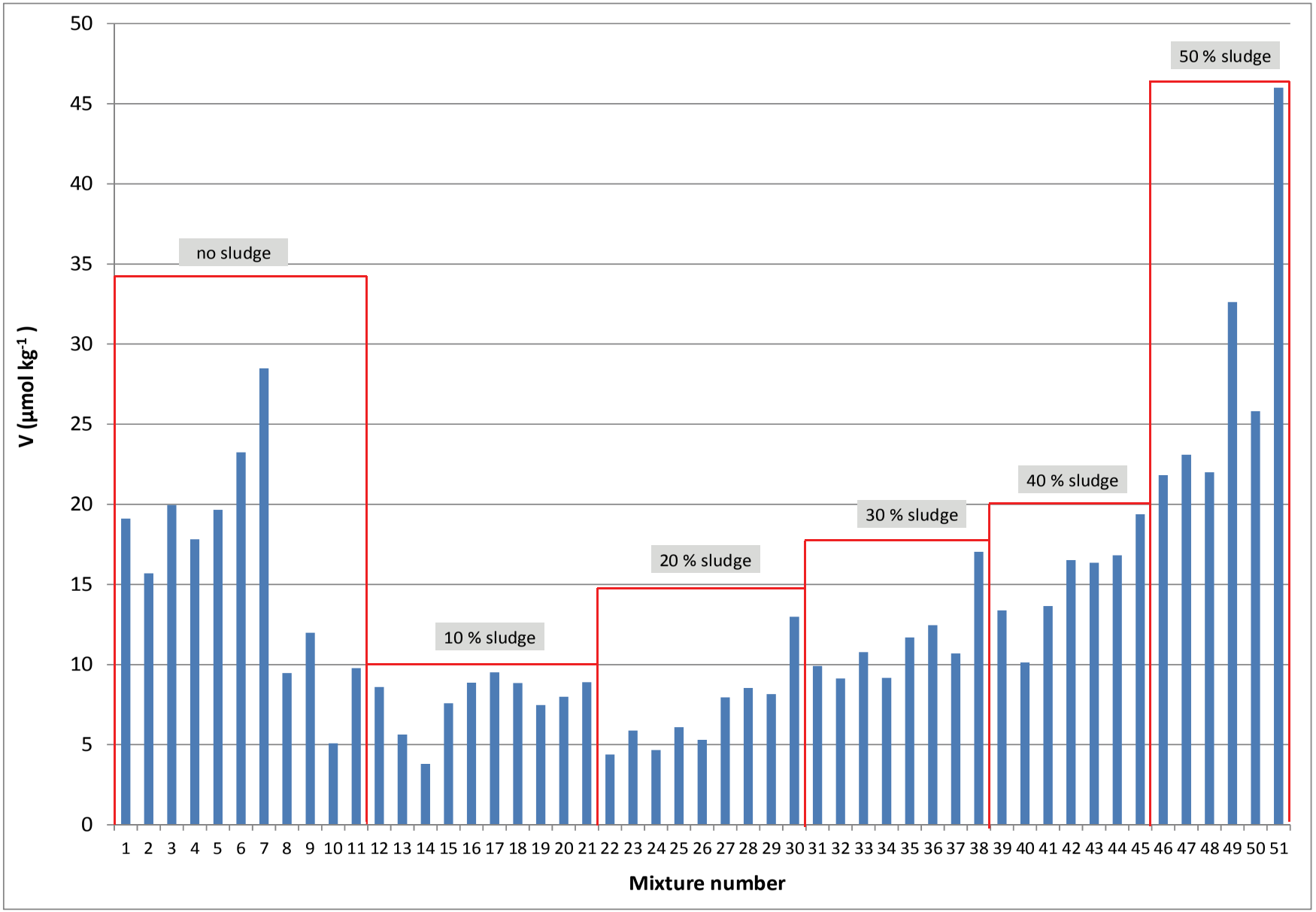


Figure 4.33 Cumulative V release after 9 leaching cycles

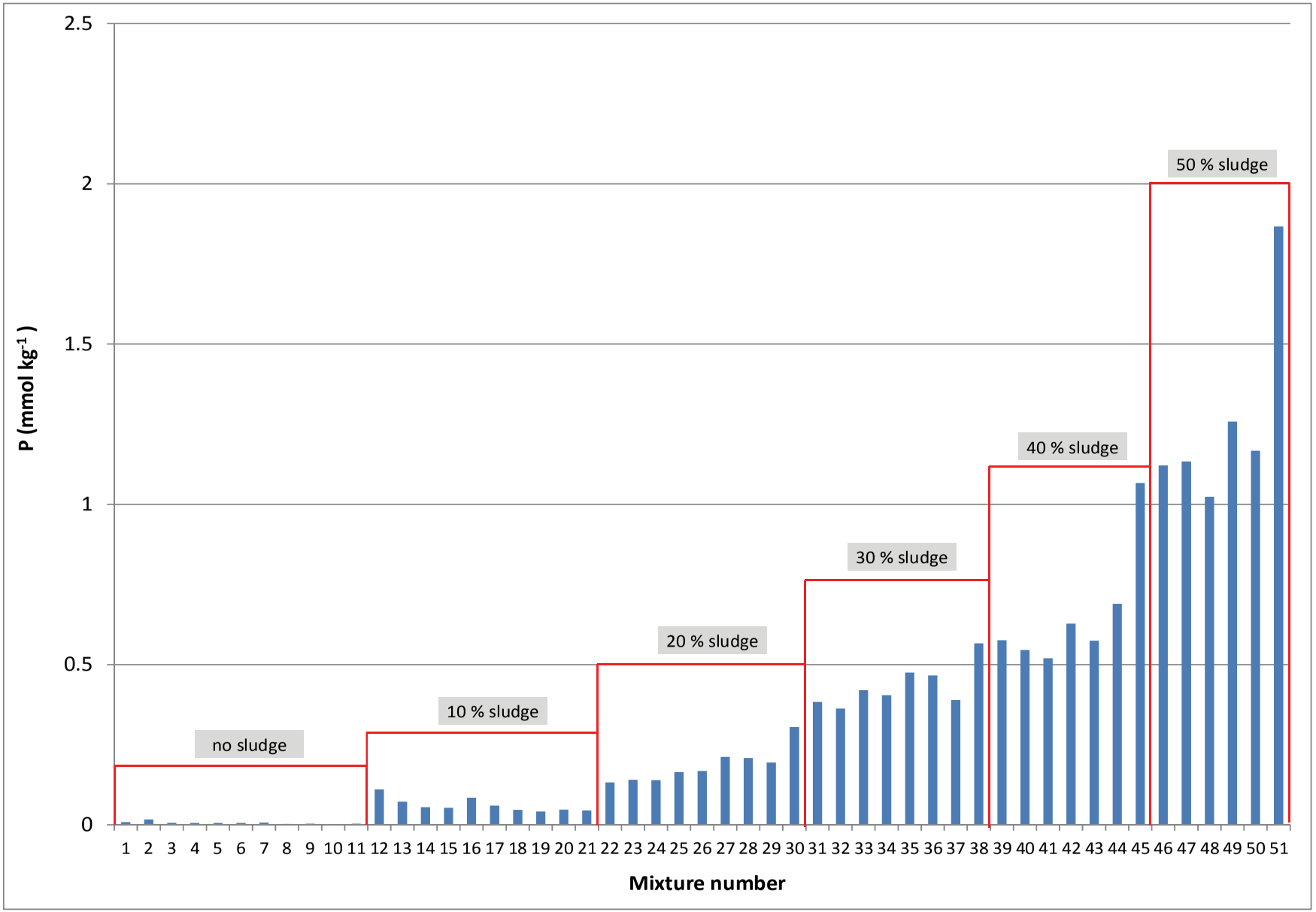


Figure 4.34 Cumulative P release after 9 leaching cycles

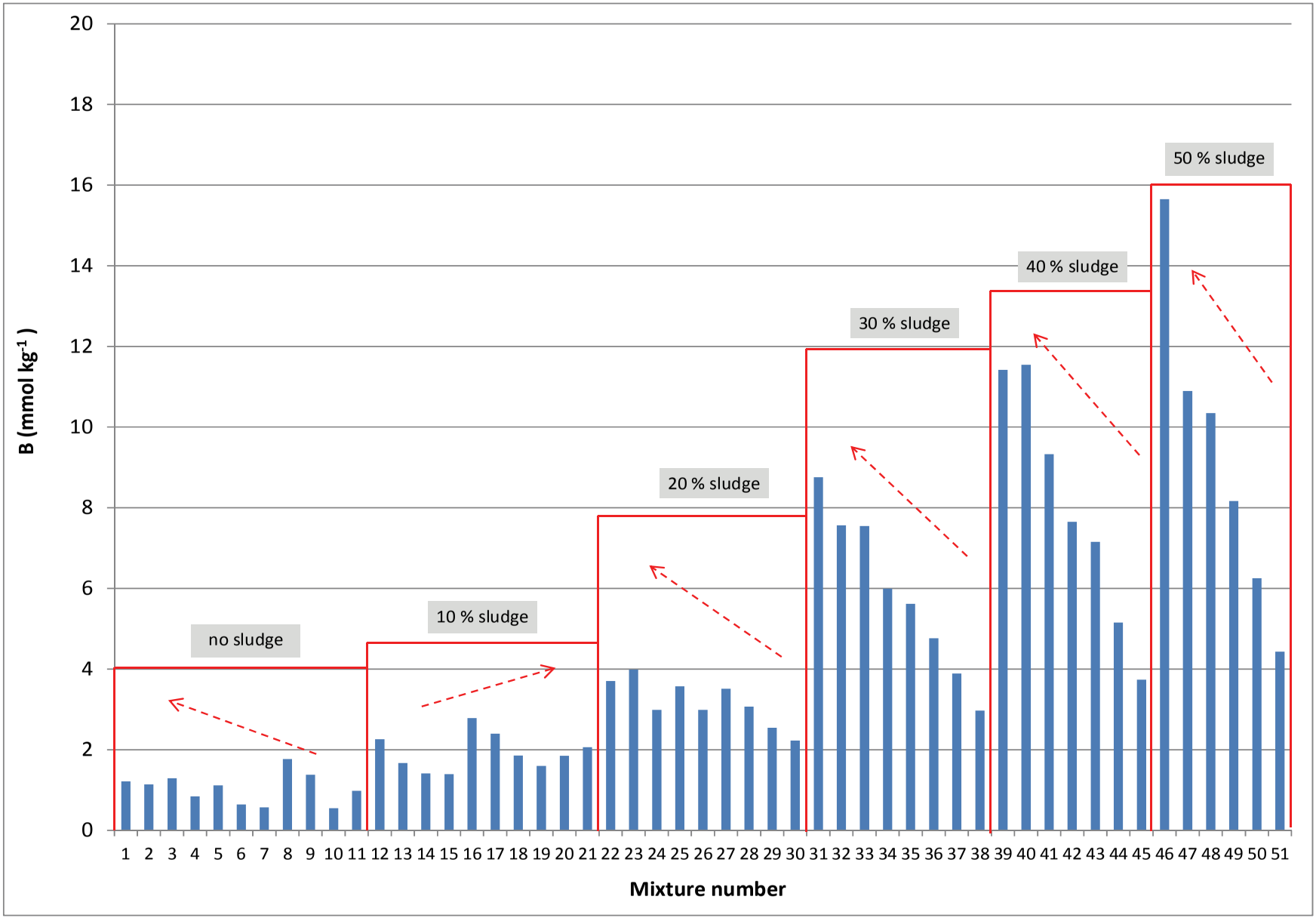


Figure 4.35 Cumulative B release after 9 leaching cycles. The arrows indicate the direction of the increasing fine ash content for each sludge treatment group

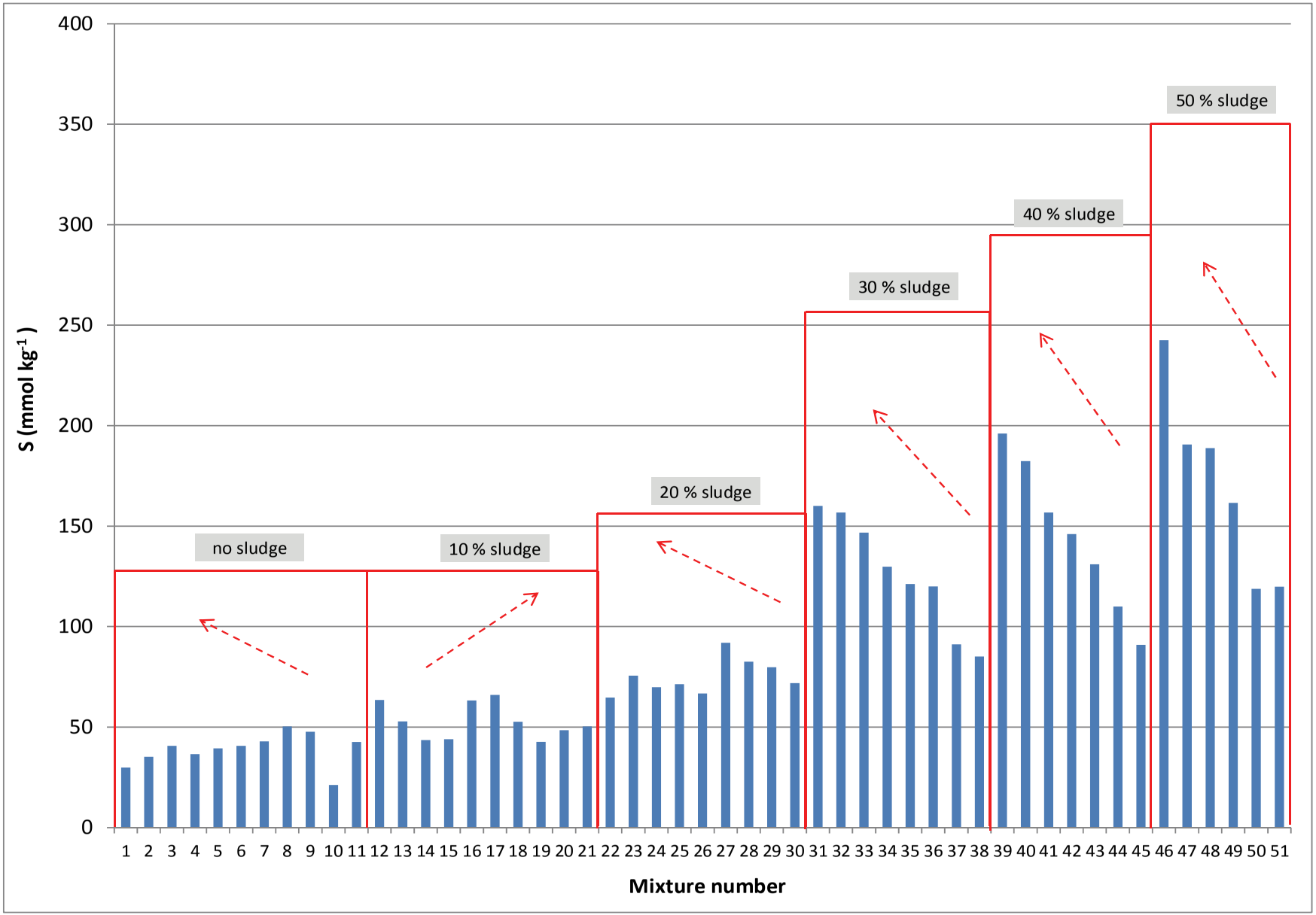


Figure 4.36 Cumulative S release after 9 leaching cycles. The arrows indicate the direction of the increasing fine ash content for each sludge treatment group

CHAPTER 5: PARTICLE SIZE DISTRIBUTION AND WATER RETENTION

5.1. Introduction

Physical soil parameters such as total pore space, pore size distribution, bulk density, air filled porosity and water holding capacity are determined by particle size distribution (Benito *et al.,* 2005). It is reasonable to expect that the same principles will apply to all porous media destined for plant growth.

Dominance of macroporosity increases aeration and decreases water retention (Jayasinghe *et al.,* 2009) and the dominance of fine particles decreases the average pore size and a results in an increase in microporosity and water holding capacity (Lal & Shukla, 2004, Jayasinghe *et al.,* 2009).

Particle size distribution will also control surface area. Larger particles (>2 mm) are not likely to release nutrients for plant uptake, whereas particles < 0.05 mm and > 0.002 mm in diameter allow weathering rapid enough to release significant amounts of plant nutrients (Brady and Weil, 2008). A measurement of particle size distribution can help in better understanding the interaction between chemical, physical and biological parameters of the mixtures.

5.2. Objective

To assess the variation in particle size distribution of fine and gasification ash and gain an understanding of the influence of gasification ash, sludge and fine ash on water holding characteristics.

5.3. Material and Methods

5.3.1. Particle size analysis

Samples of fine and gasification ash were collected from SASOL, Secunda. Samples were taken from freshly deposited heaps of fine and gasification ash, with about 200 kg of each collected. The gasification ash were spread out on a polyethylene sheet and thoroughly mixed with a spade before sampling in order to ensure representative sampling for particle size analysis. A total of thirty 200 g gasification and fine ash samples were taken for particle size analysis. The sieve method described by The Soil Science Society of South Africa (1990) was used. Nine sieves were arranged in a descending column as follows; 8, 4, 2, 1, 0.5, 0.25, 0.1, 0.05 mm. All particles smaller < 0.05 mm was also

collected. The 200 g samples were transferred to the top 8 mm sieve then washed with distilled water through the sieves while shaking and tapping lightly the column of sieves. Samples remaining on each sieve were then transferred into pre-weighed beakers and oven dried at 105^{o}C for 24 hours.

5.3.2. Water retention characteristics of fine ash – coarse ash mixtures

A preliminary study was also done to isolate the influence of fine ash amendment on water holding capacity of gasification ash. Columns (volume = 398.3 cm^3, height = 4.6 cm, radius = 5.25 cm) were filled with an equal amount of coarse ash and varying amounts of fine ash. Three different fine ash – gasification ash mixtures were established in duplicate. The fine ash content of the mixtures is given in Table 5.1. Water holding capacity of a medium is a function of its micro porosity. In this set of experiments, the influence of increasing fine ash content on water retention characteristics was investigated. This was done by determining the water content of the mixtures at matric potentials of -10, -20, -50, -100, -200, -300, -500 and -1000 J kg^{-1}, using a pressure plate apparatus.

Table 5.1 Fine ash content and bulk densities of the different fine ash – coarse ash mixtures

	Fine ash content (%)		
	a	**b**	**c**
Dry mass basis*	4.8	9.1	16.7
Dry bulk density (kg m^{-3})	1227^{x}	1254	1385

*Coarse ash water content = 13% and fine ash water content = 41%.

x) Mean of two replicates.

5.4. Results and Discussions

5.4.1. Particle size distribution

Fine ash generally did not have a diverse particle size distribution (Fig 5.1).Particles ranging between100-250 µm were consistently the dominant fraction of fine ash (CV = 9.2%). Particles > 250 µm were less than 10% of the total dry mass and the contribution of these particles was more variable. Particles > 1 mm dominated the particle distribution of the gasification ash. On average particles > 1 mm constituted more than 75% of the total mass. The contribution of particles > 1 mm to the total mass was also consistent and the variation between the 30 replicates in the end exhibited a variation of only 6.6%. The contribution of particles < 1 mm was variable and repeated analyses of these fractions

yielded CV values greater than 34% for the size fraction smaller than 1 mm. Particles < 2 mm was on average 36.2% of the total mass of the gasification ash and the replicates exhibited a 12% variation.

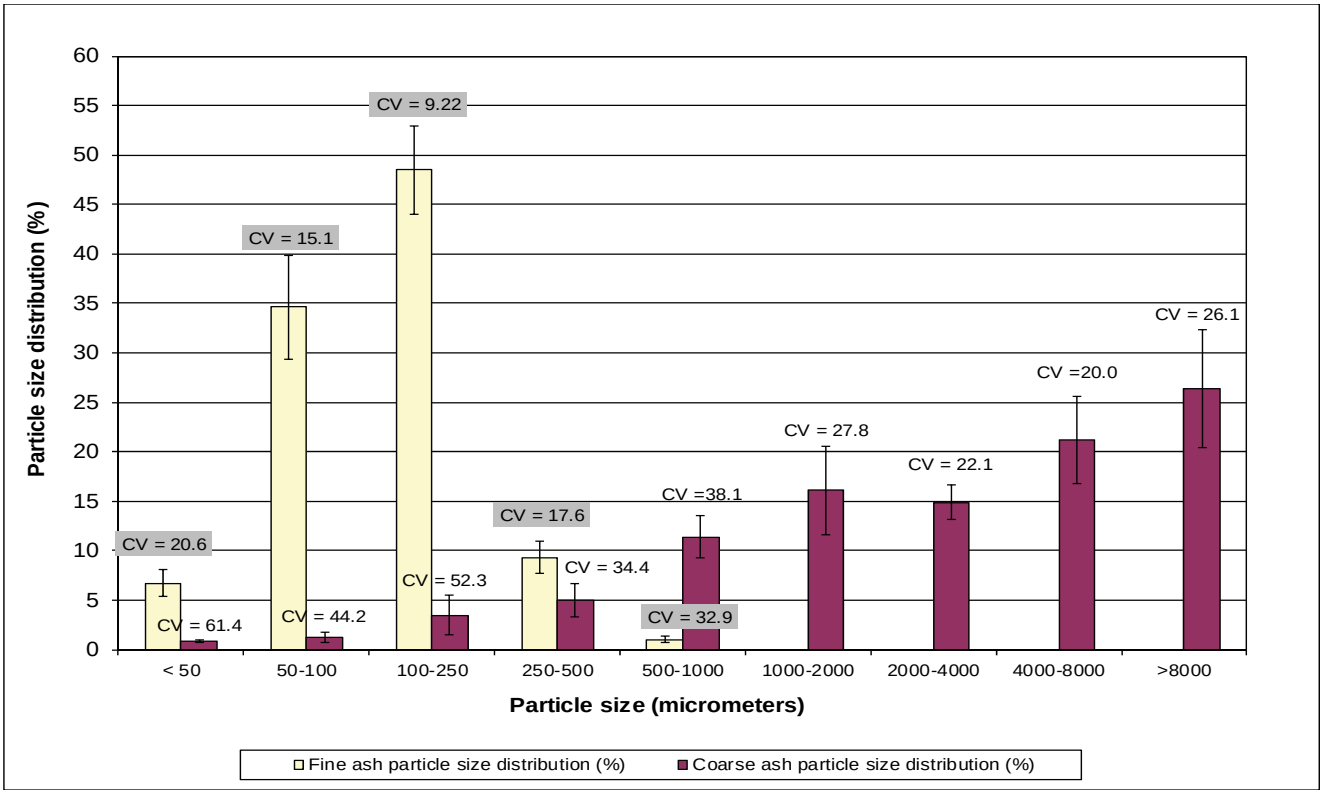


Figure 5.1 Dry-mass particle size distribution of fine and gasification ash**.** The error bars are standard deviations. The values above the bars are the coefficient of variance (CV in percentage). The shade coefficient of variance is for that of fine ash. (n = 30)

5.4.2. Water Retention Characteristics of Fine Ash – Coarse Ash Mixtures

Although the dominant particle size fraction of the fine ash corresponded to the fine and very fine sand fraction of a typical soil analysis it was hypothesised that fine ash amendment will definitely increase the water holding capacity of the much coarser gasification ash. The water retention characteristics of the coarse ash sample was done previously and was not collected at the same time as the samples used for the mixture experiment described in 5.3.2. It was also not evaluated at the same matric potentials (ψ_m). The ψ_m used for the control was: -33 J kg^{-1}, -80 J kg^{-1} -500 J $kg^{-1}$and -1500 J kg^{-1}. However, it was included as a reference to evaluate the influence of fine ash additions on the water retention characteristics of the coarse ash (Fig 5.2). The coarse ash curve was that of a typical macro porous medium with very low water holding capacity, characterized by the almost vertical slope of the water retention curve. There was little difference between the 4.8% curve and that of coarse ash at $\psi_m \leq$ -500 J

kg^{-1}. The difference in volumetric water content (θ_v) between the 4.8% fine ash mixture and coarse ash increased as the samples got wetter (increasing matric potential). At especially ψ_m > -300 J kg^{-1}, the differential between the 4.8% mixture and coarse ash curves increased as illustrated by the sudden change in the slope ($\partial\psi_m/\partial\theta_v$) of the graph from this point. This showed that the fine ash fractionally increased a specific pores size range of this mixture.

The water retained at highly negative matric potentials is assumed to be surficial water, bound (ordered/ "structured") water near mineral surfaces, a few molecular layers (3-4) thick and at a very low electrochemical potential (McBride & Baveye, 1995). In soils the upper limit at which surficial water predominate is usually at ψ_m< -1500 J kg^{-1} and the amount of water bound is directly proportional to the specific surface area of the material (Hillel, 1982). The point where only a monolayer of water molecules is present is at $\psi_m \approx$ -100 000 J kg^{-1} (Bird *et al.,* 2005). It is possible that in the gasification ash this upper limit was somewhat higher (-500 J kg^{-1}) because of the lower surface area and also the lack of highly adsorptive clay mineral surfaces and the dominance of more inert ash surfaces. Fine ash made no difference in water retention at $\psi_m \leq$ -500 J kg^{-1}, compared to gasification ash, and this could be attributed to the fact that the 4.8% fine ash mixture did not significantly increase the specific surface area of the mixture.

At all matric potentials, the 9.1% and 16.7% fine ash mixtures were able to retain more water than the coarse ash alone. These treatments further increased, relative to the 4.8% mixture, the previously mentioned pores size range that retain water at ψ_m > -300 J kg^{-1}. The 9.1% and 16.7% fine ash mixtures also increased the specific surface area of the medium represented by water retained at $\psi_m \leq$ -500 J kg^{-1}.

From a growth medium point of view, water retention at ψ_m> -100 J kg^{-1} is probably the most important especially the approximate field capacity interval estimate for soils: -10 to -33 J kg^{-1} (Fig. 5.3). However, it is expected that field capacity in coarse ash might be higher than -10 J kg^{-1}, and possibly closer to that of coarse organic growth mediums (-0.1 J kg^{-1}). The dotted intercept lines in Fig. 5.3 show that the 4.8% fine ash mixture increase the volumetric water content (θ_v), at -33 J kg^{-1}, with only 8% (from 10% to 18%) and the 16.7% fine ash mixture with 25% (10% to 35%). However, the latter translates to an increased waterholding capacity, at -33 J kg^{-1}, of 0.25 m^3 (250 litre) water per cubic metre of medium and 2500 m^3 for a hectare and medium depth of 1 m.

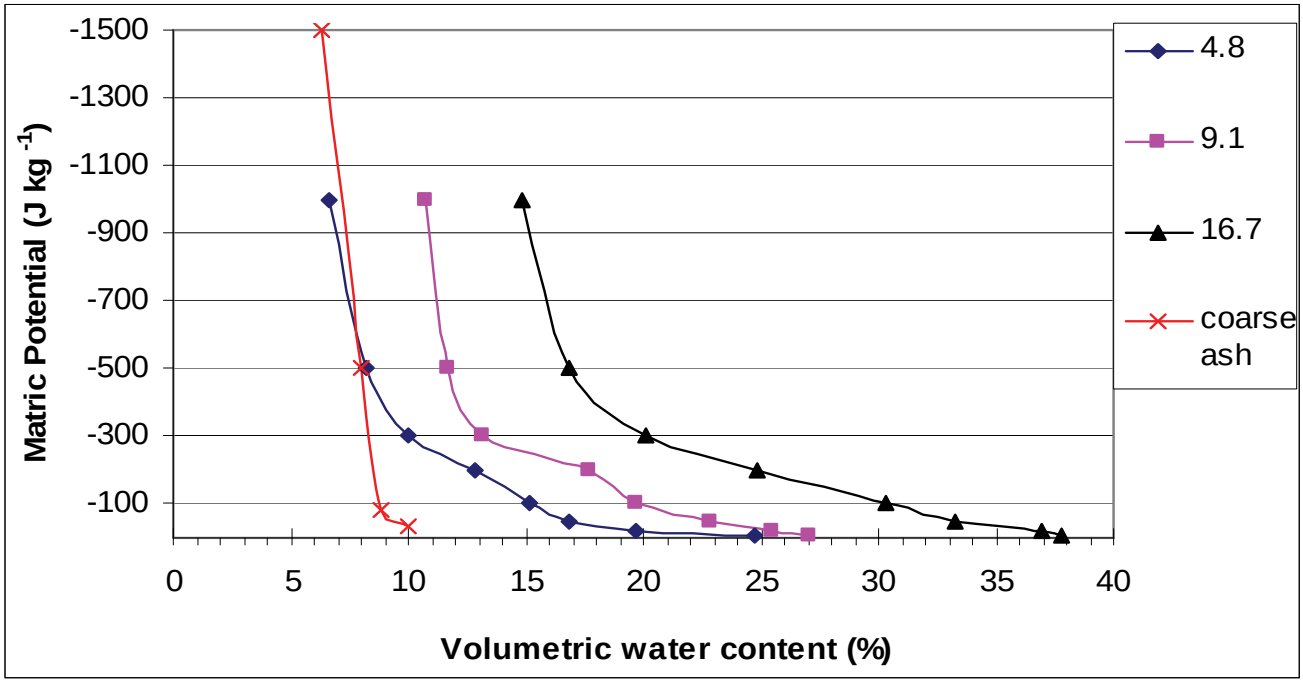


Figure 5.2 Water retention curves of coarse ash and fine ash – coarse ash mixtures containing: 4.8%, 9.1% and 16.7% fine ash (on a dry mass basis)

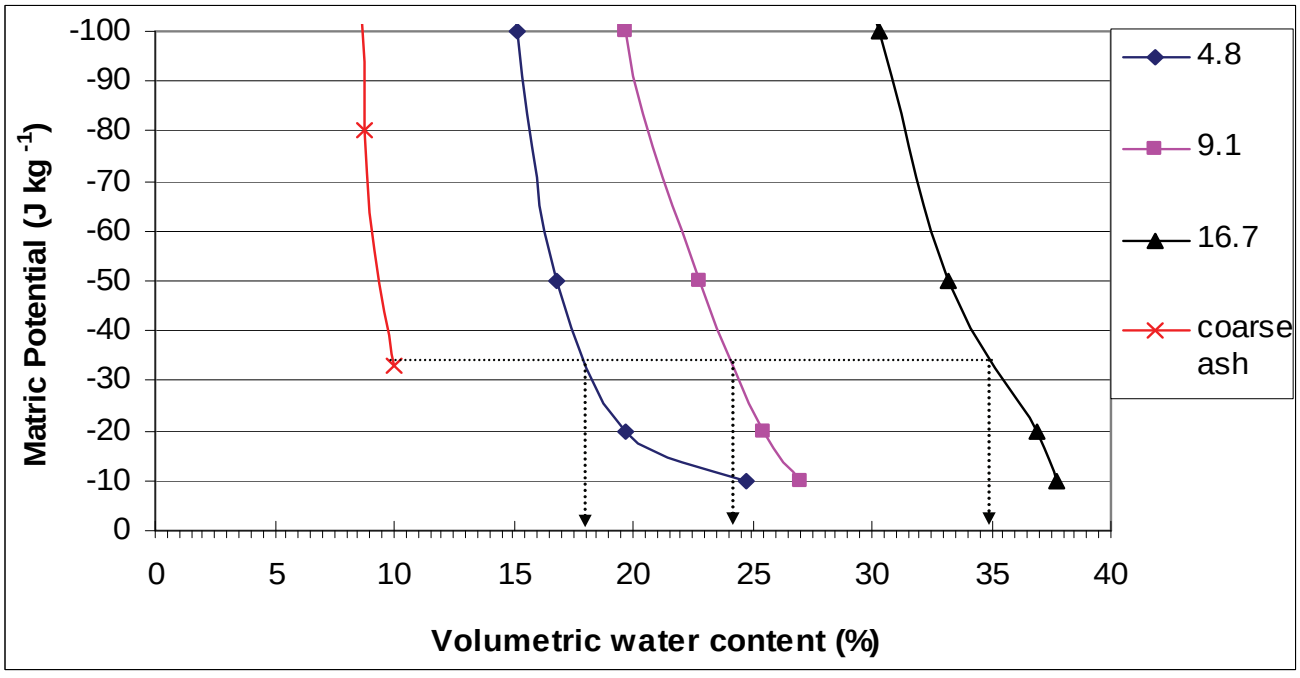


Figure 5.3 Water retention curves between -10 and -100 J kg^{-1} for gasification ash only and gasification ash amended with fine ash

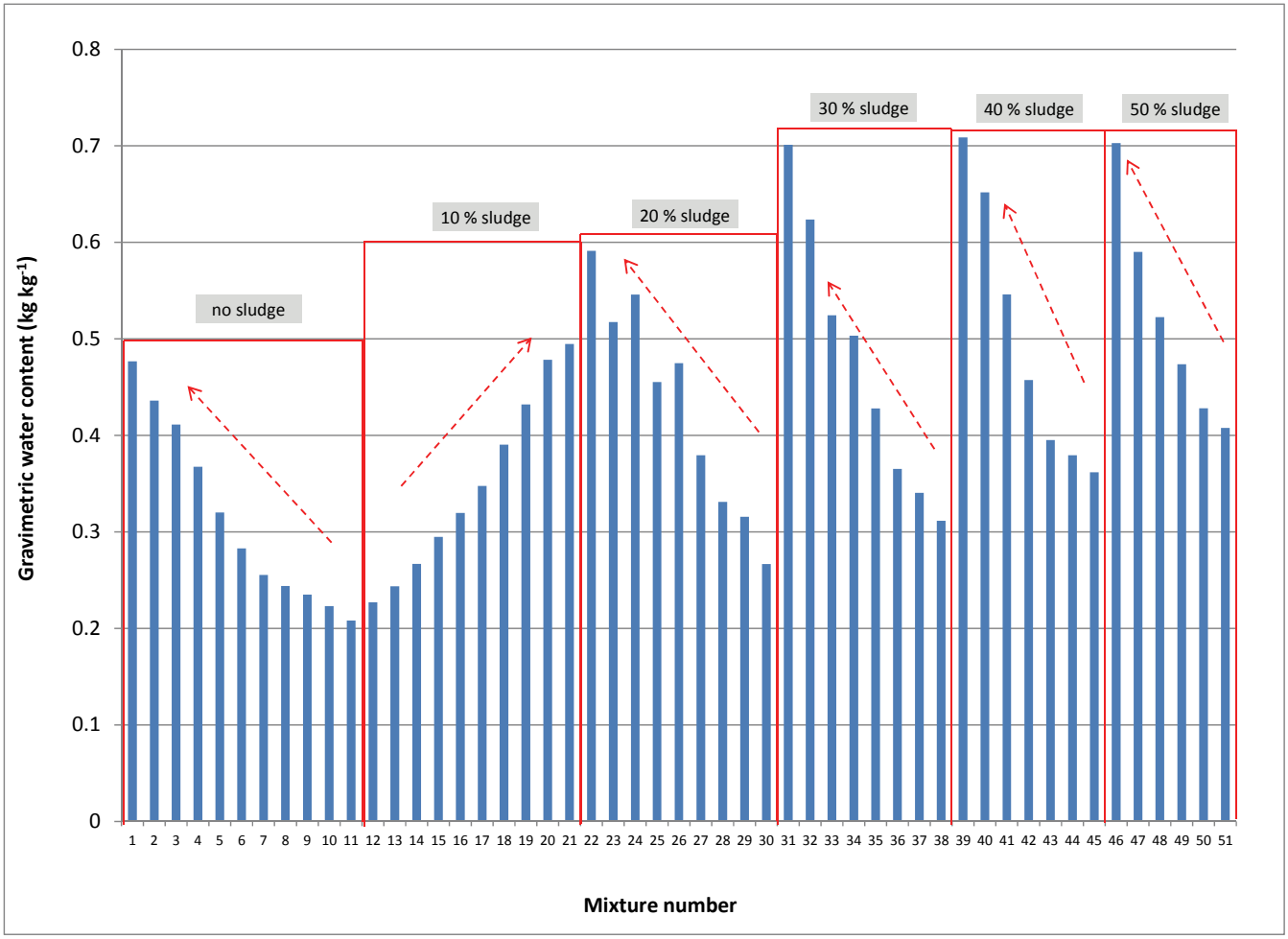


Figure 5.4 Gravimetric water content of the various mixtures after the ninth leaching cycle. The arrows indicate the increasing gradient in fine ash content

As discussed in Chapter 3, water added, leached amount and mass of columns were determined after vacuum was applied to the columns. With the dry mass of mixtures know it was possible to calculate the amount of water retained by the mixtures. The gravimetric water content was calculated as the ratio between the mass of water retained when the application of a static tension of -10 kPa was unable to remove any more water from the mixtures to the dry mass of the mixtures (Fig 5.4). The increasing fine ash content increased the water holding capacity of the mixtures. The effect of fine ash seemed to be more dominant than that of the sludge. Sludge amendment greater than 30%, even > 20%) did not drastically improve the water holding capacity of the mixtures. A similar trend observed for the chemical parameters, where various nutrients did not show any further substantial solubility when the sludge content was increased beyond 30%.

CHAPTER 6: MODELLING OF NUTRIENT AND SALT BALANCES OF A SLUDGE / COARSE ASH CO-DISPOSAL FACILITY

6.1. Introduction

6.1.1. Background

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 increased in many fields of science, more so in environmental studies. Even more important is the fact that some chemical changes, although measurable, can be slow, and it is not always feasible to wait for the long time these changes might continue for before making decisions and recommendations. Annandale *et al*. (1999) pointed out that computer models are useful tools for predicting long term environmental consequences of management practices.

In the present effort of revegetating coarse ash dumps using sludge, estimating the dynamics of nutrients and salts is of utmost importance, not only as an assessment of the medium's capacity to sustain plant life, but also as an indication of the risk to groundwater. Assessing the fate of salts and nutrients in profiles can be done in field or laboratory studies or by the use of simulation models.

Many modelling tools exist, some dealing with physical transport down a profile, others designed to model chemical changes of elements during various processes. In a problem of this nature, however, the right modelling tool should be one that combines transport with geochemical reactions. Furthermore, the modeling approach should be a multi-component one which unlike single-component models, takes into account reactions among solutes. Multiple solutes can mutually compete for sorption sites, can create various aqueous complexes, and can precipitate or dissolve depending on actual conditions in the profile of the medium.

This report is an early attempt to model the nutrient and salt balances of a sludge/coarse ash co-disposal facility using the HP1 model (Jacques *et al*., 2006), a modeling tool that was generated by coupling the one-dimensional variably saturated water flow and solute transport model HYDRUS 1D with the geochemical model PHREEQC.

6.1.2. Aim

This study aims to be a first step in predicting concentrations of major nutrients and salts within and at the bottom of a coarse ash/sludge co-disposal facility. The work seeks to simply provide predicted values against which measurements from experiments can be compared.

6.2. Materials and Methods

6.2.1. Description of model

The HP1 code incorporates modules simulating (1) transient water flow in variably-saturated media, (2) transport of multiple components, and (3) mixed equilibrium/kinetic geochemical reactions.
In HP1, the governing equations for water, heat and solute transport are solved sequentially. The multi-compartment reactive transport equations are solved using a non-iterative sequential approach meaning that the physical part is solved first without any chemical interactions, while the chemical reactions that are uncoupled in space and coupled over the components are solved subsequently (Jacques *et al*., 2008).

The model solves the Richard's equation for water flow:

$$\frac{\partial \theta(h)}{\partial t} = \frac{\partial}{\partial x}\left[K(h)\left(\frac{\partial h}{\partial x} + \cos\alpha\right)\right] - S(h)$$

where h is the soil water pressure head [L], θ is the volumetric water content [L^3L^{-3}], t is time [T], x is the spatial coordinate [L] (positive upward), S is the sink term [$L^3L^{-3}T^{-1}$], α is the angle between the flow direction and the vertical axis, and K is the unsaturated hydraulic conductivity [LT^{-1}].

6.2.2. Profile description

A 500 cm coarse ash profile with the top 25 cm amended on a mass to mass basis with 30% wet sludge (5% dry sludge) was modelled under steady-state saturated flow conditions. Choice of 30% sludge was made from observations from an earlier investigation where sludge application above 30% was shown to carry a high risk with respect to potentially toxic elements. This dosage would be about 90 tons dry sludge per hectare of dry coarse ash assuming a bulk density of 1200 kg m^{-3}. The upper boundary condition was a constant pressure head while the lower boundary condition was free

drainage. The profile was discretized into 41 nodes. Observation nodes were inserted at 125, 250 and 500 cm depths (Fig 6.1).

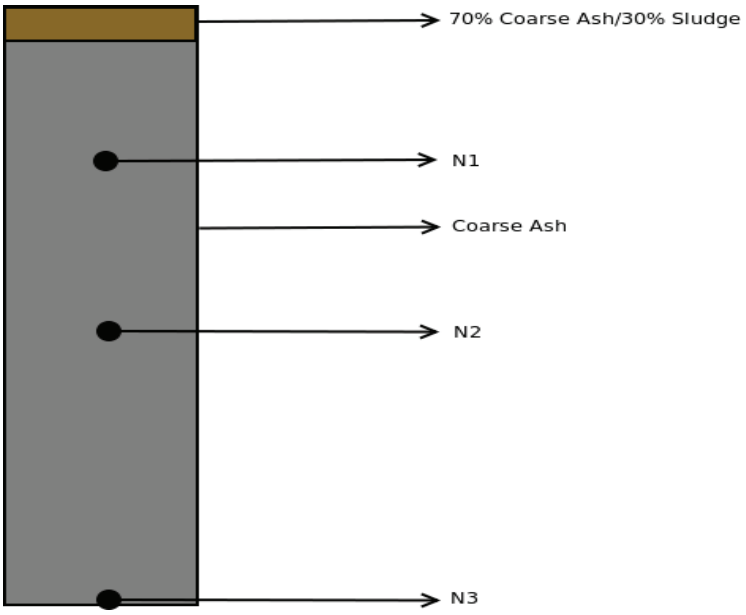


Figure 6.1 A 500 cm coarse ash profile showing observation nodes N1, N2 and N3 at depths of 125, 250 and 500 cm depths respectively.

6.2.3. Model input parameters

Input parameters were derived both from laboratory studies and from literature. A concentration of elements from unamended coarse ash was obtained from Matjie *et al*. (2005). Concentrations of coarse ash amended with 30% sludge (wet mass to wet mass) were considered in this study. Values are shown in Table 6.1.

Table 6.1 pH and solution composition of unamended coarse ash, and coarse ash amended with 30% sludge

	Coarse ash alone (Matjie *et al*., 2005)	70% Coarse ash plus 30% sludge
Ca (mg/L)	142	1192.14
Mg (mg/L)	<1	21.56
K (mg/L)	6	175.24
Na (mg/L)	10	222.29
Nitrates (mg/L)	<0.5	0.3
pH	11.6	9.7

The simulation was run for 30 days. The van Genuchten hydraulic model with no hysteresis was adopted. Water flow parameters typical of sandy soil were used except that fluid flux density was adjusted to 5 cm/day. A dispersivity of 2 cm was assumed because of the typically wide range of pore-size distributions characteristic of coarse ash dumps. Dispersivity is a measure of pore size distribution, and a large dispersivity indicates a wide range in pore-size distribution. For laboratory experiments it is typically 0.5-2 cm (Radcliffe and Simunek, 2010).

6.3. Results and Discussion

Results of the 30-day simulation are shown in figures 6.2 and 6.3. Concentrations of the nutrients began to increase rapidly at N1 (125 cm) after about 5 days and at N2 (250 cm depth) after about 15 days of simulation (Fig 6.2). Nutrient concentrations remained unchanged at 500 cm (N3), implying that at day 30 movement of solutes had not reached the bottom of the profile. Concentrations of the elements Ca, Mg, Na and K after rapid increases at N1 and N2 remained relatively stable until the end of the simulation. On the other hand, on about day 20, most of the nitrates had been leached out of N1, and had started accumulating at N2.

By day 30, most of the nitrates had leached out from the top 200 cm depth of the ash profile and had accumulated at 300 cm. No nitrates were recorded at N3 (500 cm depth), therefore nitrates did not leach out from the profile. A maximum nitrate concentration of about 0.00017 mmol/cm^3 was observed at N1 (125 cm depth) at around day 15.

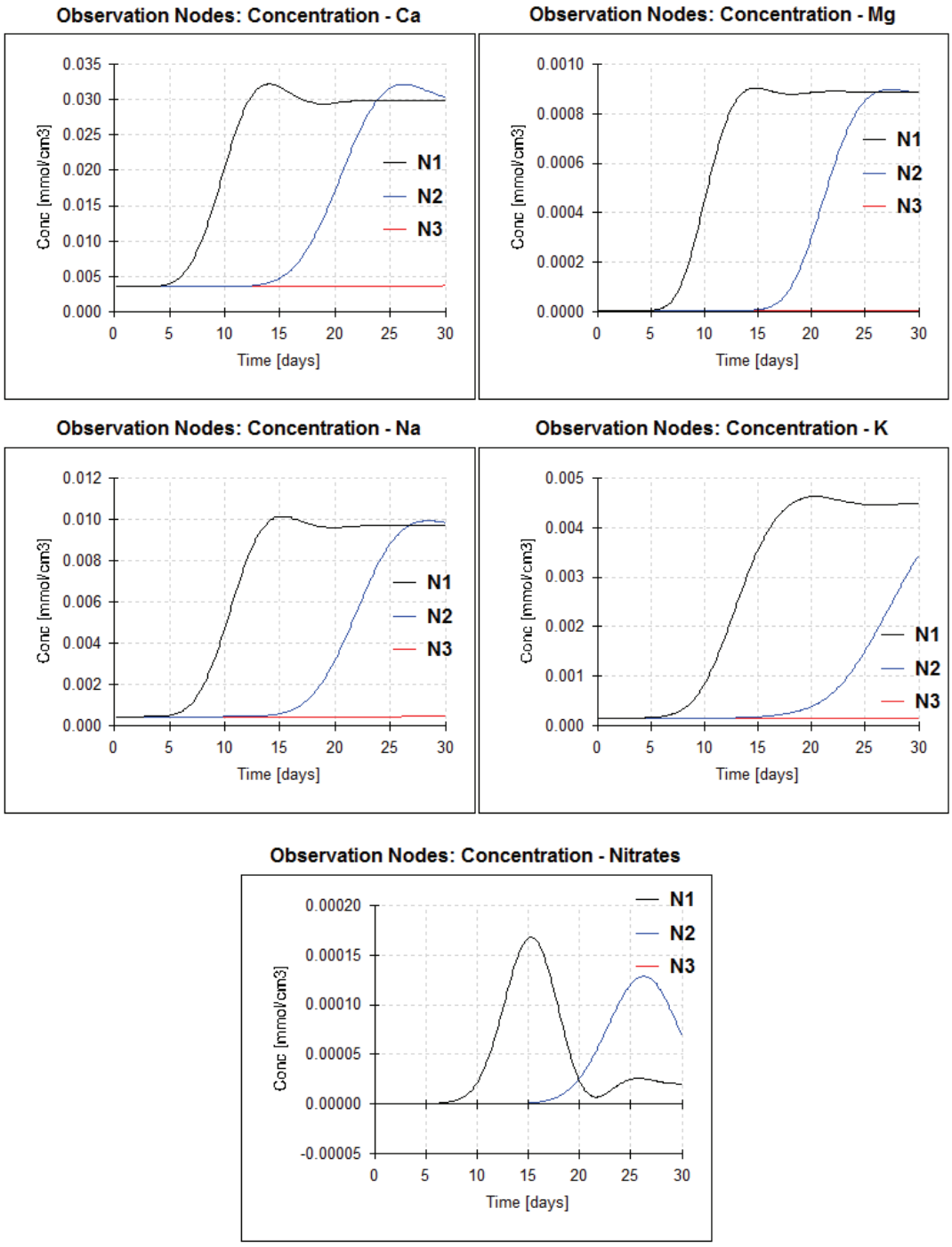


Figure 6.2 Concentration of nutrients with time. N1 = 125 cm depth; N2 = 250 cm depth; N3 = 500 cm depth

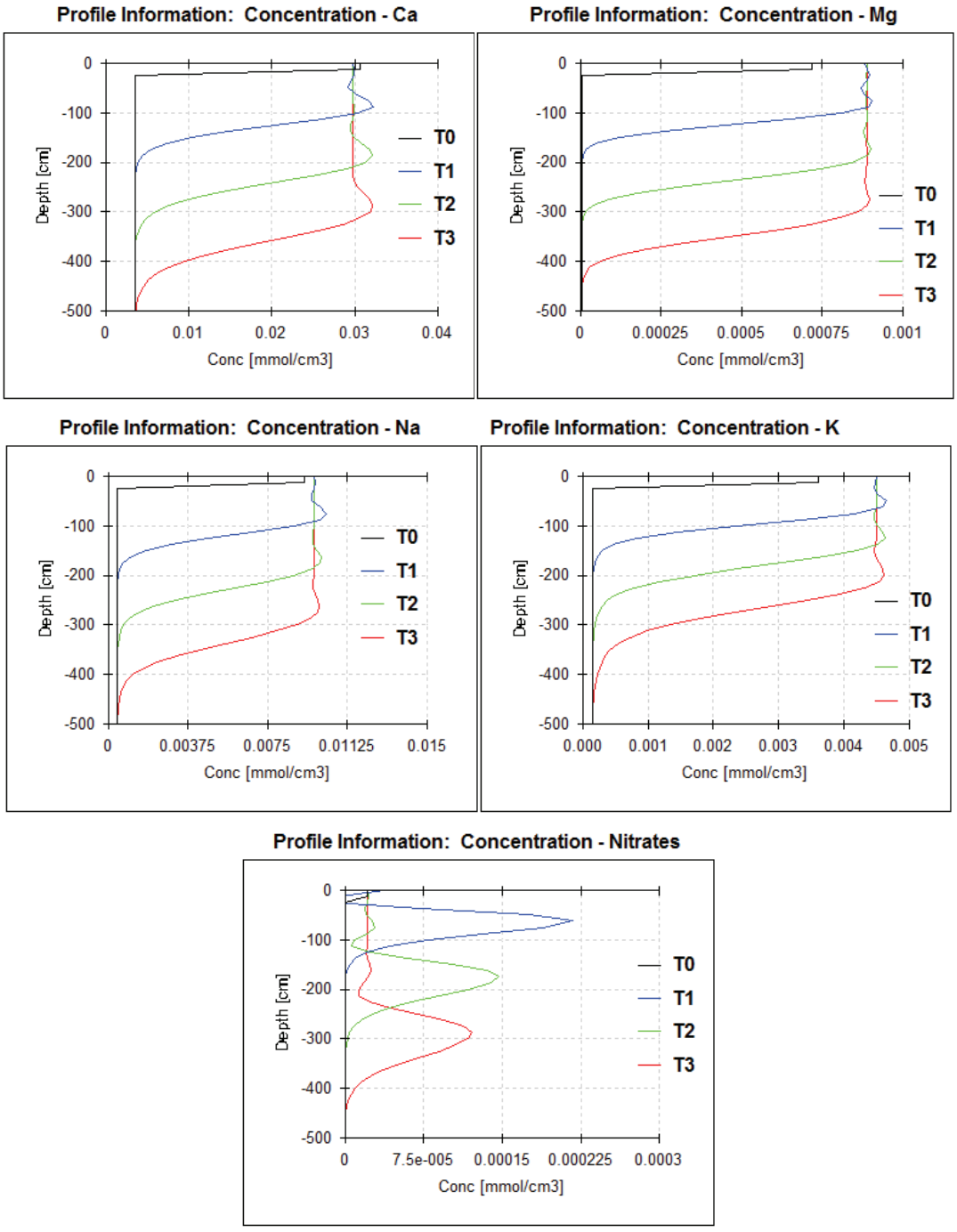


Figure 6.3 Concentration of nutrients with depth. T0 = Day 0; T1 = Day 10; T2 = Day 20; T3 = Day 30

CHAPTER 7: CONCLUSIONS AND RECOMMENDATIONS

Based on the pH and EC evolution over time enough evidence was gathered to support the conclusion that sufficient leaching is a prerequisite before attempting to establish vegetation on these media.

The sludge showed it has the ability to moderate the extreme environment created by fine ash and gasification ash. The effect of sludge can be summarised as follows:

- The pH of the media without sludge was > 11 and the addition of sludge lowered it to a pH of between 8 and 9 after nine leaching cycles. The coloured solutions of the sludge treatments was evidence of the oxidative breakdown of sludge releasing organic acids and ligands. Oxidation is an acidification process that definitely released protons into the system and contributed to the neutralisation of some of the soluble bases in solution. Furthermore the breakdown will generate CO_2 and carbonation will also play a role in decreasing the pH. The pH decrease was to a lesser extent attributed to a dilution effect;
- The pH and $CaCO_3$ equilibrium data suggest that these mixtures are moving towards systems in equilibrium with $CaCO_3$. The significance of this is that equilibrium pH and alkalinity of these systems can be predicted and the nutritional management thereof in the future might be similar to that of calcareous soils;
- Sodicity was markedly decreased with the addition of sludge and the release of the essential elements Mg and Ca was drastically increased with increasing sludge content. In mixtures without sludge, Na was by far the most dominant cation in solution. A growth medium where Na is the dominant cation in solution is not desirable. Firstly, sodium is phytotoxic and will suppress the uptake of other essential cations, like Mg and Ca, inducing nutrient deficiencies. The addition of sludge rectified this situation and for the highest sludge treatments Mg and Ca, were the dominant cations in solution. In plant nutrition, it is desirable if Ca is the dominant soluble cation. This is often the condition that is aimed for when addressing soil fertility problems with respect to the four major cations: Ca, Mg, K and Na;
- The sodium and potassium content of the ashes and the sludge were similar on a molar basis Potassium, however, illustrated a low solubility compare to Na and K release was low relative to the other major cations, and decreased substantially with time. Sludge did not liberate appreciable amounts of K from the ash. K will become a limiting macro nutrient in the long run if not supplemented;

- Sodium is quite soluble and will be removed with time, however, a management strategy to keep Na the lowest of the four major cations would be to keep the fine ash content low. The lower dependency of potassium solubility on fine ash content means that sodium levels can be decreased without unnecessarily lowering the K availability of the media;
- Phosphorus availability also increased substantially with increasing sludge amendment, while for mixtures without sludge, P exhibited a very low solubility;
- The data suggested that it will be a more prudent approach to delineating the best combination of gasification ash, fine ash and sludge based on environmental considerations. The Sasol sludge had higher Se levels compared to municipal sludge. This is an analytically challenging element to analyse in a complex matrix and the dynamics of Se release needs to be investigated in more detail because it is an element of considerable environmental concern. Sludge addition also resulted in higher As and boron (B) release from the mixtures. Based on elemental release, sludge content should be kept at or below 30%, on a wet mass basis, to keep the loading of the mixtures with these two elements low. Both As and Se are redox sensitive elements and the reduced forms are of more concern. Keeping the system continuously in an aerobic state will further reduce their environmental toxicity.

Using the 10% sludge application as a reference, the application of 3 and 6% sludge (also on a wet mass basis) currently investigated by Sasol as a disposal strategy will therefore not result in substantial elemental mobilisation from the mixtures. Although high application levels of sludge were not necessary to harness the benefits associated with its application, these application rates will be too low to have any substantially beneficial effect in terms of nutrient release.

High fine ash amendments (> 30%) resulted in the elevated solubility of aluminium and chromium and to a lesser extent vanadium. Fine ash amendment did increase the water holding capacity of the mixtures and therefore holds promise as a strategy to trap water necessary for the establishment of vegetation on coarse ash dumps. The data suggested that it is not necessary to apply high levels of fine ash to appreciably increase water holding capacity. The positive effect of fine ash amendment on water retention was evident even at low fine ash levels (<4.8%, on a dry mass basis).

Modelling of solute movement in coarse ash dumps using modelling tools such as the HP1 model may help predict future outcomes of amending coarse ash dumps with sludge. Although still in its nascent stages, modelling shows that downward movement of solutes could be rapid in these

dumps. The peculiar movement pattern of nitrates implies that all or almost all of the nitrates is leached out completely from different depths with time. Consequently, as a growth medium, addition of sludge to coarse ash heaps should be done when plants can take up maximum amounts of nitrates.

Future modelling endeavours will need to be validated with actual measurements, and must consider various scenarios, including nutrient plant uptake. Moreover, more accurate determination of hydraulic properties of coarse ash is critical to improve model prediction,

More in-depth research on various physico-(bio)chemical processes is also required:

- A better understanding of the dissolved organic carbon (DOC) dynamics is needed because it plays an important role in both the weathering of the ash and elemental transport. Organic material and DOC are important electron donors and will impact on the redox chemistry of the system and the mobility, as well as the bio- availability of redox sensitive elements;
- Weathering pathways and charge development should also be further investigated. Weathering and the formation of secondary minerals are associated with the development of either variable (pH dependant) or permanent charge development. This in turn will play a vital role in the mobility and attenuation of cations and anion. The types of secondary minerals as well as their charge characteristics are vital information to accurately predict element movement.

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APPENDIX A: MATERIAL CHARACTERISATION

A 1. Ash Characterisation

The fine and coarse ash were characterised in terms of their:

- Total elemental content by means of X-Ray Fluorescence (XRF) for the major elements in the ash (Si, Al, Fe, Mn, Ti, Ca, Mg Na, K and P). Total trace element content was determined by means of microwave acid digestion and quantitative elemental analysis with Inductively Coupled Plasma Mass Spectrometry (ICP-MS).
- Elemental release by means of a Water Leach Procedure and a Toxic Characteristic Leaching Procedure (TCLP), using EPA test method 1311. Extracts were also analysed by means of ICP-MS for Al, Fe, Mn, Ca, Mg, Na and K and Suppressed Ion Chromatography (SIC) for the anions: NO_2, NO_3, SO_4, Cl and PO_4. The TCLP extracts were not analysed for the anions because of the high ionic strength of the extractant and potential saturation/poisoning of the SIC system columns by the high acetate background concentration. The Water Leach Procedure: 100 g sample was shaken on a reciprocal shaker for 18 hours in 2000 ml de-ionized water.

A 2. Sludge Characterisation

The sludge was characterised in terms of:

- Total nitrogen (N), and carbon (C) content were determined by means of total combustion,
- Total P, Ca, Mg Na, K content by means of microwave acid digestion and quantitatively elemental analysis of the solution with ICP-MS,

Table A 1. XRF analysis of major oxides of the coarse and fine ash.

Ash	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**MnO**	**P_2O_5**
					%				
Coarse ash	47.52	25.52	1.84	7.25	2.12	0.67	0.74	0.05	0.79
Fine ash	51.24	22.09	3.36	8.04	2.23	0.33	0.60	0.04	0.71
	Si	**Al**	**Fe**	**Ca**	**Mg**	**Na**	**K**	**Mn**	**P**
					mol kg^{-1}				
Coarse ash	7.91	2.50	0.12	1.29	0.53	0.11	0.08	0.01	0.06
Fine ash	8.53	2.17	0.21	1.43	0.55	0.05	0.06	0.01	0.05

Table A 2. Major cations extracted by TCLP and the Water Leaching Procedure from the gasification ash and fine ash.

Extract	Ash	Al	Fe	Mn	Na	K	Ca	Mg
		mmol l^{-1}						
TCLP	Coarse ash	325	0.98	70.6	4.78	0.40	36.9	9.42
	Fine ash	967	1554	39.5	0.73	0.14	18.14	6.38
Water Leach	Coarse ash	105	0.91	0.16	3.83	0.25	1.23	0.02
	Fine ash	189	0.45	b.d.	0.60	0.09	1.58	0.00
		mmol kg^{-1} ash						
TCLP	Coarse ash	6.50	0.02	1.41	95.7	7.98	738.5	188.4
	Fine ash	19.4	31.1	0.79	14.6	2.76	362.8	127.5
Water Leach	Coarse ash	2.11	0.02	0.00	76.6	5.06	24.5	0.33
	Fine ash	3.78	0.01	b.d.	11.9	1.84	31.7	0.09

b.d. = Below detection

Table A 3. Major anions extracted by TCLP and the Water Leaching Procedure from the coarse ash and fine ash.

Extract	Ash	F	NO_3	Cl	SO_4	PO_4	NO_2	B
		μmol l^{-1}						
TCLP	Coarse ash	*	*	*	*	*	*	865
	Fine ash	*	*	*	*	*	*	119
Water Leach	Coarse ash	85.3	33.1	1808	2029	b.d.[x]	194	161
	Fine ash	36.9	4.68	244	743	b.d.	b.d.	19.4
		mmol kg^{-1} ash						
TCLP	Coarse ash	*	*	*	*	*	*	17.30
	Fine ash	*	*	*	*	*	*	2.39
Water Leach	Coarse ash	1.71	0.66	36.2	40.6	b.d.	3.89	3.22
	Fine ash	0.74	0.09	4.87	14.87	b.d.	b.d.	0.39

b.d. = Below detection

Table A 4. Elemental analysis of the SASOL sludge.

Sasol sludge		Units
pH	5.8	
Total N	7.87	%
Total C	51.5	
C/N Ratio	6.52	
Total P	0.78	%
Ca	0.61	
Mg	0.26	
K	0.29	
Na	0.11	
Fe	0.59	
Li	1.87	mg kg $^{-1}$
Be	0.32	
B	33.6	
Ti	48.5	
V	93.7	
Cr	33	
Mn	114	
Co	2.20	
Ni	17.5	
Cu	19.1	
Zn	195	
As	31.5	
Br	11	
Se	37.8	
Rb	1.07	
Sr	73.4	
Mo	5.36	
Cd	0.22	
Sn	11.0	
Sb	4.58	
Te	9.21	
I	4.21	
Cs	0.10	
Ba	74.21	
La	1.70	
W	1.02	
Pt	0.01	
Hg	44.4	
Tl	0.06	
Pb	5.09	
Bi	2.10	
U	0.42	

APPENDIX B: INFORMATION FOR MASS BALANCE MODELLING

Mass Balance Information for HYDRUS

******* Program HYDRUS
******* Salt and nutrient balance of a sludge/coarse ash co-disposal facility
Date: 27.11. Time: 12:32:22
Units: L = cm , T = days, M = mmol
******* Legend:
1 = Total H
2 = Total O
3 = Nitrates
4 = Ca
5 = Mg
6 = Na
7 = K

Time	[T]	.0000	
Sub-region num.		1	
Area	[L]	.500E+03	.500E+03
W-volume	[L]	.215E+03	.215E+03
In-flow	[L/T]	.000E+00	.000E+00
h Mean	[L]	.000E+00	.000E+00
ConcVol	[M/L2] 1	.949E+00	.949E+00
cMean	[M/L3] 1	.441E-02	.441E-02
ConcVol	[M/L2] 2	.950E+00	.950E+00
cMean	[M/L3] 2	.442E-02	.442E-02
ConcVol	[M/L2] 3	.321E-03	.321E-03
cMean	[M/L3] 3	.149E-05	.149E-05
ConcVol	[M/L2] 4	.980E+00	.980E+00
cMean	[M/L3] 4	.456E-02	.456E-02
ConcVol	[M/L2] 5	.665E-02	.665E-02
cMean	[M/L3] 5	.309E-04	.309E-04
ConcVol	[M/L2] 6	.165E+00	.165E+00
cMean	[M/L3] 6	.765E-03	.765E-03
ConcVol	[M/L2] 7	.609E-01	.609E-01
cMean	[M/L3] 7	.283E-03	.283E-03
Top Flux	[L/T]	-.500E+01	
Bot Flux	[L/T]	-.500E+01	

Time	[T]	10.0000
Sub-region num.		1

Area	[L]	.500E+03	.500E+03
ConcVol	[M/L2] 1	.724E+00	.724E+00
cMean	[M/L3] 1	.337E-02	.337E-02
ConcVol	[M/L2] 2	.728E+00	.728E+00
cMean	[M/L3] 2	.339E-02	.339E-02
ConcVol	[M/L2] 3	.516E-02	.516E-02
cMean	[M/L3] 3	.240E-04	.240E-04
ConcVol	[M/L2] 4	.233E+01	.233E+01
cMean	[M/L3] 4	.109E-01	.109E-01
ConcVol	[M/L2] 5	.490E-01	.490E-01
cMean	[M/L3] 5	.228E-03	.228E-03
ConcVol	[M/L2] 6	.600E+00	.600E+00
cMean	[M/L3] 6	.279E-02	.279E-02
ConcVol	[M/L2] 7	.227E+00	.227E+00
cMean	[M/L3] 7	.106E-02	.106E-02
CncBalT	[M] 1	.757E-14	
CncBalR	[%] 1	.000	
CncBalT	[M] 2	.344E-13	
CncBalR	[%] 2	.000	
CncBalT	[M] 3	.873E+00	
CncBalR	[%] 3	388.366	
CncBalT	[M] 4	.117E-13	
CncBalR	[%] 4	.000	
CncBalT	[M] 5	.517E-15	
CncBalR	[%] 5	.000	
CncBalT	[M] 6	.707E-14	
CncBalR	[%] 6	.000	
CncBalT	[M] 7	.368E-14	
CncBalR	[%] 7	.000	

Time [T] 20.0000

Sub-region num. 1

Area	[L]	.500E+03	.500E+03
ConcVol	[M/L2] 1	.500E+00	.500E+00
cMean	[M/L3] 1	.232E-02	.232E-02
ConcVol	[M/L2] 2	.507E+00	.507E+00
cMean	[M/L3] 2	.236E-02	.236E-02
ConcVol	[M/L2] 3	.626E-02	.626E-02
cMean	[M/L3] 3	.291E-04	.291E-04
ConcVol	[M/L2] 4	.369E+01	.369E+01
cMean	[M/L3] 4	.171E-01	.171E-01
ConcVol	[M/L2] 5	.920E-01	.920E-01
cMean	[M/L3] 5	.428E-03	.428E-03
ConcVol	[M/L2] 6	.104E+01	.104E+01
cMean	[M/L3] 6	.482E-02	.482E-02
ConcVol	[M/L2] 7	.393E+00	.393E+00
cMean	[M/L3] 7	.183E-02	.183E-02

CncBalT	[M]	1	.658E-08
CncBalR	[%]	1	.000
CncBalT	[M]	2	-.250E-08
CncBalR	[%]	2	.000
CncBalT	[M]	3	.307E+01
CncBalR	[%]	3	683.750
CncBalT	[M]	4	.184E-07
CncBalR	[%]	4	.000
CncBalT	[M]	5	.400E-10
CncBalR	[%]	5	.000
CncBalT	[M]	6	.110E-08
CncBalR	[%]	6	.000
CncBalT	[M]	7	.366E-09
CncBalR	[%]	7	.000

Time [T] 30.0000

Sub-region num. 1

Area	[L]		.500E+03	.500E+03
ConcVol	[M/L2]	1	.275E+00	.275E+00
cMean	[M/L3]	1	.128E-02	.128E-02
ConcVol	[M/L2]	2	.285E+00	.285E+00
cMean	[M/L3]	2	.133E-02	.133E-02
ConcVol	[M/L2]	3	.731E-02	.731E-02
cMean	[M/L3]	3	.340E-04	.340E-04
ConcVol	[M/L2]	4	.504E+01	.504E+01
cMean	[M/L3]	4	.234E-01	.234E-01
ConcVol	[M/L2]	5	.135E+00	.135E+00
cMean	[M/L3]	5	.628E-03	.628E-03
ConcVol	[M/L2]	6	.147E+01	.147E+01
cMean	[M/L3]	6	.685E-02	.685E-02
ConcVol	[M/L2]	7	.559E+00	.559E+00
cMean	[M/L3]	7	.260E-02	.260E-02
CncBalT	[M]	1	-.526E-04	
CncBalR	[%]	1	.008	
CncBalT	[M]	2	-.572E-04	
CncBalR	[%]	2	.008	
CncBalT	[M]	3	.571E+01	
CncBalR	[%]	3	847.136	
CncBalT	[M]	4	.417E-03	
CncBalR	[%]	4	.008	
CncBalT	[M]	5	.838E-06	
CncBalR	[%]	5	.000	
CncBalT	[M]	6	.296E-04	
CncBalR	[%]	6	.002	
CncBalT	[M]	7	.824E-05	
CncBalR	[%]	7	.001	