# Feasibility study on the use of irrigation as part of a long-term acid mine water management strategy in the Vaal Basin

Report to the
**Water Research Commission**

by

**Michael van der Laan, Martin Venn Fey, Gerhard van der Burgh, Pieter Christiaan de Jager, John George Annandale, Heinrich Meiring du Plessis**

Department of Plant Production and Soil Science, University of Pretoria, Pretoria 0002, South Africa

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Private Bag X03
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An Excel file containing the original data and subsets of selected data numbering about 450 samples based on Fe or sulfate concentrations or pH, is available on the WRC website as Special Publication SP 80/14

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# ABSTRACT

Protecting the environment from contaminated mine water decanting in increasing volumes from the goldfields presents an enormous challenge, probably greater than that of coal mine water because the decant points are in urban areas. Some of the water is acidic but most of it is partly neutralised through water-rock interaction. The main limitation of the water is an undesirable concentration of sulfate salts and metals, chiefly iron, and to a lesser extent manganese, aluminium and various trace elements. This project addressed some of the possibilities of irrigating land and producing crops with the mine water, primarily after it has been neutralised with lime but also as a form of land treatment in which the raw mine water is applied to soils or mine tailings that have been preconditioned with slaked lime or limestone to achieve in situ neutralisation and sequestration of many of the contaminants. Supplementary treatments were also explored using aluminium sulfate and locally mined ferromanganese wad, currently used for uranium recovery in the gold mines.

The project found it highly probable that goldfield mine water can be used cost-effectively to irrigate vegetation on mine tailings or salt tolerant crops such as wheat or soybean on agricultural land. Following irrigation the salts in the water become concentrated and the dominant ions, calcium and sulfate, precipitate as gypsum. It is calculated that about 60% of applied salts will be retained within the soil when irrigating with neutralised mine water. Crop model simulations estimate that irrigating with neutralised mine water can result in wheat yields of around 9 tonnes/ha and soybean yields of 5 tonnes/ha when grown in rotation. Even under worst case scenarios in which farmers have to pay for the infrastructure to deliver the mine water to their farms, an income of >R240 000/year can still be realised for a 40 hectare farm.

Clay soils and mine tailings have further capacity to retain many of the other salts present in the water. Results from this study indicate that 75-90% of salts can be removed when raw mine water is applied to mine tailings or clay soils. The use of aluminium sulfate – which works synergistically with lime – as part of the pre-treatment process potentially has several benefits, including smaller, more economical treatment plants.

Reverse osmosis has been proposed for treating mine water in the Vaal Basin but is expensive, energy intensive and, like other processes, leaves a saline residue which requires disposal. By contrast, irrigating with chemically treated water will enable its immediate productive use. The socio-economic benefits could be far reaching. In addition, South Africa currently is not well positioned to provide electricity for reverse osmosis and will need to accept the high carbon footprint indefinitely. A Life Cycle Assessment comparing conventional reverse osmosis with the irrigation option together with reverse osmosis of the smaller volumes of irrigation return flows demonstrated significantly lower impacts for the latter option for global warming potential, non-renewable resource (fossil fuel) depletion and acidification potential.

Following these positive results further research has been recommended, including the establishment of a pilot plant irrigating with actual purpose-treated mine water, exploring optimal geo-hydrological settings for land/irrigation treatment schemes and a thorough cost comparison with the conventional reverse osmosis option. The favourable implementation of this technology can have far reaching consequences, not only in the Witwatersrand goldfields, but also the Mpumalanga coalfields and many other regions around the world with a legacy of intensive mining.

# EXECUTIVE SUMMARY

## Background

The imminent problem of poor quality mine water facing the Vaal Basin has potentially major economic, social and environmental repercussions. Essentially it is a salt problem, because while the water can effectively be neutralised to remove acidity, metals and radioactivity, this leaves a brackish water for the dilution of which there is insufficient clean water to achieve fitness-of-use objectives. A feasibility study, commissioned by the government to find short- and long-term solutions, has recently been completed, recommending neutralisation in a high density sludge plant followed by conventional reverse osmosis (RO). This will potentially solve the salinity problem, but is accompanied by a huge economic and energy cost, with recent estimates of R6.66 billion for infrastructure and R1 billion per annum operating costs. In addition extremely saline brine from the process would still require disposal.

Previous work done by the University of Pretoria in Mpumalanga has shown that common field crops can be economically grown using poor quality coal mine water when the water contains relatively high concentrations of calcium (Ca) and sulfate. The reason for this is that as the crops transpire and concentrate the soil solution, the Ca and SO4 ions precipitate out as gypsum and so are effectively removed from the water. This results in root zone salinity being maintained at levels suitable for crop production and far below what would be expected when irrigating with saline water containing higher levels of more soluble salts such as sodium (Na), magnesium (Mg) and chloride (Cl). Furthermore, gypsum precipitation was found not to result in any physical or chemical changes that would adversely affect soil productivity over the long-term.

An opportunity to effectively use this technology as part of a treatment strategy for the more pressing gold mine water problem was therefore identified. The main aim of this project was to rapidly identify and quantify ways in which irrigation could be used to avoid the high treatment costs associated with RO, utilising laboratory studies, crop modelling, life cycle and economic assessments and geographic information system (GIS) queries.

## Laboratory study

A short, laboratory-based project (K8/1058//3) was conducted to: (a) evaluate a local iron (Fe)-manganese (Mn) wad and aluminium (Al) sulfate as alternative treatments for metalliferous mine water, and (b) experimentally simulate land treatment of the mine water using Ergo mine tailings and two soils, amended with limestone or slaked lime.

Combinations of Fe-Mn wad from a mine near Ventersdorp, Al sulfate from a factory near Springs, and reagent grade calcium carbonate ($CaCO_3$) and calcium hydroxide [$Ca(OH)_2$] were used in a series of laboratory experiments to find conditions that would be suitable for the removal of metals, chiefly Ca, Fe and Mn, and sulfate from mine water that was collected from a decant point near Randfontein.

Direct application of the same mine water to mine tailings from the Ergo tailings storage facility (TSF) near Brakpan and two soils from adjacent agricultural lands, suitably amended with either limestone or lime to neutralise the acidifying effects of the mine water, was carried out in order to simulate land treatment of the mine water by irrigation at an average rate of 5 mm day$^{-1}$ for 10 years, incorporating the amendments and precipitated solids to a depth of between 0.2 and 1 m. On the mine tailings as much as 75% of the added salts could be sequestered by this simulated land treatment. A black clay soil was able to sequester about 90% of added salts even without the addition of an alkaline amendment.

Both Fe-Mn wad and Al sulfate can be used in an auxiliary role with lime and limestone for removal of metals from mine water. The wad's effectiveness for Mn removal by oxidation may be reduced when ferrous Fe is present, however, since this will be oxidised preferentially. Similarly the cation exchange capacity of Mn oxide in the wad may preferentially be occupied by Ca because of mass action which would further reduce the capacity of the wad to remove Mn and other metals from solution. Aluminium sulfate and hydrated lime work synergistically as conditioners for mine water to effect a rapid depletion of contaminants at a near neutral pH. The order in which these reagents are added to the mine water makes a great difference to the resultant composition. The quality of the water produced is probably quite sensitive to small changes in reaction conditions, and further investigation should make use of more accurately controlled pH, temperature and gas composition.

The results represent clear proof of concept that land treatment, either with mine tailings and/or a clay soil, suitably amended with fine limestone or possibly fly ash from power stations, is technically attractive and could offer solutions to two environmental challenges at once: erodible mine tailings and large volumes of contaminated mine water.

### Cropping system simulations

Long-term simulations of crop growth and salt dynamics using the SWB-Sci model show that a large fraction of the salt can potentially be removed from the neutralised mine water as a result of irrigating with it. While uncertainties exist regarding the quality of the mine water that will be pumped from the mine voids and its quality following neutralisation, simulations estimated that 34-69% of the salts could be precipitated as gypsum. Highest gypsum precipitation was estimated for the Western Basin mine water neutralised using limestone and lime or mine water neutralised using a limed Al sulfate treatment developed in this project. Root zone salinity levels were simulated to remain below the threshold which would have an impact on wheat and soybean growth, while yields of maize were simulated to be impacted consistent with its greater sensitivity to salt. Average total dissolved solids (TDS) concentrations in the leachate were estimated to range from 3716 to 5486 mg $l^{-1}$. The sodium adsorption ratio (SAR) correlated with the electrical conductivity (EC) of the leachate, implying that the sodium hazard per se is of little concern, since when sodicity is high it is salinity that is likely to be the limiting factor. For a simulation in which irrigation with the neutralised mine water was discontinued after 25 years and the system switched to rainfed maize, it was estimated to take over 250 years for all of the precipitated gypsum to be re-mobilised through drainage.

### Life Cycle Assessment

A reduced scope life cycle assessment was used to compare conventional RO treatment of mine water with a treatment strategy which includes irrigation with and without the desalinisation of the smaller quantities of irrigation return flows. Only the environmental impacts related to electricity consumption to drive the treatment processes were considered. The functional unit considered was 1 tonne of salt removed from the mine water. Due to conventional RO being a very energy intensive process, this translated into high potential impact for all the categories considered – global warming potential, acidification potential, and non-renewable energy (fossil fuel) and blue water consumption. For the Western Basin limestone-neutralised mine water, irrigation was estimated to have an 89% lower impact, while for a treatment strategy that further involved using conventional RO on the irrigation returns flows, the impact was estimated to be 70% lower. The lowest environmental benefits of using irrigation instead of RO were estimated for the Eastern Basin, but impacts were still reduced by 52% for the irrigation plus conventional RO of return flows option. This work shows that while using conventional RO to treat mine water will have very clear benefits on water quality, some burden shifting is expected. In addition to water scarcity problems, South Africa faces electricity generation challenges which also need to be carefully considered. A major weakness in LCA is no or inadequate consideration of salinity impacts, making it a biased form of environmental impact assessment. Ongoing research aims to address this weakness.

### Availability of land and economic analysis

SWB-Sci model outputs indicate that for a wheat-soybean rotation cropping system, 1363, 3217 and 5562 ha will be needed for the Western, Central and Eastern Basins, respectively. The spatial analysis showed that, in theory, ample suitable land is available for irrigation with neutralised mine water. Water may need to be piped 17 to 30 km, depending on individual basin characteristics.

South Africa is a net importer of both wheat and soybean oilcake resulting in higher commodity prices when compared to crops which tend to be more export parity related, such as maize. The current crushing capacity of soybeans is under-utilised and additional production of roughly 500 000 t of soybean is required for the price to start trading at export parity levels. Using industry related water costs, average production expenditure when all three crops are combined was R19 900 per hectare (Scenario 1 – farmers pay for the water but not transfer from extraction points). If producers were to carry the full burden (CAPEX and OPEX) of getting the water to their production areas, this cost could increase on average to R23 300 per hectare

(Scenario 2). The model accounts for the market volatility in commodity prices and maize prices were assumed to decrease slightly, whilst wheat and soybean prices are expected to move side-ways from their current prices. Under the worst case scenario (Scenario 2), producers could still realise a farm/small business income of R243 320 per annum (excluding family and tax expenses) on 40 hectares irrigated with neutralised mine water if they continue to achieve the modelled yields as presented in Chapter 6.

From an economic sustainability perspective, more than 300 producers could benefit financially by each cultivating a 40 ha pivot as a separate business unit. If all of these hectares could come under production, approximately 10% of the current soybean crushing demand could be attained. Total gross revenue that can be generated by the 11 992 hectares under wheat and soybean rotational cropping would be approximately R73 m based on 2014 prices and costs, while it could increase to R108 m based on a higher return per hectare.

**Recommendations for future research and application of this technology**

The results of this study suggest that irrigation could well be warranted as part of a mine water management strategy. Hence the following additional research is recommended:

- Investigate more quantitatively and on a larger scale the economic feasibility of using Al sulfate and ferromanganese wad as supplementary ameliorants for mine water treatment.
- Establish a pilot plant in the Western Basin to investigate salt dynamics in a neutralised mine water wheat-soybean (or other suitable crop) irrigation system.
- Improve the SWB-Sci model's capacity to simulate bypass flow (incomplete solute mixing) and crop response to soil salinity. The latter should be informed by local field trials irrigating crops with brackish water.
- Carry out field trials to quantify the effects of direct application of raw mine water to agricultural soils and mine tailings, selected for their buffer capacity and/or availability at each of the decant locations.
- Find out, based on expected leaching loads and concentrations, whether there is assimilative capacity in the rivers of the Western, Central and Eastern Basins.
- Conduct geo-hydrological studies to identify sites where neutralised mine water irrigation schemes can be located so as to have minimal impact on the environment (for example, above an already contaminated aquifer).
- Complete a comprehensive risk assessment for mine water irrigation scenarios, including social, policy and environmental risks.

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# CHAPTER 1 INTRODUCTION

As a result of many of the large-scale mining activities in the Witwatersrand gold fields coming to an end over recent years, a critical point has been reached for the management of poor quality mine water that is, or will soon be, decanting from the mine voids. The water is contaminated primarily through the oxidation of sulfide minerals. Depending on the composition of the host rock with which the water reacts the pH may be strongly acidic and the dissolved salts dominated by acidic metal sulfates (mainly of iron and aluminium) or neutral to alkaline in which case the dissolved salts are dominated by basic metal sulfates, mainly of calcium, magnesium and sodium. The water requires treatment to neutralise the acidity, including that which develops when dissolved iron is oxidised at the surface. The typical treatment involves liming, which precipitates the more hazardous metals as sludge (especially iron, aluminium and manganese but also nickel, zinc, copper, and other trace metals such as arsenic and uranium) but leaves the water too saline with residual sulfates to achieve fitness-of-use objectives for the Vaal Barrage and further downstream (DWA, 2013a). If no action is taken therefore, assurance of supply from the Vaal Dam would be threatened, which could have unacceptable economic and social implications in the region. Water is already decanting from the Western Basin, has reached the environmentally critical level (ECL) for the Central and Eastern Basins, and is expected to begin decanting from the Central Basin after mid-2015 and from the Eastern Basin in late 2016 unless pumping and treatment commences before then (DWA, 2013a).

Around 60% of South Africa's economy and 45% of the country's population receives its water from the Vaal River System, with irrigation using 35% of this water (the Vaalharts Irrigation Scheme alone accounts for 31%) (DWA, 2013b). This fraction used by irrigation is relatively low considering that approximately 61% of our available fresh water resources is used for irrigation on average in South Africa (Annandale et al., 2011). As water resources in this region have been fully exploited for over three decades now, it has been necessary to augment supplies through water transfer schemes from the Thukela and Usutu Rivers and from the Lesotho Highlands. In an Upper Vaal Water Management Areas (WMA) Validation Study conducted in 2005, it was estimated that as much as 241 million $m^3$ per annum (660 Ml $d^{-1}$) was unlawfully used for irrigation, and the eradication thereof has since been judged essential to obtain a positive water balance in the Vaal Basin System (DWA, 2006).

Considering the imminent threat of poor quality mine water on the assurance of water supply to Gauteng and the associated wide-ranging consequences, the South African government commissioned a feasibility study to investigate short- to long-term solutions. The study group was tasked with exploring key technologies and opportunities for managing this saline water, and the final report has recently been published recommending a high density sludge (HDS) pre-treatment followed by conventional reverse osmosis (RO) (DWA, 2013a). As indicated in the report, due to the urgency of the matter 'decisions have to be based on the current understanding of the best available information and technical analyses that have been completed…'. Conventional RO qualifies as a well-established technology to remove the salts from this water, ensuring the prevention of environmental degradation following its release. But this technique is energy intensive and expensive, and creates high volumes of a brine waste product requiring disposal or value addition. While irrigation was one of the treatment technologies considered in the feasibility study, several concerns were expressed with this option which resulted in it not being included in the management strategy. These concerns include (i) that not all the salts are removed from the water, (ii) that some of the salts that are immobilised in the soil may become re-mobilised over the long-term, (iii) that the effectiveness of salt management cannot be adequately monitored, (iv) that adequate land for irrigation may not be available in the built-up Vaal Basin region, and (v) that the seasonal nature of the demand for water by irrigation would require adequate storage and larger pumping facilities (DWA, 2013b). It was also indicated in the feasibility study report that only salt tolerant crops can be irrigated, with the single crop (Annandale et al., 1999) mentioned as example being Salicornia bigelovii (dwarf saltwort), which is a halophyte. This last point highlights a common misunderstanding regarding the key principle in using irrigation as a treatment option which is discussed below.

Work done in the early 1980s using a steady-state chemical equilibrium model showed that when $CaSO_4$-rich mine water is used in irrigation, a significant quantity of gypsum precipitates (becomes insoluble) in the soil, reducing salt loads in the irrigation return flows (Du Plessis, 1983). In subsequent WRC-supported research starting in 1993 and still continuing today at the University of Pretoria (UP), this gypsum precipitation mechanism was confirmed in the laboratory, glasshouse experiments, field trials and on commercial scale cropping systems under pivot irrigation with mine water from the Mpumalanga coal fields

(Annandale et al., 1999; Annandale et al., 2006; Annandale et al., 2002; Beletse, 2008; Jovanovic et al., 2004). This immobilisation effectively results in soil salinity levels being much lower than would be the case when irrigating with saline waters which do not have Ca and $SO_4$ as the dominant ions, enabling the cultivation of a range of commonly grown field crops (including those that are only moderately salt tolerant). For the trials, multiple crops species grown using overhead irrigation did not show foliar injury symptoms and yields were higher than for dryland production. Furthermore, gypsum precipitation did not result in any observable physical or chemical changes that would adversely affect soil productivity. Following these findings, the UP team concluded that there are four components to consider in managing irrigation with saline mine water: (i) the chemical quality of the irrigation water, ii) the hydrological setting of the irrigated area, (iii) the management of the leaching fraction, and (iv) the fate of the drainage water (Annandale et al., 2011).

Compared to the more energy intensive water treatment technologies such as conventional RO, a major advantage of including irrigation in a treatment strategy is the low treatment cost while using the water in a productive manner, and potentially a lower environmental burden. Motivated by this, the purpose of this project is to build on previous WRC research on the feasibility of using irrigation to remove salts from neutralised AMD through gypsum precipitation, focusing specifically on gold mine water qualities that are expected for the Western, Central and Eastern Basins. The specific aims include:

To conduct laboratory studies to investigate the pre-treatment of waters specifically for irrigation to maximise gypsum precipitation and crop production, including the use of novel techniques that take advantage of locally available resources (Chapters 3, 4 and 5).

Make use of long-term soil water and salt balance modelling to estimate potential crop yields and salt dynamics for expected neutralised gold mine water irrigation schemes (Chapter 6).

Conduct a reduced scope life cycle assessment comparing selected environmental impacts of conventional reverse osmosis and a treatment strategy that includes the irrigation option (Chapter 7).

Use geographic information system (GIS) tools to identify suitable tracts of land which can be used for irrigation in the Vaal Basin, as well as an economic study to investigate the financial feasibility of a farming enterprise irrigating with neutralised poor quality gold mine water (Chapter 8).

Water quality issues currently being faced in the Vaal Basin are being anticipated in the Mpumalanga coal fields and elsewhere in South Africa, as well as the rest of the world. While it is acknowledged upfront that the irrigation option will not be suitable for all scenarios, this research aims to provide useful data and information which can be used for a wider range of decision-making processes for situations where this technology could be suitable.

# CHAPTER 2 EXPLORING ACID MINE WATER TREATMENT OPTIONS FOR IRRIGATION

## 2.1 MINE WATER QUALITY IN THE WITWATERSRAND GOLDFIELDS

An initial requirement for this project was to secure a set of representative chemical analyses of mine waters on the basis of which both geochemical authentication and practical neutralisation requirements could be calculated. It was expected that a statistical summary for each of the three major Vaal Basins would be ideal for this purpose. The best summary of such information is given in the recent report published by the Department of Water Affairs (DWA, 2012), from which the essential data in Table 1 are taken, representing median (50th) and poorest (95th percentile) values for water quality in each basin. From the flow data it is apparent that the Eastern Basin accounts for about half the expected total volume needing to be treated, with the most highly polluted water in the Western Basin accounting for only 15%. It is anticipated (DWA, 2012) that all of the Eastern Basin water will be discharged by pumping at Grootvlei and average underground raw water quality at that site is therefore also presented in Table 1.

The 95th percentile values in Table 1 represent (barring exceptional outliers) the poorest quality that will be encountered. (In the case of pH it is the 5th percentile because lowest values represent worst quality). For the purpose of calculating treatment costs the median or 50th percentile values are likely to be more meaningful, whereas the 95th percentile values are probably more relevant to risk assessment. Although the Central Basin waters have the most acidic pH range, a much greater concentration of acid occurs in the Western Basin, mostly in the form of ferrous iron (Fe) and to a lesser extent manganese (Mn), both of which will consume alkalinity as they are oxidised and precipitated during neutralisation. By contrast in the Central Basin dissolved Al is the main source of acidity – substantially more so than either Fe or Mn. This has consequences for choosing a suitable treatment method because efficient precipitation of Fe and Mn requires the addition of alkali to be accompanied by aeration (Maree et al., 2013) whereas that of Al does not. The waters are generally saline in biological terms, with electrical conductivity (EC) approaching or slightly exceeding 400 mS $m^{-1}$, and the anion suite is dominated by sulfate. The extent to which sulfate is balanced by magnesium (Mg) and sodium (Na) as opposed to calcium (Ca) after acidic cations have been precipitated has an important bearing on suitability for irrigation since it will affect the salinity (and sodicity) of return flow after evaporation of water and precipitation of gypsum have taken place (du Plessis, 1983). The Eastern Basin water has a small net alkalinity and aeration alone without lime addition may be sufficient to precipitate the Fe, although some acidification will occur when the Fe is oxidized. A more quantitative assessment will be made later during the discussion of treatment methods.

Statistical summaries comprising percentiles have some value for representation but caution may be needed in geochemical interpretation and in quantifying treatment costs. The values for each parameter in Table 1 are based on different sample populations (as indicated in relevant tables in DWA, 2012) and the charge balance among major ions is mostly poor (presented later in Table 6).

For the geochemical modelling and interpretation that will be undertaken in the next phase of the project it was decided that actual laboratory analyses of individual water samples would be preferable. We were able to acquire the Department of Water Affairs data base for the whole Vaal Basin, consisting of more than 80 000 analyses over the last two decades. Many of these analyses were incomplete, some consisting of only pH and EC, or only metals, or sulfate but not all major cations. These incomplete analyses were discarded. Other criteria for discarding analyses included a low concentration of sulfate relative to chloride (since sulfate is the signature ion for mine drainage in the region) and anomalous charge imbalance indicating laboratory error. An Excel file containing the original data and subsets of selected data numbering about 450 samples based on Fe or sulfate concentrations or pH, is available on the WRC website as Special Publication SP 80/14. Further selections, for purposes of representation as well as some preliminary geochemical interpretation, are presented in Tables 2, 3 and 4.

**Table 1 Summarised daily flow volumes and water quality data for the three major basins of the Witwatersrand goldfields***

| Water source | Estimated peak pumping flow ML $d^{-1}$ | Flow as % of total | Water quality class | pH | EC | Fe | Mn | Al | Mg | Ca | $SO_4$ | Na | Cl | Alkalinity as $CaCO_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Western Basin | 35 | 15 | Median | 5.4 | 385 | 662 | 56 | 2 | 150 | 549 | 3085 | 110 | 40 | 0 |
| | | | 95th %ile | 3.5 | 442 | 954 | 89 | 2 | 150 | 703 | 3623 | 227 | 40 | 0 |
| Central Basin | 84 | 37 | Median | 3.0 | 397 | 40 | 47 | 122 | 172 | 279 | 2831 | 122 | 137 | 0 |
| | | | 95th %ile | 2.4 | 465 | 108 | 50 | 193 | 258 | 563 | 3062 | 171 | 146 | 0 |
| Eastern Basin | 110 | 48 | Median | 6.5 | 280 | 74 | 3 | 0 | 54 | 77 | 1148 | 208 | 157 | 168 |
| | | | 95th %ile | 5.9 | 360 | 227 | 6 | 2 | 166 | 421 | 2289 | 264 | 254 | 12 |
| | | | Grootvlei (ave) | 6.4 | 322 | 135 | 4 | 0.3 | 197 | 422 | 1383 | 240 | 184 | 0 |

*Derived from Tables 6.12, 7.13, 8.13 and 8.14 in DWA (2012); for pH and alkalinity, 95th percentile values are replaced by corresponding 5th percentiles. EC in mS $m^{-1}$; solute concentrations in mg $L^{-1}$; Mg and Cl data were not available in DWA (2012) for the Western Basin and values in bold have been estimated from other sources

The selection of sulfate rich waters in Table 2 has pH values spanning a wide range, generally satisfactory charge balance indicating analytical reliability, and some trace element concentrations allowing for more complete speciation calculations. The PHREEQC model (Parkhurst and Appelo, 1999) was used to assess the likelihood of the mine water being in equilibrium with one or more mineral solids. In Table 5 the saturation indices for four minerals commonly encountered or expected in AMD environments show near zero values over different parts of the pH range suggesting that they could at least partly be exerting some control over Ca and $SO_4$ concentrations in the mine water. These data are plotted for easier comparison in Figure 1. If the mine water is indeed in equilibrium with one or more secondary minerals then the idea emerges of a partial sequestration of contaminants in mine voids prior to decantation, and of seeking ways to capitalise on such knowledge by manipulating the phreatic surface. In Tables 3 and 4 sulfate rich waters have been sorted into poorly and well neutralised groups (Tables 3 and 4, respectively). These will be used for geochemical modelling later in the project. It is noteworthy that three of the samples in Table 4 represent discharge from the Grootvlei high density sludge (HDS) plant and all of them contain a quite high residual Fe concentration suggesting that aeration and/or lime addition was inadequate at that time (more than ten years ago). It has been suggested (Maree et al., 2013) that Eastern Basin water has a high enough pH to allow Fe removal by aeration without the need for neutralisation, but oxidation of Fe will itself generate acidity which requires some lime addition to sustain the oxidation rate. More recent data (since 2008) for HDS discharge at Grootvlei suggest that Fe precipitation is now achieved effectively.

## 2.2 METHODS AND COST IMPLICATIONS OF PRE-TREATING ACID MINE WATER FOR IRRIGATION

### *2.2.1 Neutralisation with lime*

The most widely applied method for treating acid mine drainage is neutralisation with lime, either CaO or $Ca(OH)_2$. Limestone ($CaCO_3$) works less efficiently, but if suitable steps are taken to ensure fineness, mixing, aeration and flocculation, then a substantial degree of neutralisation can be achieved using mainly limestone with only a small supplement of lime to precipitate remaining metals and further reduce the sulfate concentration (Maree et al., 2013; Makgae et al., 2013). The data in Table 6 from the experimental neutralization by Maree et al. (2013) of Western Basin water, rich in Fe and manganese (Mn), indicate that Fe is largely removed by limestone treatment but that Mn, along with some trace metals not shown, requires subsequent lime addition to ensure its removal. Using limestone as partial replacement for lime halves the cost of chemicals (Table 6) and is therefore attractive. The quality of water for irrigation is probably satisfactory since after neutralisation it is predominantly gypsiferous; to what extent is uncertain, however, since the Ca values were calculated to obtain charge balance; seemingly the product water is supersaturated with respect to gypsum (solubility of about 2.5 g $L^{-1}$). The knowledge for irrigating crops with $CaSO_4$ or gypsiferous mine water has been well developed for neutralised AMD from collieries (Annandale et al., 2001; 2002).

## Table 2 Witwatersrand goldfields water data: Analytical selection for chemical speciation*

| Monitoring Point ID | Monitoring Point Name | Lat. | Long. | pH | EC mS/m | mmol$_c$ L$^{-1}$ | | | | | | | | | | µmol L$^{-1}$ | | | | Σ cations | Σ anions |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Ca | Mg | Na | K | Al | Fe | Mn | SO$_4$ | HCO$_3$ | Cl | Si | Ni | Co | Zn | | |
| 177840 | C2H185Q01 POORTJIE ROAD ON BLESBOKSPRUIT | -26.48 | 28.43 | 8.2 | 257 | 11.5 | 6.4 | 9.1 | | 0.019 | 0.006 | 0.004 | 19.33 | 4.08 | 5.44 | | | | | 27.1 | 28.8 |
| 100000546 | THIRTEEN AND EIGHTH SPRUIT WHICH FLOWS INTO THE LEEUSPRUIT | -26.49 | 27.69 | 7.9 | 177 | 12.9 | 4.5 | 5.1 | 0.21 | 0.012 | 0.001 | 0.000 | 16.74 | 2.32 | 2.25 | 6.4 | 0.15 | 0.02 | 0.05 | 22.7 | 21.3 |
| 191579 | KRUGERSDORP RANDFONTEIN ESTATES GOLD MINE - NEAR R24 ROAD BRIDGE ON TWEELOOPIESSPRUIT- INLET TREATE | -26.11 | 27.72 | 6.1 | 414 | 36.7 | 12.7 | 7.9 | | 0.217 | 5.696 | 2.034 | 72.50 | 0.20 | 1.27 | | | 1.58 | 0.29 | 65.3 | 74.0 |
| 1000261722 | GP00300 STERKFONTEIN | -26.05 | 27.71 | 8.1 | 213 | 14.7 | 10.3 | 3.8 | 0.11 | 0.002 | 0.024 | 0.001 | 24.04 | 3.03 | 1.17 | 5.7 | | | | 28.9 | 28.2 |
| 191580 | STERKFONTEIN 173 IQ - @ BANK OF BLOUBANKSPRUIT (RIETSPRUIT), @ SCHUTTE SURFACE | -26.05 | 27.71 | 2.8 | 393 | 26.0 | 11.7 | 4.4 | | 0.380 | 2.178 | 2.223 | 55.63 | | 1.15 | | | | | 47.0 | 56.8 |
| 90726 | C2H219Q01 KLIP RIVER AT DURBAN DEEP MINE (D/S SHAFT NO.5) | -26.18 | 27.84 | 4.4 | 185 | 13.8 | 6.5 | 2.9 | 0.42 | 0.278 | 0.011 | 0.253 | 20.83 | 0.00 | 1.30 | | | | | 24.2 | 22.1 |
| 179134 | NATALSPRUIT OFF RING RD EAST IN ALBERTON | -26.26 | 28.12 | 5.0 | 61 | 1.7 | 1.6 | 0.8 | 0.16 | 0.281 | 0.124 | 0.148 | 4.69 | 0.00 | 1.01 | | | | 0.34 | 4.8 | 5.7 |

*These water samples were selected from a DWA data set for more than 86000 samples from the western, central and eastern goldfields regions of Gauteng by stepwise elimination of analyses with incomplete or unreliable data (through charge balance evaluation) for major constituents, and then discarding closely similar analyses from the same sampling sites. The objective was to have a manageable set of analyses spanning a wide range of pH and salinity and having analyses for the most important major ions and preferably some trace elements, allowing geochemical relationships to be investigated which would enhance the interpretation of routinely collected data and allow extrapolable calculations to be made of water treatment requirements for different kinds of water use. A subset of data screened for usefulness to the current project is contained in a file submitted as Annexure A to this report.

**Table 3 Selection of mine water analyses with a high sulfate concentration and low degree of acid neutralisation***

| Monitoring Point ID | Monitoring Point Name | Lat. | Long. | Located on Feature Name | Located on Type | Sample Start Date | pH | EC | Ca | Mg | Na | $NH_4$ | Al | Fe | Mn | $SO_4$ | TAL | Cl | F | $PO_4$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 191580 | STERKFONTEIN 173 IQ - @ BANK OF BLOUBANKSPRUIT (RIETSPRUIT), @ SCHUTTE SURFACE | -26.05 | 27.71 | BLOUBANKSPRUIT RIETSPRUIT - DRAINAGE REGION A21D | Rivers | 24/02/2010 | 2.8 | 393 | 521 | 140 | 102 | 4.2 | 3.4 | 60 | 62.2 | 2670 |  | 41 | 0.3 | 0.2 |
| 191581 | STERKFONTEIN 173 IQ - @ BLOUBANKSPRUIT BANK, NEAR RESERVE - MORESTER SURFACE WATER | -26.05 | 27.70 | BLOUBANKSPRUIT RIETSPRUIT - DRAINAGE REGION A21D | Rivers | 24/02/2010 | 2.8 | 397 | 514 | 142 | 101 | 4.4 | 3.1 | 76 | 62.3 | 2650 |  | 44 | 0.3 | 0.2 |
| 188900 | KRUGERSDORP GAME RESERVE - @ AVIARY DAM ON TWEELOPIESPRUIT | -26.07 | 27.70 | TWEELOPIESPRUIT A21D TO A21D | Rivers | 24/02/2010 | 2.9 | 394 | 500 | 139 | 104 | 4.4 | 2.9 | 83 | 61.2 | 2820 |  | 41 | 0.3 | 0.2 |
| 187591 | W1S3 KRUGERSDORP GAME RESERVE - @ HIPPO DAM ON TWEELOPIESPRUIT | -26.10 | 27.72 | TWEELOPIESPRUIT A21D TO A21D | Rivers | 24/02/2010 | 3.0 | 461 | 636 | 176 | 121 | 5.5 | 2.8 | 286 | 75.5 | 3860 |  | 46 | 0.3 | 0.2 |
| 191579 | KRUGERSDORP RANDFONTEIN ESTATES GOLD MINE - NEAR R24 ROAD BRIDGE ON TWEELOOPIESSPRUIT- INLET TREATE | -26.11 | 27.72 | TWEELOPIESPRUIT A21D TO A21D | Rivers | 24/02/2010 | 3.1 | 469 | 574 | 159 | 132 | 5.8 | 1.4 | 290 | 58.3 | 3830 |  | 47 | 0.2 | 0.2 |

*EC in mS $m^{-1}$; other constituents in mg $L^{-1}$; TAL = total alkalinity as $CaCO_3$; blank cells indicate not determined. Selection was based on a requirement for analyses of both acidic and neutralised, sulfate-rich mine waters including determinations of both acid and base cations, allowing modelling of (a) water treatment with limestone/lime and (b) sequestration of gypsum by irrigation.

## Table 4 Selected mine water analyses with a high sulfate concentration and high degree of acid neutralisation*

| Monitoring Point ID | Monitoring Point Name | Lat. | Long. | Located on Feature Name | Located on Type | Sample Start Date | pH | EC | Ca | Mg | Na | $NH_4$ | Al | Fe | Mn | $SO_4$ | TAL | Cl | F | $PO_4$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 191579 | KRUGERSDORP RANDFONTEIN ESTATES GOLD MINE - NEAR R24 ROAD BRIDGE ON TWEELOOPIESSPRUIT- INLET TREATE | -26.11 | 27.72 | TWEELOPIESPRUIT A21D TO A21D | Rivers | 25/03/2008 | 6.1 | 414 | 734 | 153 | 182 | 3.9 | 2.0 | 157 | 57 | 3480 | 10 | 45 | 0.9 | 0.2 |
| 177815 | C2H207 GROOTVLEI MINE HDS PLANT EFFLUENT | -26.25 | 28.50 | GROOTVLEI DISCHARGE PIPE TO BLESBOKSPRUIT | Pipeline | 21/04/1999 | 6.0 | 377 | 421 | 134 | 244 | | | 241 | | 1667 | 95 | 205 | | |
| 177815 | C2H207 GROOTVLEI MINE HDS PLANT EFFLUENT | -26.25 | 28.50 | GROOTVLEI DISCHARGE PIPE TO BLESBOKSPRUIT | Pipeline | 15/07/2000 | 6.4 | 341 | 381 | 156 | 260 | | | 187 | | 1788 | 230 | 174 | | |
| 177815 | C2H207 GROOTVLEI MINE HDS PLANT EFFLUENT | -26.25 | 28.50 | GROOTVLEI DISCHARGE PIPE TO BLESBOKSPRUIT | Pipeline | 21/09/2000 | 6.8 | 364 | 411 | 140 | 252 | | | 176 | | 1816 | 380 | 171 | | |

*EC in mS/m; other constituents in mg/L; TAL = total alkalinity as $CaCO_3$; blank cells indicate not determined. Selection was based on a requirement for analyses of both acidic and neutralised, sulfate-rich mine waters including determinations of both acid and base cations, allowing modelling of (a) water treatment with limestone/lime and (b) sequestration of gypsum by irrigation.

According to Maree et al. (2013) the limestone treatment takes about 90 minutes with aeration to precipitate most of the Fe. Subsequent lime addition in the batch reactor not only removes the Mn but achieves some additional sulfate precipitation. Although this precipitate was assumed to consist of gypsum, it is just as likely to have been one of the double hydroxides such as ettringite, pyroaurite, hydrotalcite or even jouravskite ($Ca_6[Mn(OH)_6]_2.24H_2O(SO_4)_2(CO_3)_2$) which are known to be stable around pH 9-10; H F W Taylor (1973) provides a beautiful description of this family of compounds, while R M Taylor (1984) outlines their synthesis and significance to soil environments included polluted ones. Given the strong likelihood of a pyroaurite-like precipitate at pH 9.2 the constant Mg concentration in Table 6 may be in some doubt (confirming this, raw and treated water data for Grootvlei in Tables 8.14 and 8.15 of DWA (2012) reveal the average Mg concentration dropping from 197 to 117 mg $L^{-1}$, i.e. nearly half the Mg is precipitated by liming) and, considering the multiple metal-ligand combinations that are possible in the double hydroxides, the dissolved concentrations of all reaction products (including ions such as Cl that normally show conservative behaviour) should be checked after each neutralization step.

The costs given in Table 6 are those of chemical reactants only. Other operating and capital costs associated with HDS plants exploiting the limestone-lime combination have been updated by Makgae et al. (2013). Given the wide range in composition of the raw waters of the three basins (Table 1), it is likely that plant design at each pumping location will need to be modified to accommodate the main differences. The test results published so far have been for mine water composition that is typical of the Western Basin discharge. Cost per kilolitre is likely to be less for the Central and Eastern Basins. The extent to which the relative cost of neutralization may depend on composition is calculated in the next section.

**Table 5 Geochemical assessment of the waters in Table 2: saturation indices of secondary Ca and $SO_4$ minerals commonly appearing as metastable phases in sulfidic mine drainage**

| Monitoring Point Name | pH | EC mS $m^{-1}$ | $CaSO_4$ | $CaCO_3$ | $NaFe_3(SO_4)_2(OH)_6$ | $AlOHSO_4$ |
|---|---|---|---|---|---|---|
| | | | gypsum | calcite | natrojarosite | jurbanite |
| C2H185Q01 POORTJIE ROAD ON BLESBOKSPRUIT | 8.2 | 260 | -0.55 | 1.10 | -0.08 | -6.41 |
| THIRTEEN AND EIGHTH SPRUIT WHICH FLOWS INTO THE LEEUSPRUIT | 7.9 | 180 | -0.51 | 0.69 | -2.08 | -5.74 |
| KRUGERSDORP RANDFONTEIN ESTATES GOLD MINE - NEAR R24 ROAD BRIDGE ON TWEELOOPIESSPRUIT- INLET TREATED | 6.1 | 410 | 0.18 | -2.52 | 9.84 | 0.56 |
| GP00300 STERKFONTEIN | 8.1 | 210 | -0.39 | 0.98 | 1.60 | -7.10 |
| STERKFONTEIN 173 IQ - @ BANK OF BLOUBANKSPRUIT (RIETSPRUIT), @ SCHUTTE SURFACE | 2.8 | 390 | -0.01 | | -20.44 | -1.92 |
| C2H219Q01 KLIP RIVER AT DURBAN DEEP MINE (D/S SHAFT NO.5) | 4.4 | 190 | -0.42 | -5.97 | -13.08 | -0.44 |
| NATALSPRUIT OFF RING RD EAST IN ALBERTON | 5.0 | 60 | -1.59 | -5.50 | -5.18 | 0.12 |

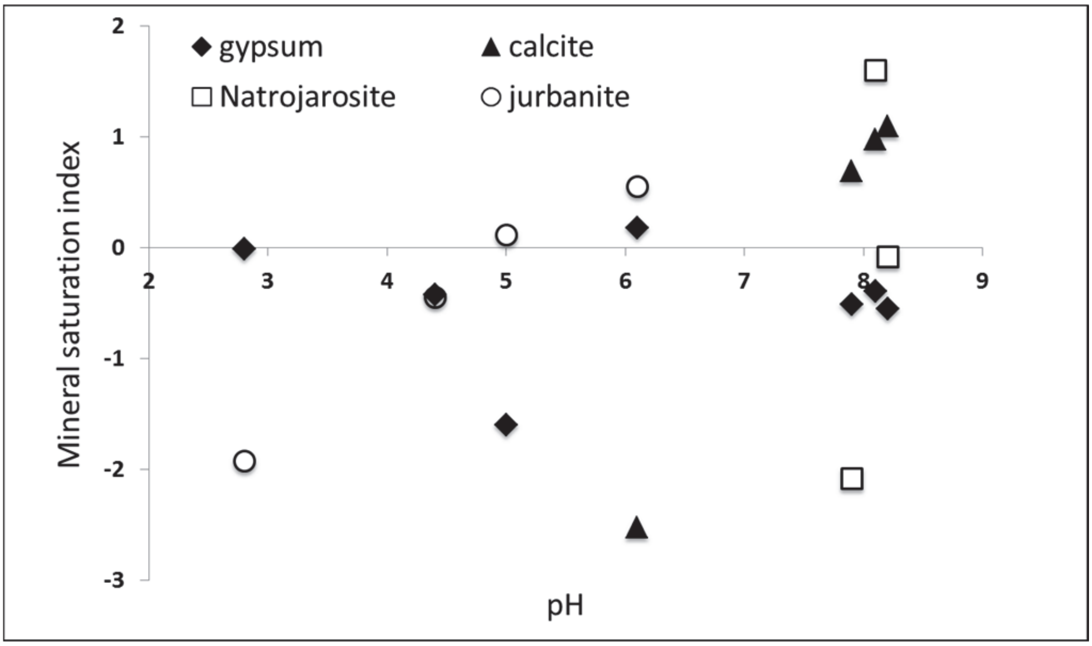


**Figure 1 Plot of the saturation index of four minerals against pH for the seven mine waters in Table 5**

**Table 6 Composition and cost of treating Western Basin mine decant with limestone and lime, alone or in combination (after Maree et al., 2013)**

| Analyte | Feed | Limestone alone | Limestone + lime | Lime alone |
|---|---|---|---|---|
| pH | 2.9 | 6.6 | 9.2 | 9.2 |
| Sulfate (mg $L^{-1}$ as $SO_4$) | 4800 | 2701 | 2285 | 2285 |
| Chloride (mg $L^{-1}$ as Cl) | 37 | 37 | 37 | 37 |
| Sodium (mg $L^{-1}$ as Na) | 50 | 50 | 50 | 50 |
| Magnesium (mg $L^{-1}$ as Mg) | 147 | 147 | 147 | 147 |
| Free acidity (mg $L^{-1}$ as $CaCO_3$) | 979 | 0 | 0 | 0 |
| Al (mg $L^{-1}$ as Al) | 6 | 0 | 0 | 0 |
| Iron(II) (mg $L^{-1}$ as Fe) | 625 | 10 | 0 | 0 |
| Iron(III) (mg $L^{-1}$ as Fe) | 100 | 0 | 0 | 0 |
| Manganese (mg $L^{-1}$ as Mn) | 228 | 228 | 0 | 0 |
| Calcium (mg $L^{-1}$ as Ca) | 602 | 720 | 760 | 760 |
| TDS (mg $L^{-1}$) calculated | 5995 | 3954 | 3410 | 3410 |
| Treatment quantity kg/$m^3$ | – | 3.94 | 3.94 + 0.52 | 2.92 |
| Treatment cost R/$m^3$ | – | 1.77 | 2.80 | 5.83 |

## 2.3 ALTERNATIVE TREATMENTS GEARED TO IRRIGATION

Certain possibilities emerged from considering the limestone-lime neutralisation process. Firstly, it is likely that Mn, Fe and other metals still in solution after the limestone step would be attenuated on soil colloid surfaces either by adsorption or by catalytic oxidation and precipitation. Two examples among many studies in support of this are those of Lee et al. (2002) and Madden and Hochella (2005). The extent of attenuation would depend strongly on properties of the irrigated soil. Perhaps supplementary lime treatment of the water could be dispensed with if irrigable soil could be found that secures a satisfactory degree of immobilization.

A second possibility was of other treatments that might complement the limestone-lime neutralisation process or be worth considering as cost-effective alternatives. Two that seemed worth exploring are aluminium sulfate with lime addition for pH control, and manganese oxide, well known as both a multi-element adsorbent and an efficient oxidant.

Thirdly, it may be feasible to irrigate the raw mine water directly onto land when combined with suitable chemical amendment of the soil to ensure neutralisation and containment of added solutes. In some situations where soil properties are unfavourable the mine water could even be regarded as an ameliorant. Direct irrigation of acid mine drainage has been tried before (Cronce et al., 1980) although current environmental regulations are more stringent and regulatory approval could be difficult to secure.

Because the cost implications cannot be quantified at this stage let us first deal with the **manganese oxide process**. The rationale comes from a paper by Duarte and Ladeira (2011) who found that soluble Mn(II) in mine water could be removed quite effectively (to < 1 mg $L^{-1}$) by passing it through a column of manganese oxide. The mechanism appears to be one of oxidation by the Mn(IV) oxide, made possible by the fact that Mn can occupy the intermediate Mn(III) valence state, also as a sparingly soluble oxide or hydroxide. Pure Mn oxide was found to be more effective than a mixture of limestone and Mn oxide in the column. The water needed first to be neutralised to about pH 7 for the oxidation to be effective. Loading rate of Mn on the oxide in the column was about 12 mg $g^{-1}$. This would amount to about 4 kg of Mn oxide being needed to remove the Mn to < 1 mg $L^{-1}$ from 1000 litres of water containing 50 mg $L^{-1}$ of soluble Mn. It is not certain whether the oxide surface could be regenerated after adsorption and reused for further scavenging of Mn. This process could be of special interest because a deposit of ferromanganese wad is currently mined on the farm Ryedale about halfway between Randfontein (where water from the Western Basin is currently being treated) and Ventersdorp. The ore has been used extensively for uranium (U) extraction by several gold mines. The deposit is substantial, about six million tonnes, and is described in detail by Pack et al. (2000). Other occurrences of wad exist regionally in association with the dolomites which are extensive in the Witwatersrand Basin. Whether it would be feasible to use the wad not only to oxidise Mn remaining in solution after limestone treatment but also to facilitate Fe oxidation is unclear and future research into this aspect could be rewarding. Manganese oxide is an effective scavenger of metals and solutes of special concern such as U. The principle behind the method is also applicable to land treatment of mine water in which soil mineral surfaces, especially Mn and Fe oxides, have the capacity not only for multi-element adsorption but also to catalyse the oxidation of soluble Fe and Mn (see, for example, Madden and Hochella, 2005).

The idea of using **Al sulfate** to treat mine water is counter-intuitive because Al and sulfate are two of the major ions in AMD. This is probably the most widely used of all chemicals, in conjunction with lime, for purifying water to a potable condition. The largest manufacturer of Al sulfate in Africa is located in Springs near to the Grootvlei mine which is to be the treatment focus of half the mine water on the Witwatersrand goldfields. The rationale for dosing mine water with Al lies once again in double hydroxide chemistry (Taylor, 1984). Specifically, one can hypothesise that Al and Fe(II) will readily co-precipitate, through induced hydrolysis, at a pH well below that required for precipitation of $Fe(OH)_2$ (around pH 9) because the pH of $Al(OH)_3$ precipitation is around 5 and the mixed hydroxide will have a pH of precipitation falling proportionately between the two. The same reasoning applies to Mn and to other divalent metals such as zinc, copper and nickel.

Hypothetical treatment with Al sulfate and lime of the waters listed in Table 1 is outlined in Table 7, with a sequential explanation in footnotes of the quantities that theoretically would be needed on the basis of reaction stoichiometry. The Al sulfate cost has not yet been established with certainty because it depends on grade, and the price used in the calculations was obtained from an international web site offering industrial grade Al sulfate for \$150 $tonne^{-1}$ (F.O.B.). An industrial grade is available at the Springs facility. It is not certain whether the double hydroxide composition of $M^{2+}/Al^{3+}$ molar = 3:1 would be sufficient to secure Fe(II) precipitation without the need for prior oxidation, but that is the general idea based on evidence from synthesis experiments (Taylor, 1984). If it did work then it would mean a gain in efficiency because oxidation could proceed leisurely in the precipitated sludge instead of being a prerequisite to precipitation. This would allow a smaller plant for a given output, consistent with the shorter residence time of water in the reactor. The chemical cost for the Central and Eastern Basins is similar to that for lime treatment of Western Basin water in Table 6, but the cost of treating the water from the Western Basin in this way, whether of median or poor quality, is probably prohibitive (between R5 and R8 per $m^3$, Table 7). The benefits of using Al sulfate for removing the large concentrations of divalent Fe and Mn from mine water remain to be tested experimentally. In principle, besides precipitating Fe and Mn without the need for aeration, Mg should also be removed (to form hydrotalcite) as well as trace contaminants; some sulfate would contribute to the anion layer in the double hydroxide. Hence the need to achieve a high pH (> 9) with lime might fall away, and water of a more suitable composition might be produced for irrigation.

The next idea, which is illustrated by the calculations in Tables 8 and 9, was to hypothetically apply the treatments in Table 7 to a **land treatment set-up** in which sludge separation and disposal would no longer be required because all solid reaction products would remain in place and only soluble salts and surplus water would leave the reactor. In this case the reactor would be as many hectares of land, to a depth determined by soil type and whatever drainage system was designed to match it, as would be needed to discharge the annual volume of water to be irrigated from each of the basins, at a rate which maximises the opportunity for evaporative concentration while leaving enough flexibility for irrigation scheduling so as to ensure a suitable leaching fraction without risk of unwanted runoff or leachate. Details of the operating variables and calculations are presented in the tables. Of special interest is that one fifth of the water applied will drain and take with it only a small fraction of the applied solids (Table 9). Such a system would go a long way towards keeping salts from mine water out of surface waters in the Vaal and Crocodile (West) catchments. At the same time there is every chance that if the soil for each irrigation farm is selected well, the added Al, Fe and Mn hydroxides (the accumulation of which from treating Western Basin-type water roughly equates to incorporating a 10 mm-thick layer of dried solid on the irrigated land each year) could significantly enhance the structure of weakly coherent sands, sodic, dispersible clays or hard-setting loams without necessarily polluting the soil if the irrigation management is well thought out.

A final thought concerns the possibility of **disposing of mine water on mine tailings storage dams**. A particular case of interest is Ergo's Brakpan Dam Tailings Storage Facility (TSF) (Figure 2) which is due for closure in the near future. This 600 ha TSF is connected by pipeline to the gold plant which is close to where the Eastern Basin water will be extracted at Grootvlei for treatment. Hence the infrastructure, including pumps, already exists for land farming of a substantial portion of Eastern Basin water. The precipitation of hydroxide solids in the tailings would be of enormous value in limiting wind erosion and facilitating the establishment of a productive cover of vegetation such as *Eucalyptus spp*. The idea of turning such a serious liability into an asset is appealing, but given the environmental status of the Blesbokspruit any uncertainty about containing salts within the TSF would have to be addressed. Currently the Grootvlei HDS plant discharges directly into the Blesbokspruit; diversion to the TSF, whether before or after treatment, could therefore be advantageous.

**Table 7 Major ion equivalent concentrations and corresponding dosage and cost of Al sulfate and lime theoretically needed to precipitate divalent ions as a double hydroxide with $M^{2+}/Al^{3+}$ molar ratio of 3:1. (Based on analytical data in Table 1)**

| Water source | Water quality class | Fe (II) | Mn (II) | Al | Mg | Ca | Na | $SO_4$ | Cl | $HCO_3$ | Sum cations | Sum anions | Sum[1] M(II) | Al reqmt.[2] | $AlSO_4$ dose[3] | Lime dose[4] | $AlSO_4$ cost[5] | Lime cost[6] | Total chem. cost |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $mol_c\ L^{-1}$ | | | | | | | | | | | | | kg $m^{-3}$ | | R $m^{-3}$ | | |
| Western Basin | Median | 24.5 | 2.0 | 0.2 | 12.5 | 27.5 | 4.8 | 64.3 | 1.1 | 0.0 | 71 | 65 | 39.0 | 13 | 1.28 | 1.93 | 1.92 | 3.85 | 5.77 |
| | 95th %ile | 35.3 | 3.2 | 0.2 | 12.5 | 35.2 | 9.9 | 75.5 | 1.1 | 0.0 | 96 | 77 | 51.0 | 17 | 1.68 | 2.52 | 2.51 | 5.03 | 7.55 |
| Central Basin | Median | 1.5 | 1.7 | 13.6 | 14.3 | 14.0 | 5.3 | 59.0 | 3.9 | 0.0 | 50 | 63 | 17.5 | 1 | 0.13 | 1.20 | 0.19 | 2.39 | 2.59 |
| | 95th %ile | 4.0 | 1.8 | 21.4 | 21.5 | 28.2 | 7.4 | 63.8 | 4.2 | 0.0 | 84 | 68 | 27.3 | 2 | 0.19 | 1.87 | 0.29 | 3.75 | 4.04 |
| Eastern Basin | Median | 2.7 | 0.1 | 0.0 | 4.5 | 3.9 | 9.0 | 23.9 | 4.5 | 3.4 | 20 | 32 | 7.3 | 2 | 0.24 | 0.36 | 0.36 | 0.72 | 1.09 |
| | 95th %ile | 8.4 | 0.2 | 0.2 | 13.8 | 21.1 | 11.5 | 47.7 | 7.3 | 0.2 | 55 | 55 | 22.5 | 7 | 0.73 | 1.11 | 1.10 | 2.22 | 3.32 |
| | Grootvlei | 5.0 | 0.1 | 0.0 | 16.4 | 21.1 | 10.4 | 28.8 | 5.3 | 0.0 | 53 | 34 | 21.6 | 7 | 0.71 | 1.06 | 1.07 | 2.12 | 3.19 |

[1] Fe+Mn+Mg [2] Al requirement = ((Sum M(II)) – Al)*0.33 [3] Al sulfate dosage = Al reqmt.*9/(0.09*1000) [4] Lime dose (as $Ca(OH)_2$) = (Al.reqmt.+Sum M(II)+Al)*74/2000 [5] Based on Al sulfate cost of R1500/tonne [6] Based on lime cost of R2000/tonne.

**Table 8 Anticipated inputs, solids retention and quality of discharge for the land treatment of mine water by amending soil with Al sulfate, lime and limestone then irrigating at a rate of 5 mm $d^{-1}$. The Table provides a basis for assessing the degree of retention of solids, the environmental impact of return flow and the cost of chemicals used for remediation. The calculations represent an extension of the water treatment in Table 7.**

| Water source | Water quality class | Flow | Area needed for 5 mm $day^{-1}$ | $AlSO_4$ dose | Lime dose | Final Ca | Final Na | Final $SO_4$ | Metal sludge load | $CaCO_3$ dose | Gypsum load | Soluble salt load | Return flow volume | Return flow TDS | Return flow SAR |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | ML $d^{-1}$ | ha | kg $m^{-3}$ | | mmolc $L^{-1}$ | | | t $ha^{-1}$ $yr^{-1}$ | | | | ML $d^{-1}$ | mg $L^{-1}$ | mmol $L^{-0.5}$ |
| Western Basin | Median | 35 | 700 | 1.28 | 1.93 | 79.5 | 4.8 | 84.3 | 52 | 24 | 155 | 18 | 7.0 | 2298 | 1.4 |
| | 95th %ile | | | 1.68 | 2.52 | 103 | 9.9 | 113.0 | 69 | 35 | 210 | 28 | 7.0 | 2893 | 2.9 |
| Central Basin | Median | 84 | 1680 | 0.13 | 1.20 | 46.3 | 5.3 | 51.6 | 32 | 3 | 69 | 19 | 16.8 | 2359 | 1.5 |
| | 95th %ile | | | 0.19 | 1.87 | 78.8 | 7.4 | 86.2 | 50 | 5 | 122 | 23 | 16.8 | 2608 | 2.2 |
| Eastern Basin | Median | 110 | 2200 | 0.24 | 0.36 | 13.6 | 9.0 | 22.7 | 9 | 3 | 18 | 27 | 22.0 | 2796 | 2.6 |
| | 95th %ile | | | 0.73 | 1.11 | 51.1 | 11.5 | 62.5 | 28 | 8 | 84 | 32 | 22.0 | 3081 | 3.3 |
| | Grootvlei | | | 0.71 | 1.06 | 49.8 | 10.4 | 60.2 | 26 | 5 | 77 | 30 | 22.0 | 2959 | 3.0 |

Assumptions: 1. A leaching fraction of 0.2 (i.e. 20% of applied water drains). 2. Mg dominates soil exchangeable cations with a proposed concentration of 50 $mmol_c$ $kg^{-1}$; this is replaced by Ca through a soil depth of 1 m and may contribute to salt load in the return flow during early stages but could also be sequestered in the precipitation product of Al sulfate addition. 3. Sulfate is not significantly immobilised by metal precipitates and remains in solution except for gypsum crystallization. 4. Ca is sequestered as gypsum and as exchangeable Ca equivalent to exchangeable Mg. 5. Soluble salts in return flow consist of chloride and sulfate with residual Na plus desorbed Mg and Ca in equilibrium with gypsum. SAR (sodium adsorption ratio) is calculated accordingly. 6. Limestone ($CaCO_3$) applications will be needed periodically to neutralise acidity from slow oxidation of Fe and Mn in the metal sludge. Annual cost at R500 $t^{-1}$ will range from about R1500 $ha^{-1}$ (central, eastern) to R17000 $ha^{-1}$ (land irrigated with western waters).

**Table 9 Total dissolved solids (TDS) in applied mine water (calculated from chemical analysis) and expected TDS in return flow water after irrigation with a leaching fraction of 0.2, and the fate of solids in the mine water and applied ameliorants (Al sulfate, lime and limestone).**

| Water source | Water quality class | Initial TDS | Return flow TDS[1] | TDS Difference | Original mine water solids[2] | Added remedial solids[3] | Solids dissolved in return flow[4] | Net solids gain on land[5] | Percentage of original solids in return flow |
|---|---|---|---|---|---|---|---|---|---|
| | | mg $L^{-1}$ | | % | t $ha^{-1}$ $year^{-1}$ | | | | % |
| Western Basin | Median | 4628 | 2298 | -50 | 84 | 83 | 8 | 167 | 10 |
| | 95th %ile | 5434 | 2893 | -47 | 99 | 112 | 11 | 211 | 11 |
| Central Basin | Median | 4319 | 2359 | -45 | 79 | 27 | 9 | 106 | 11 |
| | 95th %ile | 4592 | 2608 | -43 | 84 | 43 | 10 | 127 | 12 |
| Eastern Basin | Median | 2292 | 2796 | 22 | 42 | 14 | 10 | 55 | 24 |
| | 95th %ile | 3358 | 3081 | -8 | 61 | 42 | 11 | 103 | 18 |
| | Grootvlei | 2879 | 2959 | 3 | 53 | 37 | 11 | 90 | 21 |

[1] Expected return flow TDS was calculated on the basis that Ca concentration is that of a saturated gypsum solution, Na concentration is five times greater than in applied water because of evaporation, and sulfate concentration is sufficient to balance the charge of Ca and Na ions after chloride has been accounted for. It is assumed that no other ions are present in concentrations that would significantly contribute to TDS. [2] From initial TDS and annual depth of irrigation averaging 5 mm $day^{-1}$. [3] Sum of Al sulfate and lime dosage calculated in t $ha^{-1}$ $yr^{-1}$ from irrigation rate of 5 mm $d^{-1}$ and dosage in kg $m^{-3}$ plus limestone application rate (Table 8). [4] Calculated from return flow TDS and volume of return flow based on a leaching fraction of 0.2 (i.e. one fifth of the volume irrigated). [5] Sum of original and added solids (2 and 3 above).

**Figure 2 Ergo's Brakpan Dam tailings storage facility south of Brakpan adjoining the Blesbokspruit and the Heidelberg Road. The top of the dam is 3.5 km wide and has an area of about 600 ha. Slurry is still pumped into the facility from a site adjacent to where underground water will be pumped at Grootvlei near Springs.**

## 2.4 SUMMARY AND CONCLUSIONS

This chapter has presented an assessment of water quality data that are available, has discussed treatment methods which are most likely to be employed in the short-term, and has presented some alternative treatments that may be worth evaluating in the longer term if the irrigation option for mine water disposal is retained. The previous experimental work with the limestone-lime process that was reviewed did not include analytical data adequate for detailed calculation of the salt balance using the SWB model which is one of the main objectives of this project. Although there are some data for the composition of the effluent from one HDS plant (at Grootvlei), the more recent data relevant to effective plant operation (in terms of Fe precipitation) are incomplete with regard to solutes such as Mg and bicarbonate alkalinity and parameters crucial to assessing irrigability cannot be calculated reliably. The use of geochemical models such as PHREEQC to predict water quality after mine water treatment with chemicals is not considered to be reliable either because redox and carbonate equilibria are almost certainly subordinate to kinetics in determining solution composition. Two approaches should therefore be used for obtaining input water quality data for SWB calculation in the current project. The first is to consider a range of likely compositions based on reaction stoichiometry of mine water treatment (including some of the alternative treatments that have been discussed). The second, preferable approach would be to obtain fresh samples from whatever HDS facilities are currently running and obtain comprehensive, reliable analyses for all major constituents as well as trace elements. The extent to which these approaches could be pursued will become evident later in the report. The next three chapters will deal with laboratory experiments to simulate the land treatment option as well as assessment of the alternative chemical amendments discussed above.

# CHAPTER 3 LABORATORY SIMULATION OF A LAND TREATMENT METHOD FOR DECONTAMINATING METALLIFEROUS MINE WATER

## 3.1 INTRODUCTION

The problem of rising groundwater in the gold mines is receiving urgent attention (DWA, 2012). One option is to neutralise the water and irrigate crops (Makgae et al., 2013) as has been demonstrated for colliery waters (Annandale et al., 2002). In high density sludge (HDS) plants built to contain acidic metal loads the favoured method of neutralisation is the limestone-lime process (Maree et al., 2013). In the review of pre-treatment methods for irrigation (Chapter 2) we anticipated that limestone alone may be adequate provided the manganese (Mn), iron (Fe) and trace metals remaining in solution are not toxic. However, a key requirement in neutralising Fe- and Mn-laden mine water is aeration. This affects the size and capital cost of the HDS plant (Maree et al., 2013).

There are three ways in which dissolved Fe and Mn can be removed without prior aeration. A novel method involves contact with Mn oxide (Duarte and Ladeira, 2011) and might have been impractical but for a large deposit of Fe-Mn wad mined near Ventersdorp for uranium (U) extraction by gold mines (Pack et al., 2000). Incorporating the wad in mine water neutralisation could increase efficiency because its combined oxidative and adsorptive effect should reduce the need for aeration mentioned in the previous paragraph.

The second method is to remove divalent metal cations by alkaline co-precipitation as double hydroxides with a trivalent cation such as aluminium (Al). Besides Fe and Mn, magnesium (Mg) would also precipitate along with the trace metals nickel (Ni), copper (Cu) and zinc (Zn) (Taylor, 1984). A logical reactant would be Al sulfate, one of the most common chemicals used in water purification. It would conceivably be used in a 1:3 mole ratio of Al to divalent cations (Fey et al., 2013). Lime is used to secure metal precipitation and the additional sulfate would therefore be sequestered as gypsum prior to or during irrigation. Aluminium sulfate is produced in large quantities at Springs close to where Eastern Basin water is pumped out at the Grootvlei mine. Some preliminary estimates of quantities and costs have been presented in Chapter 2. This approach does not seem to have been tried for cleaning metalliferous, sulfuric mine water, probably because the principle is counter-intuitive: both Al and sulfate are already present as major ions in the mine water. The key justification for Al addition is to prime the water with sufficient Al to form double hydroxide precipitates with divalent cations (Fe, Mn, Mg and the trace metals mentioned above). A greater volume of sludge would be generated but the trade off, hypothetically, is a cleaner water produced more efficiently because of the reduced need for aeration and for raising the pH excessively in the process of neutralisation.

While both the above methods hold promise there is potentially an even better approach in which raw mine water is applied directly to land. Neutralisation chemicals are still added but as soil amendments. This allows more time for reaction between lime or limestone, dissolved metals and oxygen, and obviates the need to build HDS plants and dispose of the attendant sludge. It also exploits the ion exchange, adsorption and catalytic oxidation properties of soil colloids (Lee et al., 2002; Madden and Hochella, 2005). Precedents for this approach are rare (Cronce et al., 1980) but the scale, cost and urgency of the current situation demands that all options be considered especially if they could reduce cost without drastically affecting terrestrial or aquatic habitat. The factor most strongly favouring land treatment of mine water, however, is an expected improvement in soil properties, at least for some soils and mine tailings based on the properties known to be conferred by Fe oxides (Sumner, 1963). Clays would be made more friable and permeable, and sands more cohesive and retentive, by metal hydroxides and gypsum accumulated through a decade or more of land treatment. With proper irrigation and drainage management the production of crops can be envisaged and the small fraction of salts remaining soluble could probably be intercepted and dealt with as outlined by Westcot (1988). A hybrid approach involving Mn wad or Al sulfate might also work well on poor substrates such as mine tailings. These ideas can be tested in the laboratory and the objective was to do these without delay while there is still an opportunity for incorporating them if they have sufficient merit into mine water management plans.

## 3.2 MATERIALS AND METHODS

*Mine water*

Originally it was intended to study mine water from all three basins of the Witwatersrand goldfields. It was later found, however, that there is no ready basis for collecting fresh samples from the central and eastern basins. Furthermore it was considered inadvisable to work with synthetic mine water. All experiments were therefore conducted on water from the western basin. This was collected from the research site adjoining the high density sludge (HDS) plant at Randfontein gold mine near Krugersdorp (Appendix 1a). The water was pumped directly into twelve 20 L plastic tubs and kept sealed until required. The water was clear but underwent a small degree of oxidation within a few hours of collection as indicated by a fine, reddish brown deposit that developed on the walls of the storage tubs during transport to the laboratory. Such oxidation tends to be self-limiting because it produces a drop in pH that inhibits the rate of oxidation, especially if the solution is kept in an airtight container. Water from this site has been well characterised and its amelioration studied in some detail (Maree et al., 2013).

*Ferromanganese wad*

Several kg of wad (a porous, low bulk density, Mn oxide with associated Fe oxide) was collected from a stockpile at the Ryedale mine near Ventersdorp (Appendix 1b). The material had been crushed and coarsely screened ready for commercial use as an adsorbent, but for laboratory experiments the sample was further reduced in size by screening < 2 mm then further separating an even finer powder fraction of < 63 μm by wet sieving and drying in a shallow container under an infrared lamp. The deposit has been described in detail by Pack et al. (2000) and information on its availability and potential uses can be found at http://www.metmin.co.za.

*Aluminium sulfate*

Industrial grade Al sulfate powder was obtained from the manufacturers at Springs (Appendix 1c; www.pakamisa-industries.co.za/Aluchem/Aluchem_Products.html). A concentrated aqueous solution was prepared for use in the experiments.

*Liming materials*

Analytical reagent grade, finely powdered $Ca(OH)_2$ and $CaCO_3$ were used for the mine water neutralisation trials (Appendix 1c).

*Mine tailings*

A bulk sample of tailings was collected from the Brakpan Dam TSF (tailings storage facility) operated by Ergo (DRD Gold) between Springs and Heidelberg (Appendix 1d). The tailings were air-dried and passed through a 2 mm screen.

*Soils*

Two bulk soil samples were collected from farmland in the vicinity of the Brakpan Dam TSF. The first, a black clay (labelled BC in on the map in Appendix 1e), was from a cultivated fire break adjoining maize fields and is a dark coloured, strongly structured, melanic topsoil horizon. Margalitic clay soils such as this one (Bonheim form) are typically derived from basic igneous rock (dolerite), and are widespread in the Highveld region specifically in the vicinity of decant points for mine water in the Witwatersrand Basin. This soil was chosen anticipating a high buffer capacity (smectite is typically the dominant clay mineral) and water retention capacity and the likelihood that its properties, including a large specific surface and a high base saturation, would interact positively with alkaline amendments in neutralising mine water and immobilising metal contaminants. It represents the opposite extreme to the mine tailings which are mostly made up of sterile, chemically inert, acidic quartz sand.

The second soil is the orthic A horizon of a red loam (Hutton form; labelled RL in Appendix 1e) sampled adjacent to a maize field; it is probably derived from the weathering of dolomite, and was selected for its likely smaller buffering and water retention capacity compared with the black clay as well as better drainage and structural stability (low shrink-swell) imparted by a natural concentration of Fe oxides and kaolinitic clay. Such soils are common in the region. The likelihood that the red loam would have its properties altered substantially by accumulation of ferric hydroxides from mine water was expected to be much smaller than for the black clay. The idea of sampling both these soils was to find out how differently they and the adjacent mine tailings might respond to the application of large volumes of mine water, with and without alkaline amendment. Both soils were air-dried and gently crushed to pass a 2 mm screen.

*Determination of lime requirement for neutralising mine water*

The base neutralising capacity (BNC) of the mine water was determined by serial titration. Five aliquots of mine water neutralised to varying degrees by measured addition of fresh, standard 0.05 M NaOH were aerated and allowed to equilibrate overnight with occasional stirring before measuring pH and plotting a titration curve.

### *3.2.1 Simulated land treatment of mine water using amended soil and mine tailings*

In designing the project it was thought feasible to simulate the irrigation of land with mine water at a rate of 5 mm $d^{-1}$ for 10 years, allowing the water to evaporate but periodically applying a leaching fraction so as to minimise the build-up of soluble salts. It was proposed to do this over three weeks in a suitable environment for evaporation such as a glasshouse with extractor fans, at a solution: solid ratio equivalent to the mine water being applied to a depth of 1 m in the soil or mine tailings. The intention was to study two or three soils as well as mine tailings using the full range of amendments in various combinations, i.e. not only hydroxide and carbonate liming materials but also Fe-Mn wad and Al sulfate.

It transpired that the work could be done most effectively by carrying out two experiments in parallel, one at the University of the Western Cape (UWC) comparing the black clay soil with mine tailings, and the other at the University of Pretoria (UP) using a similar technique and experimental treatments but with key modifications and comparing the two soils with each other but not the mine tailings. It was also decided that including treatments with Mn oxide or Al sulfate in the land treatment simulation would have little practical relevance since the expected advantage of these amendments is to hasten the removal from solution of Fe and/or Mn in the water treatment plant, whereas land treatment would allow removal of these ions through more protracted neutralisation and oxidation and thus obviate the need for prior amendment. The effectiveness of these conditioners in mine water treatment and their possible relevance to land treatment using mine tailings will be dealt with in Chapter 4. There was some overlap of the UWC and UP experiments in terms of the applied treatments and of the black clay being common to both, which afforded an assessment of reproducibility.

#### *3.2.1.1 Comparison of the mine tailings and black clay soil (UWC-based experiment)*

A facility became available at UWC which was ideal for the land treatment trial. It was recently built for a WRC-funded project on evaporation of brines, and consists of two specially constructed trolleys each with five racks to accommodate shallow, 3 L capacity glass basins (commercial, Pyrex, oven dishes) and infrared heating lamps (175 W) mounted on an adjustable stand above each basin. The small room housing this apparatus was air-conditioned allowing for moist air to be extracted and replaced with dry air continuously. A preliminary test indicated that with the lamps mounted 35 cm above the basin, 250 mL of water added to 400 g soil in the basin could easily be evaporated to dryness overnight. The warmest temperature measured on the underside of the basins once the contents had dried did not exceed 32°C. Ten positions on the two trolleys constrained the experiment to twelve treatments, nine with soil or tailings and three in small basins placed within one large one. Table 10 is a summary of the experimental design. The procedure that follows is illustrated photographically in Appendix 2.

The 240 mL of water that for 20 days was added and mixed daily and each time evaporated overnight from 400 g tailings or soil is equivalent to an average of 5 mm $d^{-1}$ being applied to and evaporated from a 1 m depth of tailings or soil in the field for 10 years, assuming a bulk density of 1500 kg $m^{-3}$. The amendment quantities for $Ca(OH)_2$ and $CaCO_3$ have stoichiometrically equivalent neutralising value although the hydroxide is a stronger base. The amounts applied were calculated to achieve complete neutralisation (including metal oxidation and precipitation) to a pH of 7.5 based on prior determination of the mine water BNC with NaOH and assuming incorporation of the amendment and mine water to a depth of 1 m. The full amount of amendment was applied and thoroughly mixed before the first water was added. Three of the treatments (TP0, SP0 and SPH) involved pure water (label P, which was actually tap water) instead of mine water (label M), while three treatments (0M0, 0MC, 0MH) had neither soil (S) nor tailings (T) and were included in order to identify and quantify the precipitated solids from the daily evaporation of mine water, alone or reacted with Ca carbonate (C) or hydroxide (H) in the same ratio as used in the soil or tailings. For these treatments three miniature glass basins were placed within a large basin under a single infrared lamp which was lowered to ensure complete evaporation each day. No leaching was performed except at the termination of the experiment when the weighed, dry contents of the basins were equilibrated with 90 mL water overnight after which solids were separated by vacuum filtration and dried. The filtrate was also saved for analysis.

**Table 10 Soil, water and amendment combinations in the first land treatment simulation trial**

| Treatment code | Soil | Water | Amendment | Mass of soil (g) | Daily water (g) | Mass of amendment (g) |
|---|---|---|---|---|---|---|
| 0M0 | None | Mine | None | 0 | 80 | 0 |
| 0MC | None | Mine | $CaCO_3$ | 0 | 80 | 1.60 |
| 0MH | None | Mine | $Ca(OH)_2$ | 0 | 80 | 1.18 |
| TP0 | Mine tailings | Pure | None | 400 | 240 | 0 |
| TM0 | Mine tailings | Mine | None | 400 | 240 | 0 |
| TMC | Mine tailings | Mine | $CaCO_3$ | 400 | 240 | 4.80 |
| TMH | Mine tailings | Mine | $Ca(OH)_2$ | 400 | 240 | 3.55 |
| SP0 | Black clay | Pure | None | 400 | 240 | 0 |
| SM0 | Black clay | Mine | None | 400 | 240 | 0 |
| SMC | Black clay | Mine | $CaCO_3$ | 400 | 240 | 4.80 |
| SMH | Black clay | Mine | $Ca(OH)_2$ | 400 | 240 | 3.55 |
| SPH | Black clay | Pure | $Ca(OH)_2$ | 400 | 240 | 3.55 |

In the case of the soil (S) and tailings (T) treatments leaching was performed every 4 or 5 days, for which purpose additional water was added, the amount being adjusted in later leachings to ensure sufficient leachate for analysis. The amounts of extra water for leaching and the yield of leachate were recorded on each occasion. Leaching was carried out through filter paper on a large Buchner funnel under vacuum (Appendix 2). Five leachings were performed, the first four after about 30 minutes equilibration with mine water in the "M" treatments and the final one with pure (tap) water after overnight equilibration in the covered pans at room temperature. After leachate extraction the filter cake was tipped back into the basin and dried overnight under the infrared lamp. With resumption of the daily wetting, this cake, in the case of the black clay, needed to be wetted gradually and broken up with a spatula. With transfers of solids between filter funnel and basin the cumulative loss of material during the whole experiment was negligible, roughly estimated to be not more than 1 or 2 percent (see photo of filter cake removal in Appendix 2).

Electrical conductivity and pH were determined in the fresh leachates which were filtered and analysed for anions (sulphate, chloride and nitrate) by ion chromatography using a Dionex suppressed system with carbonate/bicarbonate eluent, and for metal cations and other elements by inductively coupled plasma – optical emission spectrometry (ICP-OES). The mine water, and the tap water used as "pure" water, were also analysed.

### *3.2.1.2 Comparison of the black clay and red loam soils (UP-based experiment)*

The second experiment, at the University of Pretoria, was conducted in the soils laboratory making use of electric heaters to generate an evaporating environment. The original intention had been to use the glasshouse but the space available had inadequate control to overcome winter temperatures. The soils and their treatments for this experiment are summarised in Table 11.

As can be seen from the correlation in the second column of Table 11, the first four soil-treatment combinations are a repetition of the first experiment but there were some important differences.

Firstly, although in both experiments the addition of water was based on the water content needed to achieve a saturated paste, the first experiment applied this as a fixed amount each day to dry soil whereas the second experiment determined, by weighing, and recorded the amount of water needed to restore the saturation water content, with overnight evaporation typically having been incomplete and showing some variability during the course of the experiment.

Secondly, the amount of liming materials added was based on an estimate of mine water BNC of 18.4 mmol $L^{-1}$ which is about 90% of that which formed the basis for liming in the first trial. Furthermore, the red loam was found to have a saturation water content that was two-thirds that of the black clay so the quantities of alkaline amendments applied to this soil were proportionately smaller, anticipating that the total water addition would end up being reduced by the same ratio.

**Table 11 Soils and experimental treatments in the second land treatment simulation**

| Treatment code | Correlation | Soil | Water added | Amendment | Water leached |
|---|---|---|---|---|---|
| BC-MWNL | SM0 | Black clay | Mine | None | Mine |
| BC-MWOH | SMH | Black clay | Mine | $Ca(OH)_2$ | Mine |
| BC-MWCO | SMC | Black clay | Mine | $CaCO_3$ | Mine |
| BC-DWOH | SPH | Black clay | Pure | $Ca(OH)_2$ | Pure |
| RS-MWNL | $S_rM0$ | Red loam | Mine | None | Mine |
| RS-MWOH | $S_rMH$ | Red loam | Mine | $Ca(OH)_2$ | Mine |
| RS-MWCO | $S_rMC$ | Red loam | Mine | $CaCO_3$ | Mine |
| RS-DWOH | $S_rPH$ | Red loam | Pure | $Ca(OH)_2$ | Pure |
| BC-MWOH# | $SMH_{lp}$ | Black clay | Mine | $Ca(OH)_2$ | Pure |
| RS-MWOH# | $S_rMH_{lp}$ | Red loam | Mine | $Ca(OH)_2$ | Pure |

Thirdly, the addition of amendments was split, so that each application took place following the collection of a leaching fraction. The latter was performed seven times during the 20-day experiment simulating what would roughly amount to a seasonal leaching of soluble salts under field conditions. The amount of water applied to leach the soils on each occasion was an additional 10% of that added.

Another difference between the experiments was the inclusion of a leaching treatment in which the mine water-irrigated, hydroxide-amended soil was leached with pure water (in this case deionised and not tap water water) instead of mine water (suffixes # and lp in columns 1 and 2 of Table 11). And finally, in the second experiment most of the treatments on both soils were applied in triplicate, allowing for statistical appraisal.

Analyses conducted on leachates in the second experiment were similar to those in the first but the elemental analysis by ICP was done on a single composite sample from the leachates for each treatment. Titratable acidity (residual BNC as performed on the original mine water) was determined in the fresh leachates. Some soil analyses using standard methods were conducted on soil and tailings residues from both experiments. Exchangeable acidity and Al were determined by 1M KCl extraction and the status of exchangeable base cations (including Mn) was assessed by 1M ammonium acetate (pH 7) extraction. A more detailed account of the second experiment has been included in Appendix 3.

#### *3.2.1.3 Simulation of a more concentrated land treatment in the mine tailings (Extension of the UWC trial)*

The change in physical properties as a result of secondary solids accumulating through mine water evaporation has so far been evaluated qualitatively, in terms of texture and consistence, especially in the tailings. A follow-up trial with the tailings was carried out in which all the mine water was added at once to the lime- or limestone-enriched tailings using a solid-solution ratio simulating the same 10-year, 5 mm day irrigation with mine water as was done previously but in such a way as to represent confinement of the wetting, neutralisation and precipitation reactions to the top 0.2 or 0.4 m instead of 1 m of tailings. This was achieved by means of the five treatments in Table 12 which included a preliminary test of the effects of dissolving some Al sulfate in the mine water and adding ferromanganese (Fe-Mn) wad to the tailings. In this experiment TMC and TMH have their earlier meanings, suffixes "+" and "0.5+" refer to simulation of 0.2- and 0.4-m incorporation depths, respectively, while "alwad" earmarks the additional modification with Al sulfate and ferromanganese wad. The mine water, 2.5 L initially, was stirred with the 40 or 80 g tailings once daily during evaporation which required five days to reach dryness under infrared lamps suspended 25 cm above the basins.

**Table 12 Treatments used to further enrich the mine tailings with secondary solids**

| Treatment | Mass tailings (g) | Mass Ca hydroxide (g) | Mass Ca carbonate (g) | Mass wad (g) | Mass Al sulfate in mine water (g) | Volume of mine water (mL) |
|---|---|---|---|---|---|---|
| TMC 0.5+ | 80 | 0 | 2.4 | 0 | 0 | 2500 |
| TMH 0.5+ | 80 | 1.78 | 0 | 0 | 0 | 2500 |
| TMC + | 40 | 0 | 2.4 | 0 | 0 | 2500 |
| TMH + | 40 | 1.78 | 0 | 0 | 0 | 2500 |
| TMH 0.5+ alwad | 80 | 2.00 | 0 | 2 | 1 | 2500 |

## 3.3 RESULTS AND DISCUSSION

The mine water titration data (Figure 3) are well fitted by either of two trend lines. Despite a good linear fit it is likely that two buffer ranges occur at around pH 7 and above pH 9, related to oxidation and hydrolytic precipitation of Fe and Mn and possibly involving other solutes such as Mg. The polynomial trend line may therefore be a more accurate representation. To achieve the traditional phenolphthalein end point of pH 8.4 would require the same base addition using either line, i.e. about 20 mmol $L^{-1}$ of OH, and this value was used in calculating the lime needed to counteract the mine water's acidity (base neutralising capacity) in the experimental treatments.

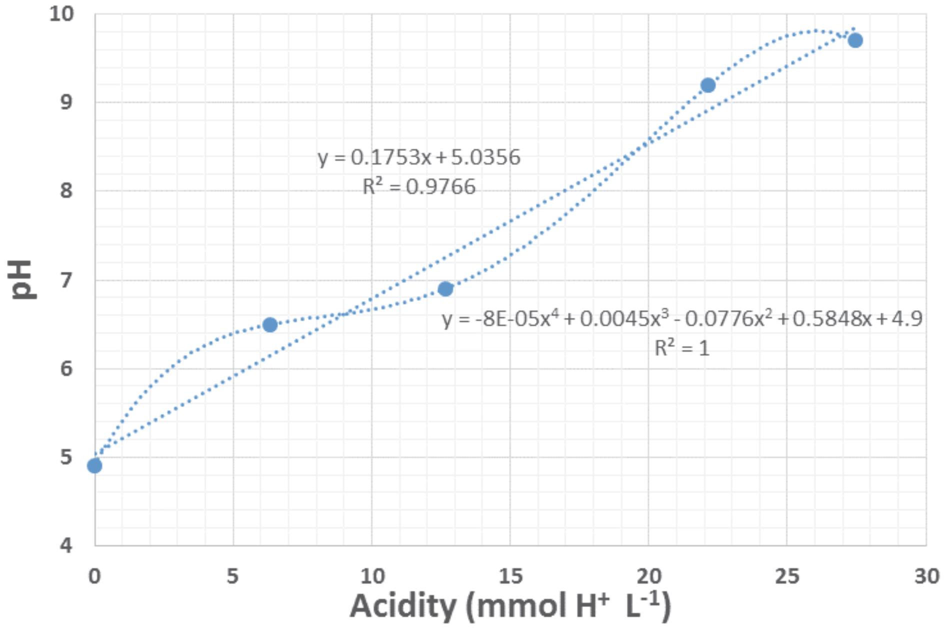


**Figure 3 Serial titration of Randfontein mine water with NaOH, plotting pH response against base addition expressed as acidity per unit volume of the mine water**

The main results of the first simulation trial are presented in Tables 13 to 19 and Figures 2 and 3. Some soil analysis results for both trials are given in Table 20, while Table 21 summarises pH and EC data for the seven leachates in the second trial. The results in Tables 13-17 consist of the volume, pH, EC and chemical composition of five leachates collected from each of the nine experimental treatments of either mine tailings (T) or the black clay soil (S) with various combinations of mine water (M) or pure water (P) and either Ca hydroxide (H), Ca carbonate (C) or zero (O) amendment. It was possible to calculate net evaporation by subtracting the leachate volume from the volume of water that had been applied up to that point. This is reported in Tables 13-17 as the cumulative net evaporation in mm, based on the ratio of volume of water to mass of soil, an assumed soil or tailings bulk density of 1.5 kg $m^{-3}$, and a depth of soil to be amended of 1 m.

It is this assumption about a field context which is key to being able to simulate 10 years of land treatment during 20 days in the laboratory. In some respects it seems rather like a magician's sleight of hand, stating that overnight, with merely an infrared lamp to dry the wet soil in a glass basin, one has achieved the same result, in terms of leaving behind a concentration of precipitated salts and metal hydroxides, as that which would affect a metre depth of soil after the evaporation of about 1000 mm of mine water, which in the field would take six months to accomplish. It can be seen from the five Tables 13-17 that cumulative net evaporation had reached about 4 m by the time the first leaching took place and progressed at a steady rate until, at the end of the experiment, it had accumulated to nearly 16 m in the tailings and more than 18 m in the clay soil. The difference of 2 m is due to the fact that water retention by the sandy tailings was much smaller, allowing the collection of double the volume of leachate in comparison with the clay soil. This is of course why sand becomes impoverished by leaching faster than clay soil and, conversely, why clayey material makes a better repository for waste than sand.

The EC and pH of the leachates have been plotted against net evaporation in Figure 4 for the mine tailings and Figure 5 for the clay soil. These plots have trend lines fitted to the data for the first four leachings only, in which mine water had been employed. Not only was the fifth leaching made with fresh water but also it took place following longer equilibration, overnight. The unamended tailings are very acidic in their raw state with pH only slightly above 2, but this climbs steadily in both the TPO and TMO treatments to about 5 and 3, respectively, after five leachings with pure water or mine water. The mine water itself had a pH of 3.4 (Table 18). The EC of the first mine tailings leachate with pure water is quite high (50 mS $m^{-1}$) but drops then levels off at a value which suggests that much of the solute derives from the dissolution of gypsum, an interpretation confirmed by the corresponding levels of sulfate and Ca in Table 17 since gypsum has a solubility of between 2 and 3 g $L^{-1}$. That the mine tailings already contain gypsum probably reflects a history of amelioration with lime during disposal, although the acidic pH suggests this is incomplete, possibly because of further oxidation of pyrite in the tailings. The presence of gypsum may explain why there were lumps in the tailings sample; these were friable but surprisingly coherent given the sandy texture and were removed by screening (see the first photo in Appendix 2). Gypsum and other salts may also accumulate at and near the surface due to capillary rise and evaporation of water within the tailings, giving an exaggerated impression of the concentration of salts, and acidity, in the TSF as a whole. The sample, from about 10-30 cm, was probably not taken deeply enough to preclude this possibility.

Returning to Figure 4 it is evident that applying mine water and evaporating it produced a gradual rise in salinity of the leachate (this is equivalent to irrigation return flow, so the trend is of practical significance), although this was contained to a large degree probably not only by the intermittent leaching but also by the precipitation of solids. The final leaching with fresh water produced a sharp drop in EC, confirming the expectation that excess soluble salts are easily removed from the tailings.

**Table 13 Yield and composition of the first of five successive leachates (four with mine water and the last with fresh water) from the first simulation trial, including the calculated equivalent, net, cumulative evaporation based on a 1 m soil depth and the salt load in the leachate based on the volume times the total mass of solutes from elemental analysis. Blank cells signify a concentration below the probable limit of detection.**

| Treatment | | Fresh mine water | Evaporated mine water | | |
|---|---|---|---|---|---|
| | | | OMO | OMC | OMH |
| Volume of leachate (mL) | | | 90 | 90 | 90 |
| Cumulative net evaporation | | | 1520 | 1520 | 1520 |
| pH | | 3.38 | 2.11 | 5.91 | 7.09 |
| EC (dS $m^{-1}$) | | 0.520 | 2.75 | 1.91 | 1.87 |
| Concentration (mg $L^{-1}$) | Ca | 696 | 393 | 380 | 384 |
| | Mg | 232 | 2800 | 2751 | 2733 |
| | Na | 92 | 1546 | 1604 | 1645 |
| | K | | 38 | 174 | 179 |
| | Fe | 342 | 3006 | 7 | |
| | Mn | 64 | 483 | 430 | 11 |
| | Al | | | | |
| | Si | 6 | 10 | 2 | 1 |
| | Ni | | 4.2 | 0.4 | |
| | Co | | 2.4 | 0.8 | |
| | Zn | | 1.1 | -0.3 | |
| | Cu | | 2.3 | 2.3 | 1.8 |
| | As | | | 2.4 | 0.7 |
| | Cl | 31 | 468 | 734 | 843 |
| | $SO_4$ | 3494 | 41321 | 17416 | 18661 |
| | $NO_3$ | | | | |
| | Total | **4942** | **50070** | **23503** | **24454** |
| $mmol_c$ $L^{-1}$ | Ca | 35 | 20 | 19 | 19 |
| | Mg | 19 | 233 | 229 | 228 |
| | Na | 4 | 67 | 70 | 72 |
| | K | 0 | 1 | 4 | 5 |
| | Fe | 12 | 107 | 0 | 0 |
| | Mn | 2 | 18 | 16 | 0 |
| | Al | 0 | 0 | 0 | 0 |
| | Total | 73 | 446 | 338 | 323 |
| % | Ca | 48 | 4 | 6 | 6 |
| | Mg | 27 | 52 | 68 | 70 |
| | Na | 5 | 15 | 21 | 22 |
| | K | 0 | 0 | 1 | 1 |
| | Fe | 17 | 24 | 0 | 0 |
| | Mn | 3 | 4 | 5 | 0 |
| | Al | 0 | 0 | 0 | 0 |
| $mmol_c$ $L^{-1}$ | Cl | 1 | 13 | 21 | 24 |
| | $SO_4$ | 73 | 861 | 363 | 389 |
| | $NO_3$ | 0 | 0 | 0 | 0 |
| Sum anion charge | | **74** | **874** | **384** | **413** |
| Sum cation charge | | **72** | **445** | **338** | **323** |

**Table 14 Yield and composition of the second leachate with mine water, as in Table 13**

| Treatment | | Second leaching | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | TPO2 | TMO2 | TMC2 | TMH2 | SPO2 | SMO2 | SMC2 | SMH2 | SPH2 |
| **Volume of leachate (mL)** | | 125 | 125 | 120 | 115 | 40 | 85 | 35 | 65 | 55 |
| **Cumulative net evaporation** | | 7200 | 7163 | 7163 | 7200 | 8288 | 8063 | 8306 | 8138 | 8138 |
| **pH** | | 2.44 | 2.52 | 5.64 | 7.15 | 7.07 | 5.08 | 7.02 | 7.20 | 7.91 |
| **EC (dS m$^{-1}$)** | | 0.37 | 1.27 | 0.96 | 0.85 | 0.09 | 0.78 | 0.69 | 0.63 | 0.10 |
| **Concentration (mg L$^{-1}$)** | **Ca** | 664 | 459 | 444 | 466 | 64 | 478 | 582 | 618 | 137 |
| | **Mg** | 30 | 921 | 904 | 848 | 35 | 541 | 366 | 272 | 29 |
| | **Na** | | 457 | 509 | 473 | 3 | 304 | 262 | 229 | 4 |
| | **K** | | | 52 | 68 | 1 | 27 | 15 | 12 | 1 |
| | **Fe** | 91 | 970 | 5 | | | 0 | | | |
| | **Mn** | 2 | 275 | 212 | 101 | | 141 | 20 | 5 | |
| | **Al** | 27 | 41 | | | | | | | |
| | **Si** | 2 | 7 | 6 | 2 | 17 | 24 | 2 | 2 | 2 |
| | **Ni** | 0.5 | 2.0 | | | | | | | |
| | **Co** | 0.2 | 0.8 | 0.5 | 0.2 | | 0.5 | | | |
| | **Zn** | | | | | | | | | |
| | **Cu** | | | | | | | | | |
| | **As** | 0.0 | | | | 0.8 | | 0.1 | | |
| | **Cl** | 21 | 122 | 671 | 243 | 75 | 295 | 720 | 289 | 77 |
| | **SO$_4$** | 1819 | 10666 | 22895 | 8273 | 103 | 5045 | 9195 | 3479 | 95 |
| | **NO$_3$** | | | | | 179 | | | | 8 |
| | **Total** | **2656** | **13921** | **25698** | **10473** | **479** | **6855** | **11161** | **4907** | **354** |
| **mmol$_c$ L$^{-1}$** | **Ca** | 33 | 23 | 22 | 23 | 3 | 24 | 29 | 31 | 7 |
| | **Mg** | 3 | 77 | 75 | 71 | 3 | 45 | 30 | 23 | 2 |
| | **Na** | 0 | 20 | 22 | 21 | 0 | 13 | 11 | 10 | 0 |
| | **K** | 0 | 0 | 1 | 2 | 0 | 1 | 0 | 0 | 0 |
| | **Fe** | 3 | 35 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | **Mn** | 0 | 10 | 8 | 4 | 0 | 5 | 1 | 0 | 0 |
| | **Al** | 3 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | **Total** | 42 | 169 | 129 | 120 | 6 | 88 | 72 | 64 | 9 |
| **%** | **Ca** | 79 | 14 | 17 | 19 | 50 | 27 | 40 | 48 | 72 |
| | **Mg** | 6 | 45 | 58 | 59 | 47 | 51 | 42 | 35 | 26 |
| | **Na** | 0 | 12 | 17 | 17 | 2 | 15 | 16 | 16 | 2 |
| | **K** | 0 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 0 |
| | **Fe** | 8 | 21 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | **Mn** | 0 | 6 | 6 | 3 | 0 | 6 | 1 | 0 | 0 |
| | **Al** | 7 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **mmol$_c$ L$^{-1}$** | **Cl** | 1 | 3 | 19 | 7 | 2 | 8 | 20 | 8 | 2 |
| | **SO$_4$** | 38 | 222 | 477 | 172 | 2 | 105 | 192 | 72 | 2 |
| | **NO$_3$** | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 |
| **Sum anion charge** | | **38** | **226** | **496** | **179** | **7** | **113** | **212** | **81** | **4** |
| **Sum cation charge** | | **41** | **168** | **128** | **119** | **5** | **87** | **71** | **63** | **8** |
| **Solids mass balance g/leach** | | 0.33 | 1.74 | 3.08 | 1.20 | 0.02 | 0.58 | 0.39 | 0.32 | 0.02 |

**Table 15 Yield and composition of the third leachate with mine water, as in Table 13**

| Treatment | | Third leaching | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | TPO3 | TMO3 | TMC3 | TMH3 | SPO3 | SMO3 | SMC3 | SMH3 | SPH3 |
| Volume of leachate (mL) | | 155 | 150 | 120 | 125 | 90 | 75 | 95 | 75 | 100 |
| Cumulative net evaporation | | 11231 | 11213 | 11325 | 11344 | 12750 | 12581 | 12750 | 12656 | 12563 |
| pH | | 3.40 | 2.66 | 6.10 | 6.01 | 6.72 | 4.49 | 6.82 | 6.83 | 7.89 |
| EC (dS $m^{-1}$) | | 0.27 | 1.48 | 1.11 | 1.06 | 0.10 | 1.04 | 0.84 | 0.82 | 0.11 |
| Concentration (mg $L^{-1}$) | Ca | 572 | 357 | 520 | 494 | 111 | 588 | 769 | 764 | 192 |
| | Mg | 9 | 1045 | 0 | 0 | 60 | 0 | 727 | 644 | 40 |
| | Na | | 524 | 896 | 888 | 25 | 693 | 667 | 622 | 15 |
| | K | | | 95 | 109 | 6 | 49 | 26 | 26 | 4 |
| | Fe | 1 | 811 | 7 | 29 | | 20 | | | |
| | Mn | | 191 | 333 | 395 | | 424 | 80 | 70 | |
| | Al | | 13 | | | | | | | |
| | Si | 1 | 7 | 13 | 10 | 25 | 45 | 4 | 5 | 5 |
| | Ni | | 1.0 | 0.8 | 0.7 | 0.1 | 1.6 | | | |
| | Co | | 0.5 | 1.6 | 1.7 | | 4.8 | 0.1 | 0.2 | |
| | Zn | | | | | | 1.2 | | | |
| | Cu | | | | | | | | | |
| | As | 0.1 | 1.0 | 5.8 | 0.4 | 3.0 | | | 1.0 | 0.3 |
| | Cl | 34 | 155 | 350 | 244 | 125 | 410 | 564 | 567 | 182 |
| | $SO_4$ | 1681 | 14957 | 11618 | 8671 | 175 | 9734 | 6573 | 5970 | 222 |
| | $NO_3$ | | | | | 136 | | | | 7 |
| | Total | **2297** | **18063** | **13840** | **10842** | **667** | **11971** | **9411** | **8669** | **668** |
| $mmol_c\ L^{-1}$ | Ca | 29 | 18 | 26 | 25 | 6 | 29 | 38 | 38 | 10 |
| | Mg | 1 | 87 | 0 | 0 | 5 | 0 | 61 | 54 | 3 |
| | Na | 0 | 23 | 39 | 39 | 1 | 30 | 29 | 27 | 1 |
| | K | 0 | 0 | 2 | 3 | 0 | 1 | 1 | 1 | 0 |
| | Fe | 0 | 29 | 0 | 1 | 0 | 1 | 0 | 0 | 0 |
| | Mn | 0 | 7 | 12 | 14 | 0 | 15 | 3 | 3 | 0 |
| | Al | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | Total | 29 | 165 | 80 | 81 | 12 | 77 | 132 | 122 | 14 |
| % | Ca | 97 | 11 | 33 | 30 | 47 | 38 | 29 | 31 | 70 |
| | Mg | 2 | 53 | 0 | 0 | 42 | 0 | 46 | 44 | 24 |
| | Na | 0 | 14 | 49 | 47 | 9 | 39 | 22 | 22 | 5 |
| | K | 0 | 0 | 3 | 3 | 1 | 2 | 1 | 1 | 1 |
| | Fe | 0 | 18 | 0 | 1 | 0 | 1 | 0 | 0 | 0 |
| | Mn | 0 | 4 | 15 | 18 | 0 | 20 | 2 | 2 | 0 |
| | Al | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $mmol_c\ L^{-1}$ | Cl | 1 | 4 | 10 | 7 | 4 | 12 | 16 | 16 | 5 |
| | $SO_4$ | 35 | 312 | 242 | 181 | 4 | 203 | 137 | 124 | 5 |
| | $NO_3$ | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 |
| Sum anion charge | | **36** | **316** | **252** | **188** | **9** | **214** | **153** | **140** | **10** |
| Sum cation charge | | **28** | **165** | **198** | **203** | **11** | **179** | **131** | **122** | **13** |
| Solids mass balance g/leach | | 0.36 | 2.71 | 1.66 | 1.36 | 0.06 | 0.90 | 0.89 | 0.65 | 0.07 |

**Table 16 Yield and composition of the fourth leachate with mine water, as in Table 13**

| Treatment | | Fourth leaching | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | TPO4 | TMO4 | TMC4 | TMH4 | SPO4 | SMO4 | SMC4 | SMH4 | SPH4 |
| Volume of leachate (mL) | | 165 | 155 | 145 | 140 | 70 | 75 | 80 | 85 | 75 |
| Cumulative net evaporation | | 14325 | 14344 | 14494 | 14531 | 16388 | 16200 | 16350 | 16238 | 16181 |
| pH | | 4.00 | 2.63 | 5.16 | 3.96 | 6.07 | 4.07 | 6.13 | 6.20 | 7.77 |
| EC (dS m$^{-1}$) | | 0.25 | 1.43 | 1.25 | 1.42 | 0.11 | 1.23 | 1.00 | 0.93 | 0.11 |
| Concentration (mg L$^{-1}$) | Ca | 719 | 471 | 454 | 421 | 112 | 519 | 626 | 634 | 179 |
| | Mg | 12 | 0 | 0 | 0 | 61 | 0 | 886 | 788 | 38 |
| | Na | 33 | 764 | 929 | 954 | 17 | 700 | 734 | 614 | 11 |
| | K | 8 | 5 | 117 | 99 | 4 | 47 | 26 | 26 | |
| | Fe | | 0 | 181 | 565 | | 76 | | | |
| | Mn | 0 | 348 | 439 | 604 | 0 | 512 | 120 | 122 | |
| | Al | | 12 | | | | 1 | | | |
| | Si | 4 | 8 | 12 | 25 | 22 | 36 | 5 | 6 | 4 |
| | Ni | | 1.5 | 1.7 | 6.4 | | 2.4 | | | |
| | Co | | 1.3 | 2.6 | 5.4 | | 6.2 | | 0.3 | |
| | Zn | | | | | | 2.0 | | | |
| | Cu | | 0.1 | | | | | | | |
| | As | | 1.0 | 4.6 | 3.4 | | 2.2 | 2.5 | 0.4 | 2.8 |
| | Cl | 87 | 166 | 276 | 306 | 119 | 374 | 604 | 422 | 116 |
| | $SO_4$ | 1518 | 14368 | 10476 | 13516 | 205 | 10178 | 9901 | 6295 | 276 |
| | $NO_3$ | | | | | 124 | | | | 9 |
| | Total | **2381** | **16146** | **12892** | **16505** | **665** | **12457** | **12904** | **8907** | **636** |
| mmol$_c$ L$^{-1}$ | Ca | 36 | 24 | 23 | 21 | 6 | 26 | 31 | 32 | 9 |
| | Mg | 1 | 0 | 0 | 0 | 5 | 0 | 74 | 66 | 3 |
| | Na | 1 | 33 | 40 | 41 | 1 | 30 | 32 | 27 | 0 |
| | K | 0 | 0 | 3 | 3 | 0 | 1 | 1 | 1 | 0 |
| | Fe | 0 | 0 | 6 | 20 | 0 | 3 | 0 | 0 | 0 |
| | Mn | 0 | 13 | 16 | 22 | 0 | 19 | 4 | 4 | 0 |
| | Al | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | Total | 39 | 71 | 89 | 107 | 12 | 79 | 142 | 129 | 13 |
| % | Ca | 93 | 33 | 26 | 20 | 49 | 33 | | 25 | 71 |
| | Mg | 3 | 0 | 0 | 0 | 44 | 0 | 52 | 51 | 25 |
| | Na | 4 | 47 | 46 | 39 | 7 | 38 | 22 | 21 | 4 |
| | K | 1 | 0 | 3 | 2 | 1 | 2 | 0 | 1 | 0 |
| | Fe | 0 | 0 | 7 | 19 | 0 | 3 | 0 | 0 | 0 |
| | Mn | 0 | 18 | 18 | 20 | 0 | 24 | 3 | 3 | 0 |
| | Al | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| mmol$_c$ L$^{-1}$ | Cl | 2 | 5 | 8 | 9 | 3 | 11 | 17 | 12 | 3 |
| | $SO_4$ | 32 | 299 | 218 | 282 | 4 | 212 | 206 | 131 | 6 |
| | $NO_3$ | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 |
| Sum anion charge | | **34** | **304** | **226** | **290** | **10** | **223** | **223** | **143** | **9** |
| Sum cation charge | | **38** | **247** | **210** | **243** | **11** | **193** | **141** | **128** | **11** |
| Solids mass balance g/leach | | 0.39 | 2.50 | 1.87 | 2.31 | 0.05 | 0.93 | 1.03 | 0.76 | 0.05 |

**Table 17 Yield and composition of the fifth leachate, as in Table 13 but with fresh water in place of mine water**

| Treatment | | Fifth leaching | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | TPO5 | TMO5 | TMC5 | TMH 5 | SPO5 | SMO5 | SMC5 | SMH5 | SPH5 |
| Volume of leachate (mL) | | 195 | 185 | 190 | 190 | 85 | 75 | 55 | 70 | 130 |
| Cumulative net evaporation | | 15506 | 15563 | 15694 | 15731 | 18169 | 18019 | 18244 | 18075 | 18094 |
| pH | | 5.04 | 2.99 | 4.16 | 3.71 | 6.01 | 4.13 | 6.47 | 6.58 | 7.56 |
| EC (dS m$^{-1}$) | | 0.29 | 0.88 | 0.76 | 0.84 | 0.10 | 1.23 | 0.87 | 0.90 | 0.11 |
| Concentration (mg L$^{-1}$) | Ca | 554 | 392 | 404 | 403 | 67 | 422 | 440 | 450 | 118 |
| | Mg | 5 | 443 | 471 | 525 | 22 | 953 | 586 | 599 | 15 |
| | Na | 12 | 237 | 262 | 283 | 12 | 600 | 506 | 461 | 10 |
| | K | 0 | | 26 | 4 | 6 | 47 | 25 | 25 | 8 |
| | Fe | | 803 | 62 | 278 | | 3 | | | |
| | Mn | 0 | 117 | 162 | 174 | 0 | 456 | 51 | 63 | |
| | Al | 1 | 8 | 5 | 3 | 2 | 3 | 1 | | |
| | Si | 21 | 10 | 26 | 35 | 23 | 43 | 4 | 6 | 6 |
| | Ni | 0.2 | 1.2 | 2.9 | 3.0 | 0.0 | 3.0 | | | 0.1 |
| | Co | | 0.6 | 1.9 | 2.1 | | 5.5 | | 0.2 | |
| | Zn | | 0.2 | 0.5 | 0.7 | | 4.9 | | | |
| | Cu | 0.5 | 1.2 | 1.0 | 1.0 | 1.1 | 1.6 | | 1.5 | 1.6 |
| | As | 0.9 | 2.5 | 1.1 | 1.7 | 4.2 | | | 1.4 | 2.1 |
| | Cl | 43 | 323 | 205 | 251 | 117 | 480 | 539 | 479 | 177 |
| | $SO_4$ | 1578 | 26641 | 5300 | 7188 | 184 | 10864 | 6131 | 6184 | 209 |
| | $NO_3$ | | | | | 52 | | | | |
| | Total | **2214** | **28981** | **6931** | **9153** | **490** | **13887** | **8283** | **8269** | **547** |
| mmol$_c$ L$^{-1}$ | Ca | 28 | 20 | 20 | 20 | 3 | 21 | 22 | 22 | 6 |
| | Mg | 0 | 37 | 39 | 44 | 2 | 79 | 49 | 50 | 1 |
| | Na | 1 | 10 | 11 | 12 | 1 | 26 | 22 | 20 | 0 |
| | K | 0 | 0 | 1 | 0 | 0 | 1 | 1 | 1 | 0 |
| | Fe | 0 | 29 | 2 | 10 | 0 | 0 | 0 | 0 | 0 |
| | Mn | 0 | 4 | 6 | 6 | 0 | 17 | 2 | 2 | 0 |
| | Al | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| | Total | 29 | 101 | 80 | 93 | 6 | 145 | 95 | 95 | 8 |
| % | Ca | 97 | 19 | 25 | 22 | 55 | 15 | 23 | 24 | 76 |
| | Mg | 1 | 37 | 49 | 47 | 30 | 55 | 51 | 52 | 16 |
| | Na | 2 | 10 | 14 | 13 | 9 | 18 | 23 | 21 | 6 |
| | K | 0 | 0 | 1 | 0 | 3 | 1 | 1 | 1 | 3 |
| | Fe | 0 | 28 | 3 | 11 | 0 | 0 | 0 | 0 | 0 |
| | Mn | 0 | 4 | 7 | 7 | 0 | 11 | 2 | 2 | 0 |
| | Al | 0 | 1 | 1 | 0 | 3 | 0 | 0 | 0 | 0 |
| mmol$_c$ L$^{-1}$ | Cl | 1 | 9 | 6 | 7 | 3 | 14 | 15 | 13 | 5 |
| | $SO_4$ | 33 | 555 | 110 | 150 | 4 | 226 | 128 | 129 | 4 |
| | $NO_3$ | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 |
| Sum anion charge | | **34** | **564** | **116** | **157** | **8** | **240** | **143** | **142** | **9** |
| Sum cation charge | | **29** | **101** | **80** | **93** | **6** | **145** | **95** | **95** | **7** |
| Solids mass balance g/leach | | 0.43 | 5.36 | 1.32 | 1.74 | 0.04 | 1.04 | 0.46 | 0.58 | 0.07 |

**Table 18 Analysis of mine water and aqueous extracts of the solid residue from evaporating mine water in the presence or absence of Ca hydroxide and bicarbonate with the same ratio as that used in the land treatment simulation. Treatment codes are explained in Table 10. Blank cells signify a concentration probably below the limit of detection.**

| Treatment | | Fresh mine water | Evaporated mine water | | |
|---|---|---|---|---|---|
| | | | OMO | OMC | OMH |
| Volume of leachate (mL) | | | 90 | 90 | 90 |
| Cumulative net evaporation | | | 1520 | 1520 | 1520 |
| pH | | 3.38 | 2.11 | 5.91 | 7.09 |
| EC (dS $m^{-1}$) | | 0.520 | 2.75 | 1.91 | 1.87 |
| Concentration (mg $L^{-1}$) | Ca | 696 | 393 | 380 | 384 |
| | Mg | 232 | 2800 | 2751 | 2733 |
| | Na | 92 | 1546 | 1604 | 1645 |
| | K | | 38 | 174 | 179 |
| | Fe | 342 | 3006 | 7 | |
| | Mn | 64 | 483 | 430 | 11 |
| | Al | | | | |
| | Si | 6 | 10 | 2 | 1 |
| | Ni | | 4.2 | 0.4 | |
| | Co | | 2.4 | 0.8 | |
| | Zn | | 1.1 | -0.3 | |
| | Cu | | 2.3 | 2.3 | 1.8 |
| | As | | | 2.4 | 0.7 |
| | Cl | 31 | 468 | 734 | 843 |
| | SO4 | 3494 | 41321 | 17416 | 18661 |
| | NO3 | | | | |
| | **Total** | **4942** | **50070** | **23503** | **24454** |
| $mmol_c$ $L^{-1}$ | Ca | 35 | 20 | 19 | 19 |
| | Mg | 19 | 233 | 229 | 228 |
| | Na | 4 | 67 | 70 | 72 |
| | K | 0 | 1 | 4 | 5 |
| | Fe | 12 | 107 | 0 | 0 |
| | Mn | 2 | 18 | 16 | 0 |
| | Al | 0 | 0 | 0 | 0 |
| | Total | 73 | 446 | 338 | 323 |
| % | Ca | 48 | 4 | 6 | 6 |
| | Mg | 27 | 52 | 68 | 70 |
| | Na | 5 | 15 | 21 | 22 |
| | K | 0 | 0 | 1 | 1 |
| | Fe | 17 | 24 | 0 | 0 |
| | Mn | 3 | 4 | 5 | 0 |
| | Al | 0 | 0 | 0 | 0 |
| $mmol_c$ L-1 | Cl | 1 | 13 | 21 | 24 |
| | SO4 | 73 | 861 | 363 | 389 |
| | NO3 | 0 | 0 | 0 | 0 |
| Sum anion charge | | **74** | **874** | **384** | **413** |
| Sum cation charge | | **72** | **445** | **338** | **323** |

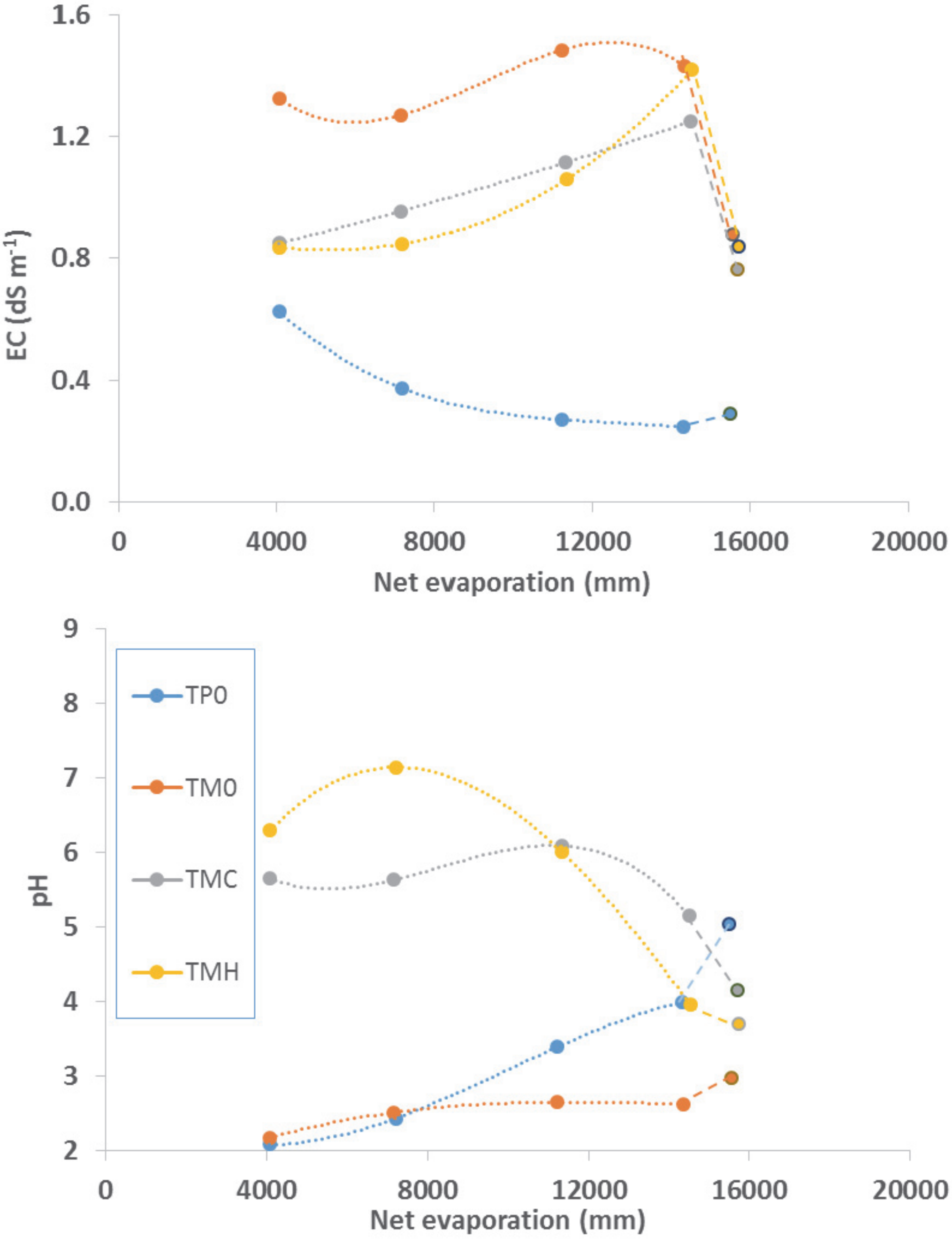


**Figure 4 pH and EC of five sequential leachates from four mine tailings treatments in relation to cumulative net evaporation calculated relative to a hypothetical receiving depth of 1 m (data from Tables 13-17). The final leachate was obtained differently from the first four (see text). (M=mine tailings; 0, C and H are zero, carbonate and hydroxide amendments; P and M refer to pure water and mine water, respectively). (Solid curves are closest fitting trend lines generated using the polynomial option in Excel)**

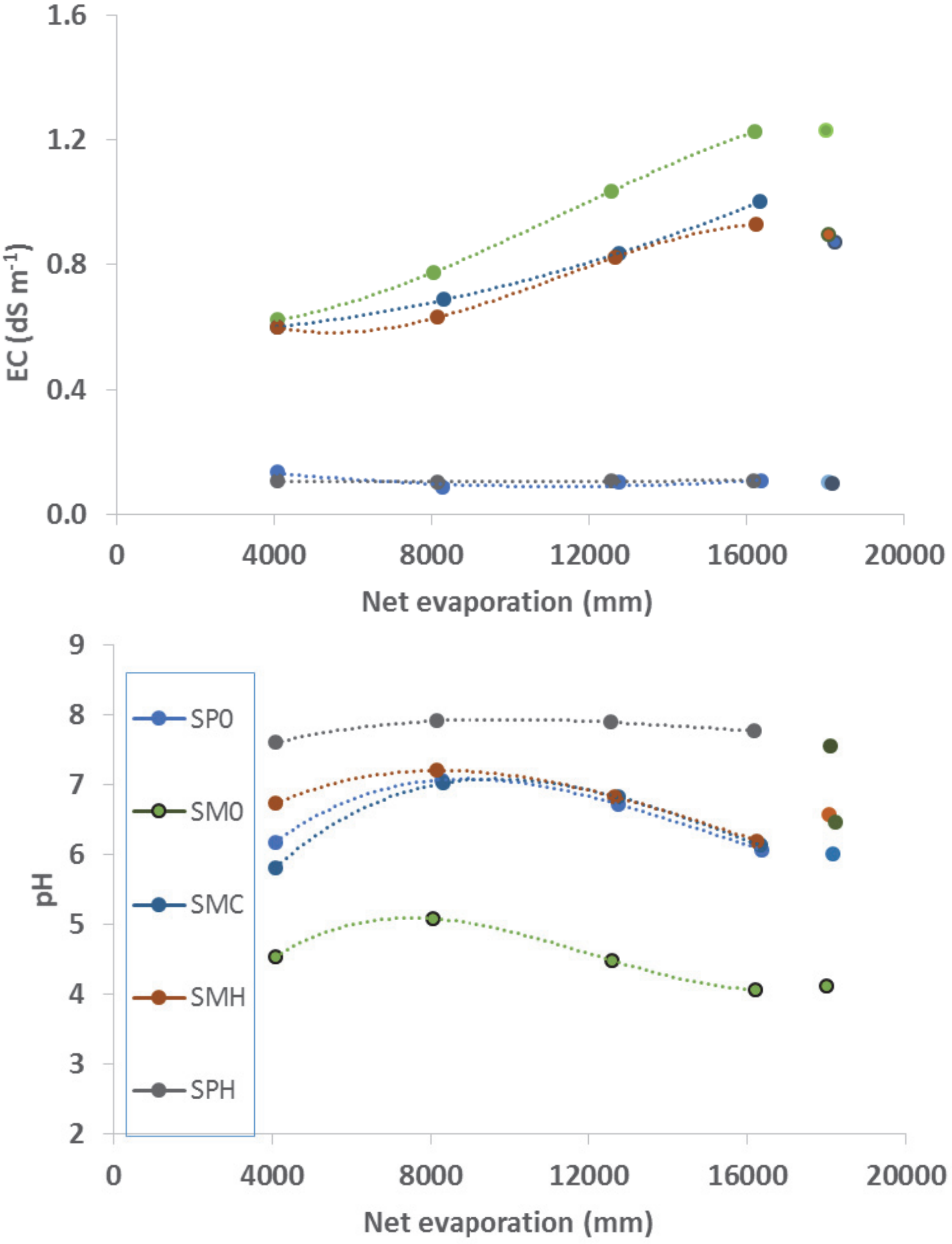


**Figure 5 pH and EC of five sequential leachates from five soil treatments in relation to cumulative net evaporation calculated relative to a hypothetical receiving depth of 1 m (data from Tables 13-17). The final leachate was obtained differently from the first four (see text). (S=soil; 0, C and H are zero, carbonate and hydroxide amendments; and P and M refer to pure water and mine water, respectively). (Solid curves are closest fitting trend lines generated using the polynomial option in Excel).**

**Table 19 Derived data comparing the physical effectiveness of mine tailings and the black clay soil in retaining water (leaching fraction derived from the Table of irrigation data in Appendix 2) and sequestering evaporated and chemically precipitated solids (calculated from Table 18).**

| | TMO | TMC | TMH | SMO | SMC | SMH | OMO | OMC | OMH |
|---|---|---|---|---|---|---|---|---|---|
| **Leaching fraction %** | 15.7 | 15.1 | 14.9 | 7.3 | 6.2 | 7.0 | 5.9 | 5.9 | 5.9 |
| **total added g** | 25.7 | 25.7 | 25.7 | 26.9 | 26.9 | 26.9 | 7.5 | 7.5 | 7.5 |
| **total leached g*** | 16.6 | 10.1 | 9.0 | 4.2 | 3.2 | 2.8 | 4.5 | 2.1 | 2.2 |
| **Fraction leached (%)** | 64 | 39 | 35 | 16 | 12 | 10 | 60 | 28 | 29 |
| **Solids sequestered (%)** | 36 | 61 | 65 | 84 | 88 | 90 | 40 | 72 | 71 |

***The quantity leached from the mine tailings with pure water (TP0) was 3.3 g which leachate analysis in Table 3 suggests is largely gypsum.**

**Table 20 Exchangeable basic cations including $Mn^{2+}$ (expressed as $mmol_c\ kg^{-1}$) extracted in ammonium acetate from dried residues after leaching all treatments in both experiments simulating land treatment. Treatment codes and the correlation of treatments are explained in Table 11 and the accompanying text.**

| Treatment/soil | K | S | Ca | Na | Mg | Mn |
|---|---|---|---|---|---|---|
| BC-MWNL3 (SM0) | 10 | 541 | 439 | 33 | 217 | 51 |
| BC-MWOH3 (SMH) | 11 | 591 | 630 | 34 | 225 | 23 |
| BC-MWCO3 (SMC) | 11 | 575 | 612 | 35 | 228 | 26 |
| BC-DWOH3 (SPH) | 7 | 9 | 326 | 3 | 102 | 1 |
| BC-MWOH# | 11 | 613 | 642 | 43 | 241 | 19 |
| RS-MWNL3 | 6 | 402 | 256 | 18 | 64 | 14 |
| RS-MWOH3 | 8 | 428 | 376 | 19 | 71 | 13 |
| RS-MWCO3 | 8 | 433 | 396 | 19 | 71 | 15 |
| RS-DWOH3 | 7 | 22 | 174 | 2 | 12 | 1 |
| RS-MWOH# | 8 | 404 | 373 | 16 | 66 | 11 |
| SM0 | 9 | 392 | 318 | 37 | 163 | 38 |
| SMH | 10 | 510 | 533 | 34 | 198 | 21 |
| SMC | 10 | 485 | 496 | 32 | 206 | 20 |
| SPH | 8 | 2 | 364 | 5 | 85 | 0 |
| SP0 | 9 | 4 | 219 | 6 | 134 | 2 |
| TP0 | 2 | 29 | 27 | 3 | 1 | 0 |
| TM0 | 2 | 358 | 318 | 8 | 15 | 2 |
| TMH | 2 | 536 | 510 | 5 | 8 | 1 |
| TMC | 2 | 564 | 535 | 5 | 8 | 1 |
| Red soil (untreated) | 7 | 4 | 29 | 2 | 11 | 2 |
| Black soil (untreated) | 8 | 2 | 206 | 4 | 131 | 1 |

**Table 21 Average pH and EC measurements relative to cumulative net evaporation for each of seven sequential leachings of the ten treatments in the second simulation experiment. Correlation with treatments in the first experiment has been inserted in the second column allowing some of these data to be compared with those plotted in Figure 5 (SMO, SMC, SMH, and SPH).**

| Treatment | Corrln. | E (mm) | pH | EC (dS/m) | E (mm) | pH | EC (dS/m) | E (mm) | pH | EC (dS/m) | E (mm) | pH | EC (dS/m) | E (mm) | pH | EC (dS/m) | E (mm) | pH | EC (dS/m) | E (mm) | pH | EC (dS/m) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **BC-MWNL3** | **SM0** | 2201 | 5.30 | 0.55 | 4333 | 4.94 | 0.57 | 7102 | 5.13 | 0.86 | 9452 | 4.51 | 0.98 | 11691 | 4.24 | 1.11 | 13971 | 4.14 | 0.96 | 16093 | 4.04 | 1.01 |
| **BC-MWOH3** | **SMH** | 2133 | 5.00 | 0.56 | 4461 | 5.16 | 0.57 | 7370 | 5.77 | 0.74 | 9316 | 5.82 | 0.88 | 11541 | 6.40 | 0.96 | 13794 | 6.27 | 0.73 | 15877 | 6.25 | 0.78 |
| **BC-MWCO3** | **SMC** | 2234 | 5.07 | 0.52 | 4326 | 5.53 | 0.55 | 7001 | 6.17 | 0.73 | 9338 | 6.26 | 0.86 | 11548 | 6.56 | 0.94 | 13811 | 6.74 | 0.69 | 16007 | 6.36 | 0.82 |
| **BC-MWOH#** | **$\text{SMH}_w$** | 2178 | 5.90 | 0.34 | 4341 | 7.12 | 0.39 | 7023 | 6.42 | 0.75 | 9030 | 6.87 | 0.82 | 11124 | 6.95 | 0.92 | 13333 | 6.97 | 0.70 | 15315 | 7.29 | 0.75 |
| **BC-DWOH3** | **SPH** | 1797 | 7.12 | 0.09 | 3874 | 6.59 | 0.08 | 6751 | 6.95 | 0.08 | 8849 | 7.28 | 0.08 | 10649 | 7.60 | 0.06 | 12332 | 7.36 | 0.05 | 14350 | 7.35 | 0.05 |
| **RS-MWNL3** | **RM0** | 1709 | 4.62 | 0.60 | 3403 | 4.65 | 0.99 | 5217 | 3.97 | 1.22 | 6924 | 3.76 | 1.28 | 8644 | 3.47 | 1.42 | 10382 | 3.42 | 1.16 | 12021 | 3.32 | 1.15 |
| **RS-MWOH3** | **RMH** | 1666 | 5.50 | 0.39 | 3252 | 6.63 | 0.76 | 4982 | 5.43 | 0.89 | 6659 | 5.81 | 1.06 | 8314 | 5.84 | 1.12 | 9934 | 5.93 | 0.93 | 11553 | 6.01 | 0.91 |
| **RS-MWCO3** | **RMC** | 1655 | 5.38 | 0.57 | 3233 | 6.75 | 0.89 | 4995 | 6.03 | 0.99 | 6675 | 6.39 | 1.07 | 8327 | 6.47 | 1.20 | 9990 | 6.32 | 0.97 | 11628 | 6.36 | 0.92 |
| **RS-MWOH#** | **$\text{RMH}_w$** | 1638 | 5.80 | 0.44 | 3102 | 6.88 | 0.80 | 4707 | 6.35 | 0.90 | 6363 | 6.71 | 0.94 | 7974 | 6.91 | 0.92 | 9543 | 6.92 | 0.74 | 11211 | 7.05 | 0.77 |
| **RS-DWOH3** | **RPH** | 1609 | 7.48 | 0.11 | 3159 | 6.65 | 0.11 | 4885 | 7.26 | 0.09 | 6506 | 7.37 | 0.07 | 8118 | 7.23 | 0.06 | 9785 | 7.34 | 0.04 | 11320 | 7.30 | 0.04 |

#(For explanation of treatment codes see Tables 10 and 11)

The pH of the amended tailings was quite well buffered at between pH 5 and 6 in the case of the carbonate amendment (TMC) and well above 6 to begin with, in the case of the hydroxide lime amendment (TMH). Towards the termination of the experiment the leachate pH of both amended tailings had begun to drop, earlier in the case of the hydroxide- than the carbonate-amended tailings suggesting that the Ca carbonate was slower acting but longer lasting than the hydroxide but that the overall effects would be similar in the end. Whether this would eventuate or not under field practice is difficult to predict, because it would depend on the concentration of carbon dioxide which in a partly confined pore space and depending on biological respiration can rise considerably above normal atmospheric levels. Some carbonation of the hydroxide lime will occur before all of it can react with mine water, especially if it is incorporated at once instead of being split as was done in the second trial. Such carbonation will reduce the difference between hydroxide and carbonate amendments.

One potentially very important difference between the effects of hydroxide and carbonate will now be discussed, with the aid of supplementary illustrations in Appendix 2. Those familiar with neutralizing metalliferous, sulfuric mine water containing substantial ferrous Fe would recognise immediately the green precipitate that formed when the water was treated with an excess of Ca hydroxide. This was evident in water added to both the miniature basins with Ca hydroxide only and the mine tailings amended with Ca hydroxide (Appendix 4). By contrast, Ca carbonate takes much longer (a day or two) to produce a noticeable change in appearance which is never green but consists of the gradual development of a reddish-brown precipitate. With time the green precipitate in the hydroxide-neutralized water begins to oxidize to a buff and eventually reddish-brown colour, similar to that which formed directly from reaction with Ca carbonate. The explanation for this different response to hydroxide and carbonate liming is far from simple. Slow, alkaline oxidation of ferrous Fe solutions can give rise to maghemite via magnetite crystallization, whereas oxidation of neutral solutions in the presence of carbonate may give rise to goethite via a green rust intermediate or, under a variety of conditions, ferrihydrite and then hematite may form when oxidation is more rapid. These are just some of the possibilities, a full account of which is given by Cornell and Schwertmann (2003). Suffice it to say that the two types of amendment produce a very different visual result but that the difference becomes smaller with time and perhaps would not be so great if the amendment was split and dispensed in small doses as was done in the second experiment, rather than the single dose which in the earlier stages would have created an excess of base in relation to the mine water. The danger of armouring has been considered since this is well known in attempts to precipitate metals from mine water using passive treatment with limestone. Quite possibly this is why the pH of the amended tailings began to drop substantially towards the end of the experiment: the acidifying effect of Fe oxidation would no longer have been fully neutralised because residual Ca carbonate particles may have been smothered by a film of ferric hydroxide. On the other hand, since the pH of the final leachate was not much less than 4 in the amended tailings it does suggest that a single large application at the start of land treatment is worth considering.

It is instructive to consider the visual evidence of Fe precipitation and oxidation in the tailings in conjunction with the chemical changes that took place in leachate composition (from Table 13 to Table 17). The first leachate, after five wetting and drying cycles with added mine water, revealed that all of the substantial Fe concentration (TMO leachate) had been removed from solution by hydroxide lime (TMH) and only a small concentration appeared in the leachate from carbonate amendment (TMC). The Fe concentrations thereafter followed the same interesting crossover pattern exhibited in the pH data which we put down to different rates of reaction, so that in the final leachate there was a significantly larger Fe concentration in TMH leachate than in TMC leachate. This suggests that the Ca hydroxide had partially been spent on reactions other than Fe hydrolysis and was consequently, and counterintuitively, less effective overall than Ca carbonate. If this was found to be applicable on a large scale in the field it would be a pleasant surprise because hydroxide is more expensive.

Having begun to consider chemical composition of the tailings leachates let us consider some other chemical aspects worth mentioning before going on to a discussion of the black clay soil. Firstly, some elements are present in the tailings to begin with that, after one or two leachings, are largely removed since they are not present to any significant degree in the mine water. Notable are Al and a suite of trace elements, the concentrations of some of which may be considered fairly serious. These are especially evident in Table 13 (Ni, Co, Zn, Cu and As). The arsenic levels in particular may be cause for special precautions to be taken in managing these tailings. We have not attempted to discuss this with site managers but it should be raised at some point in the future. While the high levels of Fe initially present in the mine water treated, unamended tailings (TMO1) are half-attributable to the mine water with the rest coming from the tailings (see TPO1), this is not the case with Mn and Mg which are both present in high concentrations in the mine water with relatively little in the tailings. Almost certainly this enrichment of the Western Basin mine water with both Mg and Mn, as well as its fairly benign pH of 3.4 after some oxidation, is due to neutralisation by contact with a dolomite which abounds in the region. As will become evident later this could have crucial implications for the disposal of both irrigation return flow and reverse osmosis reject brines since soluble Mg and Mn in this water are as important as Na, if not more so.

One of the ways in which one can track the likely reactions taking place during the simulated land treatment is to examine the relative proportions (calculated as % chemical equivalents i.e. taking both molarity and ionic charge into account) of the various cations in solution. These calculated percentages appear near the bottom of Tables 13-17. Notice how Ca dominance in the early leachate (Table 13) gives way to Mg dominance at the end (Table 17), and how Mn, although it increases substantially, never exceeds about 10% of the total cations whereas Mg may eventually account for more than half. The Fe, important initially, soon becomes of little consequence but its reappearance in the more acidic final mine water leachates reminds us of how important it is to maintain an elevated pH throughout the treatment. It seems from the work of Maree et al. (2013) on limestone use in HDS plants that the mild alkalinity of limestone is sufficient to precipitate Fe, but not Mn, by facilitating its oxidation provided aeration is carried out. The results in Tables 13-17 seem to confirm this, and it is only with Ca hydroxide treatment of the tailings that Mn concentrations are brought right down. (This is not the case with the black clay soil but that will be considered later). The loss of Ca dominance in solution despite applying Ca amendments is because gypsum precipitation has occurred. A cursory look at the increasing sulfate concentrations provides a ready explanation, in terms of the solubility product principle, for why Ca concentrations decrease while remaining in equilibrium with gypsum (see PHREEQC output files for the second leachate series in Appendix 5).

All of these chemical interpretations of course rest on obtaining analytical data that can be believed to start with. This is why a charge balance is inserted at the base of Tables 13-17. In some cases the charge imbalance is not acceptable and it was not possible to check the analyses in the time available but overall the charge balance is satisfactory given that (i) alkalinity was not determined (the black clay series showed a consistent anion deficit in hydroxide treatments without mine water, for example, which could be attributed to some bicarbonate alkalinity) and (b) the redox status of Fe and Mn is not easily accommodated without at the same time determining the total acidity; many of the samples approach charge balance if it is assumed that Fe and Mn are in their higher oxidation states.

Next, it is instructive to examine in what manner the data for the black clay soil differ from those of the mine tailings treatments. Figure 5 shows that pH buffering is much stronger throughout the experiment as was expected, with only a minor dip in pH towards the end, and part of this could well be an effect of ionic strength as the EC builds up, as is clearly shown in the upper part of Figure 5. Only the mine water-treated clay without amendment showed any substantial acidity and this remained above 4 throughout the trial.

How did this buffering affect leachate composition? Tables 13-17 indicate that the concentrations of Fe, Mn and the other metals of concern are dramatically lower than in the mine tailings; in the case of Fe and Mn this is because the added amounts are rendered insoluble by both hydroxide and carbonate amendments in conjunction with the known natural alkalinity and cation sorbing properties of this type of soil (Bonheim form). Manganese but not Fe eventually appears in the later leachates but not in concentrations that would give rise to serious concern. Again, Ca dominance gives way to Mg dominance as leaching progresses, and gypsum precipitation is strongly suggested by the complementary Ca and sulfate concentrations. In this case there was even solid evidence of gypsum precipitation in the form of a strong efflorescence of tasteless white salt crystals on the dark surface of the dried clay (Appendix 4). There was no evidence of reddening by Fe precipitation and it is interesting to speculate as to why this is so. Perhaps the black background so strongly absorbs all incident light in the visible spectrum that there is none left for the Fe oxide to differently absorb and reflect the (red) remainder?

Regarding other physical responses there was no discernible change in the consistence, moist or dry, of the black clay soil in response to amendments. On the other hand the amended mine tailings showed a distinct firming of the sediment when being stirred with added mine water compared with unamended tailings. More quantitative assessment such as with soil water retention in pressure plate apparatus is still to be carried out. The physical appearance of the treated tailings is dramatically different from the untreated control because of the Fe oxides (Appendix 4). It is expected that gypsum crystallization will also affect some physical properties. The more concentrated enrichment of solids achieved by combining the mine water with a smaller quantity of soil in an extension of the trial (Table 11) is shown in the photographs in Appendix 4. These dried products showed some evidence of particle aggregation that may hold promise for reducing the erodibility of the gold mine tailings.

An interesting feature of the black clay soil was the high concentration of nitrate in the leachates (Tables 13 to 17), all of them to begin with (Table 13) and subsequently confined to the treatments without mine water suggesting that either the salinity was inhibitory or that, more likely, the reduced Fe and Mn in the mine water functioned as a nitrification inhibitor, either by being directly toxic to nitrifying bacteria and archaea or by consuming oxygen and suffocating them. Biological responses of this kind will be critical to evaluate in any kind of land treatment system because if microbes languish so surely will plant roots.

Key results of the second simulation experiment are included in Tables 20 and 21, and show that for those treatments that were comparable in the two experiments there is a gratifying degree of confirmation of the results. The exchangeable cation data in Table 20 also provide a good indication of how valuable a cation exchange material is for metal retention and increasingly it seems appealing to think of those thousands of hectares of black clay surrounding many mine dumps as being an exceptionally valuable, mineable resource for ensuring the sustainability of rehabilitation. The savings it would afford mining companies in allowing closure of TSFs would be more than enough to compensate farmers for loss of income on these agriculturally suboptimal soils.

It may be worth offering some remarks about Tables 18 and 19. Table 18 allows us to track the evolution of the mine water from a relatively fresh start (EC 50 mS $m^{-1}$) to a potentially quite concentrated brine (EC 211 mS $m^{-1}$) from which salts are sequestered to some extent simply by adding alkaline amendments. These aqueous extracts of the evaporated residues tell us some useful things about what the brines are likely to consist of after amendment; in particular, the Mg increases from 27 to as much as 70% of the cations while Na climbs from 5 to 20%, Ca drops from 48 to 6% and Mn never exceeds 5%. According to Table 19 which is gleaned from the irrigation data in Appendix 2 and the chemical data in Table 18, the sequestration of solids in this simulated land treatment is especially effective when alkaline amendments are applied and is much more effective in the black clay than in the mine tailings, although this is partly due to the fact that the leaching fraction in the mine tailings water application was double that of the black clay, while the proportion of the sequestered solids that is in the form of sparingly soluble gypsum as opposed to effectively insoluble metal hydroxides remains to be determined. In the next chapter we will consider the pre-treatment of the mine water with novel amendments: Al sulfate and ferromanganese wad, augmented with lime or limestone.

# CHAPTER 4 LABORATORY EVALUATION OF FERROMANGANESE WAD AND ALUMINIUM SULFATE AS AGENTS FOR IRON AND MANGANESE REMOVAL FROM GOLD MINE WATERS

## 4.1 INTRODUCTION

The traditional method of dealing with metalliferous mine water is to neutralise it with lime, not only to raise the pH but also to precipitate dissolved metals. A pH well above 9 is aimed at in order to completely sequester iron (Fe) and other metals. Normally this is achieved by adding calcium hydroxide [$Ca(OH)_2$]. A multi-step process using fine limestone ($CaCO_3$) to neutralise strong acidity, aeration to oxidise and precipitate most of the Fe, and $Ca(OH)_2$ to precipitate metals [manganese (Mn), residual Fe and trace metals such as nickel (Ni), copper (Cu) and zinc (Zn)] has been proposed by Maree et al. (2013) and is the expected basis by which high density sludge plants will treat water decanting from the Witwatersrand gold mines. There is a significant cost saving associated with the partial substitution of Ca hydroxide with fine limestone. In a final step the elevated pH is lowered with carbon dioxide (Maree et al., 2013). Significant additional cost savings would be achieved if the residence time of the water in the plant could be reduced. The aeration step is a limiting one in this respect since the limestone does not achieve a high enough pH to precipitate ferrous Fe without prior oxidation to ferric Fe. Manganese largely fails to precipitate even after aeration. Any process which causes the rapid oxidation and/or precipitation of Fe(II) and Mn(II) might obviate or reduce the need for aeration coupled with a high pH.

The idea of using Mn wad for removing Mn from neutralised gold mine water in the Witwatersrand Basin was conceived during the review of literature of this project. A paper by Duarte and Ladeira (2011) in the proceedings of the International Mine Water Association claimed that Mn can be held below the Brazilian permissible limit of 1 mg $L^{-1}$ (i.e. effectively demanganated) through neutralisation to pH 7 with lime or limestone followed by contact with Mn oxide – in their case a by-product from the zinc electro-winning process. They succeeded in generating a volume of demanganated water 40 to 60 times the volume of the solid adsorbent, employing a residence time of 3-5 h in a leaching column packed with manganese dioxide ($MnO_2$), physically simulating the common practice of removing dissolved metals by passing contaminated water through a limestone drain. They attributed the effect of the Mn oxide to both adsorption and catalytic oxidation of the dissolved Mn. The water they studied had a negligible Fe concentration so it is not possible to gauge whether such treatment simultaneously removes Fe. This might be expected and would be worth testing.

A large deposit of Fe-Mn wad has been mined near Ventersdorp for uranium extraction by the gold mines. The mineralogy and reserves of the deposit are described by Pack et al. (2000). There are about six million tonnes of ore consisting of a porous wad made up of roughly equal amounts of Fe and Mn oxides (chiefly hematite or goethite, and pyrolusite, respectively). The distance to truck this ore to the Western Basin mine water decant point in Randfontein is about 70 km, making its potential use for water treatment worth investigating. There are other deposits of Mn oxide in the Witwatersrand basin, usually associated with dolomite, suggesting that this option, if feasible, might be applicable at the other decant points in the Central and Eastern Basins.

In the review in Chapter 2 another principle was proposed for removing metals from mine water. This involves the formation of layered double hydroxide-type compounds (LDH). The metals in sulfuric mine water are mostly divalent (Ca, Mg, Fe, Mn, Ni, Zn and Cu) and are capable of co-precipitating with trivalent metals (Al and, once oxidised, Fe) to form a mixed hydroxide in which the trivalent metal substitutes for the divalent cation in brucite-like sheets, imparting a positive charge which is balanced by layers of anions, for example carbonate and sulfate, between adjacent sheets. Compounds such as ettringite, hydrotalcite, pyroaurite and a variety of others are possible (Taylor, 1980), and a multi-metal, multi-ligand precipitate can form at a pH which is lower than the threshold pH required to precipitate the divalent metal cation. In theory this suggests a method by which divalent metals such as Fe and Mn can be precipitated without requiring prior oxidation, at pH values which are nearer to neutral than would otherwise have been the case. It is not certain to what extent this principle is embodied in conventional water purification, which employs a combination of lime and a salt of either Al or Fe(III). There does not seem to be any indication of such treatment having been applied to mine water, probably because such salts are often present in the mine water already – as major, deleterious constituents. Adding more would therefore seem, on first consideration, to be counter-productive. Hypothetically the trick would be to combine Al or Fe(III) with the mixture of divalent metal cations, sufficiently to induce, by liming and hydrolysis, the formation of an LDH-type precipitate. Much of the sulfate would hopefully end up in the anion layer and some would be sequestered with Ca as gypsum. Application of the principle to co-disposal of alkaline-aluminate and acidic-sulfuric effluents has been investigated (Santini and Fey, 2012).

The Al sulfate plant at Springs is near to the Eastern Basin water decant at Grootvlei mine; it has the largest output in southern Africa and supplies water purification plants over a wide area. This proximity may be fortuitous if it turns out that Al sulfate addition with lime is economically effective for removing metals from mine water.

This chapter has the following aim: To investigate, in laboratory tests using mine waters representative of the Vaal Basin, the extent to which (a) locally available Fe-Mn wad, and (b) Al sulfate with lime neutralisation, can enhance the removal of Fe, Mn and other metals from solution without the usual need for aeration.

## 4.2 MATERIALS AND METHODS

Sample collection and preparation were described in the previous chapter but certain details are briefly repeated here for convenience.

### *4.2.1 Mine water*

All experiments were conducted on water from the Western Basin. This was collected from the research site adjoining the high density sludge (HDS) plant at Randfontein gold mine near Krugersdorp. The water was pumped directly into twelve 20 L plastic tubs and kept sealed until required. The water was clear but underwent a small degree of oxidation within a few hours of collection as indicated by a fine, reddish brown deposit that developed on the walls of the storage tubs during transport to the laboratory. Such oxidation tends to be self-limiting because it produces a drop in pH that inhibits the rate of oxidation, especially if the solution is kept in an airtight container. Water from this site has been well characterised and its amelioration studied in some detail (Maree et al., 2013).

### *4.2.2 Ferromanganese wad*

Several kg of wad (a porous, low bulk density, Mn oxide with associated Fe oxide) was collected from a stockpile at the Ryedale mine near Ventersdorp. The material had been crushed and coarsely screened ready for commercial use as an adsorbent. For laboratory experiments the sample was further reduced in size by screening < 2 mm then further separating an even finer powder fraction of < 63 µm by sedimentation and wet sieving, and drying in a shallow container under an infrared lamp. The deposit has been described in detail by Pack et al. (2000) and information on its availability and potential uses can be found at http://www.metmin.co.za.

### *4.2.3 Aluminium sulfate*

Industrial grade Al sulfate powder was obtained from the manufacturers at Springs (www.pakamisa-industries.co.za/Aluchem/Aluchem_Products.html). A concentrated aqueous solution containing 36 percent Al sulfate (w/w) was prepared for use in the experiments. The solid Al sulfate contains 12% Al by mass.

### *4.2.4 Liming materials*

Analytical reagent-grade, finely powdered $Ca(OH)_2$ and $CaCO_3$ were used for neutralisation.

### *4.2.5 Experimental*

Because of time and cost constraints the experiments were designed to obtain proof of concept as efficiently as possible. One way of achieving this was initially to conduct qualitative tests for dissolved Fe(II) and Mn(II), in conjunction with pH measurement, in order to establish whether a particular treatment had a useful outcome. In this way a combination of treatments could be arrived at quickly while avoiding the expense and delay of quantitative analysis. The tests consisted of adding a few drops of 1 M NaOH to make the solution alkaline. A greenish precipitate indicated a substantial residue of ferrous Fe while a buff coloured (off-white) precipitate was taken to indicate that ferrous Fe had largely been removed but that residual Mn might be present (bearing in mind that a high concentration of Ca or Mg will also produce a precipitate when the solution is made alkaline with NaOH). Substantial Mn presence was confirmed by adding a few drops of 30% $H_2O_2$ to produce a dark brown precipitate with effervescence. This test was found to be sensitive to as little as 10 mg $L^{-1}$ Mn. Quantitative analysis was carried out on selected samples by ion chromatography (IC) for anions and inductively coupled plasma – optical emission spectrometry (ICP-OES) for cations as described in Chapter 3. For ICP analysis the solutions were passed through a 0.45 µm filter and acidified to pH < 2 with a few drops of c.$HNO_3$.

Initial experiments consisted of adding amendments to 50 mL aliquots of mine water in polypropylene centrifuge tubes, shaking, measuring the suspension pH, centrifuging at 4000 rpm for 5 minutes and decanting some supernatant into 15 mL test tubes for qualitative analysis by sequential addition of NaOH and $H_2O_2$ as described above. Later experiments were conducted with 300 mL of mine water in a 500 mL beaker placed on a magnetic stirrer with continuous pH measurement during amendment addition. The reaction was terminated by pouring some of the suspension into a 50 mL tube and centrifuging for 5 minutes at 4000 rpm. After qualitative tests a filtered, acidified aliquot of supernatant was prepared for cation analysis by ICP-OES.

### *4.2.6 Experiments*

*Experiment 1: treatment of mine water with Fe-Mn wad and Ca carbonate*

Varying amounts of Fe-Mn wad up to 1000 mg (fine powdered fraction) were weighed into centrifuge tubes to each of which 50 mg $CaCO_3$ had been added. A 50-ml aliquot of mine water was added and the stoppered tubes were shaken intermittently for 15 minutes and centrifuged. The supernatant was tested qualitatively for Fe and Mn. A subsample was pre-treated by adding about 5% by volume of a 10% Al sulfate solution before conducting the qualitative tests for Fe and Mn.

*Experiment 2: treatment of mine water with Al sulfate and Ca hydroxide*

Different volumes of a 36% Al sulfate solution were added with a micropipette to 50 mL mine water in a centrifuge tube and mixed. A mass of $Ca(OH)_2$ powder sufficient to neutralise the combination of mine water and Al sulfate was then added and the mixture was immediately shaken vigorously, then intermittently for 5 minutes. The suspension pH was measured and the supernatant was tested qualitatively for Fe and Mn as described above.

*Experiment 3: testing different methods of adding Al sulfate and lime to mine water and evaluating supplementary treatment with Fe-Mn wad*

The order and manner of adding Al sulfate and Ca hydroxide to the mine water was tested using 300 mL of mine water in a 500-mL beaker with continuous pH measurement using a magnetic stirrer. Either 4 or 5 mL of 36% Al sulfate solution and between 0.8 and 1.07 g of Ca hydroxide were added, the latter either as a solid or as an aqueous suspension (30 mL). The standard method of treatment was to mix the Al sulfate solution with the mine water then add the Ca hydroxide (in solid or suspension form) either gradually or all at once, with vigorous stirring. A variation involved first adding the lime to the mine water until the pH stabilised then adding the Al sulfate. Another variation involved combining the lime and the Al sulfate to form a white suspension of Al hydroxide and Ca sulfate (a kind of "milk of alumina") then adding this all at once to the stirred mine water. In addition to measuring pH and qualitatively analysing the supernatant from centrifugation after ten minutes, the visual appearance of the precipitates was also recorded. Supernatants from the three most promising treatment combinations were further treated by shaking for 30 minutes with the Fe-Mn wad (1% w/v addition of the fine powder), and then centrifuging again. Supernatants from before and after wad addition were filtered and acidified for quantitative analysis as described above.

In addition to the mine water experiments some additional data were collected relating to the simulated land treatment that had not been available at the time of writing up the earlier results in Chapter 3.

## 4.3 RESULTS AND DISCUSSION

### Experiment 1: treatment of mine water with Fe-Mn wad and Ca carbonate

The purpose of this experiment was to simulate the process described by Duarte and Ladeira (2011) in which the adsorptive and oxidative effects of Mn oxide are intensified by ensuring the mine water has a near neutral pH. Because they obtained fairly similar results with hydroxide and carbonate, it was decided to try $CaCO_3$ which is much cheaper. The quantity used, 50 mg in 50 mL mine water, is approximately equivalent to the base neutralising capacity of the mine water (~20 mmol $L^{-1}$) as determined earlier (Figure 3 in Chapter 3). The quantities of Fe-Mn wad added were 0, 100, 200, 300, 400, 500 and 1000 mg, creating suspension concentrations of 0, 0.2, 0.4, 0.6, 0.8, 1.0 and 2.0% (w/v), respectively.

Precipitates formed when the supernatants were made alkaline with a few drops of 1% NaOH. All except that from the highest wad treatment were greenish and changed with peroxide addition to an orange-brown colour. The precipitate from the highest wad treatment was very dilute and pale in colour but changed with peroxide addition to a strongly effervescing black precipitate. This was interpreted as indicating complete Fe but incomplete Mn removal from solution by the wad-calcite combination.

A separate aliquot of the supernatant from the 2% wad suspension was then treated with a small dose (about 5% by volume) of a 10% Al sulfate solution and the qualitative NaOH/$H_2O_2$ tests were repeated. A pale grey precipitate formed with NaOH which did not discolour on peroxide addition suggesting that Mn had been trapped by the Al hydroxide, preventing its oxidation. Since there was no pH control in adding NaOH it was not possible to draw conclusions about the nature and stability of the co-precipitate. What can be concluded, however, is that (i) a high enough concentration of wad in the presence of a mine water-neutralising concentration of Ca carbonate will remove most Fe and probably some Mn from solution and (ii) the amount of wad needed to produce a useful effect is very large (20 kg per $m^3$ of mine water) which would almost certainly not be cost-effective for water treatment. As will be discussed later, it is entirely possible that solutions whose composition is dominated by Fe, Mg and Ca with smaller concentrations of Mn will be ineffectual in removing residual Mn because the cation exchange capacity will largely be taken up by the other cations and able only to adsorb a small fraction of the Mn in solution. Furthermore, the oxidative capacity of the $MnO_2$ will likely be spent in reacting with ferrous Fe which is present in a considerably larger concentration (about 12.2 mmol $L^{-1}$) than the Mn (2.3 mmol $L^{-1}$). In one respect this amounts to a kind of redox poisoning by Fe, of the oxidative capacity of the added Mn oxide. That could explain why there is still a substantial residual concentration of soluble Mn in solution despite the fact that most of the Fe has been removed by the highest level of wad addition. Of course, the efficient removal of Fe is also a desirable outcome and the cost effectiveness of the Fe-Mn wad would need to be compared with that of $Ca(OH)_2$, which is the standard conditioner for rapid removal of Fe.

**Experiment 2: treatment of mine water with Al sulfate and Ca hydroxide**

The results of experiment 1 suggested that it might be fruitful to devise a treatment consisting of contacting the mine water with Fe-Mn wad and lime followed by Al sulfate, making sure that there is enough lime to sustain the reaction pH above 7. On the other hand sequential wad/lime-alum may not be a good idea because the wad's action is thought to be due partly to its oxidative power, and oxidising ferrous Fe would partially negate the objective of the alum which is to strip ferrous Fe from solution as an LDH compound thus obviating the need for aeration after liming. One may conclude that the roles of wad and Al sulfate overlap and are not synergistic. It was therefore decided to focus on Al sulfate as the more likely of the two amendments to complement lime in removing dissolved metals.

The treatments and their results are summarised in Tables 22 and 23. The treatment rationale is as follows: based on the lime requirement determination in the previous chapter, 50 mL mine water needs 36 mg $Ca(OH)_2$ to neutralise the acidity. We also calculated that pure $Ca(OH)_2$ and the commercial grade Al sulfate which contains 12% Al are effectively equivalent in mass terms. Hence 36 mg Al sulfate is equivalent to the acidity plus metal content of 50 mL mine water. We know that a common LDH equivalent ratio of $Al^{3+}$:$M^{2+}$ is 1:3. We should try 1:4 as one extreme and 2:1 as the other with a couple of intermediate ratios. Hence the quantities of Al sulfate shown in Table 22. The quantities of $Ca(OH)_2$ are equivalent to the acidity of the mine water plus that of the added Al sulfate. In the case of $CaCO_3$ 10% more was added than the amount which is chemically equivalent to the corresponding $Ca(OH)_2$ level. This was done to compensate for slow and therefore probably incomplete reaction. The Al sulfate was added to the mine water as a concentrated solution and mixed. Solid Ca hydroxide or carbonate powder was added and shaken with the water intermittently for 5 minutes. The precipitates described in Table 22 developed in the supernatant after adding NaOH and $H_2O_2$.

The results were unexpected: no residual Fe or Mn was evident in the 0AlH treatment (no Al addition, only $Ca(OH)_2$). However if the pH values are considered for the series, the only one that was above neutral was the 0AlH supernatant. The amount of lime added was enough in this case to precipitate all the Fe and Mn. When Al had been added, NaOH produced a light, green Fe precipitate which turned orange-brown with peroxide addition. Because Fe was present it was not possible to detect a dark precipitate that could be attributed to Mn, but since Fe oxidises and precipitates more readily than Mn as pH increases it can be assumed that a positive test for $Fe^{2+}$ holds also for $Mn^{2+}$. At the highest level of Al addition (2AlH), the initial precipitate was not green but off-white and changed to a brown colour with peroxide addition, but was still (i.e. there was no effervescence). The low pH (4.1 after 5 days) explains the ambiguous test for Mn; when an excess of NaOH was added peroxide had its usual effect of darkening the precipitate and effervescing. The reason for the low equilibrium pH at high Al levels is not clear since the addition of $Ca(OH)_2$ was adjusted to match the hydrolysis of added Al. It is possible, however, that the high Mg concentration in the mine water (about 19 $mmol_c$ $L^{-1}$, matching that of the acid cations) contributes to the formation of a hydrotalcite (i.e. LDH)-like phase when Al has been added, thus requiring more base than $Al(OH)_3$ precipitation alone would consume and resulting in some residual Fe and Mn in solution. The upward shift in pH resulting from the increase in lime addition per unit mass of Al added is seen more clearly in Figures 6 and 7 as well as the overall pattern of pH decline with increasing Al addition.

**Table 22 Quantities of Al sulfate and lime (Ca hydroxide or carbonate) added to 50 mL mine water and the resultant pH (measured after 5 days) and precipitate formation and characteristics in response to the addition of Na hydroxide and hydrogen peroxide to the supernatant**

| Treatment | Al sulfate mg | Al sulfate solution* mL | $Ca(OH)_2$ or $CaCO_3$[1] mg | pH 5 d | NaOH ppt | $H_2O_2$ ppt |
|---|---|---|---|---|---|---|
| **0 Al H** | 0 | 0.000 | 36 | 8.2 | None | None |
| **0.25 Al H** | 9 | 0.146 | 45 | 6.5 | Weak orange green | Brown, effervesc. |
| **0.5 Al H** | 18 | 0.293 | 54 | 5.9 | Strong dark green | Brown, effervesc. |
| **1 Al H** | 36 | 0.586 | 72 | 4.4 | Weak pale green | Pale brown, still |
| **2 Al H** | 72 | 1.172 | 108 | 4.1 | V weak off white | Pale brown, still |
| **0 Al C** | 0 | 0.000 | 53 | 5.3 | Strong dark green | Brown, effervesc. |
| **0.25 Al C** | 9 | 0.146 | 66 | 5.4 | Strong dark green | Brown, sl effervesc. |
| **0.5 Al C** | 18 | 0.293 | 79 | 5.3 | V strong dark green | Brown, still |
| **1 Al C** | 36 | 0.586 | 106 | 4.5 | Weak pale y brown | Pale brown, still |
| **2 Al C** | 72 | 1.172 | 158 | 4.2 | Weak off white | Pale brown, still |

* 36% w/w solution with a density of 1.28 g/mL

[1] $CaCO_3$ equivalent to $Ca(OH)_2$ +10%

Note: pale brown, still, peroxide ppt became darker brown, effervescent with excess NaOH and $H_2O_2$

The quantity of alkalinity used to neutralise the added Al was consequently increased from 1 to 1.67 dmg $Ca(OH)_2$/mg Al sulfate. This greater liming load per unit Al added was an attempt to maximise the potential for LDH formation between Al and not only Fe and Mn, but also Mg. The pH results are shown in Table 23. The pattern of precipitate characteristics was similar to that described in Table 22.

**Table 23 Follow-up experiment to that described in Table 22, in which the range of Al amounts was widened and the lime application per unit Al was increased by two-thirds**

| Treatment | Al sulfate mg | Al sulfate solution* mL | $Ca(OH)_2$ or $CaCO_3$[1] mg | pH fresh |
|---|---|---|---|---|
| 0 Al H | 0 | 0.000 | 36 | 9.1 |
| 0. 5 Al H | 18 | 0.293 | 66 | 7.2 |
| 1 Al H | 36 | 0.586 | 96 | 5.4 |
| 2 Al H | 72 | 1.172 | 156 | 4.5 |
| 2.5 Al H | 90 | 1.465 | 186 | 4.2 |
| 0 Al C | 0 | 0.000 | 53 | 5.3 |
| 0.5 Al C | 18 | 0.293 | 97 | 4.6 |
| 1 Al C | 36 | 0.586 | 141 | 4.4 |
| 2 Al C | 72 | 1.172 | 229 | 4.3 |
| 2.5 Al C | 90 | 1.465 | 273 | 4.2 |

* 36% w/w solution with a density of 1.28 g $mL^{-1}$ [1] $CaCO_3$ equivalent to $Ca(OH)_2$ +10%

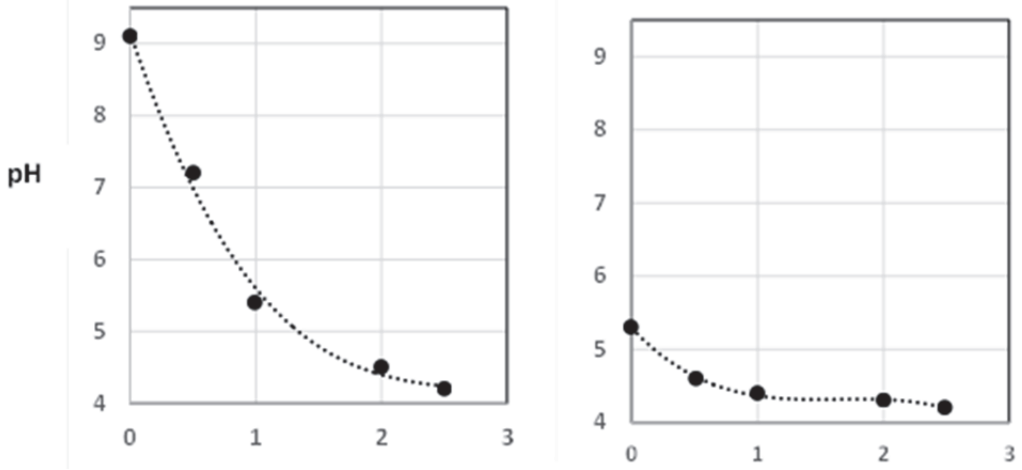


**Figure 6 pH resulting from Al addition and neutralisation with Ca hydroxide (left) or Ca carbonate (right). Data taken from Table 22. (Curves are closest fitting trend lines generated using the polynomial option in Excel).**

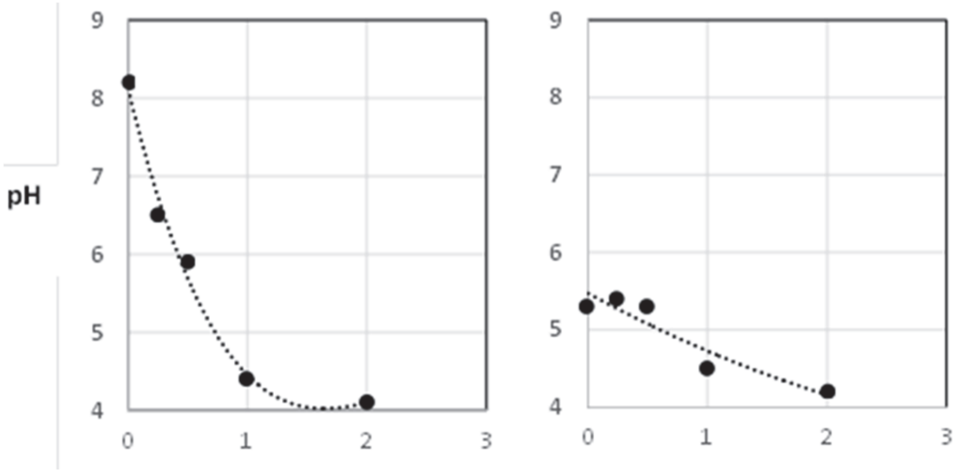


**Figure 7 pH resulting from Al addition and a greater degree of neutralisation with Ca hydroxide (left) or Ca carbonate (right) than in Figure 6. Data taken from Table 23. (Curves are closest fitting trend lines generated using the polynomial option in Excel).**

The response to greater lime addition was less than expected suggesting that there may be another factor involved such as armouring of lime particles by a film of Al or hydroxide which would slow down lime dissolution enough to prevent its full effect from being realised before pH measurement. This suggestion is supported at least in the case of carbonate lime by the higher pH after 5 days (Figure 6) than that measured fresh after adding extra lime (Figure 7).

### Experiment 3: testing different methods of adding Al sulfate and lime to mine water and evaluating supplementary treatment with Fe-Mn wad

Based on the information in experiments 1 and 2 it was possible to identify a level of Al sulfate and lime addition that might produce useful metal removal while still being practically affordable. In order to generate sufficient material for analysis and to allow continuous monitoring of pH during treatment the volume of mine water used was 300 mL. This was placed in a 500 mL beaker on a magnetic stirrer and varied quantities of Al sulfate (as a 36% solution) and Ca hydroxide (initially as a solid and finally as a suspension in 30 mL water which could be added to and mixed instantly with the stirred mine water) were added as described in Table 24.

**Table 24 Preliminary recipes for mine water treatment with aluminium sulfate and calcium hydroxide**

| Al sulfate 36% (mL) | $Ca(OH)_2$ (g) | Method of addition to 300 mL mine water | Final pH | Colour of precipitate |
|---|---|---|---|---|
| 4 | 10.72 | Mix Al sulphate with mine water, add solid lime gradually | 9.4 | Khaki green |
| 4 | 0.892 | Mix Al sulphate with mine water, add solid lime gradually | 6.4 | Brown |
| 5 | 0.900 | Mix Al sulphate with mine water, add 30 mL lime suspension instantly | 7.4 | Blue-green |
| 5 | 0.800 | Mix Al sulphate with mine water, add 30 mL lime suspension instantly | 5.2 | Pale blue-green |

Based on the pH values attained and the apparent value of instant addition of the lime as a suspension (this was done fairly readily after mixing the lime and water in a capped polypropylene centrifuge tube which pours quantitatively) a final combination was chosen consisting of:

- 4 mL Al sulfate (to give an augmented concentration in the mine water of 0.57 g Al/L),
- 0.90 g $Ca(OH)_2$ suspended in 30 mL water, and
- 300 mL of mine water.

Three orders of adding these ingredients to each other, always with vigorous stirring, were then evaluated as follows:

A. Mix Al sulfate with mine water, then add lime suspension;
B. Mix lime suspension with mine water, then add Al sulfate;
C. Mix Al sulfate with lime suspension, then add to mine water.

The following results of these three methods of addition were obtained. Method A, adding lime suspension to the aluminated mine water, produced a voluminous blue-green precipitate and the near-neutral suspension pH of 7.2 was reached rapidly. Method B, aluminating the limed mine water, achieved a suspension pH of 7.7 within 5 minutes, having descended from a pH of 12 at the instant of Al addition. The precipitate was very similar to that produced by method A. Method C, adding limed Al sulfate ("milk of alumina") to the raw mine water, achieved a pH of 9.5 immediately after addition which then dropped gradually to 8.4 within 5 minutes. The suspension was a paler blue-green colour than the other two suspensions and settled rapidly under gravity, such that the flocculated sediment occupied < 20% of the total volume after about 30 minutes of settling.

After 5 minutes of gentle stirring a 50 mL subsample of each suspension was removed and centrifuged and the clear supernatant was filtered and acidified for ICP-OES analysis after removing a small quantity for qualitative analysis. The remaining suspension was allowed to stand overnight and the pH measured again the following day. In all three cases the suspensions had equilibrated to pH 6.9, and a thin orange oxidized layer had formed at the top of the blue-green precipitates. Evidently the quite large differences in pH recorded at the time of decanting a sample for analysis were due to reaction rate differences associated with the manner of reagent addition. Since the idea of using Al sulfate as an amendment is to secure fast removal of metals, these initial differences due to method of reaction rather than quantity of reagent are crucial.

Qualitative analysis of the centrifuged supernatants gave a dilute, off-white precipitate with NaOH which turned brown and effervesced strongly after peroxide addition, suggesting that most Fe had been removed by all three methods but that there was a small amount of soluble Mn remaining in solution.

A portion of the centrifuged supernatants was reacted with the Fe-Mn wad (0.5 g finely powdered wad/50 mL solution) by shaking intermittently for 30 minutes then centrifuging and passing the supernatant through a 0.45 µm filter before acidifying for analysis.

The quantitative analysis of the mine water after being limed and aluminated by the three methods, and of the three treated waters which had received the additional treatment with Fe-Mn wad, is presented in Table 25. The data confirm the qualitative analysis indicating that Fe has essentially been removed and the Mn concentration is low. There is a suggestion that wad treatment can remove most of the remaining Mn if the solution pH is high enough (in the Cw treatment the Mn concentration was 1.8 mg $L^{-1}$). Treatment C, in which a limed Al sulfate solution is added to the mine water, appears to have the greatest effect in reducing both Fe and Mn concentration as well as leaving the smallest concentration of the main solutes, Ca and sulfate. The latter effect suggests that a solid phase such as ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) may have formed in the limed Al sulfate solution ("milk of alumina") prior to its addition to the mine water. The elevated pH of

8.4 and slightly higher Al concentration than in the other treatments are consistent with this interpretation. If an ettringite solid had formed its dissolution rate may have slowed the approach to an equilibrium pH of 6.9 recorded a day later.

**Table 25 Chemical composition of six products of mine water treatment with lime and Al sulfate in different orders of addition, and with ferromanganese wad as an optional extra treatment, compared with original mine water**

| Treatment | Method | pH | Ca | Mg | Na | K | Fe | Mn | Al | Sum | S |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | mmolc/L | | |
| A | Aluminated water + lime | 7.2 | 87.0 | 11.7 | 4.5 | 0.49 | 0.06 | 0.32 | 0.05 | 104 | 134 |
| B | Limed water + Al | 7.7 | 78.2 | 8.6 | 3.3 | 0.48 | 0.17 | 0.70 | 0.03 | 91 | 139 |
| C | Limed Al + water | 8.4 | 48.6 | 15.3 | 3.3 | 0.46 | 0.02 | 0.24 | 0.14 | 68 | 95 |
| Aw | A + wad | 7.2 | 46.2 | 12.2 | 4.2 | 0.50 | 0.02 | 0.13 | 0.03 | 63 | 80 |
| Bw | B + wad | 7.7 | 40.1 | 10.0 | 3.6 | 0.45 | 0.02 | 0.48 | 0.03 | 55 | 76 |
| Cw | C + wad | 8.4 | 38.2 | 15.0 | 3.2 | 0.47 | 0.02 | 0.07 | 0.03 | 57 | 79 |
| **Original mine water** | | **3.4** | **35** | **19** | **4** | **<1** | **12** | **2** | **<1** | **72** | **72** |

While treatment C among the three methods may have removed the most Fe and Mn and left the lowest solute concentration in solution, it had the least effect in reducing the concentration of Mg. This may have been because in treatment C the main effect is one of an elevated pH (initially 9.5, decreasing gradually to 8.4 after 5 minutes) being buffered by the presence of a slowly dissolving solid (ettringite) which might induce the hydrolytic precipitation of Fe and Mn more than that of Mg. By contrast, treatment B, which involved liming the mine water before dosing with Al sulfate, resulted in the lowest Mg concentration (less than half the original) but left the largest concentration of Fe and Mn. There appeared to be an inverse relationship between Mn and Mg in solution, as depicted in Figure 8 for all six treatments. It is not certain whether these results relate to the formation by Al with other metals of a layered double hydroxide (LDH), the likelihood of which was discussed earlier. Certainly it seems the most plausible explanation for such a marked drop in Mg solubility at a near neutral pH. The Mg-Mn relationship in Figure 8 may point to a competition between these ions for positions in an LDH-type solid. As expected, soluble Na and K show conservative behaviour and their concentration remains essentially unchanged after all water treatments.

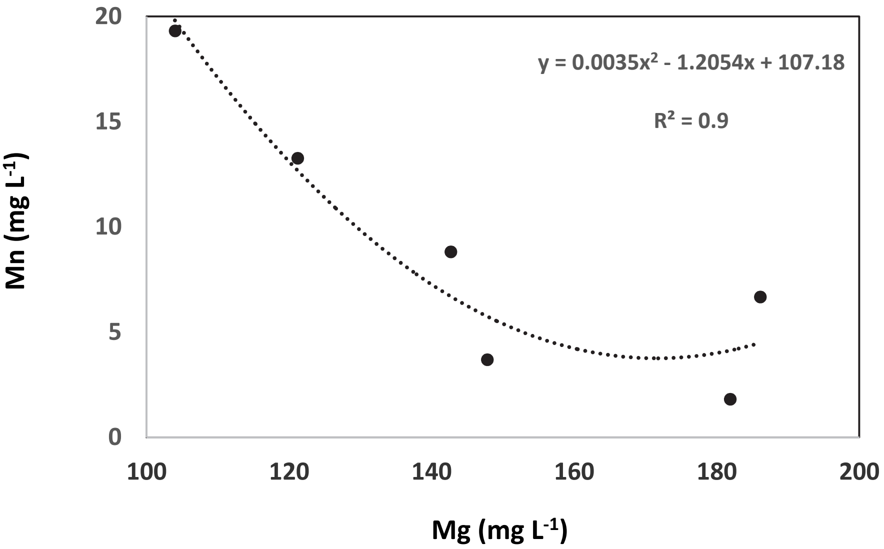


**Figure 8 Relationship between Mn and Mg concentration in the six treated mine waters (Table 11)**

The effect of the Fe-Mn wad is interesting. Its removal of Mn was not as marked as might have been expected from the experiments of Duarte and Ladeira (2011). On the other hand it did succeed in considerably reducing the concentration of both Ca and sulfate, the extent of which is best appreciated by examining each treatment separately with and without the wad (Table 25). For treatments A and B, the wad almost halved both Ca and $SO_4$ concentrations (assuming all the S is sulfate). This could be due to both the cation exchange capacity of the Mn oxide component and the capacity of Fe and Mn oxides to specifically adsorb anions such as sulfate (the Fe oxide component is probably the most influential in this respect). Practical implications of these results, as well as those of the land treatment simulation experiments, will be covered in the next chapter.

# CHAPTER 5 SUPPLEMENTARY DATA FROM EXPERIMENTAL LAND TREATMENT AND DISCUSSION OF OPTIONS FOR IRRIGATING WITH MINE WATER

## 5.1 MINERALOGY OF EVAPORATED MINE WATER RESIDUES AND FERROMANGANESE WAD

Up to this point characterisation of the secondary solids precipitated in the simulated land treatment experiment has been possible by indirect inference based on the data in Tables 4 and 5, especially for the solids made by evaporation in the presence of amendments but in the absence of a soil or mine tailings substrate. The progressive evolution could also be tracked from the sequence of photos in Appendix 4, showing colour changes of the precipitates offering clues about oxidation state and degree of neutralisation. We can calculate the chemical composition of the final precipitates by difference (mine water constituents and amendments minus leachate constituents), but ultimately require direct evidence in order to draw conclusions about mineralogical composition. X-ray diffraction data for the three evaporation residues, 0M0, 0MC and 0MH, appear in Appendix 6. They confirm that the dominant crystalline mineral in all three cases is gypsum, with accessory jarosite in 0M0 (probably natrojarosite given the dominance of sodium (Na) over potassium (K) in the mine water) consistent with the acidic leachate pH of 3.4 (Table 18), while TMC had some accessory calcite indicating incomplete reaction of the mine water with the calcium carbonate ($CaCO_3$) amendment. On the other hand the TMH precipitate consists of gypsum as virtually the only crystalline solid (there is a trace of calcite which probably formed through aerial carbonation of the excess Ca hydroxide that would have existed in the early stages of the experiment). What is noteworthy is the absence of readily detectable peaks for any of the iron (Fe) oxides (goethite, hematite), or hydroxides (ferrihydrite) or hydroxysulfates (besides the jarosite in 0M0; schwertmannite would not have been unexpected in these precipitates – Cornell and Schwertmann, 2003). This could partly be due to the eclipsing effect of the dominant, highly crystalline gypsum in all the samples, and partly to the very poor crystallinity that typically characterises secondary Fe compounds formed through hydrolysis in the presence of a variety of contaminants. This is one aspect that might merit more detailed investigation, since identifying the mineral forms of precipitated Fe could give greater certainty about the long-term stability of solids sequestrated during land treatment. What does seem likely is that if Fe minerals are not readily identified in the discreet solids formed by evaporation and neutralisation without soil or tailings, then the chances are remote of identifying any in the treated mine tailings and soil.

Regarding the ferromanganese wad a powder sample was examined twice by X-ray diffraction using a cobalt tube (University of Pretoria) and a copper tube (courtesy Dr Laure Aimoz, Olympus Industrial Systems, France). Both diffractograms (not shown) indicated hematite as the dominant mineral with accessory quartz. In the Co-generated XRD pattern some goethite and kaolinite was also identified. No crystalline phase of manganese (Mn) oxide could be detected which is apparently quite normal for supergene wad deposits of this kind (Dr Ilmarie Rencken, personal communication). The abundance of Mn oxide in the material was readily confirmed by strong exothermic reaction with hydrogen peroxide. Further work with the wad as an amendment for mine water would require specific surface determination and surface chemical characterisation (ion adsorption and zero point of charge or zeta potential).

## 5.2 LAND TREATMENT OF TAILINGS WITH MORE CONCENTRATED PLACEMENT OF AMENDMENTS AND WATER

Leachates from the more concentrated land treatment experiment have been analysed and the major cation composition (determined by ICP-OES) is shown in Table 26. The "+" and "0.5+" suffixes represent a situation in which, instead of all amendments and precipitates being mixed to a depth of 1 m, they are incorporated to a depth of about 0.2 or 0.5 m, respectively (see Table 11 and associated discussion for a fuller explanation). The data in Table 26 confirm that Ca is largely retained in the solid phase (most probably as gypsum again) while the leachate is dominated by Mg with an accessory amount of Na and a minor amount of Mn. These results are similar to those reported for TMC and TMH in Table 17 except that Mg concentrations in particular are considerably higher. The explanation for this is may lie in the more concentrated simulation having taken place over a compressed time scale of five days with continuous evaporation and no daily evaporation and desiccation as occurred in the first simulation trial. The frequency of wetting and drying and the degree of desiccation with each cycle is something that also warrants more detailed investigation in follow-up studies.

**Table 26 Metals in leachate from mine tailings after more concentrated treatment with mine water and alkaline amendments or wad and Al (treatment codes are explained in Table 10)**

| Treatment | Method | Ca | Mg | Na | K | Fe | Mn | Sum |
|---|---|---|---|---|---|---|---|---|
| | | mmolc/L | | | | | | |
| TMC+ | Tailings mine water + carbonate | 19.1 | 162 | 28.3 | 2.0 | 0.02 | 14.7 | 226 |
| TMH+ | Tailings mine water + hydroxide | 15.4 | 159 | 27.0 | 1.8 | 0.02 | 4.8 | 208 |
| TMC 0.5+ | Tailings mine water + carbonate | 15.4 | 172 | 28.1 | 1.9 | 0.02 | 13.0 | 230 |
| TMH 0.5+ | Tailings mine water + hydroxide | 16.0 | 138 | 26.5 | 2.0 | 0.02 | 11.7 | 194 |
| TMH 0.5 +Alwad | Tailings mine water + hydroxide + wad | 20.9 | 171 | 33.5 | 1.8 | 0.02 | 16.9 | 244 |

The more concentrated land treatment experiment provided an opportunity to evaluate the effect of a fivefold enrichment of the secondary solids on the mine tailings. The most obvious effect was on colour, and Figure 9 is an attempt to capture the gradation from the leached appearance of unamended mine tailings (TM0 and TP0; the former is even more bleached probably as a result of its having become acidified during leaching with mine water and oxidation) through the diffuse incorporation treatments (TMC, TMH) via the intermediate (0.5+) to the most concentrated (+) treatments of mine tailings, and at the other end of the spectrum the precipitates themselves without the diluting effect of tailings material (0MC, 0MH). The unamended precipitate, 0M0, which as indicated earlier contains jarosite in addition to the dominant gypsum, appears white when dry (Figure 9) but as shown in Appendix 4 was a pale yellow colour when wet (this is the distinctive "yellow boy" that is commonly found in acid sulfate soils; jarosite, and to a lesser extent schwertmannite, are the minerals that most likely provide this colour).

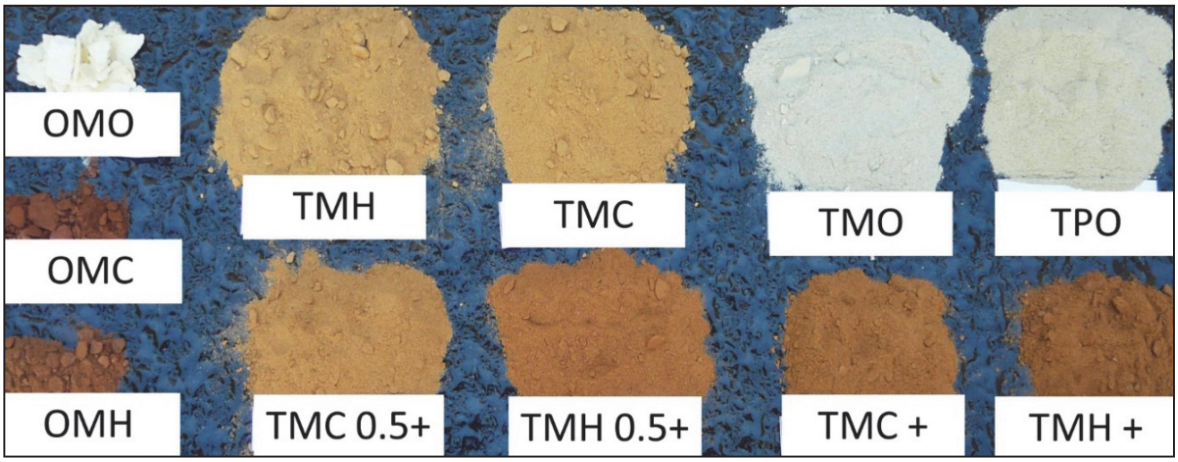


**Figure 9 Ergo mine tailings (T) after different treatments with mine water (M) or pure water (P) and either hydroxide (H), carbonate (C) or no (0) lime and simulation of land treatment that would involve mixing to depth of 1 m (TMC, TMH), 0.5 m (TMC 0.5+, TMH 05+) or 0.25 m (TMC +, TMH +). The corresponding solid precipitates obtained after evaporation of mine water, with or without lime, in the absence of tailings, are shown on the left (0M0, 0MC and 0MH).**

There is also some indication in Figure 9 of aggregation in the ferruginised mine tailings. It should be emphasised, however, that the source of this aggregation is not necessarily precipitated Fe oxides as was postulated in our earlier review (Chapter 2), since the bleached TMO material showed a degree of coherence in both wet and dry states similar to that of the Fe-enriched materials. The dominant gypsum component is, according to the sharp XRD reflections, well crystallized. It could be envisaged that interlocking gypsum crystals, which are commonly elongated and lath-shaped, would contribute to the observed aggregation. Having said this it should also be pointed out that the coherence of the aggregates was weak, even in the dry state, and that an even greater concentration of secondary solids than that achieved in TMC+ and TMH+ would be needed before any marked aggregating effect of Fe compounds could be observed. Partly for this reason, and also because the quantities of material were too small for many physical tests to be carried out, the assessment of the land treatment effects on physical properties of the tailings was not pursued beyond the qualitative observations reported above. Some physical data were obtained for the two soils, however, and these are presented in the next section.

## 5.3 MINE WATER AND CHEMICAL AMENDMENT EFFECTS ON SOIL PHYSICAL PROPERTIES

The response of the black clay (textural analysis indicated that it is more correctly classified as a silty clay loam) and the red loam to treatment with mine water and alkaline amendments was assessed by means of a swelling index, measuring the expansion of the soil when immersed in water (Table 27) and soil water characteristic curves (Figure 19), performed by the traditional method using pressure plate apparatus as described in Dane and Topp (2002).

**Table 27 Swelling of the black clay and red loam soils in response to treatments in the second land treatment simulation [swelling index obtained by the method of Sivapullaiah et al. (1987)]***

| Treatment code | Soil | Water added | Amendment | Water leached | Swelling index (%) |
|---|---|---|---|---|---|
| BC-UNTREAT | Black clay | None | None | None | 40 |
| BC-MWNL | Black clay | Mine | None | Mine | 40 |
| BC-MWOH | Black clay | Mine | $Ca(OH)_2$ | Mine | 60 |
| BC-MWCO | Black clay | Mine | $CaCO_3$ | Mine | 50 |
| BC-DWOH | Black clay | Pure | $Ca(OH)_2$ | Pure | 35 |
| BC-MWOH# | Black clay | Mine | $Ca(OH)_2$ | Pure | 50 |
| RS-UNTREAT | Red loam | None | None | None | 30 |
| RS-MWNL | Red loam | Mine | None | Mine | 25 |
| RS-MWOH | Red loam | Mine | $Ca(OH)_2$ | Mine | 30 |
| RS-MWCO | Red loam | Mine | $CaCO_3$ | Mine | 20 |
| RS-DWOH | Red loam | Pure | $Ca(OH)_2$ | Pure | 30 |
| RS-MWOH# | Red loam | Mine | $Ca(OH)_2$ | Pure | 20 |

*Data courtesy of I Storm, University of Pretoria

The results in Table 27 indicate that the black clay shows an enhancement in swelling capacity when treated with a combination of both mine water and an alkaline amendment (either lime or calcium carbonate). The red loam showed no discernible effect of treatment on swelling, perhaps because the inherent swelling tendency of this soil is comparatively small to begin with. It is not certain what the mechanism is of swelling enhancement. The results were almost identical with and without washing to remove soluble salts. An iron hydroxide precipitate forms when mine water and lime or limestone are added together, but the manner in which such a precipitate would react with existing clay surfaces to enhance swelling is not clear. It would probably be a pH dependent phenomenon because of the potential for positive surface charge to develop on the iron hydroxide at lower pH.

The soil water characteristic curves for the two soils (Figure 10) are consistent with their texture, as well as the mineralogy expected of them on the basis of soil morphology (smectitic black clay vs. kaolinitic, oxidic red loam). In neither soil, however, was there any evidence of a significant shift of the characteristic curve in response to mine water and alkaline amendments.

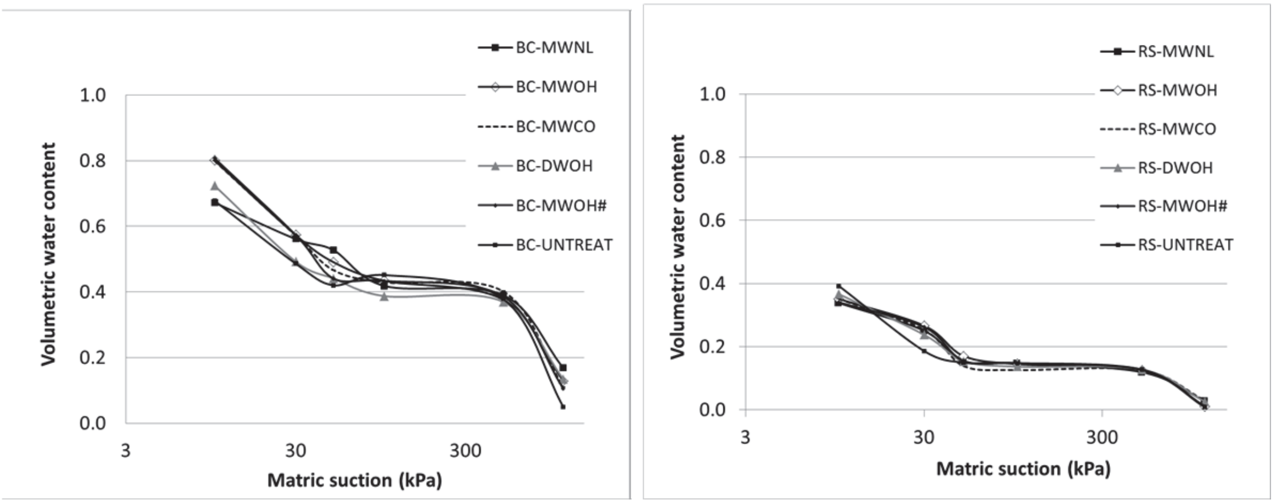


**Figure 10 Soil water characteristic curves for the black clay (left) and red loam (right) soils in the second land treatment simulation trial (see Table 13 for explanation of treatment codes; data kindly provided by I Storm, University of Pretoria)**

## 5.4 GENERAL DISCUSSION OF OPTIONS FOR IRRIGATING WITH MINE WATER

In planning the short research project the rationale behind treating the mine water was the prospect of producing water suitable for irrigated agriculture. We also speculated that the mine water composition is such that with suitable alkaline ameliorants, it might be possible to irrigate the mine water directly onto land without pre-treatment and still have a sustainable vegetation cover. In order to evaluate the land treatment option, we needed to calculate the likely sequestration of salts that would take place. Based on the leachate and mine water analyses in Tables 13-17, Table 18 and Table 26, the fraction of added metal cations, individually and combined as total salt (sulfates), which precipitates during simulated land treatment and therefore would probably not appear in irrigation return flow, is shown as a percentage in Table 28 for both the mine tailings and the black clay soil.

**Table 28 Percentage of metal and salt sequestered from mine water by simulated land treatment on Ergo mine tailings (T) and black clay soil (S) in relation to type of amendment and intensity of mine water application (for explanation of treatment codes see Table 10 and 12)**

| Treatment | Metal and salt retention (%) | | | | | |
|---|---|---|---|---|---|---|
| | Ca | Mg | Na | Fe | Mn | Total salt* |
| TM0 | 93 | 27 | 8 | 23 | 19 | 65 |
| TMC | 92 | 26 | -10 | 97 | 21 | 75 |
| TMH | 93 | 26 | -12 | 91 | 25 | 74 |
| TMC+ | 95 | 15 | 29 | 100 | 28 | 71 |
| TMH+ | 95 | 12 | 28 | 100 | 75 | 72 |
| TMC0.5+ | 96 | 10 | 30 | 100 | 36 | 71 |
| TMH0.5+ | 95 | 27 | 34 | 100 | 43 | 75 |
| TMH0.5+Alwad | 93 | -1 | 6 | 100 | 7 | 65 |
| SMO5 | 96 | 67 | 54 | 99 | 52 | 88 |
| SMC5 | 96 | 80 | 59 | 100 | 91 | 92 |
| SMH5 | 95 | 80 | 62 | 100 | 92 | 91 |

*Based on allocation of sulfate to metal cations

Interestingly, the least effective of the treatments, namely either unamended tailings (TMO) or tailings amended with a combination of lime, Al sulfate and Fe-Mn wad, still retained 65% of the added salt simply through evaporation. This salt is almost entirely gypsum, since most of the Na and Mg sulfate would be soluble (as confirmed in leachate analyses in Table 17 and Table 26), but would include some precipitated Fe and Mn. The idea of sequestering sulfate from mine water as gypsum has been in circulation for some time (Du Plessis, 1983; Annandale et al., 2002) and it certainly makes the dominant contribution in the case of the gold mine water studied here. Of concern, however, was the relatively high Mg, Fe and Mn content of the mine water from the Western Basin (Maree et al., 2013). In Table 28 it is evident that as much as a third of the Mg, between a quarter and three quarters of the Mn, and effectively all of the Fe can be sequestered by the right combination of irrigation method and amendment. In no case did mine tailings sequester more than 75% of the salt load. The black clay soil, on the other hand, removed about 90% of added solutes even without alkaline amendment, attesting to not only its powerful adsorption capacity but also its strong buffer capacity. The earlier remark about these montmorillonite clays, so widely found on the South African Highveld, being an underappreciated asset for waste treatment of various kinds bears repeating here.

In closing, some additional points may be worth making that apply more generally to the issue of mine water treatment and the irrigation option:

- Contrary to the assumptions of Maree et al. (2013), limestone has an effect on soluble Mn concentration while lime has an effect, sometimes marked, on Mg concentration. These assumptions may therefore be inappropriate and the evaluation of processes such as the limestone-lime sequence of treatments should be modified accordingly.
- The layered double hydroxide (LDH) hypothesis and the effectiveness of Al sulfate in giving substance to it appear to be supported by our results in Chapter 2.
- The ferromanganese wad idea is also supported by the results but quantitative assessment suggests that it would probably not be economic.
- Land treatment is an exciting prospect, however:
    - Mine tailings are little more than a skeletal substrate for solute sequestration by evaporation and chemical precipitation (mainly as gypsum with accessory iron hydroxide)
    - Some soils may in certain respects be an almost ideal substrate for solute retention from mine water, black clays in particular.
    - Other common Highveld soils such as red loams of the Hutton form are only moderately successful in attenuating solutes and buffering pH, and are significantly inferior to the black clay soils (see results of the second land treatment experiment comparing the red loam with the black clay, Tables 21 and 22).
- A cost-benefit analysis of Al sulfate should include its effect on the flocculation volume of the sludge.
- Nitrification inhibition in the black clay by ferrous Fe and soluble Mn is strongly indicated by nitrate data (Tables 13-17) and could be a very important result.

# CHAPTER 6 MODEL SIMULATION OF LONG-TERM IRRIGATION WITH NEUTRALISED MINE WATER

## 6.1 INTRODUCTION

Extensive work on irrigating field crops with mine water has been done for the Mpumalanga coalfields of South Africa, including laboratory studies, glasshouse trials, field trials and monitoring on commercial farms (Annandale et al., 1999; Annandale et al., 2002; Beletse, 2008; Jovanovic, Annandale et al., 2004). Work was also done to better understand the environmental impact of this practice, concluding that soils under the correct agronomic management could be sustainably irrigated over the long-term, and that when considering larger scale environmental impact, the geohydrological setting of the mine water irrigation scheme is of critical importance (Annandale et al., 1999; Annandale et al., 2006; Annandale et al., 2002; Idowu et al., 2008). Crops that have been successfully irrigated at commercial scales include sugar bean, wheat, maize, potatoes (Jovanovic et al., 2004) and planted pastures (Beletse, 2008).

Modelling has played a key role in investigating potential crop yields, the degree of gypsum precipitation, soil salinization, salt leaching loads and long-term sustainability. When irrigating with calcium sulphate ($CaSO_4$)-rich waters specifically, the model predicted that soil salinity would increase upon initiation of irrigation, and then fluctuate around acceptable levels due to gypsum precipitation and the leaching of more soluble salts such as sodium (Na) and magnesium (Mg).

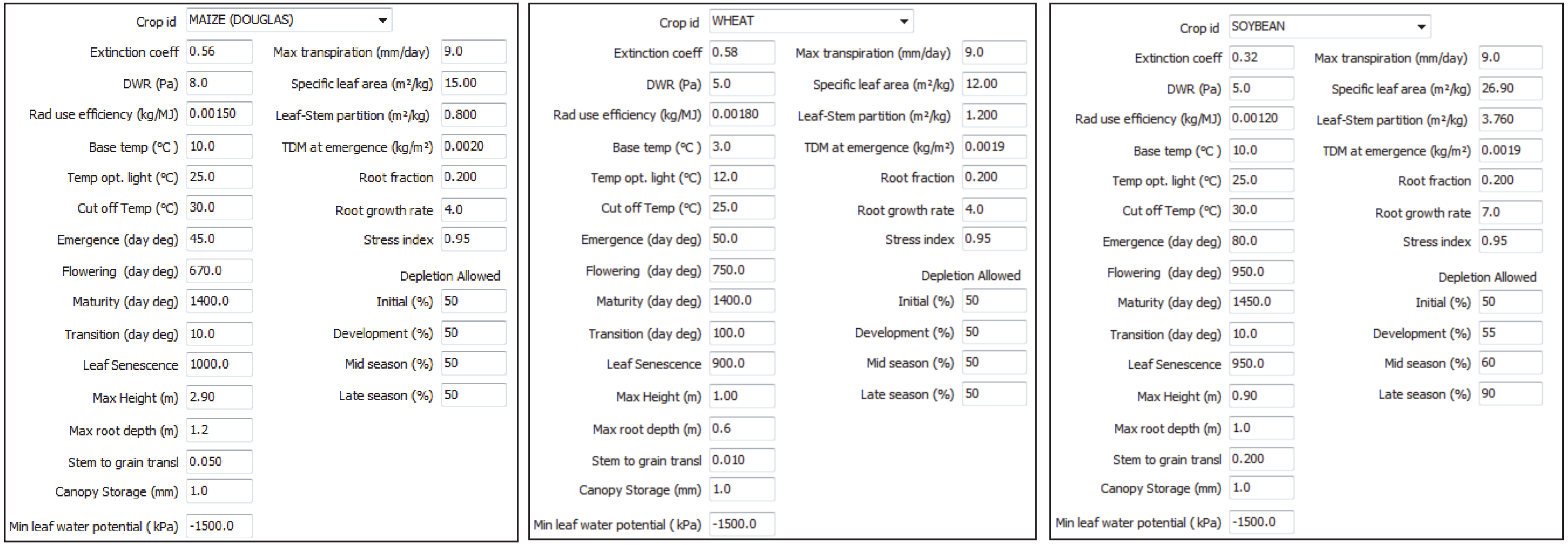
While the principle remains the same, to date no research has been done on irrigating crops using poor quality gold mine water from the Vaal Basin. The objective of this simulation study is therefore to investigate crop growth and salt dynamics when irrigating with neutralised water from gold mines in the region.

## 6.2 MATERIALS AND METHODS

SWB-Sci is a mechanistic, generic-crop, daily time-step soil water and salt balance model (Annandale et al., 2002; Annandale, 1999). The chemical precipitation or dissolution of lime and gypsum is calculated using a chemical-equilibrium subroutine based on (Robbins, 1991). A cascading soil water balance approach is used and complete mixing is assumed between the resident and draining salt fractions. SWB-Sci has been calibrated and tested using data from research conducted on the impact of irrigation with mine water on crop growth and soil and water resources in the Mpumalanga coal fields (Annandale et al., 1999; Annandale et al., 2002; Jovanovic et al., 2004, Beletse, 2008).

The influence of salinity stress on crop growth was previously simulated in SWB-Sci by adding osmotic potential, calculated as a function of ionic composition (Campbell, 1985), to the matric and gravitational potentials. For the purpose of this study, however, SWB-Sci has been modified to use an approach based on Maas and Hoffman (1977). This approach assumes that maximum yield is achieved until a salinity threshold is reached, after which yield is reduced using a linear function based on crop-specific salt sensitivity. In the model, the calculated salinity stress factor is used to reduce the transpiration occurring from each soil layer as a function of the saturated paste electrical conductivity ($EC_e$) of that layer on a daily time-step. When determining whether water stress will occur, osmotic potential is therefore not considered in this version of the model.

A summer maize (*Zea mays* L.) – winter wheat (*Triticum aestivum*) rotation was simulated. For the 50-year simulation (1950-2000), the planting date was 25 November for maize and 29 May for wheat. As relatively poor yields were simulated for maize which is a salt-sensitive crop, additional simulations were also run for soybean (*Glycine max*) using the same planting date as for maize. SWB-Sci crop parameters for these crops were obtained from data collected in WRC Project titled, 'Water use efficiency of irrigated agricultural crops determined with satellite imagery' *(WRC report no TT 602/14)* and from the SWB-Sci database for wheat and soybean (Figure 11). Centre pivot irrigation was simulated to commence when crop available soil water was depleted by 30 mm, continuing until the soil water content had returned to field capacity.



| | | | |
|---|---|---|---|
| Crop id | MAIZE (DOUGLAS) | | |
| Extinction coeff | 0.56 | Max transpiration (mm/day) | 9.0 |
| DWR (Pa) | 8.0 | Specific leaf area (m²/kg) | 15.00 |
| Rad use efficiency (kg/MJ) | 0.00150 | Leaf-Stem partition (m²/kg) | 0.800 |
| Base temp (°C ) | 10.0 | TDM at emergence (kg/m²) | 0.0020 |
| Temp opt. light (°C) | 25.0 | Root fraction | 0.200 |
| Cut off Temp (°C) | 30.0 | Root growth rate | 4.0 |
| Emergence (day deg) | 45.0 | Stress index | 0.95 |
| Flowering (day deg) | 670.0 | Depletion Allowed | |
| Maturity (day deg) | 1400.0 | Initial (%) | 50 |
| Transition (day deg) | 10.0 | Development (%) | 50 |
| Leaf Senescence | 1000.0 | Mid season (%) | 50 |
| Max Height (m) | 2.90 | Late season (%) | 50 |
| Max root depth (m) | 1.2 | | |
| Stem to grain transl | 0.050 | | |
| Canopy Storage (mm) | 1.0 | | |
| Min leaf water potential ( kPa) | -1500.0 | | |

| | | | |
|---|---|---|---|
| Crop id | WHEAT | | |
| Extinction coeff | 0.58 | Max transpiration (mm/day) | 9.0 |
| DWR (Pa) | 5.0 | Specific leaf area (m²/kg) | 12.00 |
| Rad use efficiency (kg/MJ) | 0.00180 | Leaf-Stem partition (m²/kg) | 1.200 |
| Base temp (°C ) | 3.0 | TDM at emergence (kg/m²) | 0.0019 |
| Temp opt. light (°C) | 12.0 | Root fraction | 0.200 |
| Cut off Temp (°C) | 25.0 | Root growth rate | 4.0 |
| Emergence (day deg) | 50.0 | Stress index | 0.95 |
| Flowering (day deg) | 750.0 | Depletion Allowed | |
| Maturity (day deg) | 1400.0 | Initial (%) | 50 |
| Transition (day deg) | 100.0 | Development (%) | 50 |
| Leaf Senescence | 900.0 | Mid season (%) | 50 |
| Max Height (m) | 1.00 | Late season (%) | 50 |
| Max root depth (m) | 0.6 | | |
| Stem to grain transl | 0.010 | | |
| Canopy Storage (mm) | 1.0 | | |
| Min leaf water potential ( kPa) | -1500.0 | | |

| | | | |
|---|---|---|---|
| Crop id | SOYBEAN | | |
| Extinction coeff | 0.32 | Max transpiration (mm/day) | 9.0 |
| DWR (Pa) | 5.0 | Specific leaf area (m²/kg) | 26.90 |
| Rad use efficiency (kg/MJ) | 0.00120 | Leaf-Stem partition (m²/kg) | 3.760 |
| Base temp (°C ) | 10.0 | TDM at emergence (kg/m²) | 0.0019 |
| Temp opt. light (°C) | 25.0 | Root fraction | 0.200 |
| Cut off Temp (°C) | 30.0 | Root growth rate | 7.0 |
| Emergence (day deg) | 80.0 | Stress index | 0.95 |
| Flowering (day deg) | 950.0 | Depletion Allowed | |
| Maturity (day deg) | 1450.0 | Initial (%) | 50 |
| Transition (day deg) | 10.0 | Development (%) | 55 |
| Leaf Senescence | 950.0 | Mid season (%) | 60 |
| Max Height (m) | 0.90 | Late season (%) | 90 |
| Max root depth (m) | 1.0 | | |
| Stem to grain transl | 0.200 | | |
| Canopy Storage (mm) | 1.0 | | |
| Min leaf water potential ( kPa) | -1500.0 | | |

**Figure 11** From left to right, maize, wheat and soybean crop growth parameters used for the long-term SWB-Sci simulation

A one metre deep virtual soil profile was initialized in the model with assumed values for soil chemical parameters (Table 29 and Table 30). For all 11 layers field capacity was set at 0.33 $m^3$ $m^{-3}$, permanent wilting point at 0.23 $m^3$ $m^{-3}$ and bulk density at 1200 kg $m^{-3}$. The drainage factor, which determines the fraction of water between field capacity and saturation that can drain to the layer below, was set at 0.6, while the maximum drainage rate for the profile was set at 50 mm $day^{-1}$.

**Table 29 Soil characteristics including soluble cation concentrations assumed for the hypothetical soil profile in the SWB-Sci simulations**

| | | | Soluble cations (cmol$_c$ kg$^{-1}$) | | | |
|---|---|---|---|---|---|---|
| **Depth** | **pH** | **EC$_e$ (mS m$^{-1}$)** | **Ca$^{2+}$** | **K$^+$** | **Mg$^{2+}$** | **Na$^+$** |
| 0-5 | 6.2 | 385 | 0.89 | 0.01 | 1.27 | 1.76 |
| 5-10 | 6.2 | 385 | 0.89 | 0.01 | 1.27 | 1.76 |
| 10-21 | 6.2 | 385 | 0.89 | 0.01 | 1.27 | 1.76 |
| 21-31 | 6.4 | 312 | 1.08 | 0.01 | 1.42 | 1.13 |
| 31-41 | 6.4 | 312 | 1.08 | 0.01 | 1.42 | 1.13 |
| 41-51 | 7.5 | 135 | 0.33 | 0.00 | 0.41 | 0.65 |
| 51-61 | 7.5 | 135 | 0.33 | 0.00 | 0.41 | 0.65 |
| 61-71 | 8.2 | 89 | 0.16 | 0.00 | 0.20 | 0.52 |
| 71-81 | 8.2 | 89 | 0.16 | 0.00 | 0.20 | 0.52 |
| 81-91 | 8.2 | 89 | 0.16 | 0.00 | 0.20 | 0.52 |
| 91-101 | 8.2 | 89 | 0.16 | 0.00 | 0.20 | 0.52 |

**Table 30 Exchangeable ion concentrations assumed for the hypothetical soil profile in the SWB-Sci simulations**

| **Depth** | Exchangeable ions (cmol$_c$ kg$^{-1}$) | | | | |
|---|---|---|---|---|---|
| | **Ca$^{2+}$** | **K$^+$** | **Mg$^{2+}$** | **Na$^+$** | **SO$_4^{2-}$** |
| 0-5 | 23.21 | 0.29 | 19.58 | 3.26 | 3.43 |
| 5-10 | 23.21 | 0.29 | 19.58 | 3.26 | 3.43 |
| 10-21 | 23.21 | 0.29 | 19.58 | 3.26 | 3.43 |
| 21-31 | 30.62 | 0.26 | 24.62 | 2.21 | 2.87 |
| 31-41 | 30.62 | 0.26 | 24.62 | 2.21 | 2.87 |
| 41-51 | 31.58 | 0.26 | 26.78 | 2.26 | 0.54 |
| 51-61 | 31.58 | 0.26 | 26.78 | 2.26 | 0.54 |
| 61-71 | 31.75 | 0.32 | 26.41 | 0.00 | 0.67 |
| 71-81 | 31.75 | 0.32 | 26.41 | 0.00 | 0.67 |
| 81-91 | 31.75 | 0.32 | 26.41 | 0.00 | 0.67 |
| 91-101 | 31.75 | 0.32 | 26.41 | 0.00 | 0.67 |

Neutralised mine water qualities that were used in the simulations are presented in Table 31. In addition to data obtained from Maree et al. (2013), estimated water qualities following neutralization with limestone based on stoichiometric calculations for predicted water qualities decanting from the Western, Central and Eastern Basins were used. Furthermore, resultant water quality for the limed Al treatment investigated in this project (see Chapter 4), and historical data from the Grootvlei HDS plant was also used in the simulations. It must be emphasized that the dynamic nature of the mine water composition with time and location results in a high degree of uncertainty in the final neutralised mine water quality from different locations and over time. These qualities and simulations therefore only serve to provide a guideline with regards to crop growth and salt dynamics. They also give us a range of possibilities. In addition to the simulations specified in Table 31, simulations were also run for the Western Basin with good quality irrigation water and for rainfed maize production.

**Table 31 Predicted water qualities following mine water treatment according to different approaches used in the SWB-Sci simulations**

| Basin / Treatment | Ca | Mg | Na | $SO_4$ | Cl | Ca | Mg | Na | $SO_4$ | Cl |
|---|---|---|---|---|---|---|---|---|---|---|
| | mol $L^{-1}$ | | | | | mg $L^{-1}$ | | | | |
| Western - limestone + lime* | 0.019 | 0.006 | 0.002 | 0.024 | 0.001 | 760 | 147 | 50 | 2285 | 37 |
| Western - limed Al[ꝉ] | 0.024 | 0.008 | 0.003 | 0.031 | 0.003 | 960 | 192 | 69 | 2976 | 105 |
| Western - limestone[‡] | 0.012 | 0.004 | 0.006 | 0.017 | 0.001 | 480 | 96 | 138 | 1632 | 35 |
| Central - limestone[‡] | 0.012 | 0.005 | 0.007 | 0.017 | 0.004 | 480 | 120 | 161 | 1632 | 140 |
| Eastern - limestone[‡] | 0.012 | 0.005 | 0.010 | 0.017 | 0.005 | 480 | 120 | 230 | 1632 | 175 |
| Eastern - Grootvlei HDS[#] | 0.011 | 0.006 | 0.011 | 0.017 | 0.006 | 421 | 134 | 244 | 1667 | 205 |

*Taken from Maree et al. (2013)

[ꝉ] See Chapter 4

[‡] Estimated using stoichiometric calculations

[#] Department of Water and Sanitation monitoring data

Long-term weather data for Krugersdorp were used for the Western Basin simulations and long-term weather data from Germiston were used for the Central and Eastern Basin simulations. Monthly average maximum and minimum temperature and rainfall data are presented in Table 32.

**Table 32 Monthly average maximum and minimum temperatures and rainfall for the Krugersdorp and Germiston weather stations**

| Site | Variable | Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Krugersdorp | $T_{max}$ (°C) | 26.5 | 26.3 | 25.2 | 23.0 | 20.0 | 17.8 | 17.6 | 20.3 | 24.4 | 25.0 | 25.0 | 26.0 |
| | $T_{min}$ (°C) | 14.6 | 14.1 | 12.8 | 9.6 | 5.4 | 2.3 | 2.3 | 4.3 | 9.0 | 11.5 | 12.7 | 14.0 |
| | Rainfall (mm) | 115 | 91 | 89 | 53 | 18 | 7 | 4 | 8 | 19 | 65 | 100 | 115 |
| Germiston | $T_{max}$ (°C) | 27.2 | 26.3 | 24.5 | 22.2 | 19.8 | 16.9 | 17.8 | 20.0 | 23.8 | 24.9 | 25.5 | 25.9 |
| | $T_{min}$ (°C) | 15.4 | 15.1 | 13.6 | 10.8 | 7.2 | 4.1 | 4.2 | 6.3 | 10.1 | 12.0 | 13.1 | 14.3 |
| | Rainfall (mm) | 127 | 95 | 88 | 46 | 17 | 6 | 5 | 5 | 24 | 69 | 106 | 107 |

As the water qualities and climates are relatively similar, interpretation of model outputs is focused on the Western Basin limestone + lime treated water, with the results for the other simulations mostly summarised in table form.

## 6.3 RESULTS AND DISCUSSION

### *6.3.1 Crop yields*

For the simulation with limestone + lime-treated water from the Western Basin simulation, the root zone saturated paste extract electrical conductivity ($EC_e$) was estimated to be 178 mS $m^{-1}$, ranging from 3 to 403 mS $m^{-1}$. Soil $EC_e$ stabilised as a result of the continued precipitation of gypsum and a fraction of 9.2% of irrigation and rainfall draining beyond the root zone, leaching salts in the process. These root zone $EC_e$ values are suitable for the growth of a number of crops (Figure 12). Root zone $EC_e$ was observed to generally be lower in the summer than in winter as a result of higher rainfall in summer which has a diluting effect. An implication of this is that crops that are slightly more salt sensitive are best grown in the summer months.

Moderate to poor maize and good wheat yields were simulated for irrigation with the neutralized mine water (Table 33), and there was no trend in declining yield over time predicted to result from soil profile salinization. For the simulations in which salinity stress was not accounted for (irrigation with good quality water), lower maize yields in some seasons were related to cooler temperatures which resulted in slower developmental rates.

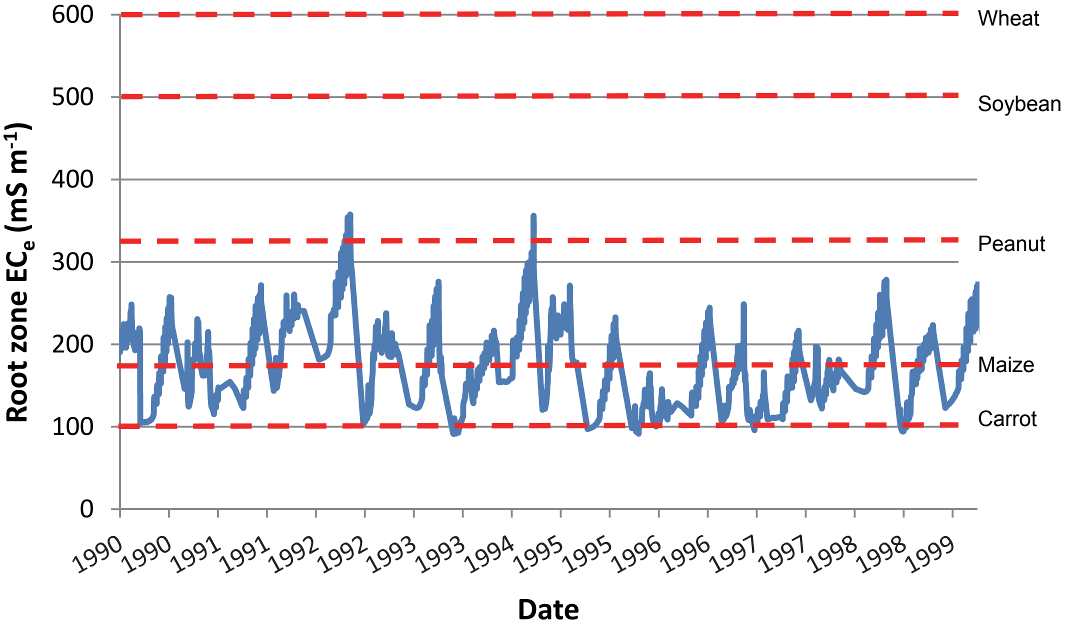


**Figure 12 Root zone saturated paste extract electrical conductivity (ECe) for the final 10 years (1990-2000) of the Western Basin limestone + lime treated water simulation (salt tolerance thresholds reported in Tanji and Kielen (2002) for selected crops are also shown)**

For the limestone treated water quality, slightly higher yields were estimated for the Central and Eastern Basins than for the Western Basin. This is most likely due to slightly higher rainfall and more favourable temperature ranges for the Germiston weather data. For the Western Basin limestone + lime treated water, maize yields were on average 4 t ha$^{-1}$ lower relative to the simulation with good quality irrigation water. Irrigation with this water still resulted in a 2 t ha$^{-1}$ average higher yield than what was simulated for rainfed production. Poorest maize yields were estimated for the Grootvlei HDS effluent-irrigated crop, which was on average 0.2 t ha$^{-1}$ lower than for rainfed production. Cultivating the more salt tolerant summer crop, soybean, resulted in yields that matched those produced using good quality irrigation water, as the salinity threshold root zone ECe of 500 mS m$^{-1}$ was not reached for soybean (Table 34). As SWB-Sci only considers dry matter production and yield as being limited by solar radiation, water availability and salinity stress, these estimates are potential yields only, and do not account for other limiting factors, e.g. pests and diseases. Economic analyses based on these crop yield data are presented in Chapter 8.

It must be clearly stated that there is a high degree of uncertainty linked to our (the international crop modelling community) ability to simulate the impact of soil salinity on crop growth and development. For example, when roots are exposed to a region in the vadose zone with high salinity and a region with lower salinity, compensative root water uptake may take place from the region with lower salinity levels. While maize is a salt sensitive crop, based on observations from irrigating maize using poor quality coal mine water in Mpumalanga, the simulated reduction of maize yields due to salinity stress may have been overestimated using the newly incorporated approach based on Maas and Hoffman (1977). Further research is required to improve our ability to simulate crop response to salinity.

**Table 33 Wheat and maize yield data, irrigation requirement and area required for the Western, Central and Eastern Basins estimated using SWB-Sci**

| Basin / Treatment | Ave wheat yield (t ha$^{-1}$) | Std dev (t ha$^{-1}$) | Ave wheat irrig/yr (mm) | Ave maize yield (t ha$^{-1}$) | Std dev (t ha$^{-1}$) | Ave maize irrig/yr (mm) | Ml/day | Area required (ha) |
|---|---|---|---|---|---|---|---|---|
| Western<br>- limestone + lime | 8.9 | 0.7 | 306 | 7.7 | 3.2 | 256 | 23 | 1589 |
| Western<br>- limed Al | 8.9 | 0.7 | 304 | 5.6 | 3.3 | 200 | 23 | 1778 |
| Western<br>- limestone | 8.9 | 0.7 | 307 | 7.6 | 3.3 | 254 | 23 | 1597 |
| Central<br>- limestone | 9.1 | 0.8 | 270 | 7.9 | 3.5 | 220 | 46 | 3569 |
| Eastern<br>- limestone | 9.1 | 0.8 | 275 | 5.8 | 3.8 | 181 | 80 | 6826 |
| Eastern<br>- Grootvlei HDS | 9.1 | 0.8 | 274 | 5.3 | 3.9 | 164 | 80 | 7120 |
| Western<br>- good quality water | 9.0 | 0.7 | 316 | 11.7 | 1.1 | 332 | - | - |
| Western<br>- rainfed | -* | - | - | 5.5 | 3.0 | - | - | - |

*Wheat cultivation not possible due to lack of rain

**Table 34 Wheat and soybean yield data, irrigation requirement and area required for the Western, Central and Eastern Basins estimated using SWB-Sci**

| Basin / Treatment | Ave wheat yield (t ha$^{-1}$) | Std dev (t ha$^{-1}$) | Ave wheat irrig/yr (mm) | Ave soybean yield (t ha$^{-1}$) | Std dev (t ha$^{-1}$) | Ave soybean irrig/yr (mm) | Ml/day | Area required (ha) |
|---|---|---|---|---|---|---|---|---|
| Western<br>- limestone + lime | 8.9 | 0.7 | 306 | 5.4 | 0.7 | 312 | 23 | 1429 |
| Western<br>- limed Al | 8.9 | 0.7 | 304 | 5.3 | 0.9 | 307 | 23 | 1440 |
| Western<br>- limestone | 8.9 | 0.7 | 307 | 5.4 | 0.7 | 333 | 23 | 1363 |
| Central<br>- limestone | 9.1 | 0.8 | 270 | 5.4 | 0.5 | 265 | 46 | 3217 |
| Eastern<br>- limestone | 9.1 | 0.8 | 275 | 5.3 | 0.6 | 267 | 80 | 5562 |
| Eastern<br>- Grootvlei HDS | 9.1 | 0.8 | 274 | 5.4 | 0.5 | 265 | 80 | 5610 |

*Wheat cultivation not possible due to lack of rain

### *6.3.2 Gypsum precipitation and salt leaching dynamics*

For the Western Basin limestone + lime treated water simulation, 50 years of irrigation resulted in a total of 888 t ha$^{-1}$ of salt being added to the soil via the irrigation water, of which 68% was predicted to precipitate as gypsum (Figure 13). An average of 145 mm drained from the root zone per annum with an average EC of 614 mS m$^{-1}$ and SAR of 2.24. Summarised results for the other simulations are shown in Table 35. Estimated root zone ECe ranged from 177 to 232 mS m$^{-1}$ for the simulations, and was highest for the HDS effluent irrigated soil. The lowest relative salt precipitation was observed for the Eastern Basin HDS effluent, maize-wheat simulation, with only 34% of the salts being removed via gypsum precipitation. As growth and water use for the soybean crop was not negatively impacted on by salinity as was the case for maize, greater volumes of irrigation water (and salts) could be applied to the soybean-wheat cropping systems (Table 36). Percentage gypsum precipitation was also slightly higher for the soybean-wheat system compared to the maize-wheat cropping systems as a result of the soybean crop more effectively concentrating the soil solution.

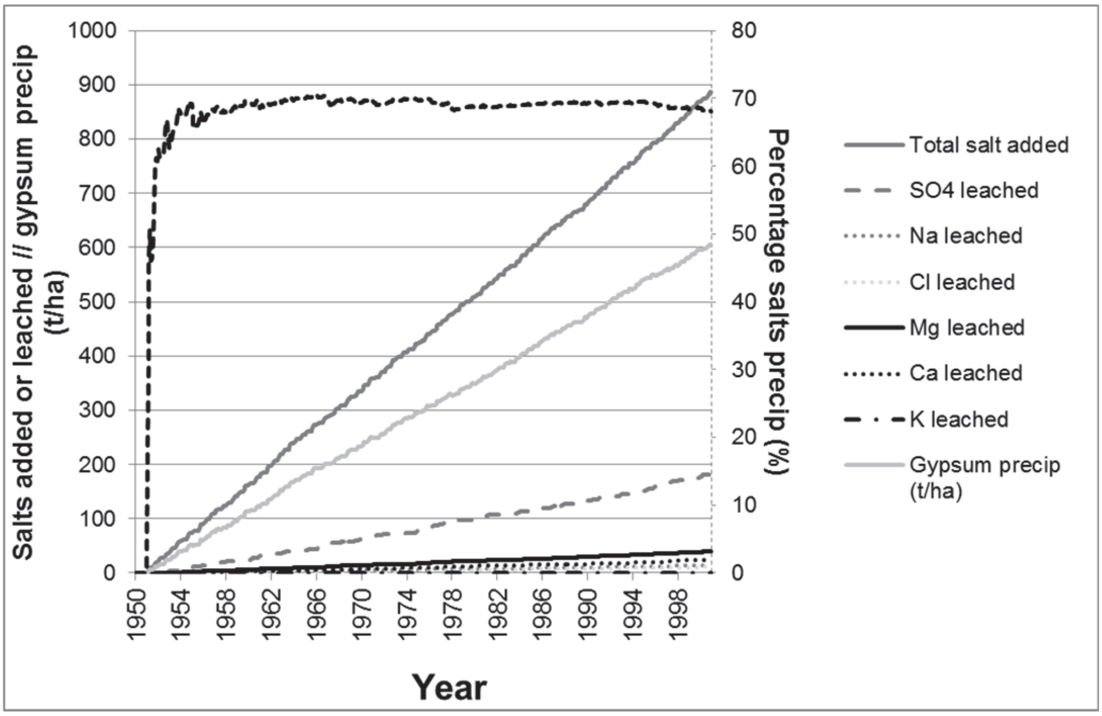


**Figure 13 Total salt added, gypsum precipitation and ion leaching load for the Western Basin limestone + lime treated water simulation over the 50 year simulation period**

Average leachate TDS concentrations ranged from 3716 to 4076 mg l$^{-1}$. Periodic spikes are evident in the salinity of drainage water (expressed as TDS or EC in Figure 14). These correlate with very small drainage volumes, however, implying that salt loading to the environment from these spikes will be correspondingly reduced. It is suggested that the average salinity level and quantity of leachate would form a sound basis for calculating the annual quantity of soluble salt draining per hectare from a mine water irrigation scheme. Alternatively this can be done simply by subtracting the quantity of gypsum precipitated from the total salt load in Table 35 and Table 36. This turns out to be very similar for all simulations: between 5.7 and 7.5 tonne ha$^{-1}$ per annum of soluble salts. Hence all that is required for impact assessment is the area of land irrigated and the volume of catchment runoff into which the salts will be deposited. It should also be noted that due to the nature of irrigation, most irrigated cropping systems in South Africa will result in return flows with elevated salt levels.

Table 35 Summary of maize-wheat cropping system simulation results for the Western, Central and Eastern Basins

| **Basin / Treatment** | **Irrigation /annum (mm)** | **Drainage /annum (mm)** | **Percentage salts precipitated (%)** | **Salt load added (tonnes ha$^{-1}$annum$^{-1}$)** | **Gypsum precipitated (tonnes ha$^{-1}$annum$^{-1}$)** | **Ave root zone EC$_e$ (mS m$^{-1}$)** | **Ave leachate TDS (mg l$^{-1}$)** |
|---|---|---|---|---|---|---|---|
| Western<br>- limestone + lime | 539 | 145 | 68 | 17.8 | 12.1 | 178 | 3931 |
| Western<br>- limed Al | 482 | 153 | 67 | 20.1 | 14.1 | 200 | 3922 |
| Western<br>- limestone | 537 | 147 | 55 | 12.8 | 7.0 | 177 | 3946 |
| Central<br>- limestone | 480 | 169 | 47 | 12.2 | 5.8 | 179 | 3787 |
| Eastern<br>- limestone | 437 | 183 | 41 | 11.6 | 4.8 | 196 | 3716 |
| Eastern<br>- Grootvlei HDS | 467 | 184 | 34 | 11.3 | 3.8 | 201 | 4076 |

Table 36 Summary of selected (best and worst) soybean-wheat cropping system simulation results for the Western, Central and Eastern Basins

| **Basin / Treatment** | **Irrigation /annum (mm)** | **Drainage /annum (mm)** | **Percentage salts precipitated (%)** | **Salt load added (tonnes ha$^{-1}$annum$^{-1}$)** | **Gypsum precipitated (tonnes ha$^{-1}$annum$^{-1}$)** | **Ave root zone EC$_e$ (mS m$^{-1}$)** | **Ave leachate TDS (mg l$^{-1}$)** |
|---|---|---|---|---|---|---|---|
| Western<br>- limestone + lime | 600 | 142 | 69 | 19.7 | 13.7 | 183 | 4225 |
| Western<br>- limed Al | 595 | 144 | 69 | 25.8 | 17.9 | 217 | 5486 |
| Eastern<br>- Grootvlei HDS | 531 | 169 | 39 | 14.3 | 5.6 | 232 | 5148 |

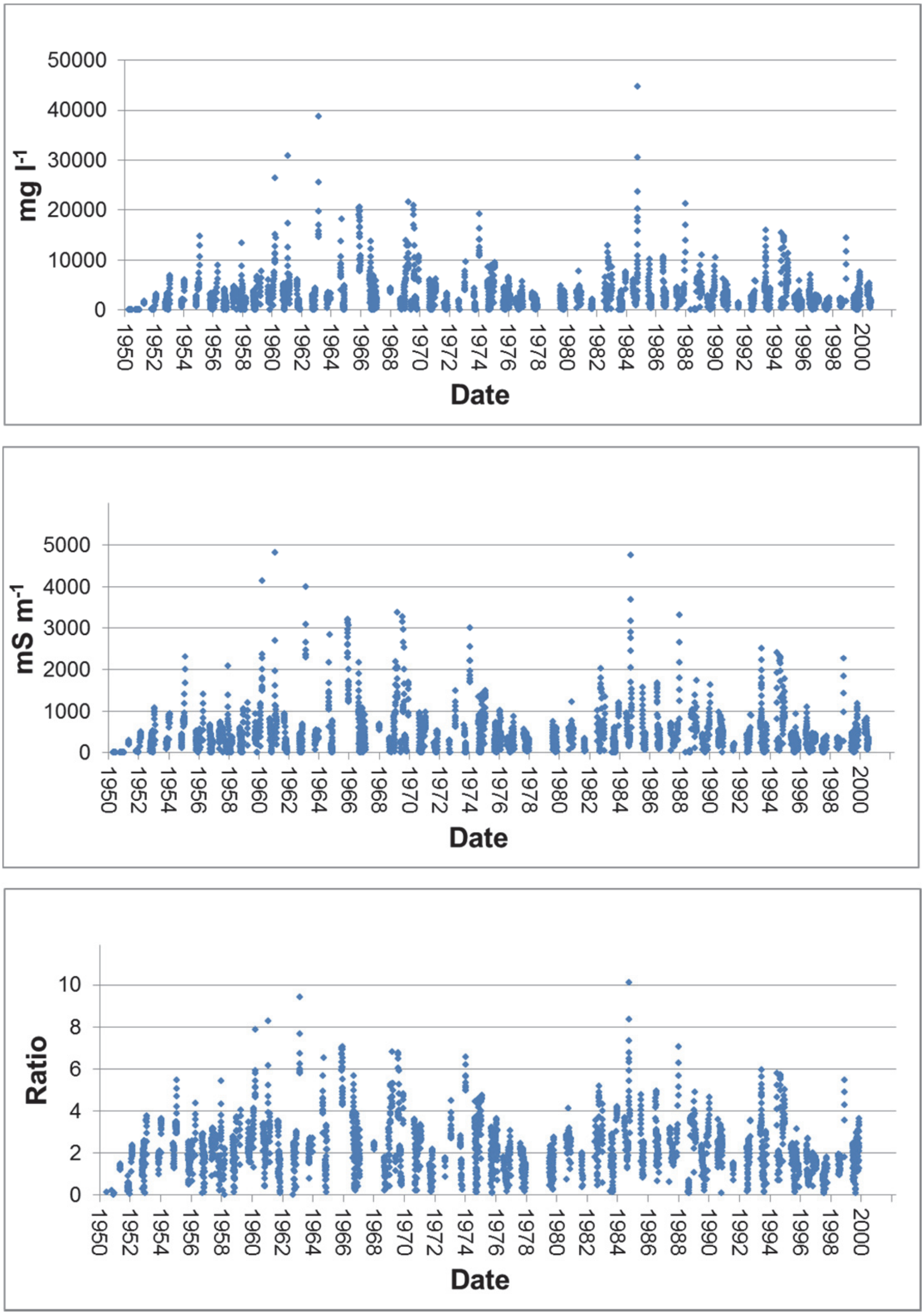


**Figure 14 Simulated leachate total dissolved solid (TDS) concentration (top), electrical conductivity (EC) (middle) and sodium adsorption ratio (bottom) and for the Western Basin limestone + lime treated water simulation over the 50 year simulation period**

The composition of the leached salts for the same simulation case is evident in Figure 15. The dominant soluble ion is Mg, followed by Ca and then Na. To get some idea of how sodicity varies the SAR was plotted against salinity for the full 50 year period of simulation, and there was a highly significant relationship between the two variables (Figure 16). The most important result of this analysis is that the irrigation return flow except in a few saline spikes would be only slightly sodic and high relative concentrations of Na would only materialise in the most saline of leachates, under which conditions the question of composition is eclipsed by that of concentration. High Mg concentrations per se are not found to be deleterious to soil physical properties except under circumstances where there are high Na levels in which case if Mg is co-dominant with Na the effect of the Na on soil properties is worse than when Ca is co-dominant with Na. Under such circumstances of high Mg levels it may be better to use a modified index such as the cation ratio of soil structural stability (CROSS) rather than SAR (Rengasamy and Marchuk, 2011).

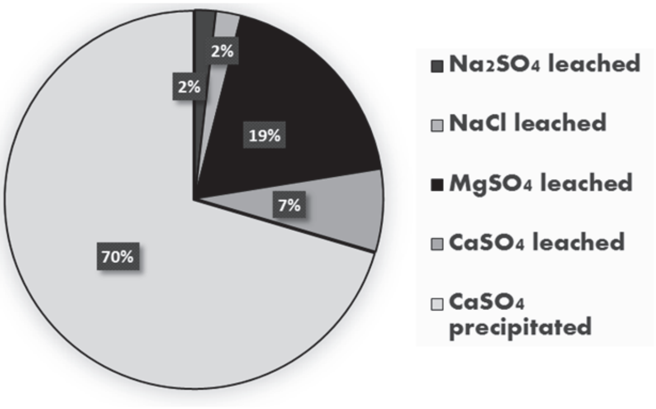


**Figure 15 Fate of added salts expressed as relative fractions for the Western Basin limestone + lime treated water simulation over the 50 year simulation period**

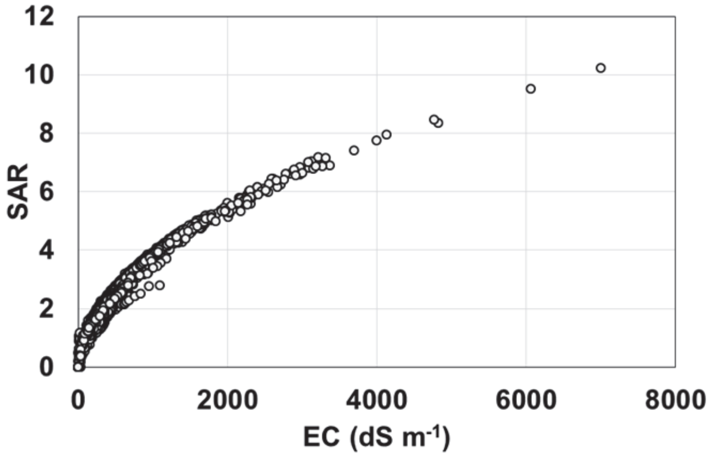


**Figure 16 Relationship between sodium adsorption ratio (SAR) and salinity of the simulated leachate for the Western Basin limestone + lime treated water simulation over the 50 year simulation period**

Sodium is the dominant cation in the leachate. While the SAR is relatively high, this value needs to be considered within the context of EC, as high salinity results in limited Na dispersion effects and structural breakdown (Ayers and Westcot, 1985). In other words, this water can be considered to have a low Na hazard because of the high salinity. High Mg concentration, coupled with a low Ca concentration, is also sometimes linked with dispersion. However, it is expected that a combined effect of high salinity, and ion paring of Mg with $SO_4$ would limit Mg affecting soil physical condition adversely. The Ca present in the leachate would further decrease this risk.

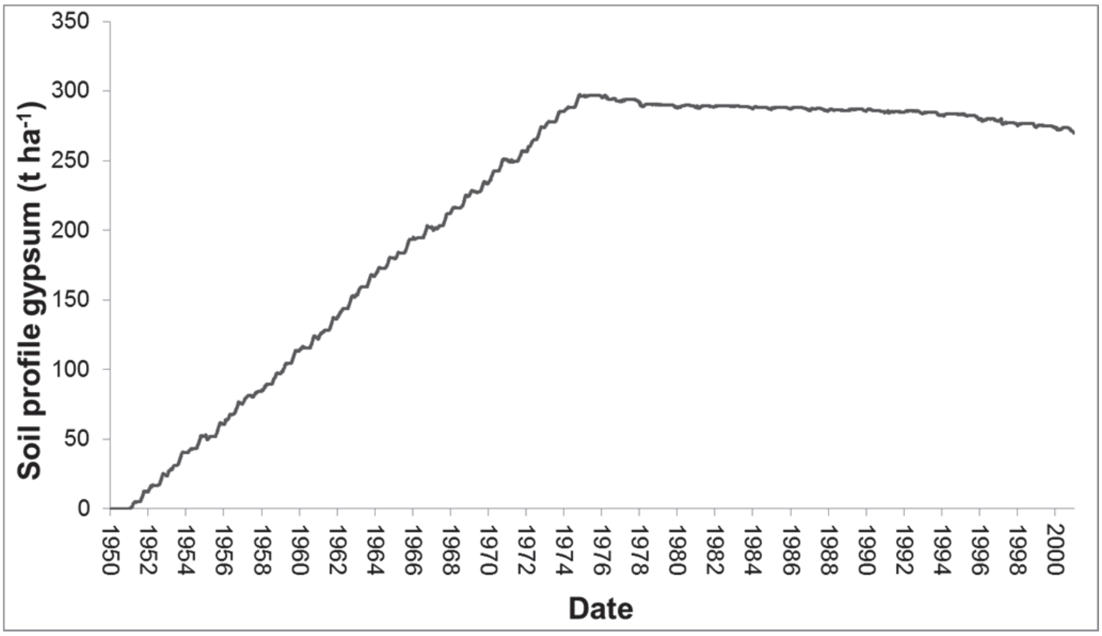


**Figure 17 Simulated soil profile gypsum dynamics following the discontinuation of irrigation and conversion to rainfed maize production after 25 years**

For a Western Basin limestone + lime treated water simulation, discontinuing irrigation with this poor quality mine water and switching to rainfed maize production (with a relatively late planting date of 26 November) showed that it would take over 250 years to remobilise the gypsum that has been precipitated (Figure 17). Switching to perennial vegetation (e.g. pastures) which will reduce deep drainage even more than the rainfed maize would result in even less gypsum re-mobilisation. SWB-Sci currently simulates complete mixing between any water entering a soil layer and the water currently in the layer following an irrigation or rainfall event, so no bypass flow of the cleaner water through the macropores is considered. As gypsum is a slow dissolver, again Figure 17 most likely represents an exaggerated estimate of gypsum re-mobilisation. Future work should aim to include an incomplete mixing algorithm (e.g. (Corwin et al., 1991)) into SWB-Sci in order to more mechanistically investigate gypsum precipitation and re-mobilisation.

## 6.4 SUMMARY AND CONCLUSIONS

Based on the results from this simulation study, irrigation of crops has the potential to be an effective component of mine water management in the Vaal Basin as it is a much less expensive alternative than some of the more sophisticated options of water treatment and disposal. For neutralised gold mine water, irrigation was estimated to result in up to 69% of the salt added being precipitated as gypsum, representing a significant immobilisation of salts. With Western Basin water between 55 and 69% of the salt load was precipitated as gypsum whereas for Central and Eastern Basin water, less than half (34-47%) of the total salt loaded was sequestered as gypsum. Since the Eastern Basin accounts for more than half the total expected volume from the Vaal Basin as a whole, this implies that the irrigation option is not quite as attractive as previous results for coal mine water have indicated. Switching from maize to soybean, which is more salt tolerant, resulted in higher relative yields and greater irrigation volume demands per hectare, which in turn reduced the total area of land needed for the irrigation treatment option. Using a salt tolerant perennial crop with even greater potential water use, for example salt tolerant Eucalyptus species, could result in even greater irrigation demands per hectare. It is noteworthy that following the simulated gypsum precipitation, soluble salts in the irrigation return flow would be dominated by Mg, with Ca the next most and Na the least concentrated of the cations. Despite the high predicted SAR of the leachate, the high EC of this water results in it having a low Na hazard. Careful agronomic management including irrigation scheduling, and storage of mine water during phases of lower demand (e.g. high rainfall periods) are important considerations that need to be taken into account.

# CHAPTER 7 ENVIRONMENTAL IMPACTS ASSOCIATED WITH ELECTRICITY GENERATION FOR CONVENTIONAL REVERSE OSMOSIS VERSUS THE IRRIGATION OPTION FOR TREATING NEUTRALISED ACID MINE WATER IN THE VAAL BASIN

## 7.1 INTRODUCTION

As South Africa is a water scarce country, the potential impact of the imminent acid mine water problem in the Vaal Basin on our freshwater resources is receiving the most focused attention. Buckley et al. (2011) noted that the water, electricity and electricity generation sectors are interconnected. Saving water can lead to saving electricity, as well as the water required to generate that electricity. When electricity generation results in the release of greenhouse gases, a longer term connection to water availability can also be expected as a result of anthropogenic climate change. Electricity generation using coal can also result in acidified rain water which can lead to aquatic and terrestrial acidification. Reverse osmosis (RO) desalination processes are recognised as being very energy intensive, with the pre-treatment operation, intake system, pumping system and application of high pressure to drive the RO stage all requiring energy (Fritzmann et al., 2007). Energy also makes up the greatest economic cost component in a desalination plant (Fritzmann et al., 2007). The design and operation conditions will greatly influence the amount of material and energy required to operate a particular desalination system (Zhou et al., 2011).

Life cycle assessment (LCA) aims to quantify the full environmental burden of a product or process. A number of studies have used LCA to compare the supply of potable water through RO with water conveyance schemes (Raluy et al., 2004; Shrestha et al., 2011). Buckley et al. (2011) reviewed key water-related LCA studies conducted in South Africa, and concluded that 'LCA and life-cycle thinking should be used regularly for water related planning, decision-making and debates'. To the best of our knowledge no LCA studies have been done to compare RO desalination versus crop irrigation to remove salts via gypsum precipitation.

In the context of developing a mine water treatment strategy for the Vaal Basin, LCA can be used to compare different treatment options with a key advantage being that it monitors multiple environmental impacts simultaneously, and can therefore detect any problem or burden shifting. For example, while one treatment option may have a more favourable impact on fresh water quality, this may come at the expense of increased air pollution and greenhouse gas emissions. In this study we use LCA methodology to compare conventional RO with a management strategy that includes irrigation to precipitate gypsum in the soil profile, as well as an option that further uses RO to remove all salts from the irrigation return flows.

## 7.2 METHODOLOGY

### *7.2.1 Goal and scope definition*

The goal of this reduced scope LCA is to compare treating neutralised mine water from the Vaal Basin using conventional RO with an approach using the 'irrigation option'. A comparison is also made with an option that includes treating the irrigation return flows from the Western, Central and Eastern Basins using conventional RO. As the products of these two activities are different, namely pure water and a brine requiring disposal for conventional RO versus agricultural produce and associated impacts (e.g. eutrophication) in the case of irrigation, the functional unit (FU) that has been selected is 'one metric tonne of salt removed from neutralised mine water' (considering that this is the ultimate objective in this context). The categories of environmental impacts that can be considered are vast, and not all are common to the two processes being compared, so a select number of categories that could be directly compared were selected.

Reverse osmosis desalination LCAs have shown that the main environmental impact comes from the operation of the plant, with the construction and disposal phases being almost negligible in comparison (Buckley, Friedrich and Von Blottnitz, 2011; Raluy, Serra, Uche and Valero, 2004). For this reason the main focus is on the impacts resulting from electricity consumption for the two activities.

The mid-point impact categories that are compared are global warming potential (relating to the carbon dioxide equivalent ($CO_2$-e) emissions as a result of generating the electricity to power the two processes), non-renewable energy consumption (relating to the use of coal fossil fuel to generate the electricity required for RO or irrigation), acidification potential (resulting from the burning of sulphur containing fuels), and blue water consumption.

As irrigated agriculture is essential in providing South Africa with food and the demand for agricultural produce is expected to increase as a result of a growing population, the impacts of other activities such as fertiliser mining or production, nitrogen and phosphorus leaching resulting in eutrophication and other impacts are not included in this assessment from the standpoint that such agricultural systems need to exist anyway. While the same argument may exist for the production of pure water using conventional RO for use by specific industries, the requirement to produce this water from saline neutralised AMD is not necessary.

### *7.2.2 Inventory analysis*

The analysis is based on conventional RO data obtained from DWA (2013c), as well as SWB-Sci simulations and upscaling exercises done in this project. Refer to Chapter 6 for additional information on the cropping systems modelled and simulation outputs. For both the RO and irrigation options, feed water was assumed to be neutralised acid mine water of a suitable quality for either activity and no conveyance electricity requirements from the point of discharge to the point of treatment are considered.

*Irrigation electricity requirements*

For the irrigation option*,* a 50 ha centre pivot with its own dedicated pump and motor is assumed. An estimated 19.9 kW is required by the pump to meet the flow and pressure needs, and an additional 4 kW to drive the wheels. The total power requirements for the 50 ha irrigation system is therefore 23.9 kW, or 0.48 kW ha$^{-1}$. For the management strategy involving irrigation with the neutralised mine water followed by conventional RO of the irrigation return flows, an electricity requirement of 3 kWh m$^{-3}$ was assumed necessary for the RO treatment. Further information on water volumes, salt concentrations and loads, and electricity requirement is provided in Table 37.

*Conventional RO electricity requirements*

Information on the energy requirement of conventional RO to treat neutralised mine water from the Western, Central and Eastern Basins was obtained from DWA (2013c). Some of the data presented in the tables in DWA (2013c) is unclear, for example, what water quality/quantity values were used in the calculations and the units used. From this information, it was assumed for the purposes of this study that 3, 1.8 and 2.2 KW is required to treat every m$^3$ of neutralised 50th percentile mine water from the Western, Central and Eastern Basins, respectively. Tables 6.17 and 6.18 in DWA (2013c) show that the electricity operating costs remain the same whether treating 50, 75 or 95th percentile water qualities. Further information on water volumes, salt concentrations and loads, and electricity requirement is provided in **Error! Reference source not found.**.

### *7.2.3 Impact assessment*

The following environmental impact categories were assessed (Table 38):

- Global warming potential calculated according to IPCC (2006) and expressed as kg $CO_2$-e (equivalents). Global warming potential is based on a 100 year time horizon is 310 for $N_2O$ and 21 for $CH_4$. $N_2O$ and $CH_4$ emissions and indirect emissions of $N_2O$ from atmospheric deposition of N in $NO_x$ and $NH_3$ are not considered.
- Acidification potential, calculated according to the Eco-indicator 95 approach (Goedkoop et al., 1995) and expressed as kg $SO_2$-e. The release of NOx and $NH_3$ gases during electricity generation was not considered.
- Non-renewable energy consumption considered total fossil fuel energy used by Eskom to provide the electricity;
- Blue water consumption, with the definition of blue water being surface and sub-surface water resources available for multiple uses.

The impact of salinity on the environment is not commonly accounted for in LCAs due to complexities with quantifying this impact. This issue is addressed further in the discussion section.

Table 37 Volumes, total dissolved solids (TDS) concentrations and electricity requirements for the methods considered for mine water treatment: conventional reverse osmosis (RO), irrigation and irrigation plus RO of return flows

| Basin | RO power requirements (kW m$^{-3}$)* | Irrig power requirements (kW m$^{-3}$) | Ave AMD flow* (ML d$^{-1}$) | Raw AMD TDS at 50th percentile (mg l$^{-1}$) | Salt load in AMD (tonnes yr$^{-1}$) | Irrig return flow volume (ML d$^{-1}$) | Irrigation return flow ave TDS (mg L$^{-1}$) | RO - salts removed (%) | Irrig - salts removed (%) | RO MWh/tonne salt | Irrig option + return flow RO MWh/tonne salt | Irrigation only MWh/tonne salt |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Western | 3 | 0.2 | 23 | 4313 | 36208 | 5 | 3978 | 98 | 58 | 0.71 | 0.21 | 0.08 |
| Central | 1.8 | 0.2 | 46 | 4363 | 73255 | 15 | 3849 | 98 | 43 | 0.42 | 0.19 | 0.11 |
| Eastern | 2.2 | 0.2 | 80 | 2292 | 66926 | 31 | 3851 | 98 | 49 | 0.98 | 0.47 | 0.18 |

* DWA (2013c)

Table 38 Environmental impact indicators per functional unit (FU) (1 tonne of salt removed) according to the treatment approach

| DESCRIPTION | Unit | Basin | Conventional reverse osmosis (RO) | Irrigation | Irrigation + RO of return flow | Emission factor /Coefficient | Units/Reference |
|---|---|---|---|---|---|---|---|
| Global warming potential | kg $CO_2$-e FU$^{-1}$ | Western | 696 | 78 | 207 | 0.98 | kg $CO_2$ kWh$^{-1}$ |
| | | Central | 413 | 104 | 183 | | (ESKOM, 2010) |
| | | Eastern | 960 | 175 | 461 | | |
| Acidification potential | kg $SO_2$-e FU$^{-1}$ | Western | 5749 | 648 | 1712 | 8.1 | g $SO_x$ kWh$^{-1}$ |
| | | Central | 3410 | 863 | 1516 | | (ESKOM, 2010) |
| | | Eastern | 7934 | 1442 | 3807 | | |
| Non-renewable energy input | MJ FU$^{-1}$ | Western | 2555 | 288 | 761 | 3.6 | MJ kWh$^{-1}$ |
| | | Central | 1516 | 384 | 674 | | (Statistics South Africa, 2005) |
| | | Eastern | 3526 | 641 | 1692 | | |
| Blue water use for electricity generation | L FU$^{-1}$ | Western | 958 | 108 | 285 | 1.35 | litres water kWh$^{-1}$ |
| | | Central | 568 | 144 | 253 | | (ESKOM, 2011) |
| | | Eastern | 1322 | 240 | 635 | | |

## 7.3 RESULTS AND DISCUSSION

The high energy requirements of conventional RO translated into relatively high environmental impacts for all categories considered, with impacts being significantly reduced when using irrigation as part of the treatment strategy due to the associated low energy requirements (Table 38). For the Western Basin as example, the global warming potential of using irrigation to remove a tonne of salt resulted in an 89% reduction compared to conventional RO, while irrigating and using RO on the irrigation return flows resulted in a 70% reduction in global warming potential (Figure 18). The smallest difference between global warming potential of the RO versus irrigation plus RO of return flows options was observed for the Eastern Basin, with a 52% reduction. Reductions for the other impact categories – acidification potential, non-renewable energy use and blue water consumption – were the same as the percentages mentioned above for global warming potential (Figure 18).

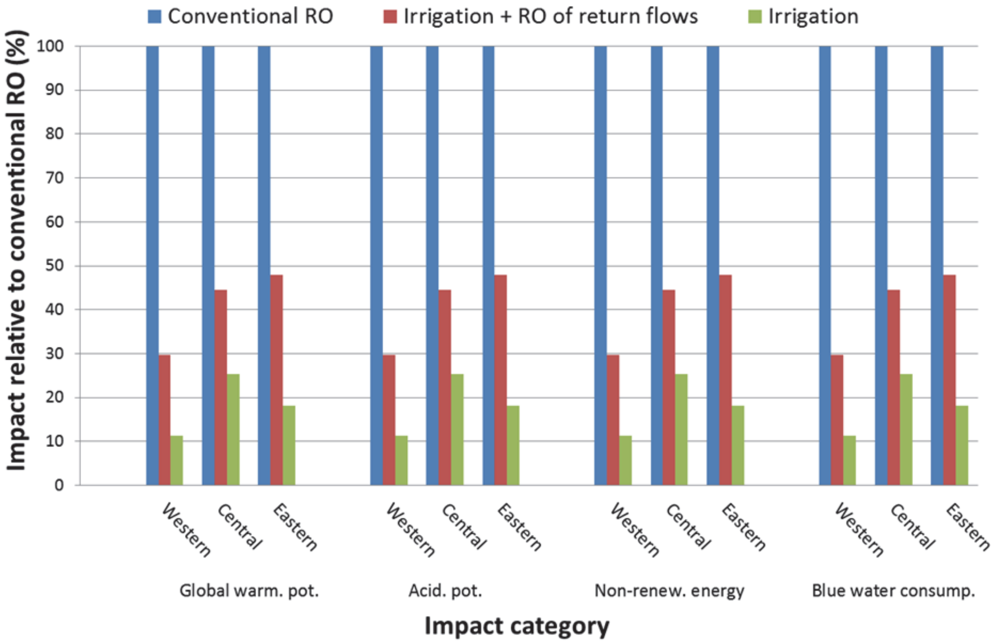


**Figure 18 Relative impact reduction of the irrigation and irrigation plus reverse osmosis (RO) of return flows options compared to conventional reverse osmosis (RO)**

Total annual energy requirements for conventional RO treatment ranged from 25 185 MWh yr$^{-1}$ for the Western Basin and 30 222 MWh yr$^{-1}$ for the Central Basin, to 64 240 MWh yr$^{-1}$ for the Eastern Basin. In contrast, irrigating with the neutralised mine water and using RO only on the irrigation return flows energy requirements were estimated to range from 7 498 MWh yr$^{-1}$ for the Western Basin to 30 826 MWh yr$^{-1}$ for the Eastern Basin.

As the design and operation conditions of the RO plant will determine energy requirements, there is uncertainty relating to the 3 kWh m$^{-3}$ that was assumed to be required to treat the irrigation return flow water for all three basins, and better estimates are not easily obtainable. Were this value to be lower, the irrigation option would have an even lower impact relative to conventional RO. that conventional lime treatment for metals removal involves an electricity cost associated with calcination (rather like cement manufacture, this is very expensive and $CO_2$ emitting, etc.). If the liming pretreatment is different for RO and irrigation then this becomes part of the LCA differential. It is also not clear whether the irrigation return flows will require further treatment, or if there is enough dilution capacity in the rivers, especially for the Western Basin scenario where return flows can potentially be directed into the Crocodile West system rather than the more sensitive Vaal system.

Irrigation has the added advantage that it will not use energy to remove salts only to blend them back into the treated water as proposed in DWA (2013a) for the conventional RO strategy. It must also be noted that according to DWA (2013a), Eastern Basin brine will require further treatment to manage the concentrated stream of mainly monovalent species that cannot be precipitated.

Reverse osmosis energy requirements have improved from as much as 20 kWh $m^{-3}$ in the 1970s to 3.5 kWh $m^{-3}$ by the end of the 1990s, with consumption below 2.0 kWh $m^{-3}$ being feasible today in some cases (Fritzmann, Löwenberg, Wintgens and Melin, 2007). Further improvements will reduce the environmental impact of RO, although eventually thermodynamics limits will confine the efficiency limits that can be achieved. Switching to a renewable energy source will also drastically reduce the environmental footprint of RO.

Other environmental impacts that have not been assessed but should be considered in a more intensive study include the effect of brine disposal in causing toxicological impacts on humans and ecosystems, land use impacts, abiotic/biotic resource use and ozone depletion. As the ultimate useful products between the two systems are clean water for RO and food for irrigation, conducting a comprehensive LCA with a common FU is challenging. A commonality is that both produce brines or saline return flows which may require further handling and safe disposal. Socio-economic impacts of the risks of reducing energy availability and assurance of supply in South Africa should also be considered (although this is out of scope of the LCA technique). A weakness of LCA methodology is that it does not adequately address impacts on fresh water salinity, a particularly important issue for South Africa. This can result in current LCA being a rather biased from of environmental impact accounting. Ongoing work described by Buckley et al. (2011) linking salt-fate models to quantifying salinity as an environmental impact may be very relevant to better understand environmental trade-offs when treating mine water using different strategies.

## 7.4 CONCLUSIONS

While using conventional RO to desalinate acid mine water in the Vaal Basin has clear benefits for fresh water quality, it is important to also consider other environmental and economic implications. In addition to the need for brine disposal, the high energy requirement of conventional RO results in significant releases of greenhouse gases and other air pollutants, as well as fossil fuel depletion. LCA can be a valuable instrument in the water sector as a comparative tool to select the most sustainable water treatment option as it monitors for any potential burden shifting. The recent release of the ISO 14046 standard for water footprinting can further assist these analyses. Comprehensive LCA studies are data intensive and expensive, but can be justified where the stakes and complexity are high (Buckley et al., 2011). Weaknesses in considering salinity impacts in LCA will need to be addressed for the useful application of LCA in the current context.

# CHAPTER 8 LAND AVAILABILITY AND ECONOMIC EVALUATION OF A MINE WATER IRRIGATED WHEAT-MAIZE/SOYBEAN CROPPING SYSTEM SCENARIO

## 8.1 INTRODUCTION

According to Vink et al. (2013) the National Planning Commission (NPC) identified the creation of ‘a million jobs in agriculture and the development of integrated rural economies’ as key goals for achieving vision 2030 of the National Development Plan (NDP). Taking into consideration the goals of the NDP, the proposed incorporation of neutralised mine water in irrigation as part of the growth path for expanding agriculture both commercially and from an emerging famer perspective is attractive. The rationale being that nationally, irrigated agriculture has reached its threshold from a water allocation perspective as only specified cases will receive additional water for agriculture.

This section aims to evaluate potential long-term financial feasibility scenarios in which neutralised mine water is used to irrigate wheat and maize/soybean in a double cropping production system (see Chapter 6 for details). Furthermore, land availability for irrigated cash crop production making use of treated mine water whilst considering locational constraints is also spatially evaluated. The emphasis fell on objectively evaluating irrigated agriculture in general and the possibilities of treated mine water usage to achieve rural economic development though irrigation.

Over the past decade the Bureau for Food and Agricultural Policy (BFAP) developed a system of models and maintained them for various crops and livestock enterprises. These linked systems of sector and farm-level models give quantitative analyses and projections of how different policy options as well as a range of macro-economic variables will affect the supply and demand of agricultural products in South Africa. The models further allow for quantitative analysis using scenario planning techniques. The models, assumptions and techniques will serve as a baseline for possible economic scenarios in using treated water for irrigated agriculture.

## 8.2 APPROACH

### *8.2.1 Production*

Based on simulated irrigation needs from Chapter 6, approximately 1597, 3569 and 6826 ha is required for the Western, Central and Eastern Basins, respectively, to fully utilise the treated water. These allocated hectares take the natural rainfall into consideration as well as the moisture needed at different growth stages. The crop modelling outputs (see Chapter 6) indicate that although wheat and soybean production utilising neutralised mine water is comparable to production with good quality irrigation water, maize yields were estimated to decrease on average by 46% when irrigating with treated water due to this crop being more salt sensitive.

**Table 39 Modelled irrigation yields from neutralised mine water**

| Basin | Ave wheat yield (t ha$^{-1}$) | Ave wheat irrig/yr (mm) | | Ave maize yield (t ha$^{-1}$) | Ave maize irrig/yr (mm) | | Ave soybean yield (t ha$^{-1}$) | Ave soybean irrig/yr (mm) | Ml/day | Area required (wheat & maize) (ha) |
|---|---|---|---|---|---|---|---|---|---|---|
| Western | 8.9 | 307 | | 7.6 | 254 | | 5.4 | 333 | 23 | 1597 |
| Central | 9.1 | 270 | | 7.9 | 220 | | 5.4 | 265 | 46 | 3569 |
| Eastern | 9.1 | 275 | | 5.8 | 181 | | 5.3 | 267 | 80 | 6826 |

Taking the estimated reduction in maize yields into consideration, the argument is made that none of the existing or currently allocated irrigated fields will switch to using neutralised mine water. The approach was rather to make use of old fields or planted pastures, as most of this land is currently under-utilised. The opportunity cost of using this land tends to be lower which results in irrigated cash crop production expansion being a possibility if gross margins per hectare are higher than in the case of other land-uses. Therefore, the identification of this type of land for irrigation with neutralised water would not necessitate the cultivation of virgin land.

### *8.2.2 Economics*

Following on the modelled production data is the FinSim financial results. This model made use of baseline data from the BFAP sector model to calculate gross margins and where possible net margins for farming enterprises. This is done by means of advanced quantitative analyses of how different policy options, macroeconomic variables, and volatile commodity market conditions could impact the financial position of farming businesses in Western, Eastern and Central production regions of Gauteng.

The following economic assumptions were used in the BFAP FinSim model:

1) Macro-economic (International) assumptions:
   - The global economic outlook remains stable as slow recovery in seen in the European area and expected to continue through the next two years, while improved prospects in North America and emerging Asia are expected to expand the global economy by 2.8% in 2014. The World Bank projects a further growth of 3.4% in 2015 in these regions. The outlook for crude oil prices remains stable, trading around $104 per barrel for the benchmark period, even though current crude oil prices are trading below $80 per barrel over the short term.

**Table 40 Baseline assumptions**

| | 2013 | 2014 | 2015 | 2016 |
|---|---|---|---|---|
| **Crude Oil Persian Gulf: Fob [$/barrel]** | 104.0 | 104.6 | 104 | 105.4 |
| **Population [Millions]** | 51.1 | 51.4 | 51.7 | 52.0 |
| **Exchange Rate[SA R/US$]** | 9.23 | 10.65 | 11.00 | 11.38 |
| | | | | |
| **SA GDP [%]** | 2.55 | 1.5 | 2.50 | 2.80 |
| **Repo Rate [%]** | 5.00 | 5.75 | 6.00 | 6.25 |

Source: BFAP, September 2014

2) Local (South African) commodity conditions:
   - Following a period of exceptionally high field crop prices, the baseline projects a sharp decline in grain and oilseed prices over the next two years, as global stocks reach record levels. This drop in prices was already anticipated in previous reports, however, production forecasts continue to rise, possibly implying an even sharper decline.
   - Domestically, favourable weather has resulted in upward revisions of maize and sorghum yields, resulting in softer prices for both commodities. While yellow maize exports have progressed well, particularly into Asian markets, white maize exports into Africa have yet to gather momentum. The SAFEX price has not fallen below export parity levels, which indicates that carryover stocks will remain high into 2015, unless prices decline significantly below export parity levels over the next few months.
   - Global wheat prices have declined in recent months, with larger than expected crops coming from Russia, China and the EU. Domestic prices will however be supported by a weaker rand, as well as the wheat tariff which is expected to become a factor in 2015, when the projected wheat price drops below the current reference price of $294 ton$^{-1}$. The domestic barley price tracks this price, and the model assumes the current barley pricing mechanism.
   - Assuming favourable rainfall conditions, most South African grain and oilseed prices are expected to trade softer in 2015, as rapidly declining global prices outweigh the effect of continuous depreciation of the exchange rate. Weather remains uncertain, however, and poor weather conditions could result in a vastly different price outlook.
3) Assumptions and calculations used in the respective gross margin calculations:
   i. Firstly, this particular adapted gross margin calculation is based on: (A) Income = yield * price, (B) all variable costs, (C) factor costs and overheads, (D) interest. Therefore, Gross Margin = A - (B + C) - D. In this gross margin calculation, land was rented (at an average rate over all three basins) and directly allocated as a cost per hectare, and interest per hectare was also deducted to finally calculate the gross margin, which is very close to a net margin per hectare. From this explanation it can be said that family living expenses as well as tax is not included, hence not a net margin. This gross margin is the closest we can get to an average possible net calculation and should not be used to benchmark against other irrigated districts. This is rather to show sustainability per hectare

ii. As shown in scenario 2, capital expenditure (CAPEX) and operating expenditure (OPEX) costs of transferring water from the neutralising facility to irrigation areas are included in the gross margin calculation. In other words, these costs are carried by the producer and directly allocated as mm ha$^{-1}$ used.

iii. Neutralisation costs are not carried by the producers.

iv. All scenarios make use of a 40 ha pivot irrigation system, which is discounted over a 20 year period at prime +2% (capital and maintenance). This down payment and operational costs are added to the production cost per hectare. Land clearing and levelling from planted pastures or old fields to accommodate pivot functionality is also included and paid over a 10 year period.

v. All production operations are carried out by contractors, which include; ripping, disking, planting, spraying (if required) and harvesting. No mechanical equipment is therefore bought as assets.

vi. Opportunity cost of the land is included based on a rented land price.

## 8.3 SPATIAL LOCATION RESULTS

### *8.3.1 Areas evaluated*

Spatial assessments were done for land in close proximity to the proposed pumping locations for the Eastern, Central and Western Basins (provided by Aurecon) (Figure 20).

**Figure 19 Proposed extraction locations and co-ordinates**

Based on remote-sensed data gathered by GDARD (2012), spatial analyses show that more than 7000 hectares is irrigated in a combined radius of 20 km surrounding all three extraction sites. If all the current irrigated land is excluded, as well as all the current dry-land cash crop fields then only the fallow, old land and pasture fields remain. From this analyses it was calculated that there is more than 19 000 hectares of pasture fields in a 20 km radius surrounding the combined three extraction sites, of which roughly 2 500 hectares were identified as small holder fields.

### *8.3.2 Western Basin*

A total of 2000 hectares of cultivated pastures fields and fallow land was identified within the selected area highlighted in Figure 20. Approximately 17 km of main piping would be required to distribute the water from the proposed extraction site. All of the selected fields are allocated on land identified as land capability class III (suitable for agriculture).

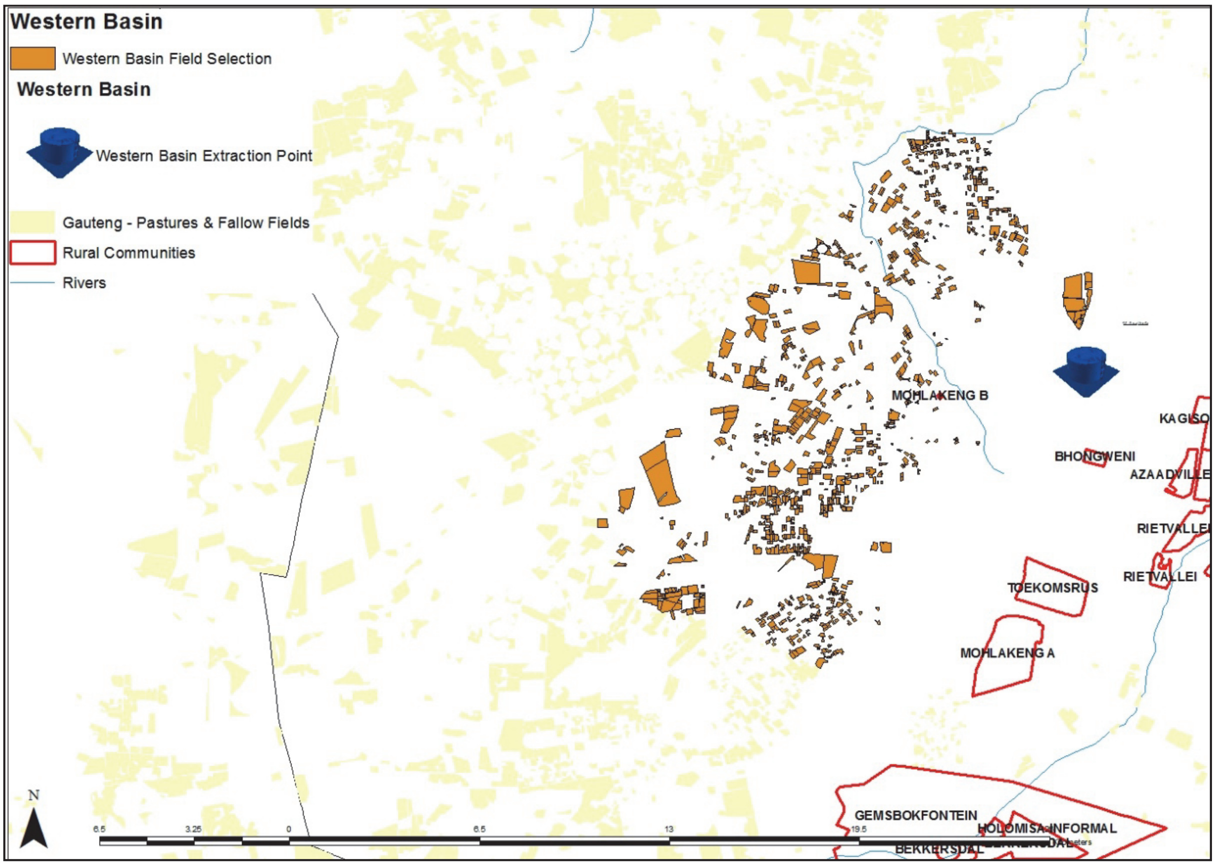


Figure 20 Western Basin – available fields for irrigation

### *8.3.3 Central Basin*

A total of 3800 hectares of cultivated pastures and fallow land was identified within the selection area highlighted in Figure 21. The furthest point being 28 km from the proposed extraction site and approximately 30 km of main piping would be required for the Central Basin. From the fields selected, roughly 40% are allocated to land capability class II (highly suitable for agriculture) and the remainder to land capability class III (suitable for agriculture). The alternative option would be to pump this water to the Eastern Basin, which would expand the irrigation area available.

### *8.3.4 Eastern Basin*

A total of 6900 hectares of suitable cultivated pastures fields and fallow land was identified within the selection highlighted in Figure 22. The furthest field is 22 km from the proposed Eastern Basin extraction site and roughly 20 km of main piping would be required. At least 90% of the fields fall into land capability class II (highly suitable for agriculture).

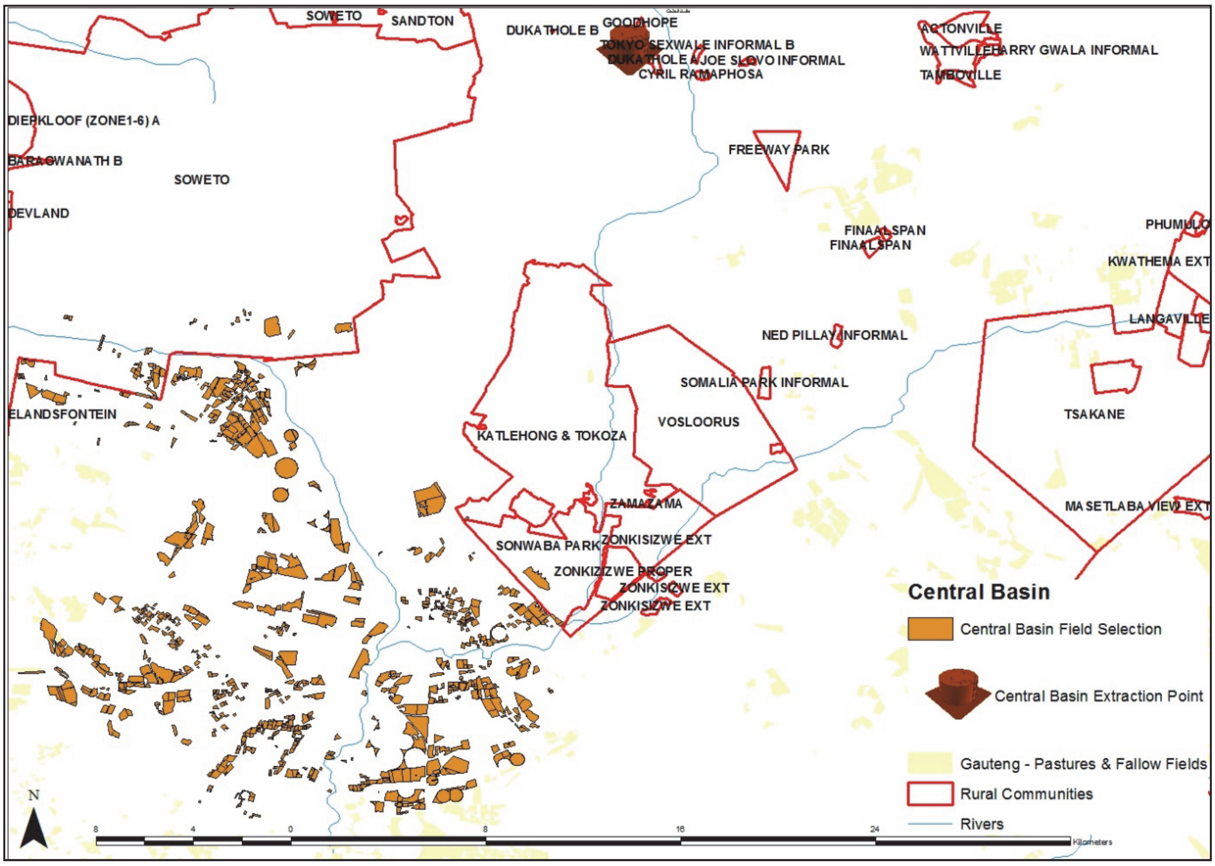


**Figure 21 Central Basin – available fields for irrigation**

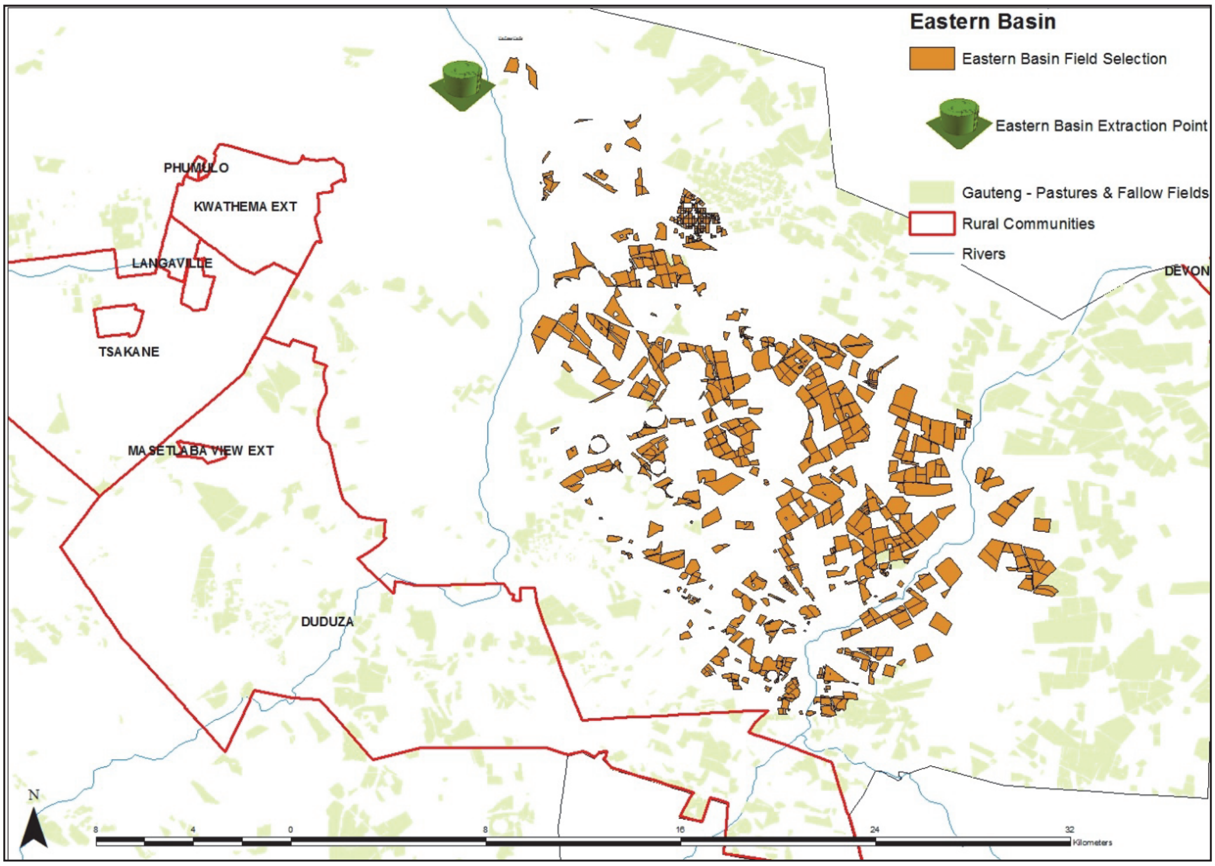


**Figure 22 Eastern Basin – available fields for irrigation**

### *8.3.5 Risk awareness*

Some of the possible unforeseen risks in allocating neutralised mine water for irrigation at these locations can include unauthorised/uncontrolled domestic or household usage, challenges in normal irrigation practices, livestock drinking the water and salinisation in current or irrigated fields. These risks are not only related to using treated water, but current irrigation farmers are faced with many risks which are similar  This being said, it is recommended that further studies should specifically focus on risks associated with using treated water in irrigated agriculture, with current irrigation risks a departure point.

## 8.4 IRRIGATION SCENARIOS CONSIDERED

All the scenarios discussed in Section 8.4 made use of the production (yield and volumes) data modelled in Chapter 6, as well as the irrigation requirements (water costs per mm used) to achieve these yields.

### *8.4.1 Scenario 1 – Farmers pay average commercial irrigation water prices for the water*

*Assumptions*

- A comparative national average water cost of R1.50 mm$^{-1}$ was used and average electricity cost of R4.80 kWh.
- Gross margins on wheat, soybean and maize could on average increase by approximately R450 ha$^{-1}$ if this water is provided **free of charge.**

*Results*

Water utilization throughout the three basins (Figures 24, 25, and 26) does not seem to differ greatly, which resulted in marginal differences through the basins. The Central Basin (Figure 25) showed the most promising results, with an average annual gross margin of R19 224 ha$^{-1}$ annum$^{-1}$ when rotating wheat and soybeans within the 5 year projected period. Even though the Western Basin showed a R1500 reduction from the Central Basin, it is still projected to realise an R17 702 ha$^{-1}$ annum$^{-1}$ over 5 years, double cropping wheat and soybeans.

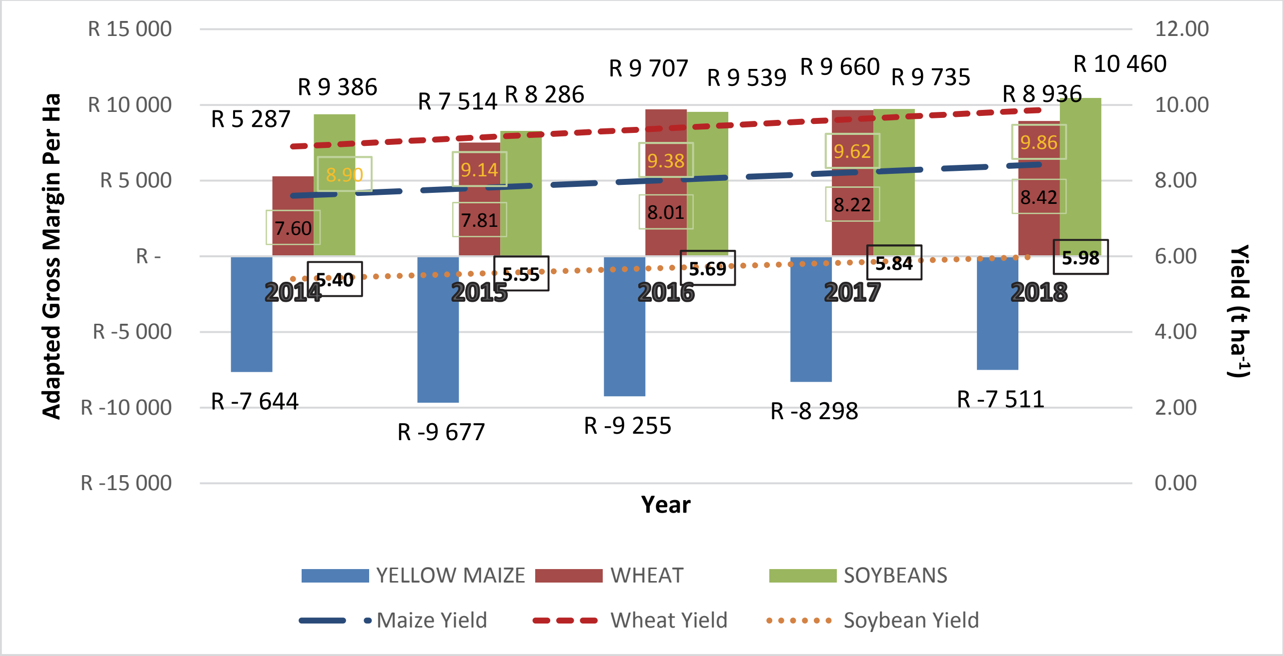


**Figure 23 Scenario 1 – Western Basin – Gross margin analyses**

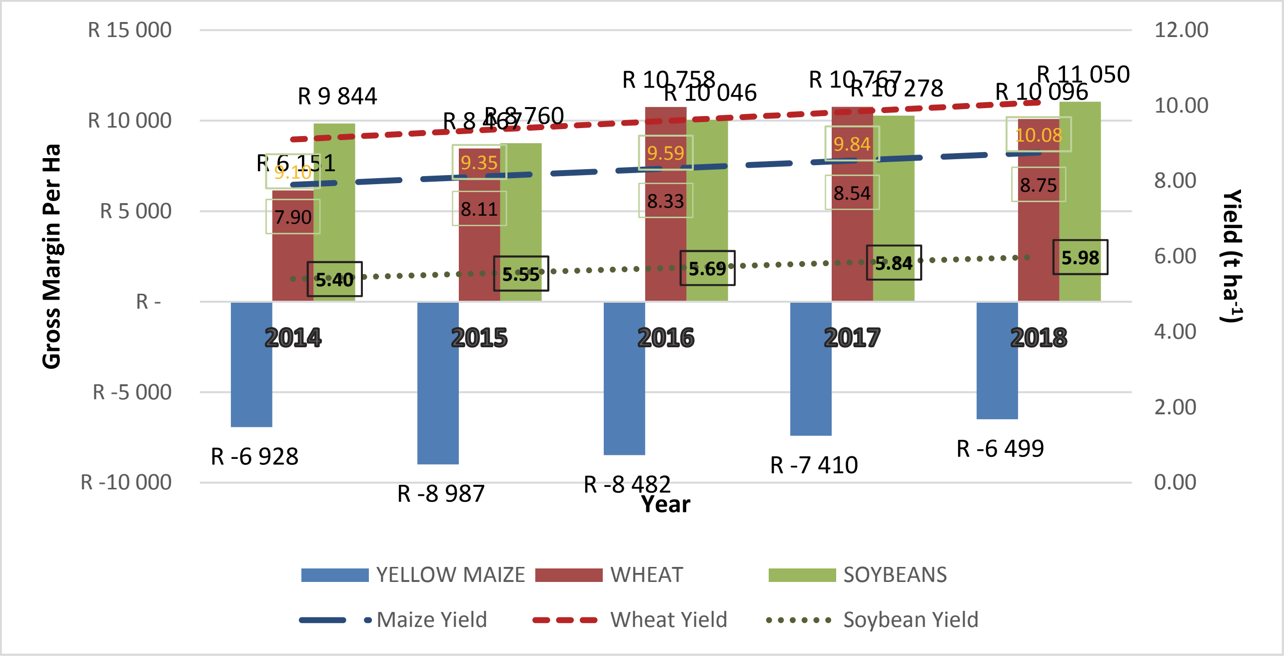


Figure 24 Scenario 1 – Central Basin – Gross Margin Analyses

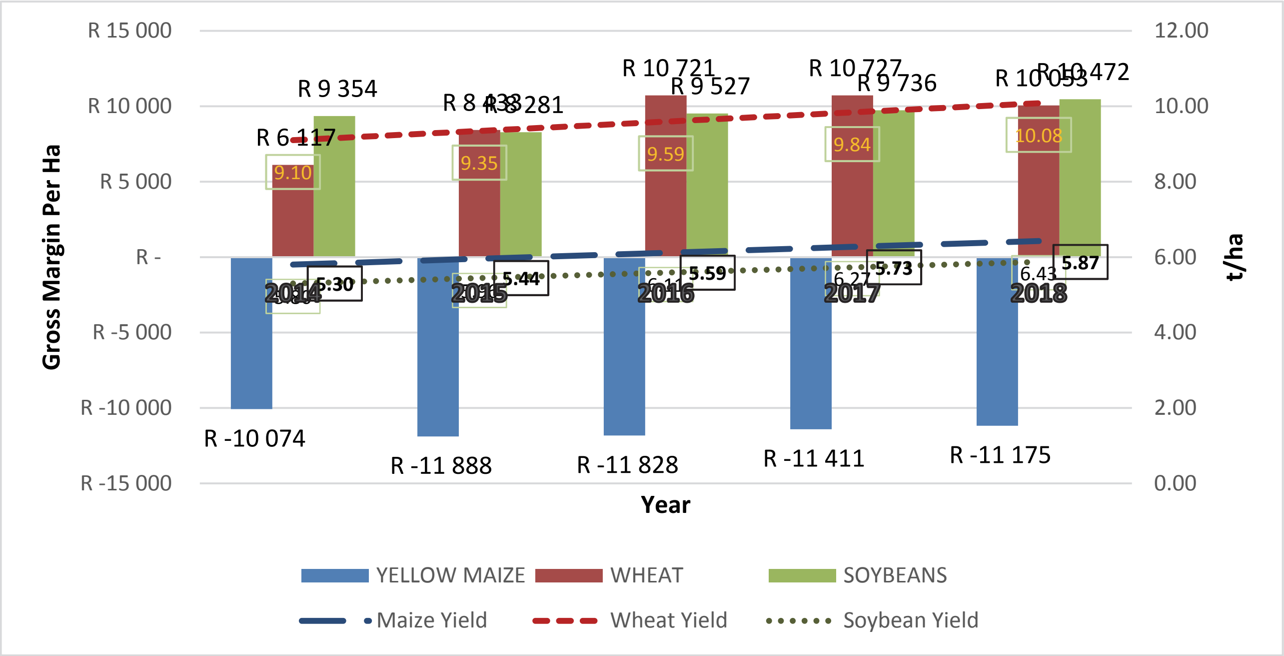


Figure 25 Scenario 1 – Eastern Basin – Gross Margin Analyses

### *8.4.2 Scenario 2 – Capital (CAPEX) and Operating (OPEX) expenditure of transferring the treated water is paid by the farmer*

Capital and operating costs (Table 41) were calculated using the costs provided by Aurecon, which prepared an AMD feasibility study for DWA 2014. Each basin has a different pricing based on the infrastructure needed. These costs do not account for the lime or gypsum plant. The costs was calculated as the distance from each extraction point to final water usage point, which is a similar approach as in Hopetown Irrigation Area (water is pumped from the Orange River in an 800 mm pipe, and along this main-pipe, farmers tap in and extract for their usage). The calculation assumes that the CAPEX and OPEX is paid over a 45 year period at a 5.5% interest rate.

**Table 41 CAPEX and OPEX for irrigation**

| | mm/annum | CAPEX/mm/annum | OPEX/mm/annum | Total Main-line Water Costs/mm/annum |
|---|---|---|---|---|
| **Western** | 895 917 | R11.08 | R3.35 | R14.43 |
| **Central** | 1 748 810 | R14.67 | R3.60 | R18.27 |
| **Eastern** | 3 112 656 | R13.12 | R6.17 | R19.29 |

Source: Aurecon (2014) compiled by van der Burgh (2014)

*Assumptions*

- Western Basin: average water cost of R14.43 mm$^{-1}$ and average electricity cost of R4.80/kWh.
- Central Basin: average water cost of R18.27 mm$^{-1}$ and average electricity cost of R4.80/kWh
- Eastern Basin: average water cost of R19.29 mm$^{-1}$ and average electricity cost of R4.80/kWh.

*Scenario 2 – Results*

Figures 27-29 show that again the Central Basin had the highest average gross margin (Figure 28), with an average annual gross margin of R9 500 ha$^{-1}$ annum$^{-1}$ with the wheat and soybean rotation. Under Scenario 2, we found that the Western Basin showed an R8 790 ha$^{-1}$ annum$^{-1}$ average gross margin over 5 years, double cropping wheat and soybeans. This is the worst case scenario for all scenario`s and all basins. In conclusion, we can argue that if this farmer produces wheat and soybeans on a 40 hectare pivot, from which he contracts all the tillage, planting and harvesting operations, he or she would still realise a total gross margin greater than R300 000 per annum.

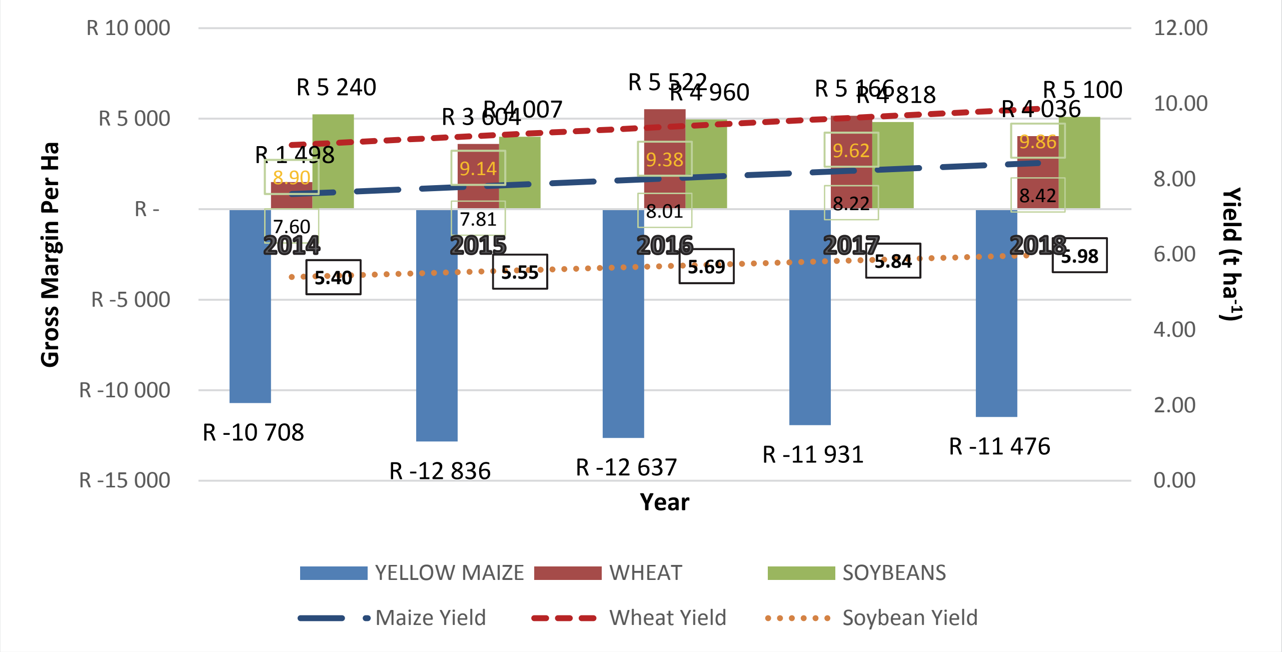


**Figure 26 Scenario 2 – Western Basin – Gross Margin Analyses**

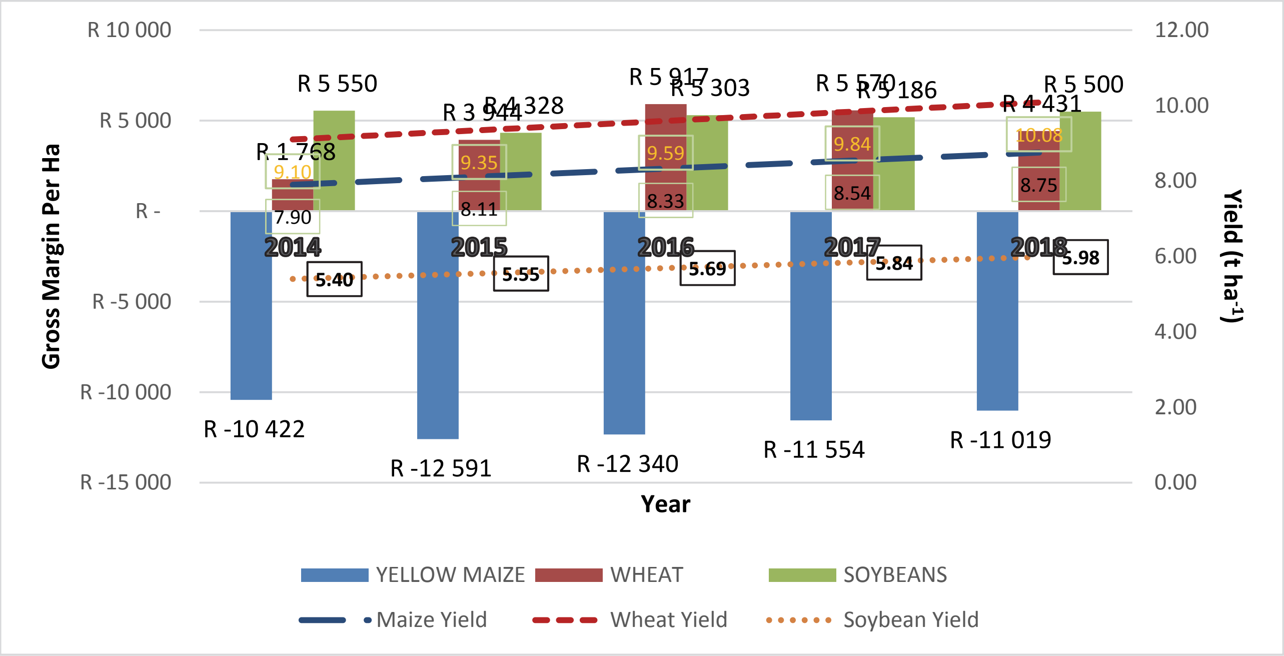


Figure 27 Scenario 2 – Central Basin – Gross Margin Analyses

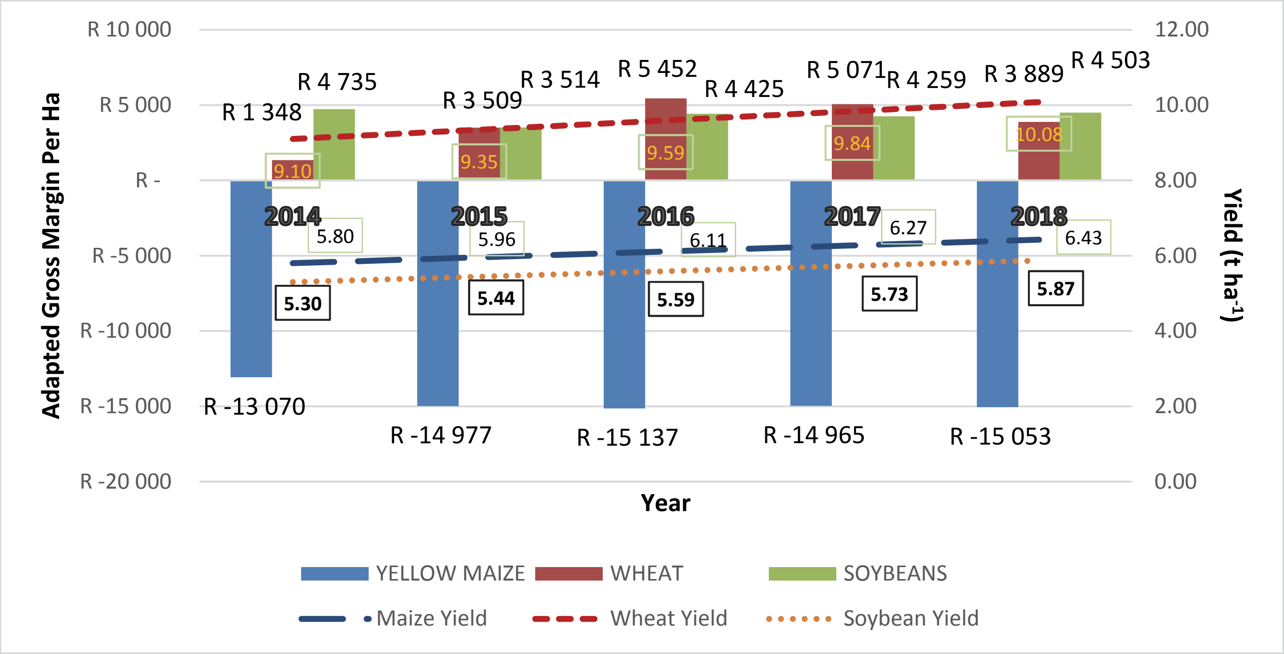


Figure 28 Scenario 2 – Eastern Basin – Gross margin analyses

## 8.5 RESULTS

Following the spatial selection approach as specified in the land allocation section, in theory, ample suitable land was found for the proposed neutralised mine water irrigation of the selected crops. Besides the land availability, the market factors also counts in favour of the crops, as wheat millers and soybean crushers are close to all production areas which allows for reduced transport differential rates. As explained earlier, this adapted gross margin is actually what any producer/business could realise on 40 hectares of land irrigated with neutralised mine water, as it accounts for all costs including rent paid.

### *8.5.1 Gross margin results*

*Wheat*

Both scenarios resulted in positive gross margins for wheat production. On average, Scenario 1 resulted in a 16% reduced gross margin when compared to current normally irrigated gross margins. This lowered 16%

accounts for the rented land being included in the gross margin calculation, hence this specific benchmarking can be done with other regional irrigation margins. Scenario 2 resulted in about 62% lower gross margin returns per hectare. This is substantially lower than the benchmark, but considering that all capital costs are paid for and the opportunity cost of using the land for unproductive/fallow pastures is estimated at R750 $ha^{-1}$, this remains to be a fairly good return especially if the return is expected to increase over the next five years.

*Soybeans*

From a market and yield perspective, soybeans would be a better option than maize for this rotation. We do, however, caution that a modelled 5.1 t $ha^{-1}$ yield is very optimistic and in-field trials will have to be conducted. By any margin, soybeans are comparable to that of normal irrigation and actually even higher than expected.

*Maize*

The simple fact that maize yields were below a break-even 10 t $ha^{-1}$ makes a negative case for this crop, as yields and prices needs to significantly improve before it would be a viable option.

The overall advantage of using these cash crops are not merely production based, but also demand driven, as South Africa is a net importer of both wheat and soybean oilcake. The current crushing capacity of soybeans is under-utilised and additional production of roughly 500 000 t of soybean is required for the price to start trading at export parity levels. The country currently produces maize surpluses and internationally stock levels are at an all-time high, hence the reason for a poorer economic performance from maize.

## 8.6 CONCLUSIONS

More than 2.7 million rural and urban township households were calculated in a combined 50 km radius area surrounding the extraction points. This leads to the question whether some form of economically sustainable rural development programmes could be part of the solution if the current and foreseeable future neutralised mine water can be redirected to productive uses?

Taking the principles of the NDP 2030 and its vision towards job creation and rural development into consideration, irrigated agriculture features as a main theme and driver to facilitate transformation. Unfortunately water is a scare resource in South Africa and alternatives have to be evaluated. The outcomes of this section substantiates the need to do more research in utilising neutralised mine water in cash crop production as industry related gross margins are realised under certain production scenarios.

Under the worst case scenario (scenario 2), any producer can realise an average gross farm income >R300 000 per annum (over the 5 year period) on 40 hectares irrigated with neutralised mine water which achieves the modelled yields as presented in Chapter 6.

# CHAPTER 9 FINAL CONCLUSIONS AND RECOMMENDATIONS

Utilising laboratory studies, crop growth and soil water and salt balance modelling, life cycle assessment approaches, economic assessment and GIS queries, information has now been generated on the feasibility of using irrigation as part of a long-term neutralised mine water treatment strategy in the Vaal Basin.

Both Fe-Mn wad and Al sulfate can be used in an auxiliary role with lime and limestone for removal of metals from mine water. The wad's effectiveness for Mn removal by oxidation may be reduced when ferrous Fe is present, since this will be oxidised preferentially. Similarly the cation exchange capacity of Mn oxide in the wad may be preferentially occupied by Ca because of mass action which would further reduce the capacity of the wad to remove Mn and other metals from solution. Aluminium sulfate and hydrated lime work synergistically as conditioners for mine water to effect a rapid depletion of contaminants at a near neutral pH. The order in which these reagents are added to the mine water makes a great difference to the composition. The quality of the water produced is probably quite sensitive to small changes in reaction conditions, and further investigation should control temperature, gas composition and pH more accurately.

Proof of concept now exists that land treatment, either with mine tailings and/or a clay soil, suitably amended with fine limestone or an equivalent material such as fly ash from power stations, is technically attractive and could offer solutions to two environmental challenges at once: erodible mine tailings and large volumes of contaminated mine water. The photo below was taken adjacent to the Ergo tailings storage facility (TSF) and the results of this study hopefully provide some inspiration in suggesting that such scenes may be more achievable on the mine tailings than has hitherto been thought possible.

**Figure 29 Area adjacent to the Ergo tailings storage facility**

Irrigation with neutralised mine water from the Western Basin that has been treated with limestone and lime was shown by simulation using the SWB model to immobilise the largest fraction of salts (69% precipitated as gypsum) compared with other waters and treatments. A similar degree of immobilisation was also achieved using the limed Al sulfate approach developed in Chapter 4, which potentially has several advantages during the neutralisation step, including a reduced aeration requirement. Uncertainties exist regarding the quality of the mine water that will be pumped from the mine voids and its quality following neutralisation. For the range of water qualities used in our simulations, between 34 and 69 percent of salts was estimated to precipitate as gypsum. Lowest gypsum precipitation was predicted for irrigation with Grootvlei HDS effluent. Using the limestone + lime and limed Al approaches resulted in higher salt loading, however, with the pre-treatments considered (excluding Grootvlei HDS effluent) resulting in similar salt leaching loads of 5.7-6.8 t $ha^{-1}$ $a^{-1}$. This equates to average total dissolved solids (TDS) concentrations in the leachate ranging from 3716 mg $l^{-1}$ for the Eastern Basin limestone treated water to 5486 mg $l^{-1}$ for the Western Basin limestone treated water.

Root zone salinity levels were simulated to remain below the threshold which would have an impact on wheat and soybean growth, while maize yields were simulated to be impacted because this is a more salt sensitive crop. There is a high degree of uncertainty linked to our ability to simulate the impact of soil salinity on crop growth and development. Current models are most likely not mechanistic enough to predict this adequately. Based on observations from irrigating maize using poor quality coal mine water in Mpumalanga, the simulated reduction of maize yields due to salinity stress may have been over-estimated in this study. Further research is required to improve our ability to simulate salinity impacts of crop growth.

A major concern of the feasibility study team with the 'irrigation option' was that the salts would simply re-dissolve and enter the groundwater (DWA, 2013a). Simulations done for this project show that if irrigation with poor quality mine water was to discontinue after 25 years and the system switched over to one of rainfed maize production, the re-mobilisation of gypsum would be very gradual, taking over 250 years for all precipitated gypsum to re-mobilise. This represents a conservative estimate, if perennial vegetation were to be established on the previously irrigated fields and deep drainage reduced further, the re-mobilisation of salts would take even longer.

A reduced scope life cycle assessment (LCA) study was conducted comparing conventional reverse osmosis (RO) with a treatment strategy that included irrigation with the water as well as irrigation followed by conventional RO of the saline irrigation return flows. The functional unit (FU) on which the analysis was based was 1 tonne of salt removed from the water. Due to the complexities of comparing these very diverse treatments options, only impacts relating to the generation of electricity to drive the approaches was accounted for.  Considerable reductions in the environmental footprint of treating the water were observed for the scenario including irrigation and conventional RO of the irrigation return flows compared to only using conventional RO. For the Western Basin, for example, global warming potential, acidification potential, non-renewable resource use and blue water consumption were all reduced by 70%. For the Central Basin this reduction was 56% and for the Eastern Basin 52%. LCA can be a very useful tool for monitoring multiple environmental impacts simultaneously, and to detect whether any burden shifting may be occurring. In this study, while conventional RO can be expected to have direct benefits on water quality in the Vaal Basin, the release of air pollutants and greenhouse gases and the consumption of finite fossil fuel resources should be of major concern. Detailed LCA studies are expensive and data intensive, but essential in important decision-making processes such as the one on determining how to manage poor quality mine water in the Vaal Basin. A major current weakness of LCA is its inadequacy in estimating salinity impacts. Until this is rectified, the application of LCA in contexts where salinity is a major issue will lead to biased results.

SWB-Sci model outputs indicate that for a wheat-soybean rotation cropping system, approximately 1363, 3217 and 5562 ha will be needed for the Western, Central and Eastern Basins, respectively. The spatial analysis showed that, in theory, ample suitable land is available for irrigation with neutralised mine water. Water may need to be piped 17 to 30 km, depending on individual basin characteristics.

South Africa is a net importer of both wheat and soybean oilcake resulting in higher commodity prices when compared to crops which tend to be more export parity related, such as maize. The current crushing capacity of soybeans is under-utilised and additional production of roughly 500 000 t of soybean is required for the price to start trading at export parity levels. Using industry related water costs, average production expenditure when all three crops are combined was R19 900 per hectare (Scenario 1 – farmers pay for the water but not transfer from extraction points). If producers were to carry the full burden (CAPEX and OPEX) of getting the water to their production areas, this cost could increase on average to R23 300 per hectare (Scenario 2). The model accounts for the market volatility in commodity prices and maize prices were assumed to decrease slightly, whilst wheat and soybean prices are expected to move side-ways from their current prices. Under the worst case scenario (Scenario 2), producers could still realise a farm/small business income of R243 320 per annum (excluding family and tax expenses) on 40 hectares irrigated with neutralised mine water if they continue to achieve the modelled yields as presented in Chapter 6.

From an economic sustainability perspective, more than 300 producers could benefit financially by each cultivating a 40 ha pivot as a separate business unit. If all of these hectares could come under production, approximately 10% of the current soybean crushing demand could be attained. Total gross revenue that can be generated by the 11 992 hectares under wheat and soybean rotational cropping would be approximately R73 m based on 2014 prices and costs, while it could increase to R108 m based on a higher return per hectare.

The results of this study suggest that irrigation could well be warranted as part of a mine water management strategy. Hence the following additional research is recommended:

- Investigate more quantitatively and on a larger scale the economic feasibility of using Al sulfate and ferromanganese wad as supplementary ameliorants for mine water treatment.

- Establish a pilot plant in the Western Basin to investigate salt dynamics in a neutralised mine water wheat-soybean (or other suitable crop) irrigation system.
- Improve the SWB-Sci model's capacity to simulate bypass flow (incomplete solute mixing) and crop response to soil salinity. The latter should be informed by local field trials irrigating crops with brackish water.
- Carry out field trials to quantify the effects of direct application of raw mine water to agricultural soils and mine tailings, selected for their buffer capacity and/or availability at each of the decant locations.
- Find out, based on expected leaching loads and concentrations, whether there is assimilative capacity in the rivers of the Western, Central and Eastern Basins.
- Conduct geo-hydrological studies to identify sites where neutralised mine water irrigation schemes can be located so as to have minimal impact on the environment (for example, above an already contaminated aquifer).
- Complete a comprehensive risk assessment for mine water irrigation scenarios, including social, policy and environmental risks.

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## Appendix 1. Sampling locations and miscellaneous photos of the study area

### Appendix 1a. Mine water collection at Randfontein

Sampling location, Randfontein

Mine water neutralization pilot plant, Randfontein

Chris de Jager transporting fresh mine water

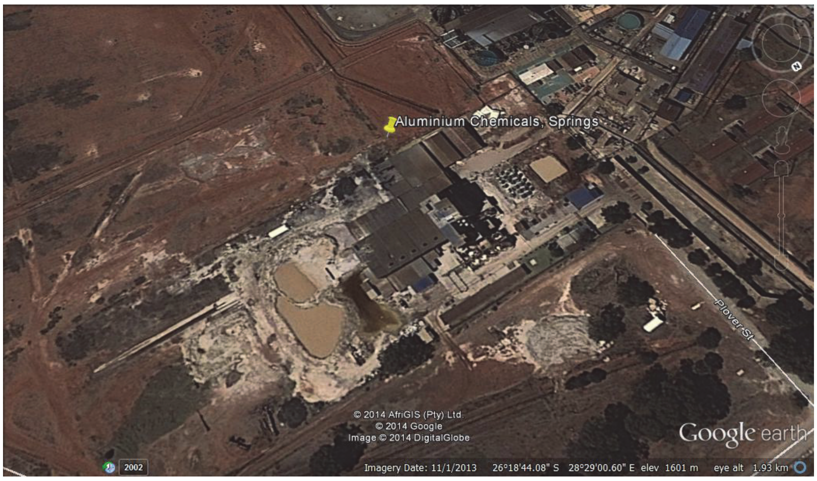
## Appendix 1b. Ferromanganese wad collection at Ryedale, Ventersdorp

Location of Ryedale mine between Ventersdorp and Randfontein

Open pit, Ryedale

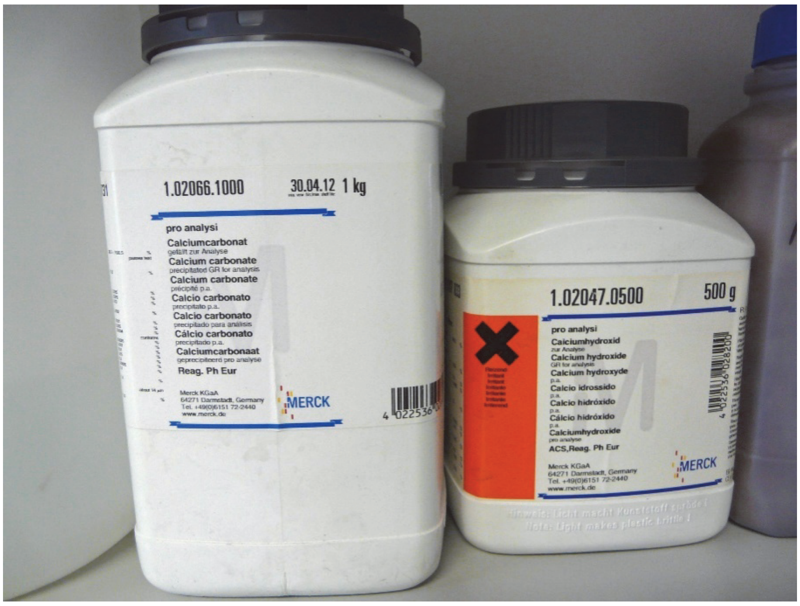
Sampling from the ore stockpile at Ryedale

## Appendix 1c. Aluminium sulfate and liming chemicals



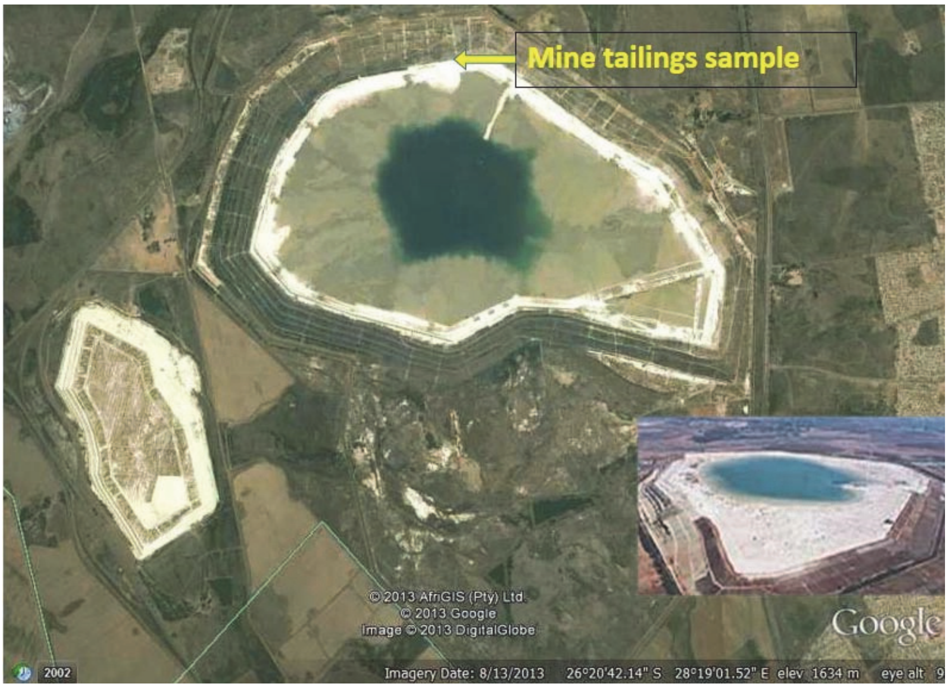
Aluminium sulfate factory, Springs

Aluminium sulfate used in experiments



Liming materials used for neutralisation (Ca carbonate and hydroxide)

## Appendix 1d. Mine tailings collection

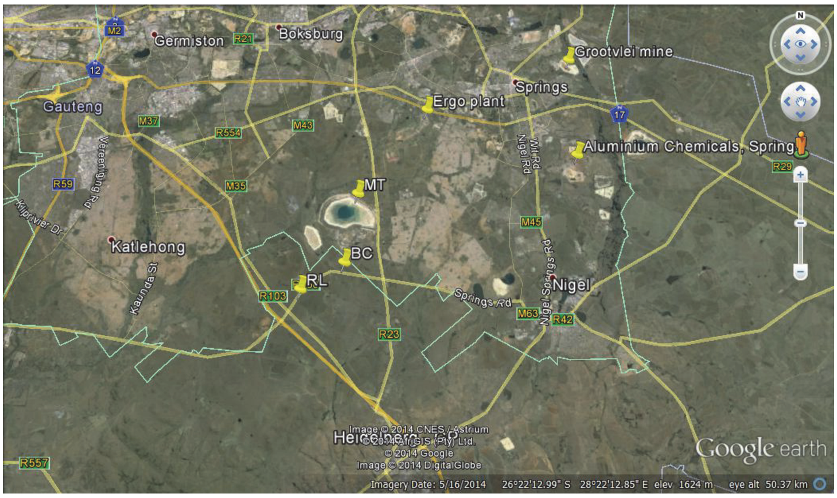


Ergo tailings storage facility (TSF) Brakpan Dam

View southwards from northern rim of the TSF where the tailings sample was taken

Wind erosion at the TSF

## Appendix 1e. Soil sampling locations



Location of black clay (BC) and red loam (RL) soils in relation to mine tailings (MT) and other key sites (Grootvlei mine, Ergo and Aluminium Chemicals plants near Springs)

The black clay sampling site (Bonheim form)

The red loam sampling site (Hutton form). Background hills are the Suikerbosrand.

## Appendix 2. Experimental procedures in the land treatment simulation

Mine tailings and black clay soil sieved (left) and alkaline treatments applied (right)

Soil and tailings in evaporation basins with amendments (left) and mixed with lime (right)

Mine water dispensed from storage tub (left) and added to tailings (right)

Small basins for mine water neutralisation and evaporation without soil

Vacuum extraction of black clay: caking facilitated return to the evaporating basin

Ignus Storm using the soils laboratory for evaporation at the University of Pretoria

**Schedule of water applications to the black clay soil and mine tailings indicating leaching days and volume of water additional to the regular application to ensure sufficient leachate from 400 g soil or tailings. The final column indicates mine water addition to the small evaporating basins without soil but containing an alkaline amendment in two of them. Leachate yield and the salt balance are shown in Table 4.**

| Date | Water applied (mL) | Leaching stage | Extra water for leaching (mL) | | Volume of mine water added (mL) |
|---|---|---|---|---|---|
| | | | Black clay | Mine tailings | 0M0 0MC 0MH |
| 20-Jun | 240 | | | | 80 |
| 21-Jun | 240 | | | | 80 |
| 22-Jun | 240 | | | | 80 |
| 23-Jun | 240 | | | | 80 |
| 24-Jun | 240 | Leaching 1 | 80 | 80 | 80 |
| 25-Jun | 240 | | | | 80 |
| 26-Jun | 240 | | | | 80 |
| 27-Jun | 240 | | | | 80 |
| 28-Jun | 240 | Leaching 2 | 80 | 0 | 80 |
| 29-Jun | 240 | | | | 80 |
| 30-Jun | 240 | | | | 80 |
| 1-Jul | 240 | | | | 80 |
| 2-Jul | 240 | | | | 80 |
| 3-Jul | 240 | Leaching 3 | 80 | 30 | 80 |
| 4-Jul | 240 | | | | 80 |
| 5-Jul | 240 | | | | 80 |
| 6-Jul | 240 | | | | 80 |
| 7-Jul | 240 | Leaching 4 | 80 | 30 | 80 |
| 8-Jul | 240 | | | | 80 |
| 9-Jul | 240 ml fresh water | Fresh water in all treatments | | | 80 |
| 10-Jul | 0 | Extra drying | | | 0 |
| 11-Jul | 240 | Leaching 5 | 80 | 30 | 90 (fresh water) |
| Total | 4800 | | 400 | 170 | 1520 |

## Appendix 3. Additional details of the second land treatment simulation experiment

This experiment was conducted by Ignus Storm and formed part of his Honours project in Environmental Soil Science. This experiment was conducted in a laboratory where the temperature was kept between 25-27°C and the humidity between 23-24% for the duration of the experiment (21 days). In this environment it was possible to evaporate 92% of the water added to prepare a saturated paste of the red loam soil in 24 hours. For the black clay soil the water loss was about 80%. The degree of desiccation of the soil in this experiment was therefore slightly less than that of the UWC experiment. Lime and limestone treatments also formed part of this study (Table 1, treatment no. 2, 3, 6 & 7) and were compared to unlimed treatments that received mine water only (Table 1, treatment no. 1 & 5) as well as treatments that received the same amount of liming material but treated with deionised water instead of mine water (Table 1, treatment no. 4 & 8). All these treatments were replicated three times. Two extra treatments were included that were not replicated (Table 1, no. 9-10). For these treatments mine water was used to prepare saturated pastes, however, for the leaching fraction deionised water was used instead of mine water. Smaller soil samples were used (250 g) to ensure enough raw mine water was available for the treatment thereof.

**Table A1. The various mine water, soil and liming treatment combinations used in the UP based experiment**

| No. | Treatment code | Detail of treatment combination |
|---|---|---|
| 1 | BC-MWNL | Black clay, Mine water, No lime |
| 2 | BC-MWOH | Black clay, Mine water, $CaOH_2$ |
| 3 | BC-MWCO | Black clay, Mine water, $CaCO_3$ |
| 4 | BC-DWOH | Black clay, Deionized water, $CaOH_2$ |
| 5 | RS-MWNL | Red soil, Mine water, No lime |
| 6 | RS-MWOH | Red soil, Mine water, $CaOH_2$ |
| 7 | RS-MWCO | Red soil, Mine water, $CaCO_3$ |
| 8 | RS-DWOH | Red soil, Deionized water, $CaOH_2$ |
| 9 | BC-MWOH# | Black clay, Mine water, $CaOH_{2,}$ Leached with water |
| 10 | RS-MWOH# | Red soil, Mine water, $CaOH_{2,}$ Leached with water |

It was also aimed to apply the equivalent of 10 years of irrigation in this experiment (based on an average evaporation rate of 5 mm day$^{-1}$).

The experiment started on the 23rd of June 2014. For the liming material + mine water treatments, lime or limestone was added and saturated pastes were prepared using mine water. For the control treatments saturation were prepared using deionized water instead of mine water. The soils were then placed into the plastic lined trays and spread thinly and left to dry for 24 hours. Afterwards, the treatments were transferred to pre-weighted mixing bowls and brought back to their saturated paste water content (and the amount of mine water added recorded). The treatments were then transferred back to their respective plastic trays, spread out and dried for another 24 hours.

Every third day the soil samples were left to dry for 22 hours, however, on this occasion 10% more mine water was added (than needed to bring it to a saturated paste). The soils were left to equilibrate for two hours and were then transferred to Buchner funnels. Leachate were obtained under vacuum and collected in Schott® bottles from each treatment. Afterwards, the samples were transferred back to their respective trays, lime or limestone was added to the liming treatments, and the treatments were brought back to saturated paste water content. The amount of lime or limestone required was based on the amount needed to neutralise the total acidity that would be added during the experiment. However, this was not added all at once instead it was divided in seven equal fractions. After each leaching event an increment of lime or limestone was added.

Aliquots of each leachate collected (15 ml) were membrane filtered through a 0.45 µm membrane filter under vacuum, 5 ml of the filtered solution was then preserved with 1 ml of concentration (65%) nitric acid and stored at 4°C. The remaining sample of each treatment was used to determine titratable acidity by titration with NaOH with a concentration of 0.002M and using phenolphthalein as indicator. The electric conductivity (EC) as well the pH of the leachates were also determined.

At the end of the experiment composite samples were prepared for each treatment. This was done by combining an equal volume of each of the seven preserved leachates collected. The combined samples were analysed for Ca, Mg, K, Na, S, Mn, Fe and Al with ICP-OES.

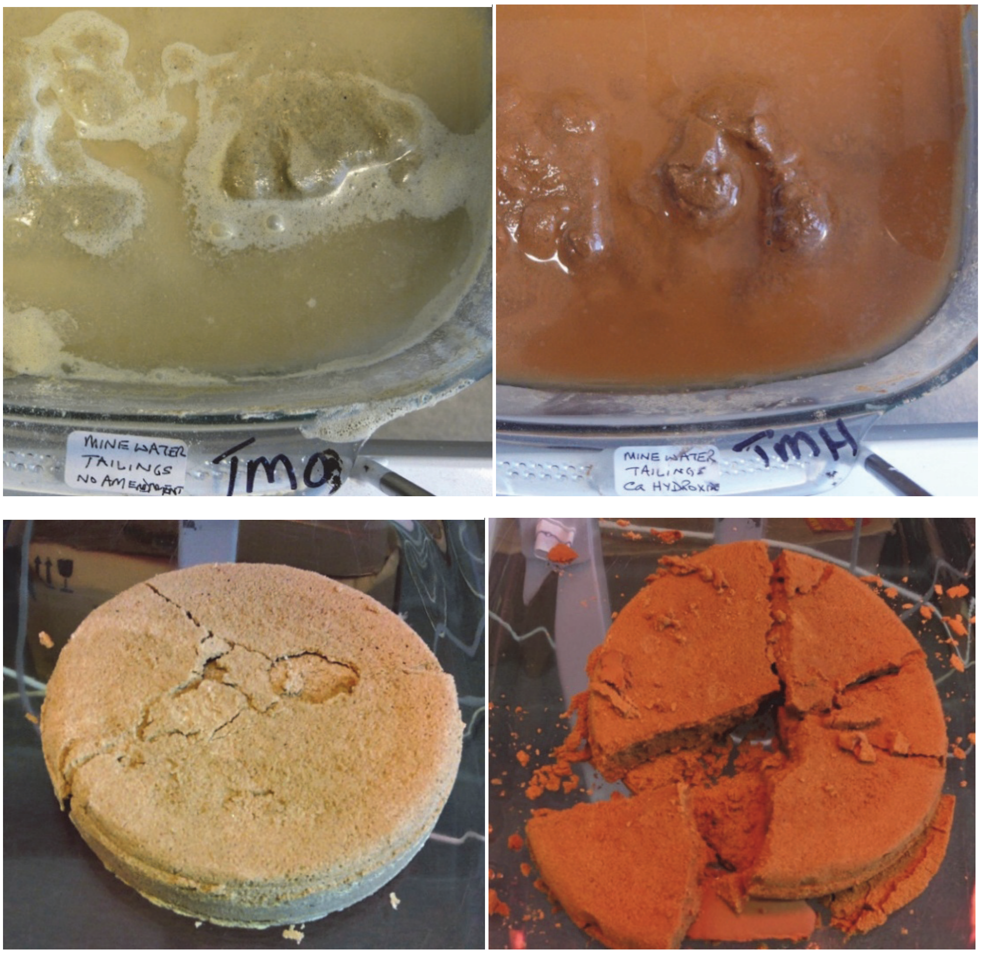
Upon completion of the experiment the soils were air-dried, homogenised and prepared for soil analysis. The samples were extracted with 1 *M* $NH_4OAc$ (1:10 soil to solution ratio) and the extracts analysed for above mentioned elements.

Evaporation trays and soil analysis in the second land treatment experiment

## Appendix 4. Visible effects of mine water and alkaline amendments in the first simulation trial

Sequence of residue development during the neutralisation and evaporative concentration of mine water. In each of the four pictures, the basin on the left is untreated mine water, in the middle is neutralised with $CaCO_3$ and on the right with $Ca(OH)_2$. These are treatments OMO, OMC and OMH, respectively, as described in Table A1. The full amount of liming material was added to the basins at the start and the mine water was then added and evaporated daily for twenty days.

Initial result of mine water addition to tailings limed with $Ca(OH)_2$ (left) and $CaCO_3$ (right).



Late stage of treating tailings with alkaline amendment and mine water: no amendment (TMO, left); $Ca(OH)_2$ (TMH, right); before (above) and after (below) vacuum extraction of leachate.

Outcome of the more concentrated land treatment simulation (Table 2)

Saturated pastes of the black clay soil after rewetting and mixing

Black clay soil after drying with efflorescence of (mainly) gypsum crystals on peds.

## Appendix 5. PHREEQC output (trimmed) for the second leaching of selected treatments showing saturation indices for selected mineral solids (Treatment codes are explained in Table 1)

```
Initial solution 1.      SMO
-----------------------------Solution composition------------------------------
      Elements           Molality       Moles
      Al                1.611e-04   1.611e-04
      Ba                3.085e-07   3.085e-07
      C(4)              1.161e-04   1.161e-04  Equilibrium with CO2(g)
      Ca                1.037e-02   1.037e-02
      Cl                8.905e-03   8.905e-03
      Co                2.396e-05   2.396e-05
      Cr                3.433e-06   3.433e-06
      Fe                1.647e-04   1.647e-04
      K                 6.888e-04   6.888e-04
      Mg                2.365e-02   2.365e-02
      Mn                3.727e-03   3.727e-03
      N(5)              3.645e-07   3.645e-07
      Na                1.518e-02   1.518e-02
      Ni                1.734e-30   1.734e-30
      S(6)              6.946e-02   6.946e-02
      Si                6.530e-04   6.530e-04
      Sr                1.738e-05   1.738e-05
      Zn                1.064e-05   1.064e-05
----------------------------Description of solution----------------------------
                                          pH  =   5.080
                                          pe  =   4.000
                           Activity of water  =   0.998
                              Ionic strength  =   1.489e-01
                          Mass of water (kg)  =   1.000e+00
                    Total alkalinity (eq/kg)  =  -1.998e-05
                          Total CO2 (mol/kg)  =   1.161e-04
                         Temperature (deg C)  =  25.000
                     Electrical balance (eq)  =  -5.552e-02
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  = -34.40
                                  Iterations  =  14
                                     Total H  = 1.110165e+02
                                     Total O  = 5.578765e+01
 -----------------------------Saturation indices-----------------------------
      Phase              SI log IAP   log KT
      Al(OH)3(am)      -1.69    9.11   10.80  Al(OH)3
      AlOHSO4           0.40   -2.83   -3.23  AlOHSO4
      Calcite          -4.82  -13.30   -8.48  CaCO3
      Gypsum            0.01   -4.60   -4.61  CaSO4:2H2O
      Quartz            0.83   -3.17   -4.00  SiO2
```

```
Initial solution 1.      SMC
-----------------------------Solution composition------------------------------
      Elements           Molality       Moles
      Al                1.272e-04   1.272e-04
      Ba                2.784e-07   2.784e-07
      C(4)              8.085e-04   8.085e-04  Equilibrium with CO2(g)
      Ca                1.320e-02   1.320e-02
      Cl                8.003e-03   8.003e-03
      Co                6.317e-06   6.317e-06
      Cr                3.425e-06   3.425e-06
      Fe                1.265e-04   1.265e-04
```

```
      K                 5.069e-04   5.069e-04
      Mg                1.689e-02   1.689e-02
      Mn                5.622e-04   5.622e-04
      Na                1.405e-02   1.405e-02
      Ni                1.181e-08   1.181e-08
      S(6)              4.670e-02   4.670e-02
      Si                1.736e-07   1.736e-07
      Sr                1.504e-05   1.504e-05
----------------------------Description of solution----------------------------
                                       pH  =   7.020
                                       pe  =   4.000
                        Activity of water  =   0.999
                           Ionic strength  =   1.088e-01
                       Mass of water (kg)  =   1.000e+00
                 Total alkalinity (eq/kg)  =   1.199e-03
                       Total CO2 (mol/kg)  =   8.085e-04
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  =  -2.609e-02
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  = -21.66
                               Iterations  =   9
                                  Total H  = 1.110152e+02
                                  Total O  = 5.569664e+01
------------------------------Saturation indices-------------------------------
      Phase               SI log IAP  log KT

      Al(OH)3(am)       0.82   11.62   10.80  Al(OH)3
      AlOHSO4          -1.12   -4.35   -3.23  AlOHSO4
      Calcite          -0.74   -9.22   -8.48  CaCO3
      Gypsum            0.06   -4.55   -4.61  CaSO4:2H2O
      Quartz           -2.75   -6.75   -4.00  SiO2
```

---

```
Initial solution 1.      SMH
-----------------------------Solution composition------------------------------
      Elements           Molality       Moles
      Al                1.122e-04   1.122e-04
      Ba                1.597e-06   1.597e-06
      C(4)              1.183e-03   1.183e-03  Equilibrium with CO2(g)
      Ca                1.519e-02   1.519e-02
      Cl                7.576e-03   7.576e-03
      Co                1.212e-05   1.212e-05
      Cr                3.424e-06   3.424e-06
      Fe                1.297e-04   1.297e-04
      K                 3.525e-04   3.525e-04
      Mg                1.370e-02   1.370e-02
      Mn                2.380e-04   2.380e-04
      Na                1.335e-02   1.335e-02
      Ni                5.262e-04   5.262e-04
      S(6)              4.550e-02   4.550e-02
      Si                9.543e-05   9.543e-05
      Sr                1.584e-05   1.584e-05
----------------------------Description of solution----------------------------
                                       pH  =   7.200
                                       pe  =   4.000
                        Activity of water  =   0.999
                           Ionic strength  =   1.053e-01
                       Mass of water (kg)  =   1.000e+00
                 Total alkalinity (eq/kg)  =   1.533e-03
                       Total CO2 (mol/kg)  =   1.183e-03
                      Temperature (deg C)  =  25.000
```

```
                  Electrical balance (eq)  =  -2.652e-02
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  = -22.76
                               Iterations  =   9
                                  Total H  = 1.110159e+02
                                  Total O  = 5.569336e+01
-------------------------------Saturation indices-------------------------------
      Phase               SI log IAP  log KT
      Al(OH)3(am)       0.60   11.40   10.80  Al(OH)3
      AlOHSO4          -1.71   -4.94   -3.23  AlOHSO4
      Calcite          -0.31   -8.79   -8.48  CaCO3
      Gypsum            0.12   -4.49   -4.61  CaSO4:2H2O
      Quartz           -0.01   -4.01   -4.00  SiO2
```

---

Initial solution 1.      **TPO**

```
------------------------------Solution composition------------------------------
      Elements           Molality       Moles
      Al                1.502e-03   1.502e-03
      Ba                2.124e-16   2.124e-16
      C(4)              1.081e-04   1.081e-04  Equilibrium with CO2(g)
      Ca                1.194e-02   1.194e-02
      Cl                5.375e-04   5.375e-04
      Co                1.719e-05   1.719e-05
      Cr                7.330e-07   7.330e-07
      Cu                6.314e-06   6.314e-06
      Fe                2.604e-03   2.604e-03
      K                 1.353e-27   1.353e-27
      Mg                1.321e-03   1.321e-03
      Mn                5.477e-05   5.477e-05
      N(5)              5.071e-08   5.071e-08
      Na                3.621e-04   3.621e-04
      Ni                1.470e-05   1.470e-05
      S(6)              2.395e-02   2.395e-02
      Si                3.673e-05   3.673e-05
      Sr                2.518e-06   2.518e-06
      Zn                6.289e-06   6.289e-06
----------------------------Description of solution----------------------------
                                       pH  =   2.440
                                       pe  =   4.000
                        Activity of water  =   0.999
                           Ionic strength  =   5.283e-02
                       Mass of water (kg)  =   1.000e+00
                 Total alkalinity (eq/kg)  =  -7.123e-03
                       Total CO2 (mol/kg)  =   1.081e-04
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  =  -4.521e-03
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -7.89
                               Iterations  =  10
                                  Total H  = 1.110212e+02
                                  Total O  = 5.560311e+01
-------------------------------Saturation indices-------------------------------
      Phase               SI log IAP  log KT

      Al(OH)3(am)      -8.14    2.66   10.80  Al(OH)3
      AlOHSO4          -1.20   -4.43   -3.23  AlOHSO4
      Calcite          -9.77  -18.25   -8.48  CaCO3
      Gypsum           -0.08   -4.69   -4.61  CaSO4:2H2O
      Quartz           -0.43   -4.43   -4.00  SiO2
```

```
Initial solution 1.      TMO
-----------------------------Solution composition------------------------------
      Elements           Molality       Moles
      Al                2.163e-03   2.163e-03
      Ba                9.828e-09   9.828e-09
      C(4)              1.077e-04   1.077e-04  Equilibrium with CO2(g)
      Ca                1.035e-02   1.035e-02
      Cl                3.920e-03   3.920e-03
      Co                1.613e-05   1.613e-05
      Cr                1.449e-05   1.449e-05
      Cu                1.560e-05   1.560e-05
      Fe                2.555e-02   2.555e-02
      K                 1.568e-05   1.568e-05
      Mg                4.213e-02   4.213e-02
      Mn                5.395e-03   5.395e-03
      N(5)              1.072e-09   1.072e-09
      Na                2.343e-02   2.343e-02
      Ni                5.015e-05   5.015e-05
      S(6)              1.882e-01   1.882e-01
      Si                1.531e-04   1.531e-04
      Sr                5.249e-06   5.249e-06
      Zn                1.922e-05   1.922e-05
----------------------------Description of solution----------------------------
                                       pH  =   2.520
                                       pe  =   4.000
                        Activity of water  =   0.996
                           Ionic strength  =   3.454e-01
                       Mass of water (kg)  =   1.000e+00
                 Total alkalinity (eq/kg)  =  -1.905e-02
                       Total CO2 (mol/kg)  =   1.077e-04
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  =  -1.643e-01
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  = -44.45
                               Iterations  =  12
                                  Total H  = 1.110335e+02
                                  Total O  = 5.626059e+01
------------------------------Saturation indices-------------------------------
      Phase               SI log IAP  log KT
      Al(OH)3(am)      -8.65    2.15   10.80  Al(OH)3
      AlOHSO4          -1.12   -4.35   -3.23  AlOHSO4
      Calcite         -10.17  -18.65   -8.48  CaCO3
      Gypsum            0.10   -4.51   -4.61  CaSO4:2H2O
      Quartz            0.22   -3.78   -4.00  SiO2
```

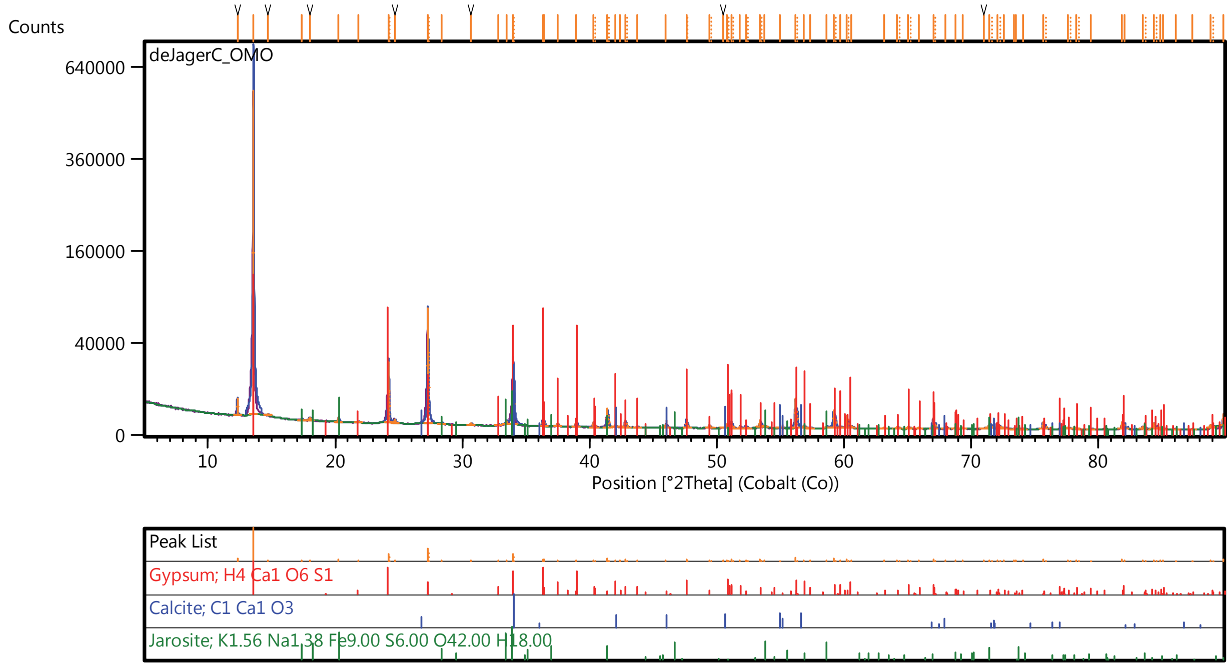
```
Initial solution 1.      TMC
-----------------------------Solution composition------------------------------
      Elements           Molality       Moles
      Al                9.688e-05   9.688e-05
      Ba                1.157e-10   1.157e-10
      C(4)              1.078e-04   1.078e-04  Equilibrium with CO2(g)
      Ca                9.809e-03   9.809e-03
      Cl                8.259e-03   8.259e-03
      Co                2.338e-05   2.338e-05
      Cr                3.293e-06   3.293e-06
      Cu                4.783e-06   4.783e-06
      Fe                3.266e-04   3.266e-04
      K                 1.291e-03   1.291e-03
      Mg                4.006e-02   4.006e-02
```

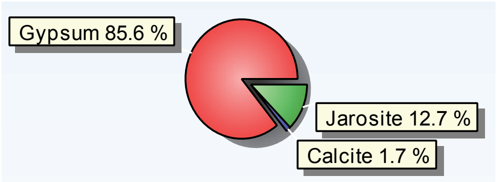
```
      Mn                5.035e-03   5.035e-03
      N(5)              7.757e-14   7.757e-14
      Na                2.587e-02   2.587e-02
      Ni                3.453e-08   3.453e-08
      S(6)              1.101e-01   1.101e-01
      Si                1.197e-04   1.197e-04
      Sr                5.897e-06   5.897e-06
----------------------------Description of solution----------------------------
                                       pH  =   2.520
                                       pe  =   4.000
                        Activity of water  =   0.997
                           Ionic strength  =   2.148e-01
                       Mass of water (kg)  =   1.000e+00
                 Total alkalinity (eq/kg)  =  -1.271e-02
                       Total CO2 (mol/kg)  =   1.078e-04
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  =  -7.770e-02
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  = -32.53
                               Iterations  =  10
                                  Total H  = 1.110271e+02
                                  Total O  = 5.594790e+01
------------------------------Saturation indices-------------------------------
      Phase               SI log IAP  log KT

      Al(OH)3(am)      -9.73    1.07   10.80  Al(OH)3
      AlOHSO4          -2.41   -5.64   -3.23  AlOHSO4
      Calcite         -10.05  -18.53   -8.48  CaCO3
      Gypsum            0.02   -4.59   -4.61  CaSO4:2H2O
      Quartz            0.10   -3.90   -4.00  SiO2
```

```
Initial solution 1.      TMH
-----------------------------Solution composition------------------------------
      Elements           Molality       Moles
      Al                1.006e-04   1.006e-04
      Ba                9.487e-09   9.487e-09
      C(4)              1.111e-03   1.111e-03  Equilibrium with CO2(g)
      Ca                1.083e-02   1.083e-02
      Cl                5.666e-03   5.666e-03
      Co                1.268e-05   1.268e-05
      Cr                3.281e-06   3.281e-06
      Fe                1.292e-04   1.292e-04
      K                 1.740e-03   1.740e-03
      Mg                4.000e-02   4.000e-02
      Mn                2.536e-03   2.536e-03
      N(5)              5.591e-18   5.591e-18
      Na                2.459e-02   2.459e-02
      Ni                1.998e-16   1.998e-16
      S(6)              7.406e-02   7.406e-02
      Si                5.208e-05   5.208e-05
      Sr                8.411e-06   8.411e-06
----------------------------Description of solution----------------------------
                                       pH  =   7.150
                                       pe  =   4.000
                        Activity of water  =   0.998
                           Ionic strength  =   1.659e-01
                       Mass of water (kg)  =   1.000e+00
                 Total alkalinity (eq/kg)  =   1.409e-03
                       Total CO2 (mol/kg)  =   1.111e-03
                      Temperature (deg C)  =  25.000
```

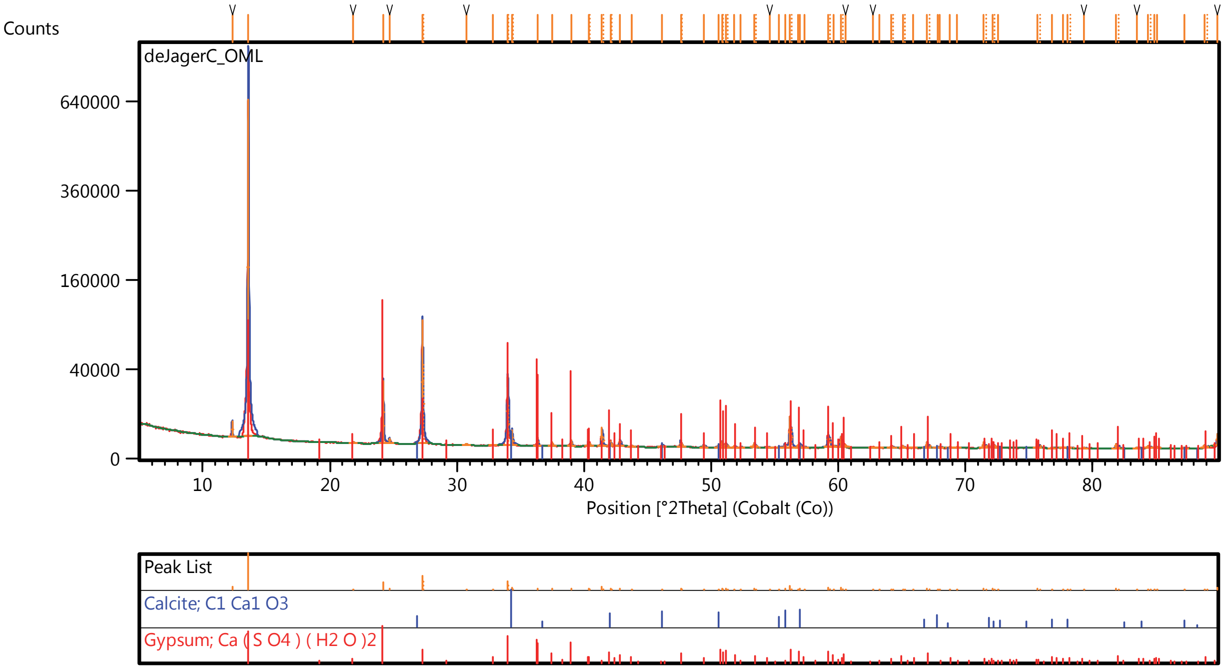
```
                  Electrical balance (eq)  =  -2.159e-02
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  = -11.83
                               Iterations  =  11
                                  Total H  = 1.110156e+02
                                  Total O  = 5.580714e+01
------------------------------Saturation indices-------------------------------
      Phase               SI log IAP  log KT

      Al(OH)3(am)       0.59   11.39   10.80  Al(OH)3
      AlOHSO4          -1.50   -4.73   -3.23  AlOHSO4
      Calcite          -0.65   -9.13   -8.48  CaCO3
      Gypsum            0.01   -4.60   -4.61  CaSO4:2H2O
      Quartz           -0.27   -4.27   -4.00  SiO2
-----------
End of run.
```

**Appendix 6a. Treatment 0M0: XRD data for the leached, dried cumulative precipitate after daily addition and evaporation of 80 mL mine water without alkaline amendment (see Table 4 for leachate composition)**

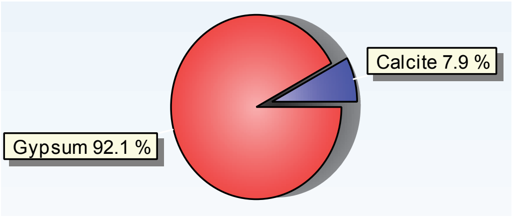




**Appendix 6b. Treatment 0MC: XRD data for the leached, dried cumulative precipitate after daily addition and evaporation of 80 mL mine water with prior application of sufficient calcium carbonate to neutralize the full quantity of mine water (see Table 4 for leachate composition)**



Quantitative for OML:



**Appendix 6c. Treatment 0MH: XRD data for the leached, dried cumulative precipitate after daily addition and evaporation of 80 mL mine water with prior application of sufficient calcium hydroxide to neutralize the full quantity of mine water (see Table 4 for leachate composition)**