

INTEGRATING NANO IRON PRODUCTION INTO THE ACID MINE DRAINAGE NEUTRALISATION TREATMENT PROCESS

A Preliminary Technical Feasibility Study

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Report to the
Water Research Commission

by

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EXECUTIVE SUMMARY

BACKGROUND

The emission of acid mine drainage (AMD) from mine workings and waste impoundments is of particular concern in South Africa, especially in the Witwatersrand gold fields and the Mpumalanga coal fields. In response to these concerns, and in recognition of mine water as a valuable resource in a water scarce region, the coal mining industry in South Africa implemented the eMalahleni Mine Water Reclamation Plant (EWRP) in the Mpumalanga Province in 2007. This plant, which uses a combination of High Density Sludge (HDS) lime neutralisation, ultrafiltration, and reverse osmosis (HiPRO process) to convert AMD into potable water, is not, however, without its challenges. The costs of the treatment processes are relatively high, and the plant generates significant quantities of low-quality wastes in the form of gypsum-rich sludge and salt-laden brine. Recovery of by-products from AMD, and/or the wastes generated from the treatment of AMD, can both reduce costs of waste disposal and offset costs of the treatment process, whilst also being consistent with the principles of sustainable development and related concepts such as resource efficiency, the circular economy and industrial ecology. Of relevance to AMD from the Mpumalanga coalfields, is the potential recovery of iron and sulphur-based products as these components are typically present in elevated levels (up to 4 g/L and 13 g/L iron and sulphate respectively). One potentially valuable iron-product that could be recovered from iron-rich AMD, is zero-valent iron in the nanoparticle size range (<100 nm), also known as zero-valent nano iron (ZVNF). Zero-valent nano iron offers a number of advantages over micro- and macro-iron in water treatment applications due to its high reactivity, and is traditionally prepared from ferric chloride using chemical reductants, such as sodium borohydride, or polyphenolic compounds extracted from green plants such as lemon, grape, sorghum, etc. It is, furthermore, posulated that the pre-removal and recovery of iron from AMD in the form of nano iron also provides the opportunity to generate a purer, and potentially more valuable, gypsum product during subsequent lime neutralisation.

PROJECT SCOPE

It is this opportunity that this study sets out to explore, through a preliminary investigation of the feasibility of generating nano iron from AMD, and the effects of this on the downstream neutralisation process parameters and outputs, particularly gypsum which constitutes one of the major wastes from the EWRP. More specifically, laboratory-scale tests were conducted to investigate the technical feasibility of extracting nano iron from a typical AMD solution using both chemical reductants and polyphenolic plant extracts, and to assess the effect of this extraction on the compositions of the effluents and residues generated during subsequent lime neutralisation of the iron-depleted supernatant. Empirical test work was supported by thermodynamic equilibrium modelling to identify predominant aqueous species and likely precipitate formation during neutralisation of AMD both before and after treatment. A review and assessment of the potential uses local markets and specifications for gypsum was also conducted to explore potential downstream applications of the gypsum-rich neutralisation residues generated.

RESULTS AND DISCUSSION: EMPIRICAL TEST WORK

Laboratory test work showed that both the chemical reductant, sodium borohydride, and polyphenol extracted from green tea can be effectively applied to generate nano iron from field AMD solutions containing elevated iron concentrations (~2-4 g/L), with sodium borohydride being more effective in removing iron ($\geq 99.9\%$ removal in 8 minutes) than the green tea extract (89% removal in 12 hours). In both cases, treatment of the AMD was accompanied by significant removal of other metals, particularly Al, Zn, Ba, Ni and Co, as well as partial removal of Mn, Mg and Ca. However, pre-treatment with sodium borohydride resulted in an increase in the concentrations of soluble boron and sodium, and neutralisation effluents still contained elevated levels of sulphate (~11 g/L), calcium (~1 g/L), boron (1-2 g/L) and sodium (5-6 g/L), which may adversely affect the performance of the subsequent reverse osmosis treatment process. In contrast, neutralisation of the AMD after

treatment with green tea extract resulted in neutralisation effluents with similar pH values and compositions of inorganic elements than those obtained from neutralisation of untreated AMD, but at lower lime dosages. The nano iron product generated using the green tea extract was, furthermore, more stable and had a smaller particle size on average (< 55 nm) than that generated through the application of sodium borohydride. However, the presence of residual polyphenol compounds in the feed to, and the potential effects on, the subsequent reverse osmosis process requires further investigation, as does the effectiveness of the nano-iron product for downstream water treatment.

RESULTS AND DISCUSSION: THERMODYNAMIC MODELLING

Thermodynamic modelling indicated that, whilst the gypsum content in the neutralisation residue after treatment with green tea extract is likely to be higher than that obtained from the neutralisation of raw AMD ($\sim 67\%$), the presence and subsequent co-precipitation of residual Fe and Al means that the residue is unlikely to be suitable for the manufacture of high-end gypsum products such as plasterboard. Nevertheless, the improved purity (~ 75 - 87% gypsum) may render the residues suitable for construction applications (e.g. manufacture of cement or cement bricks), or as feed to the Gyp-SLiM or similar process for the manufacture of higher value sulphur, magnesite, and limestone. Thermodynamic modelling also showed the potential to form carbonate precipitates, such as calcite, during neutralisation in the presence of air, with concomitant additional lime consumption, elevated sulphate concentrations in the effluent, as well as reduced gypsum content in the residue.

Whilst the study highlighted the valuable role of thermodynamic equilibrium models such as OLI, Visual MINTEQ and PHREEQ in understanding the controlling neutralisation reactions and in informing and interpreting empirical test work, it also indicated that there are several challenges in the application of these models for simulation purposes. This is particularly the case for OLI which requires a licence and does not provide flexibility in terms of the user's ability to manipulate the operational conditions or access the database.

CONCLUSIONS AND RECOMMENDATIONS

Given its potential for recovery of nano iron and generation of a purer, and potentially more valuable, neutralisation residue, it is recommended that additional test work be conducted to further explore the feasibility of using polyphenolic plant extracts to pre-treat AMD with specific emphasis on the distribution and stability of polyphenols in the treated AMD; the local availability of alternative and potentially more effective green reductants to green tea; the feasibility of using the nano iron products for downstream water treatment; and the characteristics of the subsequent neutralisation residue. It is also recommended that further studies be conducted to explore and compare options for a more holistic and integrated approach to value recovery from gypsum-rich neutralisation residues, which includes the manufacture of higher-end by-products and applications, as well as niche local applications of the gypsum for rehabilitation and remediation of local coal mines. Such studies should be aimed at establishing both the technical feasibility and the business case, taking into consideration the environmental, economic, social, and regulatory aspects of the proposed options. Finally, it is recommended that a more detailed investigation is carried out to explore the potential for using a combination of thermodynamic models such as Visual MINTEQ and PHREEQ for guiding and informing the simulation and optimisation of lime neutralisation process systems.

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ACRONYMS & ABBREVIATIONS

AMD	Acid mine drainage
ARD	Acid rock drainage
CFA	Coal fly ash
EBRU	Environmental Biotechnology Group
EC	Electrical conductivity
EFC	Eutectic Freeze Crystallisation
EWRP	Water Reclamation Plant
EWTP	eMalahleni Water Reclamation Plant
FGD	Flue-gas desulphurisation
FRAP	Ferric reducing
FRAP	Ferric Reducing Antioxidant Property
GRTE	Green rooibos tea
GTE	Green tea
HDS	High Density Sludge
HiPRO	High Pressure Reverse Osmosis
MWCB	Water Coordinating Body
NMD	Neutral mine drainage
ORP	Oxidation Reduction Potential
PG	Phosphogypsum
PRBs	Permeable reactive barriers
RO	Reverse osmosis
RTE	Rooibos tea
SD	Saline drainage
SDS	Sodium dodecyl sulphate
SPARRO	Slurry Precipitation and Recycle Reverse Osmosis
WEGD	Wet flue gas desulphurization
ZVF	zero-valent iron
ZVNF	zero-valent nano iron

CHAPTER 1: BACKGROUND

1.1 Introduction

Increasing stress is being placed on South Africa's water resources, demanding the development of integrated water management solutions and cross-sectoral partnerships. Acid mine drainage (AMD) is of particular concern in South Africa, especially in the Witwatersrand gold fields and Mpumalanga coal fields. Acid mine drainage has a significant environmental and economic impact, due to its corrosive nature and elevated content of salts and metals. Several approaches and technologies have been identified and developed for the treatment of acid mine drainage, the most commonly applied approach entailing neutralisation with limestone and/or lime, due to its simplicity and cost-effectiveness. The enhanced and widely applied High Density Sludge (HDS) process configuration produces a denser and more stable sludge than conventional lime neutralisation, thus reducing disposal space requirements and costs. However, the scale of the AMD problem in South Africa means that the HDS neutralisation process is generating considerable quantities of sludge, whilst the treated effluent still contains elevated soluble sulphate salts, and is generally not fit for consumption or use, and poses a risk to major water sources and the natural environment because of salinization. In response to these concerns and the growing recognition of mine water as a potentially valuable resource in a water scarce country, the coal mining industry in South Africa has successfully implemented two mine water reclamation plants in the Mpumalanga coal fields. These plants use multi-staged processes, incorporating reverse osmosis (RO) to recover potable water which is used to supplement local municipal water supply. A further paradigm shift has also taken place in the handling and management of the HDS sludges and RO brines, with recovery of useful and saleable by-products being actively researched and, in some cases, pursued. For example, the sludge produced in the current HDS process at the eMalahleni Water Reclamation Plant (EWTP) is currently being used in the agricultural sector, whilst Glencore has recently announced that it intends to recover salts and ice from the RO brines, based on the Eutectic Freeze Crystallisation (EFC) process developed at UCT. These mine water treatment plants, whilst progressive and integrative, are not without their challenges, both from an operational and economic perspective. The costs of the treatment processes are relatively high, and the mixed sludge that is produced by the HDS process is of low quality and value. Performance is also increasingly adversely impacted by the variability in the feed stream compositions, making it difficult for the treatment processes to achieve and maintain optimum efficiency. Although the EWTP has traditionally blended mine waters to generate a relatively consistent feed stream, the plant is currently undergoing expansion and modification for the treatment of mine waters that are high or low acidity in separate circuits. Preliminary commissioning trials have, however, indicated the need for further investigation of the relationship between the chemical composition of the feed solution and plant operating conditions, particularly the interrelated parameters of lime dosage and pH, to optimise plant performance, from both a perspective of output characteristics (effluent water and sludge) and economic efficiency.

The recovery of higher-end products from the HDS process sludge has the potential to render the treatment technologies more cost effective and economically attractive, whilst being consistent with the principles of sustainable development and related concepts such as resource efficiency, the circular economy and industrial ecology. The high iron content of acid mine drainage creates the opportunity for the recovery of iron products, such as pigments and other industrial products. Iron oxides, such as magnetite and ferrite, and zero-valent iron (ZVF) have numerous applications, including water treatment and coal washing. Iron oxide and ZVF in the nanoparticle size range (<100 nm) has been found to offer several advantages over micrometric particles for wastewater treatment, with nanotechnology being one of the fastest growing sectors of the high-tech economies. Previous studies (see for example Alegbe et al., 2018; Akinwekoma et al., 2017 a and b; Alexander and Ristow, 2010; Cheng et al., 2011; Cook, 2009; Ristow and Brauer, 2010; Wei and Vaideri, 2007) have demonstrated the feasibility of recovering iron oxides (magnetite and ferrite) and zero-valent nano iron (ZVNF), and their subsequent use in the removal of metals, from AMD. These studies have, however,

been relatively limited, with little attention having been given to the integration of iron recovery into a multi-stage water management system which generates fit-for-purpose water and useful by-products in a cost-effective manner. This is not a trivial task and requires a comprehensive understanding of the effects of key parameters on the performance of individual processes and their interface with upstream and downstream processes, particularly in terms of the properties of the outputs. Thermodynamic aqueous modelling tools such as MINTEQU, PHREEQ and OLI can play a valuable role in understanding the effect of neutralisation parameters, such as pH, neutralising reagents, and feed solution compositions, on the reaction mechanisms controlling the removal of metals and salts from solution and the compositions of the sludges. This understanding can in turn serve to inform R&D campaigns to optimise the neutralisation process in terms of desirable properties of output streams, as well as assist in the effective operation of an operating neutralisation operation by enabling the potential effects of variability in the compositions of input streams (AMD feed and neutralising reagents).

1.2 Project aims

This project sets out to explore the feasibility of generating additional value from AMD, by establishing the technical feasibility of incorporating a nano iron recovery step into the conventional AMD treatment process at the eMalahleni Water Reclamation Plant.

Specific project objectives are to:

1. Review opportunities and processes for the recovery of useful by-products from AMD and the AMD neutralisation sludge
2. Investigate the technical feasibility of generating nano iron from AMD
3. Establish the potential effects of the pre-removal of nano iron on the subsequent neutralisation process
4. Explore the application of thermodynamic models for simulating the AMD neutralisation process

1.3 Scope and limitations

The project scope is divided into four interconnected phases, each of which is designed to meet a specific objective. The outcomes of these four phases are synthesised in the form of recommendations pertaining to the application and optimisation of a multi-stage process for the integrated treatment of AMD which produces useful by-products. Whilst the eMalahleni Water Reclamation Plant has been used as the primary case study, the application of the findings in this study could also be extended to other local AMD case studies, including that arising in the Witwatersrand Goldfields.

1.3.1 Phase 1: Literature review and assessment

Phase 1 entails a preliminary review and assessment of opportunities and processes for the recovery of useful by-products from AMD and AMD neutralisation sludge (Objective 1). The focus of this review is on the production, properties and uses of gypsum and iron products, particularly nano iron, with specific focus on opportunities for the recovery of these products from AMD in the local context. This entails a comprehensive review and analysis of published literature, supplemented by interviews with local producers and consumers (or potential producers and consumers) of these products.

1.3.2 Phase 2: Laboratory-scale synthesis of nano iron

Phase 2 of the project entails a laboratory-scale study on the production of nano iron from coal-related AMD (Objective 2). This study builds on previous work at the University of the Western Cape (Alegbe et al., 2018) which established the feasibility of recovering zerovalent nano iron (ZVNF) from ferric chloride and ferric sulphate solutions using sodium borohydride and phenolic plant extracts. A particular focus of this study is on the type and dosage of these reductants and contact time on the properties of the nano iron and effluent water. Experiments have been conducted on typical AMD samples, collected from the Mpumalanga coalfields.

1.3.3 Phase 3: Laboratory-scale neutralisation

Phase 3 of the project entails a laboratory-scale study of the AMD neutralisation process both with and without prior iron removal (Objective 3). Particular focus is on the key parameters (specifically feed solution compositions and lime dosage) effecting the performance of the neutralisation process, with respect to the properties and characteristics of the sludge (in line with key physical and chemical specifications identified in Phase 1) and effluent solution (pH, major cations such as Ca, Mg, K and Na, sulphate and metals identified as being of relevance). Feed solutions to this reactor configuration include typical AMD samples collected from the Mpumalanga coalfields, and AMD that has been pre-treated for selective iron recovery (Phase 2). In this way the effect of pre-separation of iron on downstream operations has been established.

1.3.4 Phase 4: Thermodynamic modelling of AMD neutralisation

Phase 4 of the project entails the set-up and application of three different thermodynamic equilibrium models, namely VISUAL MINTEQ, PHREEQ and OLI, to simulate the distribution and attenuation of chemical species during lime neutralisation of AMD solutions (Objective 4). Three different systems have been modelled in this study, namely the chemical speciation modelling of typical AMD and NMD solutions, the simulated lime neutralisation of typical acidic and neutral mine drainage solutions from the Mpumalanga coalfields and modelling of laboratory-scale neutralisation experiments before and after treatment with reductants. Based on the findings, the potential strengths, and limitations of thermodynamic models in terms of simulating and predicting the performance of the AMD neutralisation have been assessed.

CHAPTER 2: REVIEW AND ASSESSMENT OF OPPORTUNITIES AND PROCESSES FOR THE RECOVERY OF USEFUL BY-PRODUCTS FROM AMD TREATMENT

2.1 Introduction

Mine water has become a major hydrological and geochemical problem arising from human exploitation of the geosphere. Mine water composition depends on the mined ore and the chemical additives used in the mineral and hydrometallurgical processing. This study is mainly concerned with the iron and sulphate rich acid mine drainage, occurring within the Mpumalanga coalfields of South Africa. The findings of this study could also be extended to the AMD occurring in the Witwatersrand goldfields.

This chapter provides an overview of published literature pertaining to AMD and its treatment, with specific emphasis on the recovery of by-products, particularly nano iron. A survey of potential uses, markets, and specifications for both gypsum and iron by-products in the local context was also conducted.

2.2 Background: Sources, characteristics, impacts and mitigation of AMD

2.2.1 Origins and sources of AMD

Acid mine drainage occurs as a result of the weathering of naturally occurring sulphide minerals, when exposed to air and water. These sulphide minerals include pyrite (FeS_2), pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$), arsenopyrite (FeAsS), bornite (Cu_5FeS_4), chalcocite (Cu_2S), covellite (CuS), galena (PbS), millerite (NiS), sphalerite (ZnS) and molybdenite (MoS_2). Of these minerals, the sulphides of iron, particularly pyrite, are by far the most common, and typically occur as unwanted (gangue) material in several metallic ore coal deposits. Whilst acid mine drainage can occur naturally, it is largely associated with anthropogenic activities, such as construction and, in particular, the extraction and early beneficiation of sulphide-bearing hard rock ores and coal deposits. This is because the excavation of sulphide-bearing ores, and the subsequent liberation of targeted minerals, exposes the surfaces of sulphide minerals to water and oxygen. As an unwanted or gangue mineral, this exposed pyrite is separated from the targeted minerals as much as possible during the extraction and early processing stages, and largely reports to the mined rock face or the large volume wastes generated during the subsequent crushing, milling and concentration of the run-of-mine ore. Point sources of AMD thus typically include sulphide-bearing rock faces in defunct mine shafts, mine waste impoundments (tailings, waste rock, discards, and overburden) and ore stockpiles. In South Africa, both the gold and coal mining industry are associated with significant AMD pollution, particularly in the Witwatersrand Basin and Mpumalanga Province. Several previous Water Research Commission reports provide details on the sources of AMD pollution in South Africa (see for example Harrison et al., 2010 and Broadhurst et al., 2018).

2.2.2 The mechanisms of AMD generation

The key chemical reactions involved in the formation of AMD are shown in Equations 2.3-2.4 (Evangelou and Zhang, 1995; Stumm and Morgan, 1996). Sulphide minerals, such as pyrite, are oxidised in the presence of oxygen and water to form ferrous iron, sulphate, and acid (Equation 2.1).



The ferrous iron formed undergoes further oxidation in the presence of dissolved oxygen to yield ferric iron and acid (Equation 2.2).



At pH > 3.5, hydrolysis of Fe^{3+} results in precipitation of ferric hydroxide, $\text{Fe}(\text{OH})_3$, with the release of additional acid (Equation 2.3).



At lower pH values, soluble ferric ions act as a rapid oxidant of pyrite, in accordance with Equation 2.4.



This cyclic propagation of acid generation continues until the supply of Fe^{3+} or FeS_2 is exhausted. Naturally occurring micro-organisms play a significant role in the oxidation of tailings or wastes from the mines, by catalysing both the oxidation of intermediate soluble sulphur forms and ferrous iron (Dumett and Keener, 2013; Evangelou and Zhang, 1995; Johnson, 2003; Kucera et al., 2013; Scheetz and Earle, 1998). The most common of the micro-organisms involved in AMD formation are *thiobacillus ferrooxidans* (iron and sulphur oxidising bacteria), *thiobacillus thiooxidans* (sulphur oxidising bacteria) and *ferrobacillus ferrooxidans* (iron oxidising bacteria).

Acid formed through the oxidative dissolution of pyrite is neutralised by acid-consuming minerals, such as carbonates, silicates, and clays, which may occur in the ores, wastes and local geology. The acid-neutralising minerals can vary quite significantly in terms of their neutralising capacity and reaction rates. Carbonate minerals, the most common being limestone (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$), are relatively fast weathering, whilst silicates typically have slower dissolution rates and lower neutralising capacities. Ultimately the net generation of AMD at any point source is a function of the relative rates and extents of the acid forming and acid neutralising reactions and will vary according to the mineralogy and geochemistry of the ores, wastes and host environments. Other factors influencing the rate and extent of AMD generation and dispersion in the natural environment include the local hydrogeology, climate (temperature and rainfall), microbial populations and waste/mine management practices. Most of these factors are inter-related and entail protracted spatial and temporal scales, making the reliable prediction of AMD a challenging undertaking.

2.2.3 Characteristics of AMD

Several characteristics are typically used to classify mine water (Lottermoser, 2007). A key characteristic of mine water is the pH, with mine waters being classified as acidic (pH <6), alkaline (pH >8) or circumneutral (pH 6-8) (Morin and Hutt, 1997). The classification of mine waters in terms of their *major cations and anions* involves plotting the major cation (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and anions (Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^-) on Piper or trilinear diagrams. In accordance with these diagrams, uncontaminated shallow ground waters are typically classified as calcium bicarbonate water, deep ground waters as sodium bicarbonate water, and contaminated mine water as calcium sulphate water. Also, of particular relevance to the quality of mine water is the concentration of transition *metals* and *metalloids* (or semi-metals). Contaminated mine water is typically enriched in metals and semi-metals, the concentration of which is generally highly dependent on both the local geology and the pH of the water. The pH-metal concentration relationship is illustrated by the so-called “Ficklin diagrams” which classify mine water in accordance with both pH and the total concentration of six dissolved heavy metals (Cd, Co, Cu, Ni, Pb, Zn) considered typical for mine waters (Ficklin et al., 1992). The total concentration of cations, anions, metals, and semi-metals is often measured as Total Dissolved Solids (TDS) content, with “good quality” water having a TDS of <1000 mg/L and “low quality” water a TDS of > 5000 mg/L (MCA, 2014).

In accordance with INAP (2009), there are three types of mine water:

- *Acid mine drainage (AMD)/Acid rock drainage (ARD)*: Acid mine drainage, also known as acid rock drainage, is characterised by acidic pH (< 6), moderate to high metal content (Fe and Al > 100 mg/L and Cu, Cr, Ni, Pb and Zn > 10 mg/L) and elevated sulphate concentrations (> 1000 mg/L). Acid mine/rock drainage (AMD/ARD) is formed when the geological composition of the acid forming mineral pyrite at source exceeds that of the relatively reactive acid-neutralising carbonate minerals (e.g. dolomite and limestone).
- *Neutral mine drainage (NMD)*: Neutral mine drainage is characterised by near neutral to alkaline pH values (>6) and low to moderate levels of metals and sulphate (TDS < 1000 mg/L). Neutral mine drainage occurs when the geological composition of relatively reactive acid neutralising carbonate minerals at source are equivalent to, or exceed, the acid metal pyrite composition.
- *Saline drainage (SD)*: saline drainage is typically characterised by neutral to alkaline pH (>6), low pH, transition metal content, and moderate concentrations of the anions sulphate, calcium and/or magnesium (TDS>1000 mg/L)

This study is mainly concerned with the iron and sulphate rich acid mine drainage, typically occurring within the Mpumalanga coalfields. Although varying quite significantly within regions and over time, the typical characteristics of AMD treated in water treatment plants in the Mpumalanga coalfields, as well as the Witwatersrand goldfields are shown in Table 2-1.

The results in Table 2-1 show that AMD decant from coal mines has a low pH and a high TDS, with elevated levels of sulphate, Ca, Mg, Fe, Mn, and Al. The metals Fe, Mn and Al are particularly high relative to drinking water limits (400-700 times higher). This is consistent with literature reports (see for example Annandale et al., 2009; Gunther et al., 2006) that mine water from collieries in the Mpumalanga, Free State and Limpopo Provinces contains elevated levels of metals and salts, even in cases where the pH is neutral.

Similar trends are observed for the decant water from the Witwatersrand goldfields, although the compositions vary quite considerably across the Western, Central and Eastern basins. Of particular concern in the case of AMD generated from defunct mine workings and tailings dumps in the Witwatersrand goldfields, is the elevated levels of uranium as well as other potentially harmful trace metals and semi-metals such as Ni, Cr, As, Cd, Zn and Pb (see discussions in previous WRC report by Broadhurst et al., 2018). Many of these elements are associated with pyrite in the gold ore deposits, and hence report to the leachate during AMD formation.

Table 2-1 Typical characteristics of AMD in the Witwatersrand goldfields (DWAF, 2013) and Mpumalanga coalfields (Gunther et al., 2006)

Water quality parameter	Units	Drinking water limits	Mpumalanga coalfields	Witwatersrand goldfields		
				Western basin	Central basin	Eastern basin
pH	@ 25°C	6.5-8.5	2.7	2.7	2.4	5.9
Acidity	mg/L as CaCO ₃		1050	1255	34	560
Conductivity	mS/m @ 25°C		460	426	465	363
TDS	mg/L	500	4930	5388	5118	3358
Ca	mg/L	32	660	823	563	421
Mg	mg/L	30	230	-	258	166
Na	mg/L	200	130	243	171	264
SO ₄	mg/L	400	3090	3410	3062	2289
Cl	mg/L	250	70	-	146	254
Fe	mg/L	0.3	210	799	108	227
Al	mg/L	0.1	40	-	193	2
Mn	mg/L	0.1	35	114	50	6
U	µg/L	30	—	100	695	470

Where: Drinking water limits are derived from IRMA (2016), except for values in italics which are from DWAF (1996)

2.2.4 Impacts and effects of AMD

The emissions of salt-laden and metal-enriched AMD from mine workings and waste dumps can result in contamination and pollution of the local environment, with concomitant adverse effects on natural ecosystems, human health, and the livelihoods of local communities through activities such as farming and fishing. These inter-related impacts and effects are summarised in Section 2.2.4.1-2.2.4.4 below. More detailed discussions are provided in a previous WRC report by Broadhurst et al. (2018).

2.2.4.1 Environmental pollution and degradation

AMD is considered to be the most significant surface water and groundwater water quality concern relating to the mining industry in many parts of this world, including the Witwatersrand goldfields and the Mpumalanga coalfields in South Africa (Oelofse, 2007; Vermeulen et al., 2007). AMD also results in degradation in soil quality and fertility, through acidification, salinisation, and the deposition of metal-rich secondary precipitates.

A 2011 study by the South African Department of Water Affairs (now Department of Water and Sanitation) found coal mining around the Wilge, Bronkhorstspuit, Klein Olifants and Olifants Rivers to be the main contributor to poor water quality and in-stream conditions (CER, 2016). Of particular concern is the increase

in the levels of salinization of local rivers, with elevated salt levels in the Witbank and Middleburg dams over the period 1972-2007 having been attributed directly to coal mining (McCarthy and Pretorius, 2009). This concern has also been highlighted in the recent Mine Water Atlas compiled by the South African Water Research Commission (WRC, 2017):

“the upper Olifants catchment is predominantly in an unacceptable state for the main stem Olifants River and many of the tributaries, but improves to a tolerable status at Loskop Dam. The salinity in the middle Olifants River falls in a tolerable range, and improves to an acceptable state in the Lower Olifants within the Kruger National Park. Many of the tributaries, including the Elands River, Wilge River, Steelpoort and the Ga-Selati, are in a good to acceptable status in the upper reaches of the catchments but deteriorate to unacceptable salinity ranges in the lower reaches before confluence with the Olifants River”.

Several studies bear testament to the contamination of water sources and soils because of AMD containing elevated salts and high concentrations of metals in the Witwatersrand goldfields (see for example Bobbins, 2015; Durand, 2012; Naicker et al., 2003; Ngigi, 2009; Pulles et al., 1992, Rösner and van Schalkwyk, 2000; Taylor and Maphorogo, 2015; Tutu et al., 2003; Winde and van der Walt, 2004). These studies show that the concentration of pollutants, including As, Cd, Hg, Pb and Al, regularly exceed international and national guidelines in waters around defunct mine dumps within in the region. In accordance with reports by the IHRC (2016), Kootbodien et al. (2012), Ngigi (2009) and a study conducted by the Federation for a Sustainable Environment (Cairncross et al., 2013), soils in the proximity of defunct gold mines and tailings facilities are also contaminated with toxic and radioactive metals, including aluminium, arsenic, cadmium, cobalt, copper, mercury, manganese, nickel, zinc, and uranium. In 2011, the National Nuclear Regulator of South Africa confirmed that the radiation levels were 15 times higher than the regulated levels (Cairncross et al., 2013).

2.2.4.2 *Eco-system health*

Eco-systems contaminated by AMD pose a significant threat to plants and living organisms, because of the exposure to acidity, dissolved metals, and deposition of secondary precipitates (Merovich and Petty, 2007; Petty et al., 2010).

AMD discharges into freshwater system reduce the diversity and assemblages of invertebrates, algae, fish, and amphibians (LeFevre and Sharpe, 2002). Acid and metals have detrimental toxicological effects on the aquatic ecosystems, resulting in deformities, mortality, injuries, growth disorders and low reproduction rates (Chadwick et al., 2013; Chibuike and Obiora, 2014; Clark, 1996; Gerhardt, 1993; Lewis and Clark, 1997), whilst the formation of secondary precipitates affects the organisms living at the bottom of the stream by blocking vision, contaminating food sources, and physically impairing breathing systems. In accordance with Simate and Ndlovu (2014), fish populations can be severely reduced or even eliminated altogether.

High concentrations of metals also affect soil microbial activities negatively, causing reduction in soil microbial population and distribution, and low microbial enzymatic activities (Sobolev and Begonia, 2008; Ngole-Jeme and Fantke, 2017). Due to the high concentrations of metals in soils, arthropod populations, as well as small and large mammals, are also negatively affected (Migliorini et al., 2004; Gall et al., 2015). Studies conducted by Eisler (2004) have shown that arsenic (As) doses of 17 mg/kg to 48 mg/kg body weight are terminal to birds, while some mammals are adversely affected by As doses of 2.5 mg/kg body weight after oral exposure (Ngole-Jeme and Fantke, 2017). The effects on plants can also be indirect. Contamination of soils by ARD presents adverse effects for plant growth and development (Simate and Ndlovu, 2014). The toxicity and acidity (low pH) of the metals contained in ARD affects soil fertility; the soils become water-logged and compact, forming crust which restricts seedling growth and entry of water and air into the soil system.

2.2.4.3 *Human and mammalian health*

As previously discussed, AMD pollution can result in elevated concentrations of metals and semi-metals in water sources, soils, and food sources, such as crops and fish. Some metals are essential nutrients (for example iron, cobalt, and zinc) or relatively harmless (such as the platinum group metals and gold) but may

have physical or aesthetic effects and can become toxic at elevated concentrations. Other metals (for example cadmium, mercury, lead, and arsenic) are highly toxic, even at relatively low concentration levels (Duruibe et al., 2007; Hawkes, 1997; Lenntech, 2004; Morais et al., 2012). Since these metals are not easily biodegradable, they can accrue in vital organs and glands such as the heart, liver, kidney, and brain upon ingestion, impairing their function and causing varying degrees of ailments based on acute and chronic exposures (Dermirezen and Ahmet, 2006; Farooq et al., 2008). These ailments vary from neurotoxic to carcinogenic actions, with poisoning due to exposure to metals affecting most major human physiological systems including the skeletal, nervous, respiratory, excretory, and digestive systems (ATSDR, 2008; Bobbins, 2015; Castro-Gonzalez and Mendez-Armenta, 2008; Jomova and Valko, 2011; Morais et al., 2012). Children are often at higher risks of absorbing metals from the environment and subsequently suffering from associated health problems and contact with contaminated soil and consumption of food grown in local vegetable gardens, remains a matter of concern (IHRC, 2016).

2.2.4.4 *Community livelihoods*

Apart from health effects, contamination of soils and water can reduce the productivity of soils and have adverse effects on the viability of crops and health of livestock, thus affecting the ability of the land to support agricultural and other farming activities (Mangena and Brent, 2006; Simate and Ndlovu, 2014). As indicated earlier, exposure of soils to AMD through seepage, run-off, or irrigation, can reduce the soil fertility and productivity, thus affecting the growth and quality of vegetables and other crops (IHRC, 2016). In addition, and similarly to humans, water that has come into contact with AMD is unsuitable as drinking water for animals and can affect livestock fertility and milk production (Bench Marks Foundation, 2015; Greenpeace International, 2008; Simate and Ndlovu, 2014).

In their study to assess the cost of coal mining on agriculture and human health in Odisha, Hota and Behera (2015) found the cost incurred by the local communities, in terms of loss of agricultural production and increase in medical expenses, to be substantial. Pollution of land and water by AMD arising from coal mining resulted in a loss in livelihood from both fishing and farming. Locally, a report by the Centre for Environmental Resources (CER, 2016) has claimed that the impact of mining activities in the Mpumalanga region is in most cases so severe that farming activities cannot be sustained on the land. Of particular concern was the adverse effect of soil acidification from AMD on maize production, with a very large area of the province's open pit workings situated on the old maize triangle. In accordance with the Bench Marks Foundation (2015), this has also affected farming exports, as farmers have lost European clients due to poor crop quality.

2.2.5 *AMD management and mitigation*

Approaches for the mitigation of AMD can be effectively classified into two main groups: those that treat and contain AMD after it has been generated, and those that prevent AMD formation and/or its subsequent generation. These approaches are summarized in Sections 2.2.5.1 and 2.2.5.2. A more detailed review of approaches and techniques for AMD management and mitigation is available in the INAP gardguide (http://www.gardguide.com/index.php?title=Chapter_7) and in Mujuru and Mutunaga (2016).

2.2.5.1 *AMD treatment techniques*

Treatment strategies do not prevent the actual generation of AMD at source, but rather aim to prevent its transport and dispersion into the surrounding environment. Although end-of-pipe and largely considered to be inconsistent with cleaner production principles, treatment strategies may still be required as a temporary or permanent measure to prevent off-site contamination by AMD from historical operations and/or for use in conjunction with AMD minimisation and prevention techniques. AMD treatment strategies are commonly categorised as active or passive, although hybrid active-passive treatment processes also exist.

i Active treatment strategies

Active treatment strategies improve the quality of mine water through the application of technologies that require continuous inputs of artificial energy, and biochemical or chemical reagents. Active treatment methods involve a water treatment plant that is monitored regularly by a skilled workforce. The major advantage of active treatment is the capability to handle any changes in mine water quality and quantity, because of the precise process control in response to these changes. Active treatment is also a preferred technique to passive treatment if land availability is a limiting factor. However, the continuous input of energy and reagents, and the need of skilled manpower to run and maintain AMD treatment plants, makes this approach resource intensive and expensive. Furthermore, active treatment processes generate large quantities of wastes such as the brines and sludge which are difficult to dewater and expensive to handle and dispose.

Active technologies include neutralisation, chemical precipitation (often used in combination with neutralisation), membrane processes, ion exchange and biological sulphate reduction. The most common and well-developed active AMD treatment technique entails neutralisation with limestone and/or lime. Treatment of mine water using limestone removes acidity of the mine water by the alkalinity generated by the dissolution of limestone (Equation 2.5-2.7).



Metals, such as Fe and Al, are removed through formation of hydroxide precipitates (Equations 2.8 and 2.9 respectively), whilst sulphate concentration in mine water is decreased due to the reaction with Ca^{2+} ions from lime or limestone to form gypsum (Equation 2.10)



Limestone raises the pH to neutral or circum-neutral values (6-7). These pH values are not sufficiently high to remove many metals, including base metals, Mg and Mn. The use of lime allows the pH to be adjusted to alkaline levels (9-11) to promote removal of metals as hydroxides or oxyhydroxides. Limestone and lime can also be used in an integrated two-stage neutralisation process. Conventional lime/limestone neutralisation produces a low density (2-5% solids) sludge that is difficult to thicken and filter. The high density sludge (HDS) process is a refinement on this low-density treatment method and acts to substantially reduce the sludge volume (by up to 95%) by greatly increasing its density (normally to around 20-30%). The HDS process begins by mixing incoming effluent with a neutralizing agent (limestone/lime) and recycled sludge from a clarifier/thickener unit. After neutralisation, this mixture is fed to the main lime reactor where a combination of aggressive aeration and high shear agitation ensures optimum process chemistry and clarifier performance. The discharge from the lime reactor is then treated with flocculant in the flocculation tank to promote precipitation and sent to the clarifier/ thickener unit. The clarifier separates the treated effluent from the sludge, a portion of which is recycled to the head of the process. The HDS process is well established and relatively cost-effective and is thus the most widely applied method for treatment of AMD. The HDS process is used as a short-term measure to manage AMD decant from defunct gold mines in the Witwatersrand basin, with plants on the Western, Central and Eastern limb having a capacity to treat 35, 84 and 110 ML/day AMD respectively. Sludge production, nevertheless, remains significant, the disposal of which adds significantly to the costs of operation.

Lime and limestone can be expensive and are associated with significant environmental footprints. A potential alternative approach is to use relatively inexpensive and locally available waste materials as neutralising reagents. AMD treatment with coal fly ash is one of the innovative technologies being studied for sustainable treatment of acid mine drainage in South Africa. Coal fly ash (CFA) is an aluminosilicate waste resulting from the combustion of coal in the production of electricity in coal power stations. The lime in the CFA is the species that is mainly exploited for the neutralisation and treatment of mine water (Gitari et al., 2011). These power stations are mostly found close to coal mines in South Africa, thus reducing the transportation costs of the CFA to the treatment facility. Research has also demonstrated that the use of high energy mixing devices such as a jet loop reactor increases the dissolution of the fly ash matrix and the kinetics of the reactions, whilst simultaneously reducing the amount of fly ash used in the treatment (Madzivire et al., 2010).

Whilst neutralisation processes such as the HDS process can effectively remove most metals to acceptable levels for human consumption, sulphate concentration usually remains above the required WHO and DWA limit for potable water (< 400 mg/L) because gypsum is partially soluble in water. Solubility of gypsum ranges from 1500 mg/L to 2000 mg/L depending on the composition and ionic strength of the solution, and increases in the presence of Mg^{2+} , Na^+ and K^+ ions. As such, HDS is best applied as a pre-treatment for AMD prior to further desalination. Several processes for desalinisation of pre-treated AMD, or direct treatment of NMD and SD, have been proposed in a special report to the South African Inter-ministerial committee on Acid Mine Drainage (IMC, 2010):

- The SAVMIN process developed by Mintek, a research and development organisation in South Africa, relies on the *selective precipitation* of insoluble complexes at different stages during the treatment process and the recycling of some of the reagents used in the process. This process provides potable water quality and potentially saleable by-products.
- High Pressure Reverse Osmosis (HiPRO) *membrane process* developed and commercialised by Keyplan Pty (Ltd) in South Africa transforms saline water into superior-quality drinking water.
- The Slurry Precipitation and Recycle Reverse Osmosis (SPARRO) process is a variation of the *membrane desalination process*. The concept of the SPARRO process is based on the protection of the membrane surfaces by providing a slurry suspension onto which the precipitation products can form. High water recoveries have been achieved in a demonstration scale plant (Pulles et al., 1992).
- The Environmental and Remedial Technology Holdings (EARTH Ion Exchange) process is an *ion exchange process* that was developed by Environmental and Remedial Technology Holdings (Earth) (Pty) Ltd for the purification of mine water for discharge or re-use as agricultural, process, industrial or potable water. The process produces potable water and useful and saleable products waste such as ammonium sulphate solution and mixed metal nitrate solution. The viability of this technology depends on stable prices and available markets for the products.
- The Rhodes BioSURE process was developed by the Environmental Biotechnology Group (EBRU) of Rhodes University in the early 1990s. The process involves *biological sulphate reduction* using free waste feedstock, such as sewage sludge, in place of expensive carbon and electron donor sources (ethanol and hydrogen). BioSURE has been applied on a demonstration plant scale at Grootvlei gold mine by ERWAT (the East Rand Water Care Company).
- The Magnesium-Barium-Alkali (MBA) Process, developed by the Tshwane University of Technology is another *chemical precipitation process*, modified from the CSIR ABC Process. This process uses $Mg(OH)_2$ as a neutralising reagent, and $Ba(OH)_2$ for sulphate removal in the form of $BaSO_4$.

Of these processes, only the HiPRO process has been applied on a commercial scale. One of the plants to apply this process is the eMalahleni Water Reclamation plant (EWRP) which uses a combination of lime neutralisation (HDS process), reverse osmosis (HiPRO process) and ultrafiltration to treat contaminated mine water from three operating Anglo mines and one defunct coal mine belonging to South32 in the Mpumalanga Province, removing 99% of the metals and salts. First commissioned in 2007, this plant was producing 30 ML/day potable water, of which 25 ML/day was sold to the eMalahleni municipality and has recently undergone expansion and modification to treat mine water from additional collieries and extend capacity to 50 ML/day.

On the back of the success of the EWRP, a mine water reclamation demonstration plant was commissioned at Optimum opencast coal mine (Cogha and van Niekerk, 2009), followed by a second full-scale plant at Glencore's Tweefontein Colliery in 2016, both in the Mpumalanga Province. The Tweefontein plant uses the HiPRO desalination process to treat NMD to drinking water standard, producing 15-20 ML/day potable water, a portion of which is to be supplied to the local municipality at municipal tariffs.

The choice of a suitable treatment technology depends on several factors, including the mine water composition, discharge rates and quantities, the end-use of the treated water and legislative requirements for use, and the entailed costs. In reality, there is no technical limit to the quality of the water which can be achieved using current existing techniques, but cost and the financial risk associated with the development and implementation of unproven technology is frequently the limiting factor. Therefore, the selection of a treatment technique tends to depend on economics and environmental considerations, rather than technology limitations.

ii Passive treatment strategies

As indicated above, active treatment processes are expensive and, historically, this has led to AMD being untreated or only partially treated, particularly in cases where the discharges were from "orphan" or remote sites (Akcil and Koldas, 2006). A potential alternative is to use less resource intensive passive treatment strategies. Although they cannot be regarded as "walk-away solutions, passive treatment refers to processes that do not require regular human intervention, operations, or maintenance. They should thus ideally be designed to function for many years without a major retrofit to replenish materials, and without using electrical power. Passive treatment strategies should also employ natural construction materials and processes as far as possible. Passive mine water treatment methods can be broadly classified as biological or chemical methods. Biological passive treatment technologies typically entail directing contaminated mine water through an environment containing sulphate reducing bacteria or plants, such as constructed wetlands (Hedin et al., 1994; Neculita et al., 2007; Steed et al., 2000; Wieder and Lang, 1982;). Constructed wetlands are typically used to treat low flow, acidic streams, or as a final polishing stage for pre-treated AMD. In practice wetlands remediate mine water through several physical, chemical, and biological processes, such as adsorption, reduction, and oxidation, to reduce acidity and remove metals and salts. Passive chemical methods typically entail the use of drains filled with limestone gravel or some form of reactive barrier. In the latter case, permeable reactive barriers are constructed by excavating a portion of aquifer ahead of the contaminated plume and replacing it with a reactive mixture. These reactive mixtures are normally organic carbon based to promote bacterial sulphate reduction and simultaneous precipitation of metal sulphides. Other reactive mixtures can also be used to remove contaminants such as uranium and chromium.

The advantages of passive treatment methods for mine water include relatively low operating costs and low maintenance. Passive treatment systems are also generally more aesthetically pleasing and can be integrated into surrounding eco-systems. However, passive systems require large areas of land to accommodate high flow and/or highly contaminated discharges of mine water, tend to be unpredictable (particularly in term of long-term sustainability), and offer limited opportunities for the recovery of treated water.

2.2.5.2 AMD prevention

In contrast to AMD treatment strategies, preventative strategies are aimed at minimising or avoiding the formation or generation of AMD at the source (i.e. by preventing exposure of pyrite surfaces to oxygen and/or water at the rock face or waste pile) or point of origin (e.g. by generating wastes that are non-acid generating in the first instance).

i Generating benign mine wastes

Strategies to generate non-acid generating wastes prior to their disposal include desulphurisation and waste blending. Desulphurisation essentially entails the removal of acid-forming sulphide minerals, using physical separation techniques such as gravity separation or froth flotation. Although, yet to be used on a commercial scale, laboratory-scale studies have shown that flotation can be used to effectively remove sulphide sulphur

from base metal tailings and fine coal wastes, generating bulk waste streams that are non-acid generating (see for example studies by Harrison et al., 2010). The sulphide-enriched stream can either be encapsulated or, preferably, converted into valuable by-products.

Non-acid generating mine wastes composites can also be produced prior to disposal by blending or agglomerating the waste with acid-neutralising materials. For instance, the blending of pyritic tailings (an acid producing material) with coal fly ash (CFA) forms a composite material which poses minimal harm to the environment. The lime present in the CFA combines with the liquid to form hydrated calcium silicate which resists corrosion and ingress of liquids (Adriano et al., 1980; Halstead, 1986; Scheetz and Earle, 1998). Other alkaline materials that have been used as blends include kiln dust and steel slag.

ii Preventing exposure of sulphide surfaces

A number of techniques have been developed to avoid exposure of sulphide surfaces to air and oxygen within mine waste deposits and rockface surfaces, at both a bulk and particle level:

- *Bactericides* are detergent-based reagents which break down the greasy film at the surface of the bacterial cell wall of the acidophilic bacteria which accelerate AMD formation. The application of anionic surfactants such as sodium dodecyl sulphate (SDS) is highly toxic to microorganisms and relatively affordable. However, the effect is temporary and hence the control of AMD is only short term. (Johnson and Hallberg, 2005; Loos et al., 1989; Schippers et al., 1998; Watzlaf, 1988).
- *Micro-encapsulation* entails the generation of inert coatings, for example through the reaction of AMD-generating mine waste with hydrogen peroxide and phosphate. During the process hydrogen peroxide oxidises pyrite and produces ferric iron which precipitates as iron phosphate to coat the pyrite surfaces. Other suggested coating agents include humic acid, oxalic acid, and sodium silicate.
- *Macro-encapsulation/capping* entails the use wet covers, dry covers (such as soils, geofabrics and/or alkaline materials), or covers made up of oxygen consuming materials (such as peat, sewage sludge and composted municipal solid waste). These covers create barriers between the mine waste and the elements (oxygen and/or water) which react with sulphide minerals. Tailings blended with alkaline materials can also be used as capping material. For example, agglomerates formed by mixing mine tailings with fly ash and Portland cement have been found to be effective in reducing the release of AMD formation in base metal tailings impoundments (Benzaazoua et al., 2004; Misra et al., 1996).
- *Sub-aqueous deposition* minimises oxidation of sulphides in tailings, as the oxygen diffusion coefficient is 10 000 times lower in water than in air and can be affected through the disposal of waste into flooded open pits or subsurface workings, man-made or natural lakes or impoundments or the marine environment. However, disposal at natural lake and marine sites may be restricted due to public and regulatory concerns. Furthermore, whilst acid generation is decreased, metal release might still be significant. A biologically active organic layer (wetland) and the presence of sulphate reducing bacteria may alleviate this problem.
- As in the case of sub-aqueous disposal of tailings, *flooding and/or sealing* can be used to reduce the formation of AMD in defunct underground shafts. Mineral-oxidising microorganisms in the mine water consume the dissolved oxygen present, and the replenishment of dissolved oxygen by mass transfer and diffusion is further hindered when the mine is sealed (Johnson, 2003). Sealing of underground mine shafts, adits and stopes reduces AMD formation by preventing the ingress of water and air (Johnson and Hallberg, 2005), and also prevents polluted water from flowing out from flooded mine workings. The primary factor that can affect the selection, design and construction of underground mine seals is the anticipated hydraulic pressure that the seal will have to withstand when the sealing process is completed.
- *Backfilling* of defunct mine provides opportunities for reducing surface disposal of mine waste whilst simultaneously avoiding the formation of AMD in defunct mine workings. Materials commonly used for

backfill include waste rock, sand, or mine tailings, often blended with cement. Coal combustion fly ash (FA) has pozzolanic properties which makes it suitable as a replacement for cement in backfill applications. The permeability of the CFA slurry backfill has been found to be lower than that of mine tailings or soils, resulting in reduced leaching of hazardous elements (Jorgenson and Crooke, 2003). Fly-ash residues after treatment of AMD, combined with 3% of cement, has also been proposed as potentially suitable backfill material (Gitari et al., 2008; Gitari et al., 2009; Vadapalli et al., 2008).

In many cases, more than one approach or method will be required to effectively prevent AMD formation and dispersion. For example, sulphide separation combined with water covers, elevated water table, and barrier covers may prove to be the best combined system for a given tailings impoundment. Whilst the costs and economic viability will vary from site-to-site, preventative measures such as covers, and mine sealing are normally costly. Application costs of synthetic and complex multi-layer covers, in particular, can be double that of soils and are thus only applied at smaller sites.

2.3 Value recovery from, and uses of, AMD

2.3.1 An overview of potential products from AMD

Historically AMD has been considered a waste emission, requiring treatment only in order to comply with local legislative limits for discharge into the environment. These treatment processes are expensive and, as regulations become increasingly stringent, are becoming more so. Conventional treatment processes also generate considerable quantities of sludges and brines, the disposal of which can amount to between 25% and 30% of the total costs of the process. It is increasingly recognised that AMD and/or the sludges generated during AMD treatment are a potential source of useful, or even valuable, by-products. Recently, emphasis has been placed on the recovery of water and additional commodities such as rare earth and base metals, sulphuric acid, iron salts and oxides, and gypsum-based products. Recovering by-products from AMD and AMD treatment sludges can both reduce costs of waste disposal and offset costs of the treatment and value recovery process. The various products that can be derived from AMD are presented in Sections 2.3.1.1 to 2.3.1.6.

2.3.1.1 *AMD as a water treatment agent*

AMD, itself, has in fact been found to be an effective flocculant for the removal of metals and deleterious elements, from wastewaters. In particular, AMD containing Ca, Al and Fe can be used to remove phosphorous, present in wastewaters from industrial, agricultural, and domestic sectors. For example, studies have shown that AMD can be used for the treatment or removal of metals and phosphorous in dairy waste-product (Reddy et al., 1999), whilst mine water from a copper mine complex at Falun, Sweden, was used as a flocculating agent in the treatment of municipal sewage at Framby treatment plants (Banks et al., 1996).

2.3.1.2 *Water*

Arguably one of the most valuable products that can be derived from AMD is water. Many mining operations around the world occur in water-scarce regions and, whilst mines may be struggling with an excess of ingress groundwater in mine workings, the surrounding communities are struggling with a shortage of water on the surface. It is this dilemma that prompted the construction of the eMalahleni Water Reclamation Plant (EWRP) in the Mpumalanga Province of South Africa for the treatment of AMD from coal mines in the area. For the past 10 years, this plant has provided approximately 25 ML/day potable water to the local municipality, supplying 12% of the cities daily water needs and effectively providing drinking water for 60 000 people. A second AMD treatment plant in the area uses the HiPRO desalination process to produce 15-20 ML/day potable water. The treatment of AMD to potable water standards is energy intensive and expensive, and the cost of the supply of drinking water to local municipalities in Mpumalanga is heavily subsidised by the mining companies. Lower quality water, requiring less extensive treatment, could be generated from AMD for

agriculture or even industrial use. In this way treatment costs, energy consumption and sludge generation can be reduced whilst still producing “fit-for-purpose” water from AMD. For instance, the Mine Water Coordinating Body (MWCBC), the South African Water Research Commission (WRC), Anglo Coal, Exxaro and South32 are conducting a demonstration project on 60 Ha of allocated land on the Mafube Colliery in the Mpumalanga Province, using poor quality NMD and SD to cultivate salt tolerant crops such as soybean and wheat (Mining Review 2017).

2.3.1.3 *High-value metals*

Several processes have been used to recover potentially high-value metals (e.g. Cu, Zn, Co) from AMD. These include sulphide precipitation, copper cementation with metallic iron, direct electrowinning, ion exchange, solvent extraction, and electrowinning, and/or combinations of these technologies. Diffusion dialysis has also been used to recover sulphuric acid from AMD. These processes have been discussed in detail by previous authors such as Howell et al. (2016).

2.3.1.4 *Salts*

Desalination processes such as nanofiltration and reverse osmosis produce considerable quantities of salt-laden brine, which are conventionally disposed of in the ocean or in large evaporating ponds. Treatment of these brines by means of evaporative or freeze crystallisation allows for the simultaneous recovery of potable quality water and individual monovalent and divalent metal sulphate salts, such as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, MgSO_4 , Na_2SO_4 and K_2SO_4 (Randall et al., 2011; Randall and Nathoo, 2015). In 2017, the world's first commercial plant for the eutectic freeze crystallization (EFC) of brines from the reverse osmosis treatment of AMD was commissioned at the Tweefontein Colliery in Mpumalanga. The unit has been purchased by Glencore and built and designed by Prentec, based on the technology developed at the University of Cape Town's Department of Chemical Engineering. This plant recovers 5 ML/day desalinated water, as well as potentially useable salts from the hypersaline brines (Nicolson, 2017).

2.3.1.5 *Sulphur-based products*

Processes for the treatment of AMD are seldom designed to recover sulphur as a primary product, due partly to its relatively low monetary value and the difficulty of obtaining sufficiently purity. However, a number of processes create opportunities for at partial recovery of sulphur or for the generation of gypsum products.

i Gypsum products

Gypsum or calcium sulphate dehydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is the main component of the sludge generated through lime or limestone neutralisation of AMD. It has a number of potential uses, particularly in the agricultural and construction sectors. Gypsum can be used as a physical ameliorant for soils, increasing the workability and moisture retention, and as a source of sulphate for alkaline soils. It is particularly useful for alfalfa, corn, wheat, and peanuts which require a high sulphate content. Gypsum is also used extensively in the construction industry as a main constituent in plaster and for the manufacture of gypsum board, which is used in wall, ceiling, and partition systems in residential, institutional, and commercial structures. Finally, gypsum can also be converted into elemental sulphur which can be processed further into sulphuric acid. A number of applications for synthetic gypsum from AMD and other industrial sources have been explored in the South African context and are discussed further in Sections 2.3.2 and 2.3.4.

ii Sulphur and sulphuric acid

Elemental sulphur can be recovered from AMD both directly, using biological processes, or indirectly via the conversion of sulphate compounds such as barium sulphate and gypsum which are precipitated from AMD in chemical processes. Elemental sulphur is used in the manufacture of a number of products, including fungicides, matches, gunpowder and synthetic rubber. However, the major application is in the manufacture of sulphuric acid and, to a lesser extent phosphatic and nitrogenous fertilisers (DMRE, 2012).

Biosulphate reduction removes sulphate through microbial reduction to hydrogen sulphide, simultaneously generating hydroxide ions which neutralise acid. The biogenic hydrogen sulphide reacts with divalent metals

(Zn(II), Cu(II), Ni(II), Pb(II), Cd(II) and Fe(II)) to form insoluble sulphide precipitates, whilst hydroxide ions react with trivalent metals (Al(III) and Fe(III)) to form oxyhydroxide/hydroxide precipitates, resulting in a mixed metal residue with potential for metal recovery. Biological processes for the treatment of AMD, such as the Paques SULFATEQ process, the BioSURE process and the VitaSOFT process, typically entail two stages. In the first stage, sulphate is anaerobically converted to sulphide by sulphate-reducing bacteria with the removal of metals in the form of metal sulphides. In the second stage, the residual sulphide in the effluent from the first stage is converted to high purity elemental sulphur by sulphur-oxidising bacteria with further production of alkalinity (see reviews by DWAF, 2007; IMC, 2010 and Mogashane et al., 2020).

Elemental sulphur can also be recovered from AMD in chemical processes through the conversion of barium sulphate or gypsum. Barium processes, such as the CSIR Alkali-Barium Calcium™ (ABC) and the modified Magnesium-Barium-Alkali (MBA) Process developed by the Tshwane University of Technology, employ barium salts such as barium hydroxide or barium carbonate (Akinwekomi et al., 2017b; DWAF, 2007; IMC, 2010; Mogashane et al., 2020). Barium treatment processes generally involve the pre-treatment of AMD using limestone and/or lime to remove metals in the form of a mixed metal oxide/gypsum sludge, prior to the addition of barium to form a relatively pure barium sulphate precipitate. As barium salts are expensive and environmentally toxic, barium treatment processes normally entail a barium recovery step. This step entails the thermal conversion of barium sulphate into barium sulphide and carbon dioxide. Barium sulphide is then treated with water and carbon dioxide to generate barium carbonate and hydrogen sulphide, which is subsequently converted into elemental sulphur. Whilst the technical viability of the ABC technology was demonstrated at a gold mine in 2007/2008, barium processes are reportedly three times more expensive than lime neutralisation (DWAF, 2013).

Elemental sulphur can also be generated as a secondary by-product from gypsum. In a process developed and patented by the Council for Scientific and Industrial Research in South Africa (de Beer et al., 2014; Mbhele et al., 2009), elemental sulphur is generated from waste gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in a three-step process:

- Conversion of gypsum to carbon sulphide and carbon dioxide through the thermal reduction with carbon at of 900 to 1100°C (Equation 2.11)



- Direct aqueous carbonation of CaS to produce hydrogen sulphide (H_2S), and low-grade CaCO_3 as a by-product (Equation 2.12):



- Recovery of elemental sulphur from H_2S via the commercially available PiPco process (Equation 2.13):



This process has been applied in laboratory-scale tests using waste gypsum from Stage 2 of the eMalahleni Water Reclamation Plant, and from FOSKOR. Sulphur produced from the stripped H_2S had a purity of between 95% and 96% at a recovery of 76% to 81%, compared to 91% recovery from pure gypsum. The calcium carbonate (limestone) produced was classified as low-grade, with a CaCO_3 content of <90%. The major contaminants included apatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) and anhydrite (CaSO_4). In a further study by de Beer (2014), the carbonation of CaS was conducted in two stages, to generate both a “low purity” and a “high purity” (>99%) CaCO_3 , with the latter comprising 12-23% of the total calcium carbonate recovery. In a modified version of this patented process, termed the Gyp-SliM process, the combined metal-rich gypsum sludge from both stages 1 and 2 of the eMalahleni Water Reclamation Plant is converted into elemental sulphur, low purity limestone (CaCO_3) and magnesite (MgCO_3). This process (shown in the simplified diagram in Figure 2-1) includes an additional crystallisation step to separate magnesium carbonate from the sludge generated in the carbonation step, which is comprised of a mixture of calcium carbonate, magnesium bicarbonate and metal-bearing ash (Gunther and Naidu, 2008).

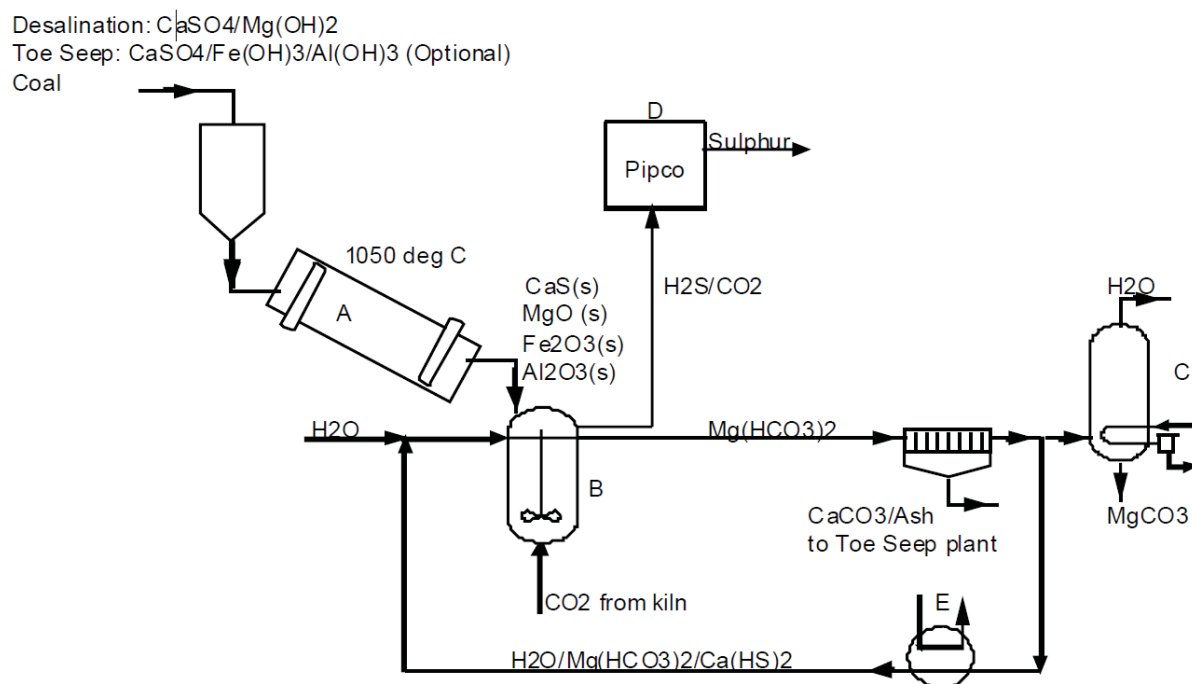


Figure 2-1 Simplified process flow diagram of the Gyp-SLiM process (Gunther and Naidu, 2008).

2.3.1.6 Iron-based products

Iron-rich AMD can provide a source of a number of potentially useful iron products.

i Goethite and haematite pigment production

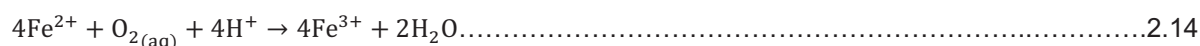
The iron oxides goethite and hematite can be used as pigments (yellow and red pigments respectively) in the manufacture of paint, ceramics, resins, etc. (Hedin, 2003, 2008; da Silva et al., 2017; da Silva et al., 2019). In the method proposed by da Silva et al. (2017), iron is initially precipitated from AMD as ferric hydroxide at pH 3.6 using alkali metal hydroxide (e.g. NaOH or KOH). The ferric hydroxide precipitate is then re-dissolved using nitric acid followed by goethite crystallisation with potassium hydroxide at pH 12. The goethite produced can then be converted to hematite using either thermal dehydration, dehydroxilation or oxidation/reduction (da Silva et al., 2012; da Silva et al., 2017).

ii Magnetite

Magnetite has numerous industrial applications, such as waste wastewater treatment, ore processing, and as a magnet in navigational devices. Although normally produced from pure ferric or ferrous chlorides and sulphates, da Silva et al. (2012) and Akinwekomi et al. (2017a) have demonstrated that magnetite can also be produced from AMD, through the application of a chemical precipitation process. In both cases, mixed Fe(II)/Fe(III) hydroxides were formed from Fe(II) rich solutions, before being converted to magnetite. The Fe(II) rich solutions were generated by da Silva et al. (2012) in a number of stages, involving precipitation of ferric hydroxide, re-dissolution of ferric hydroxide in sulphuric acid, and subsequent photoreduction of ferric to ferrous iron using UV radiation. This process resulted in over 96% iron recovery.

iii Ferrous sulphate heptahydrate (menlanterite)

Ferrous sulphate heptahydrate can be produced by reducing ferric iron in AMD to ferrous under UV radiation (Vigânico et al., 2011). The iron reduction with UV results in the formation of a $\cdot\text{OH}$ radical, causing a bactericidal effect, which retards the formation of the ferric iron (see Equation 2.14)



Subsequent evaporation results in the formation of melanterite, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, crystals, which can be used in agricultural applications. Vigânico et al. (2011) generated commercial grade melanterite (99.5% purity) from acidic solution produced through the leaching of pyrite-rich coal processing wastes.

iv Ferric sulphate coagulant

Ferric sulphate is one of many reagents commonly used for the treatment of industrial effluents and supply of domestic water (Colling et al., 2011). Studies conducted by Menezes et al. (2009) and Colling et al. (2011) involved the production of ferric sulphate through bioleaching of pyrite present in coal tailings. The solutions were then evaporated to generate a coagulant containing 12% iron (w/w). The ferric sulphate rich coagulant was found to be effective in the treatment of wastewater as commercial poly-ferric sulphate produced from iron scraps (Colling et al., 2011).

v Zero-valent nano iron (ZVNF)

Zero-valent nano iron offers a number of advantages over micro- and macro-iron in water treatment applications due to its high reactivity. A preliminary study by Alegbe et al. (2018) has shown that treatment of AMD with sodium borohydride results in the formation of ZVNF, which can be used for the in-situ removal of metals. The iron content in AMD was reduced from 3400 to 1 mg/L, whilst simultaneously reducing soluble levels of cadmium, selenium, and mercury. The most common application for ZVNF is in water treatment. Further discussions on the ZVNF applications are presented in Section 2.3.3

2.3.2 Value recovery and the eMalahleni Water Treatment Plant (EWRP)

2.3.2.1 An overview of the EWRP

As discussed in Section 2.2.5, the eMalahleni Water Reclamation Plant (EWRP) in the Mpumalanga coalfields in South Africa was specifically designed to recover potable water for local consumption from AMD and NMD emanating from the surrounding coal mines and dumps, using a combination of lime neutralisation (HDS process), reverse osmosis (HiPRO process) and ultrafiltration in a three-stage process (see Figure 2-2). In **stage 1** water the HDS process is neutralised using slaked lime or limestone, precipitating the majority of the sulphate and metals in the form of a gypsum sludge which is removed by clarification. Ultrafiltration (UF) acts as a pre-treatment for reverse osmosis (RO) where the permeate recovery is 65%. The RO retentate is conveyed to **stage 2** where precipitation is followed by hydrocyclones, clarification and membrane processes similar to stage 1 (permeate recovery 65%). The RO retentate is further treated in **stage 3** which is similar to stage 2, with the formation of a final liquid brine containing the residual salts, not removed in the stage 1 and 2 neutralisation steps. (Hutton et al., 2009).

In total, the EWRP plant effectively removes 99% of the metals and salts from the contaminated mine water in the form of “waste”, with the wastes from each of the stages varying in quantity, form, and composition. The HDS neutralisation process in stage 1 generates a metal-rich gypsum sludge comprising a mixture of gypsum and oxyhydroxides of Fe, Al, Mg, Mn, and Zn. The sludge, sometimes referred to as a “clay-based gypsum” is also reported to contain elevated concentrations of Ba, Cu, Ni, Ti and Zr (Gunther and Naidu, 2008). An additional gypsum sludge is generated from the neutralisation of the RO retentate in stage 2 of the plant. This gypsum, which accounts for 20% of the total gypsum generated by the EWRP, contains fewer metals than the stage 1 gypsum sludge and is sometimes referred to as “white gypsum”. It is, however, also reported to contain traces of Mg, Al, Cr, Cu, Fe, Mn, Sr, Ti, Zn and Zr (Gunther and Naidu, 2008). Finally, the liquid brine reject generated in stage 3 is comprised mainly of salts, namely Na, K, Ca, sulphate, and chloride, along with Mg, ammonium, chloride, and bicarbonate (Randall et al., 2011). The brine waste has also been reported to contain trace concentrations of other metals such Fe, Li, Mn, and Sr (Gunther and Naidu, 2008).

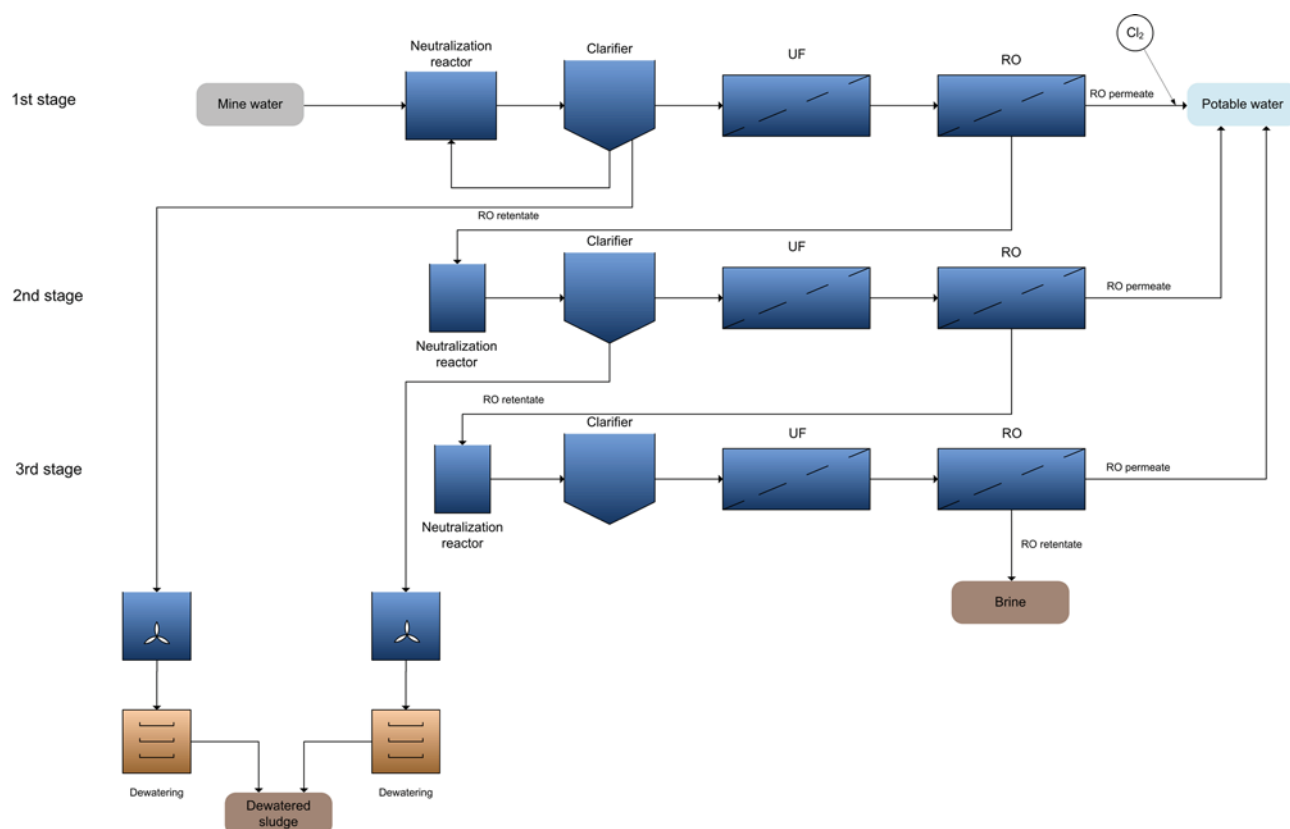


Figure 2-2 The eMalahleni Water Reclamation Plant (modified from Hutton et al., 2009)

In accordance with the data reported by Gunther and Naidu (2008), the EWRP generates between 4-5 tons of gypsum waste (dry basis) and 6-8 m³/day of liquid (brine) waste per 1000 cubic meter (i.e. 1 ML) of potable water produced. In an attempt to reduce the costs of waste disposal (which typically accounts for 25% and 30% of the total costs of the water reclamation process) and potentially generate additional income to cover the costs of water treatment, the EWRP has explored a number of options to convert the gypsum and brines into useful downstream products. The Gyp-BuMP (**G**ypsum converted into **B**uilding and **M**ining **P**roducts) project was funded by Anglo Coal to develop the processes to convert gypsum waste into building products (such as bricks, plasterboard, paint extenders, fire resistant doors, etc.) or mining products (such as stone dust for the prevention of underground combustion) (Gunther and Naidu, 2008). Although approximately 29 potential building and mining products were identified, the main focus of the Gyp-BuMP project has been on housing (Gunther and Naidu, 2008). In a pilot project, 66 houses were constructed in 2010 using gypsum from the second stage of the EWRP plant. Whilst it has been proposed that the stage 1 gypsum sludge could also be used to replace river sand in conventional brickmaking for housing purposes currently this sludge is sold to SA Lime and Gypsum for agricultural applications. A second project termed the Gyp-SLiM (**G**ypsum processed into **S**ulphur, **L**imestone and **M**agnesite) project explored the use of technology from Anglo Coal, the CSIR and Sulphide Tech. for the conversion of waste gypsum from the EWRP (stages 1 and 2) into sulphur, limestone (CaCO₃) and magnesite (MgCO₃) in accordance with the process described in Section 2.3.1.4. The project funded 18 months of laboratory test work and market research. Whilst a pilot project was planned, there is no evidence that this process has been demonstrated beyond the laboratory-scale.

Two options have been identified for the potential recovery of potable water and useable salts from the HiPRO brines generated in stage 3 of the EWRP, namely algal brine beneficiation using algae to produce by-products like spirulina and beta-carotene, and eutectic freeze crystallisation (EFC) for the selective recovery of individual salts (Gunther and Naidu, 2008). Laboratory test work by Randall et al. (2011), conducted on EWRP brine, established that EFC could recover potable water (amounting to 80% by volume of the brine generated), as

well the salts Na_2SO_4 (96.4% purity) and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (96.4% purity), each amounting to approximately 13 kg per m^3 of brine. Currently the brine waste generated at the EWRP is, however, currently still disposed of in two evaporation ponds, which require a significant amount of land and cost upwards of R100 million each to construct. Furthermore, the life span for such ponds is only about five years and the risk of leaks into the surrounding soil is a danger.

2.3.2.2 A conceptual approach for integrated value recovery

Whilst the discussion in Section 2.3.2.1 shows that efforts have been made to recover value from AMD within the EWRP in a manner that extends beyond potable water, options explored to date have been limited and relatively few of these opportunities have been realised beyond the sale of gypsum for agricultural purposes.

It is postulated that further opportunities could be realised by adopting a more holistic approach to value recovery, which considers the integration of wastes streams across the entire coal deposit-energy mechanistic chain. Such an approach is outlined in Figure 2-3.

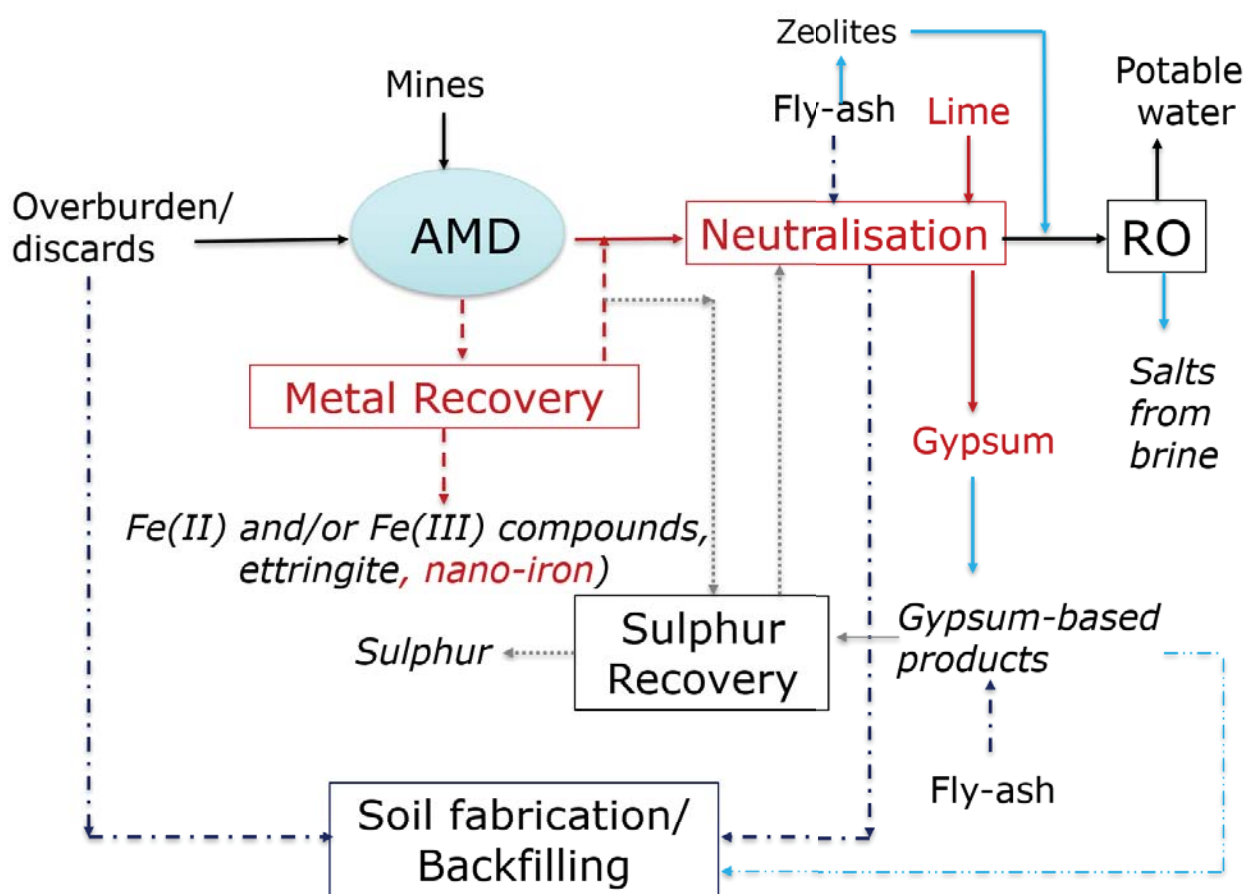


Figure 2-3 Conceptual approach for the integration of value recovery from coal production and combustion waste (the focus of this study is indicated in red print)

As discussed in Section 2.3.2.1, the use of limestone and/or lime in the HDS neutralisation process results in co-precipitation of several the metals, including Fe, Al, Mg and, to a lesser extent Zn and Mn, typically present in the AMD from the coal mines, generating a gypsum sludge with significant quantities of metal hydroxides. The prior removal of iron, in the form of Fe(III), Fe(II), Fe(II)/Fe(II) or zero-valent nano iron (see discussions in 2.3.1.6), offers the opportunity to recover useable iron products whilst simultaneously improving the quality- and hence the potential value-of the gypsum sludge generated in the subsequent neutralisation stage. Incorporation of a sulphur recovery circuit using either chemical or biological processes, as outlined in Section 2.3.1.5., could provide an opportunity to recover higher value elemental sulphur for sulphuric acid production.

Alternatively, elemental sulphur, together with metal carbonates, could be generated from the gypsum using the Gyp-Slim or a modified version thereof (see Section 2.3.1.5). Apart from recovery of iron and sulphur-based products, salts could also be recovered from the HiPRO brines, using processes such as Eutectic Freeze Crystallisation (EFC).

Further opportunities for maximum value recovery can, however, potentially be realised by adopting a more holistic view which integrates wastes across the entire coal value chain, including wastes from primary extraction, coal processing or washing, and coal combustion. As discussed in Section 2.2.5.1, laboratory studies have demonstrated that fly-ash generated from coal-fired power plants, mostly located in proximity (<25 km) to the coal mines in Mpumalanga, is a potentially suitable replacement to lime in the treatment of AMD (Gitari et al., 2011; Madzivire, 2010), capable of effectively neutralising acid and simultaneously removing sulphate and metals from a range of feed AMD solutions. Studies by Petrik et al. (2006) have, furthermore, shown that the fly-ash/gypsum residue generated from the fly-ash neutralisation process can potentially be applied as backfill material for mine voids, or to generate zeolite products. Based on previous studies using fly-ash as a source of silicate and aluminium for the synthesis of zeolites aluminium, Petrik et al. (2006) generated a relatively pure faujasite zeolite with high cation exchange capacity through the hydrothermal conversion of the solid waste sludge generated from the neutralisation of a coal AMD sample with fly-ash from a local power station. The zeolite prepared from the fly-ash/gypsum residue was found to be more efficient at toxic element removal than the commercial resin (LewatitTP207) and had a similar capacity of metal removal compared to a commercial faujasite. Petrik et al. (2006) proposed that the zeolite could be used for the further treatment of AMD in the EWRP to remove residual metals (either to replace or improve performance of the HiPRO process), and/or be sold as an additional by-product.

As a potential alternative to zeolite production, the fly-ash/gypsum sludge generated from the neutralisation of fly-ash could also potentially be used as a replacement for cement to generate the strength of the solid residues (Petrik et al., 2006). In laboratory-scale studies Petrik et al. (2006) found that the sludge-cement mixture had a high compressive strength and appeared to be suitable for the purpose of confinement of mined-out areas. Apart from cement, fly-ash, with its pozzolanic properties, has also been used in backfill applications in combination with lime, or with both lime and gypsum as binders (Mishra and Karana, 2006). Yet other authors (Palariski, 1993; Chugh and Dutta, 1998) have used mixtures of both fly-ash and coal mine waste with binders to make consolidated backfill material for coal mines. The potential thus exists to combine wastes from coal extraction and processing (overburden, discards, and tailings), coal AMD neutralisation and coal combustion (fly-ash) in the generation of backfill material for coal mine voids. In a similar application, waste materials such as fly ash, lime and gypsum can be used as a partial replacement or alternative for sand or cement in the manufacture of clay or cement bricks respectively (Karthikeyan et al., 2019; Naik et al., 2014; Sivapullaiah and Moghal, 2011). Studies by Sivapullaiah and Moghal (2011) showed that, whilst lime improves the compressive strength of fly-ash mixtures, gypsum accelerates the gain in strength for these lime-stabilized fly ashes, particularly in the initial curing periods.

Another potential application entailing multiple waste streams from the production and combustion of coal is in soil conditioning or fabrication. Studies have shown that the properties of fly-ash render it potentially suitable as an ameliorant for improving soil quality (Ram and Masto, 2014; Skousen et al., 2013; Tchuldjian et al., 1994). Such properties include the silt-sized particles, low bulk density, higher water holding capacity, alkaline pH, and significant presence of potential plant nutrients (Ram and Masto, 2014). In most cases, fly-ash blended with organic and inorganic materials (lime, gypsum, animal manure, sewage sludge, compost, soil and rocks, biochar, etc.) yielded better results than fly-ash alone (Ram and Masto, 2014). Similarly, one of the most important and widely used applications of gypsum is a soil amendment and fertiliser (Koralegedara et al., 2019). As an ameliorant, gypsum is usually used to improve quality of sodic soils, water infiltration, porosity, and particle aggregation. Gypsum also provides Ca and S for plant growth (Koralegedara et al., 2019). Studies at the University of Cape Town have demonstrated the feasibility of using the desulphurised fraction of coal processing slurry waste, together with organic matter and nutrients such as compost and anaerobic sludge, as the main substrate for the manufacture of fabricated soils (Amaral Filho et al., 2020). According to this study, the use of mixtures of soil, coal waste and additional organic matter and nutrients can reduce the amount

of topsoil used in coal mine restoration, whilst also significantly reducing the amount of fine coal disposed in dump deposits. The reported land applications of fly-ash, gypsum and coal processing waste indicate that it may thus be possible to combine these wastes in the replacement or conditioning of soils for rehabilitation of coal mine sites.

Whilst multiple opportunities for integrating downstream application of wastes from coal production, coal AMD treatment and coal combustion have been proposed here, in most cases technical feasibility of the technologies and their integrated application still needs to be demonstrated, either at the laboratory or pilot scale. Even in cases where these technologies are demonstrated, commercial implementation will require the development of a more rigorous business case, which considers the environmental, economic, socio-technical, and regulatory aspects of the proposed options.

As already indicated in the previous chapter, this specific study is concerned largely with the technical feasibility of generating nano iron from AMD, and the effects of this on the downstream neutralisation process parameters and outputs, particularly gypsum which constitutes one of the major wastes from the EWRP. In line with this focus, a more detailed overview of the applications of nano iron gypsum is provided in Sections 2.3.3 and 2.3.4 respectively.

2.3.3 Overview of Zero-Valent Nano Iron (ZVNF) applications

Nanotechnology has received considerable attention due its capability for manipulation of inherent desirable properties of materials such as reactivity, catalysis, strength, photo-activity, and selectivity (Cayuela et al., 2016; Sun et al., 2017). The application of nanoparticles (< 100 nm) in the environment offers advantages such as improved performance, lower energy consumption and reduction in residual waste (Ali et al., 2008). Zero-valent nano iron (ZVNF) or zero-valent iron nanoparticles (nZVF) is one of the most researched and efficient nanomaterials for the mineralisation of a host of pollutants in contaminated water, soil, and aquifers (Cao et al., 2005; Bae et al., 2016; Lopez-Telleza et al., 2011; Pullin et al., 2017; Yaacob et al., 2012).

Generally, iron-based materials are widely used in wastewater treatment, pharmaceuticals, medicine, food production and other manufacturing processes because of their low toxicity, biodegradability, and cost effectiveness (Adeleye et al., 2016).

The most common application for ZVNF is in water treatment. Granular iron has been used for many years at numerous sites in the form of permeable reactive barriers (PRBs) (Mueller and Nowack, 2010; Nowack, 2008) and PRBs are still the state-of-the-art method. Their major drawback is that they can only address contaminants that flow through the barrier. Recently, the use of zero valent iron nanoparticles has become very attractive in adsorption (Lopes et al., 2016) or recovery of metal ions from industrial wastes or natural water streams due to the high number of active sites for adsorption, thereby reducing the amount required per litre of solution (Parbs and Birke, 2005). In addition, the high surface area to mass ratios of nanoparticles can greatly enhance the adsorption capacities of sorbent materials. Complementing their high specific surface areas, nanoparticles also have unique adsorption properties due to different distributions of reactive surface sites and disordered surface regions (Tiwari et al., 2008). Pollutants that have been removed from water using ZVNF include metals (Ba, Cd, Cr, Cu, Pb, Hg, U and Zn), semi-metals (As, Se), anions (nitrates, perchlorates, sulphates) and organic compounds (Cundy et al., 2008; Li et al., 2006).

2.3.4 Overview of local gypsum applications and markets

2.3.4.1 Gypsum applications

Natural gypsum is widely used in a range of applications (see Section 2.3.1.5). Synthetic gypsum, such as phosphogypsum (PG) and flue-gas desulphurisation (FGD) gypsum, can be used in most of these as a

replacement material. The main commercial applications for gypsum presently include use in construction as an additive in cement and floor screed; in the manufacture of building products such as plasterboards, cornices, and other moulded products; and in agriculture, as a soil conditioner or nutrient (DMRE, 2009, OTM, 2009). The gypsum market in South Africa is well established in all three of these applications. Companies OMV, Gyproc and Etex appear to dominate the construction and building applications, whilst Kalkor and SA Lime & Gypsum are major national suppliers of agricultural gypsum products. Further details on gypsum product applications and specifications are outlined in the sub-sections below.

i Cement additive

Uncalcined gypsum is used as an additive to cement, at a ratio of 2-6%, to act as a retarder to delay setting times, and to enhance grinding characteristics of the clinker. Relatively low-grade gypsum (<95%) is generally considered suitable for application as a cement additive. Although the average purity of natural gypsum used for cement manufacture ranging from 88% to 92% (OTM, 2009), in accordance with Schutte (2018) gypsum with a purity as low as 82% can be used. This application accounts for 50-60% of global gypsum use (Schutte, 2018). Available data for 2006-2008 (DMRE, 2018; OTM, 2009) indicate that, on average, the annual application of gypsum as a cement additive in South Africa amounted to between 500 and 600 kt/a over this period (approximately 60% of total gypsum consumption).

ii Gypsum plasterboard

Gypsum plasterboard is used worldwide for ceilings, drywall partitioning in offices and homes, and for fire-resistant assemblies. The manufacture of gypsum plaster and plasterboard entails drying and calcining gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to monohydrate ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$) and further to hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$). The hemihydrate gypsum (also known as plaster, plaster of Paris or stucco) is then mixed with water, a foaming agent and various binders and catalysts in a form mould. Upon rehydrating the hemihydrate plaster forms crystals of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ which have a needle-like structure and interlock with each other, creating a firm, fire-resistant material (DMRE, 2009). A relatively high purity (>95%) gypsum is required for the manufacture of plasterboard as soluble salts, such as P_2O_5 , MgO, F and K_2O , result in efflorescence on the plasterboard surfaces. OMV, who supply approximately 60% of South Africa's gypsum demand, reportedly limit the P_2O_5 and F content in gypsum for both cement and plaster production to 0.01%. Another local supplier, Gyproc, will tolerate up to 6% impurities, if soluble salts comprise less than 0.1% of this 6% (i.e. < 0.02% soluble salts in total). A non-soluble salt content of 2.5% is also specified, as insoluble inclusions act as inert fillers and lower the compressive strength of the gypsum when calcined for plasterboard (OTM, 2009). Further data on the specifications for synthetic (FDG) gypsum used in plasterboard applications are presented in Appendix A. Available data for 2007 (OTM, 2009) shows that plasterboard accounted for approximately 17% of total gypsum consumption in South Africa.

iii Land applications

Gypsum is widely used in agriculture to improve the chemical and physical condition of soils, serving both as an ameliorant and fertiliser (see reviews by Schutte, 2009 and Koralegedara et al., 2019). Reported agricultural benefits of gypsum include:

- Reduction of surface soil acidity;
- Supplying Ca and S as nutrients, thereby improving plant growth and yield;
- Enhancing physical properties of clay soils, by improving the flocculation of soil particles and keeping the soil crumbly, thus increasing the penetration of water;
- Alleviating sodic soils by displacing the sodium through cation exchange reactions.

Apart from agricultural purposes, gypsum has also been used in the remediation of degraded and contaminated land. Application of gypsum (either alone or mixed with compost), in the remediation of a coal mine was found to reduce the acidity of the soil as well as the bioavailability of contaminants, such as Pb, P and Ba, through the formation of insoluble salts (Koralegedara et al., 2019). As in the case of the application of gypsum as a cement additive, gypsum used in land applications does not require pre-calcination and

relatively low-grade products (as low as 70% purity) can be used (Schutte, 2018). In fact, certain contaminants, such as Mg, K, Fe and Se, may be beneficial as they serve as additional nutrients. As indicated in Section 2.3.2.1, the metal-rich gypsum sludge from stage 1 of the EWRP is currently sold to SA Lime and Gypsum for agricultural purposes. Communications with representatives of this company indicate that the EWRP gypsum is blended with lime at varying ratios, depending on the requirements. There thus appears to be little advantage in providing a “purer” gypsum for agricultural purposes. Data from 2007 and 2008 showed a consumption of lime in the South African agricultural sector of between 200 and 210 kt/a respectively (OTM, 2009).

iv Other direct applications

Although not as widely applied commercially, another construction application that has been explored for gypsum is as a replacement for river sand in the manufacture of clay-fired bricks (Hamid et al., 2021). As discussed in Section 2.3.2.1, this application has been demonstrated in a pilot project in which gypsum sludge from stage 2 of the EWRP was used in the construction of 66 houses. Dehydrated gypsum (CaSO_4) is also used commercially as a filler and coating in the plastics, paint, adhesives, food, and pharmaceutical industries. For pigment, filler and extender applications, gypsum must have a high degree of whiteness and a purity more than 97-98% CaSO_4 (DMRE, 2009). Pure, dehydrated gypsum for specialist applications is largely imported to South Africa.

v Manufacture of downstream products

As discussed in Section 2.3.1.5., gypsum can also be processed further into downstream products, such as sulphur, limestone, and magnesite, using Gyp-SLiM or similar technologies. In South Africa, sulphur is mainly used to manufacture sulphuric acid, although globally, the single largest end user for sulphur is in the manufacture of phosphate fertilisers (DMRE, 2018). In South Africa, cement producers have traditionally been the main consumer of limestone (accounting for 75 percent), followed by metallurgical and agricultural applications, accounting for 10 percent and 6 percent respectively (DMRE, 2018). Significant quantities of limestone will, however, also be needed for the planned flue-gas desulphurisation (FDG) units which will be installed at the Kusile and Medupi power plants during the 2021-2025 period. Magnesite, once converted to magnesium oxide, is mainly used in refractory brick making.

2.3.4.2 Local supply and demand of gypsum products

In South Africa, gypsum is available from natural deposits or as a synthetic by-product from industry. The natural gypsum deposits in South Africa vary in grade from high-grade powdery gypsum, which contains about 90% pure gypsum, to gypsum mixed with clay containing around 65% to 85% gypsum (OTM, 2009). The deposits occur in 3 m thick layers close to the surface, therefore requiring relatively simple and inexpensive quarrying operations (OTM, 2009). These terrestrial deposits are found in remote and relatively terrains, concentrated in the Northern Cape Province and the northern section of the Western Cape Province, with smaller deposits in the Eastern Cape Province and KwaZulu-Natal Province (DMRE, 2009; OTM, 2009). The South African gypsum production sites as @ 2008 are shown in Appendix B. The relatively low costs of mining and large distances between the mines and markets means that the economic viability of natural gypsum is related largely to the cost of transport. Data published by the DMRE (2018) indicates that annual production of natural gypsum declined from between 500 and 600 kt over the period 2006-2013, to between 230 and 260 kt in 2015 and 2016.

As in the rest of the world, synthetic gypsum in South Africa is becoming increasingly important as a source of gypsum. Historically, synthetic gypsum production in South Africa has been dominated by phosphogypsum (PG) from the phosphoric acid and fertiliser producers located in Phalaborwa, Phokeng, Potchefstroom, Modderfontein and Richards Bay areas (OTM, 2009). In general, PG is higher grade than natural gypsum with a purity of between 93% and 95%. Whilst other sources of synthetic gypsum have also been generated by Sasol, Lonmin Platinum, Sappi and Anglo Coal, the volumes produced have been relatively minor and the quality low in comparison with PG (OTM, 2009). Although no data on the net production or utilisation of synthetic gypsum could be sourced for South Africa, available data of net gypsum consumption (1159 kt) and

natural gypsum supply (627 kt) in 2007 (OTM, 2009; DMRE, 2009) indicate that synthetic consumption accounted for approximately 527 kt (46% of total gypsum consumption) in that year. Data published by the DMRE (2018) indicate, furthermore, that South Africa typically imported between 2 and 4 kt of gypsum per annum prior to 2014, mainly in the form of high purity gypsum for speciality applications. However, this number increased significantly in the period 2014-2016, with imports amounting to 144 and 143 kt in 2015 and 2016 respectively (DMRE, 2018). This is consistent with the reported decline in natural gypsum production over the same period (DMRE, 2018). Whilst this reflects a net shortage of gypsum in the country, it does not consider the planned installation of flue-gas desulphurisation (FGD) technology at the Kusile and Medupi power station for SO₂ capture. Eskom is in the process of implementing wet flue gas desulphurization (WFGD) technology on its 6 × 800 MWe Kusile coal-fired power station that is under construction in the Mpumalanga region (unit 3 of 6 having been commissioned in March 2021) and has committed to retrofitting the same SO₂ abatement technology to its operational 6 × 800 MWe Medupi power station in the Waterberg region by 2025 (Creamer, 2020; Strickroth et al., 2020). According to Schutte (2018), Kusile alone will produce approximately 900 kt/annum FDG gypsum which will likely cover current and future demand for both cement and agriculture applications. Whilst the purity of the FGD gypsum will be largely dependent on the quality of the limestone used in the process, it appears unlikely that the FDG gypsum produced by the power stations will meet the stringent requirements to produce plasterboard (OTM, 2009; Schutte, 2018).

Based on the predicted supply of, and demand for, local gypsum products, it appears that there will be a national surplus of low-grade gypsum for construction and agricultural applications in the short to medium term. On the other hand, the market survey by OTM (2009) showed that the national market for gypsum plasterboard showed good potential for sustained growth. Although alternatives such as fibre-reinforced cement board provides a potential alternative to gypsum plasterboard and is thus favoured for exterior applications where weathering is a concern, it does not offer the same advantages in terms of flexibility and is more expensive than conventional plasterboard (OTM, 2009). Approximately 90% of all ceilings and office partitioning in South Africa is made from locally produced gypsum plasterboard (OTM, 2009). The feasibility of generating gypsum for the plasterboard market will, however, depend on the ability to consistently and reliably produce gypsum of a suitable quality (> 95% purity with low soluble salt content). Given the large number of contaminants, of varying concentrations, typically present in the AMD feed stream, it is unlikely that the EWRP stage 1 gypsum sludge will meet these requirements without pre-removal of salts and metals. Niche local applications of the gypsum for rehabilitation and remediation of local coal mines, as presented in Section 2.3.2.2, may be preferable. The key driver in such a case would be the mitigation of long-term (post-closure) risks and liabilities associated with contaminated land, polluting waste deposits and defunct mine workings, as opposed to direct profits from the sale of gypsum by-products. An advantage of this approach is that it would eliminate the costs of transporting bulk material from source to market. This is an important consideration as the long distances between economic centres in South Africa and poor rail infrastructure often render product-to-market options uneconomical (see for example studies by OTM, 2009 and Stander et al., 2022). Alternatively, consideration could be given to the manufacture of downstream products, such as sulphur, magnesite, and limestone, with sufficiently high market value and demand to offset cost of production and supply. South Africa has historically been a major importer of sulphur for sulphuric acid production, and other mining-intensive countries in Africa are similarly importing large quantities of sulphur at relatively high cost for the manufacture of sulphuric acid (DMRE, 2018; Nengovhela et al., 2007). The demand for limestone in South Africa is also likely to increase significantly with the installation of FDG units at Eskom power stations. Ultimately, a more detailed market and feasibility study would be required to explore the viability of this alternative.

2.4 Summary

This review has identified several options for the recovery of iron and sulphur from coal-related AMD. One potentially valuable iron product is zero-valent nano iron (ZVNF) which has application in water treatment. Nano iron is conventionally produced from pure Fe(III) solutions, with the production of nano iron from AMD remaining largely unexplored. The prior removal and recovery of iron also provides the

opportunity to generate a purer, and potentially more valuable, gypsum product during subsequent lime neutralisation. A preliminary assessment of local supply and demand indicated that whilst there is likely to be a local surplus of low-grade gypsum for cement manufacture and agricultural applications ($\geq 82\%$ and $\geq 70\%$ respectively) in the medium to long-term, the market for high-grade plasterboard shows good potential for sustained growth. Alternatively, gypsum can be converted into down-stream products such as sulphur, limestone, and magnesite – all of which have a potentially high local demand going forward-using existing technologies such as the Gyp-SLiM process. Whilst a number of these options have been investigated for the case of the gypsum-rich residues from the eMalahleni Water Reclamation Plant, none of these opportunities have been realised beyond the sale of gypsum for agricultural purposes. Key challenges when generating high-value products from AMD and AMD treatment sludges include the ability to produce a consistent quality of product, and the economics of production and supply. The composition of AMD field samples within the Mpumalanga coalfields varies significantly, whilst the cost of transporting products, especially bulk commodities, from source to market can be significant.

As an alternative to the production of marketable gypsum or gypsum-derived products, gypsum residues can be applied for rehabilitation and remediation of local coal mines, as part of an integrated approach which utilises wastes streams across the entire coal deposit-energy mechanistic chain. Options include combining gypsum-rich AMD neutralisation residues with coal combustion fly-ash and/or coal processing wastes for the generation of fabricated soils, or for mine backfill. Fly-ash from neighbouring coal-fired power stations could, furthermore, be used as an alternative to lime for the neutralisation of AMD, generating a gypsum-rich fly-ash sludge directly. The key driver here would be the mitigation of long-term (post-closure) risks and liabilities associated with contaminated land, polluting waste deposits and defunct mine workings, as opposed to direct profits from the sale of gypsum by-products. An additional benefit of such an approach is that it reduces the high costs of transporting bulk material over long distances. Fly-ash neutralisation and downstream applications of wastes for rehabilitation of mine workings and degraded land are, furthermore, relatively robust processes which can accommodate significant variability in compositions of AMD and waste streams.

In most cases technical feasibility of the technologies and their integrated application still needs to be demonstrated, either at the laboratory or pilot scale. Even in cases where these technologies are demonstrated, commercial implementation will require the development of a more rigorous business case, which considers the environmental, economic, social, and regulatory aspects of the proposed options.

CHAPTER 3: METHODS, MATERIALS AND MODELS

Chapter 3 provides details on the methods and materials used in the experimental phases of this project (Section 3.1), as well as the framework for the thermodynamic modelling phase (Section 3.2).

3.1 Experimental method and materials

As indicated in Figure 3-1, these phases include laboratory-scale test work on (i) the production of nano iron from ferric chloride solution (conventional feed) and AMD solutions, and (ii) the neutralisation of AMD solutions both with and without prior removal of nano iron.

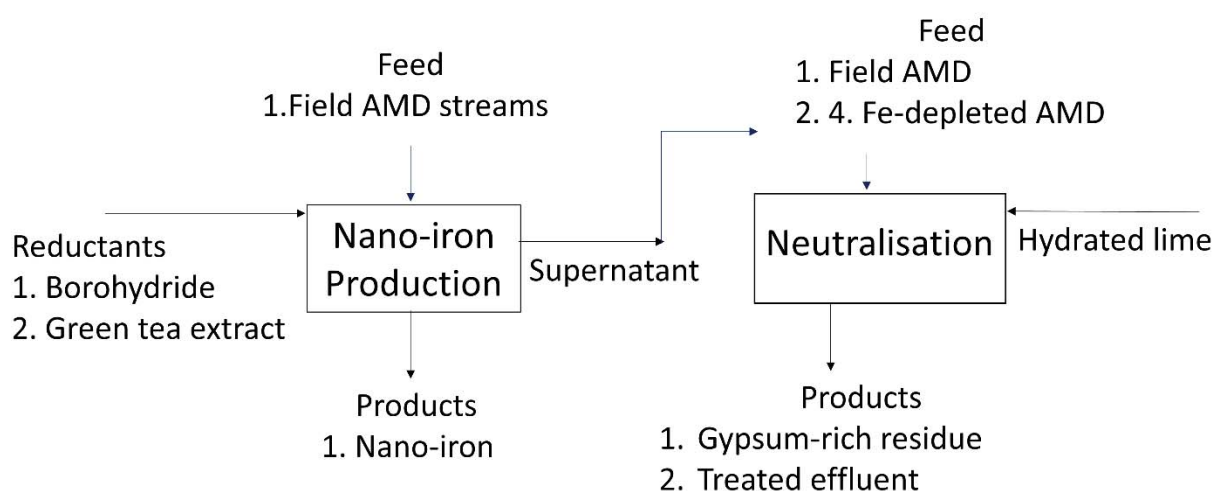


Figure 3-1 Outline of the laboratory-based experimental programme

Experimental details are provided on the collection and preparation of feed samples (Section 3.1.1); the method used for the preparation of nano iron products (Section 3.1.2.) and neutralisation of AMD (Section 3.1.3); and the analytical methods used to characterise the physical and chemical properties of the feed samples and generated products (Section 3.1.4).

3.1.1 Sample collection and preparation

3.1.1.1 AMD samples

AMD samples from field sites (labelled K, T and P) were collected from the Mpumalanga coalfields. These AMD samples were stored in airtight plastic containers to prevent the ingress of air, which can further oxidise ferrous iron to ferric iron. Prior to physical and chemical analyses, the AMD samples were filtered with a 0.45 µm pore size membrane filter paper using a vacuum pump. The chemical and physical properties of the synthetic and field AMD samples are presented in Table 3-1. Analytical methods are described in Section 3.1.4.

Table 3-1 Properties of AMD samples used in the laboratory test work

Parameters	Unit	Field AMD K	Field AMD T	Field AMD P
pH		2.08 ± 0.03	2.20 ± 0.02	2.14 ± 0.06
Electrical conductivity (EC)	mS/cm	3200 ± 1.27	2500 ± 2.30	2900 ± 4.10
Redox potential	mV vs SHE	458 ± 1.1	425 ± 0.91	448 ± 0.72
<u>Anions</u>				
Sulphate	mg/L	13200 ± 72.3	9910 ± 68.1	11500 ± 29.0
Nitrate	mg/L	3.89 ± 1.0	2.2 ± 0.2	2.13 ± 0.20
Chloride	mg/L	15.3 ± 0.2	10.1 ± 1.2	10.2 ± 1.0
<u>Major metals</u>				
Fe	mg/L	4420 ± 14.3	1930 ± 10.8	3990 ± 22.1
Ca	mg/L	527 ± 22.4	508 ± 19.3	503 ± 18.9
Mg	mg/L	575 ± 8.21	414 ± 4.46	85.4 ± 15.2
Al	mg/L	460 ± 18.2	246 ± 3.58	367 ± 21.2
Mn	mg/L	126 ± 1.21	48.3 ± 0.95	85.4 ± 3.8
<u>Minor metals</u>				
Na	mg/L	33.5 ± 1.21	64.2 ± 0.21	33.1 ± 0.92
Si	mg/L	33.8 ± 2.55	12.0 ± 0.08	28.1 ± 1.02
Zn	mg/L	13.1 ± 0.07	6.10 ± 0.05	9.8 ± 0.01
<u>Trace metals</u>				
As	mg/L	0.16 ± 0.07	0.21 ± 0.01	0.32 ± 0.02
B	mg/L	0.11 ± 0.02	0.17 ± 0.04	0.14 ± 0.03
Be	mg/L	0.15 ± 0.08	0.13 ± 0.05	0.14 ± 0.04
Cd	mg/L	0.001 ± 0.01	0.001 ± 0.03	0.001 ± 0.01
Co	mg/L	1.84 ± 0.08	0.52 ± 0.02	1.11 ± 0.05
Cr	mg/L	0.42 ± 0.22	0.51 ± 0.09	0.34 ± 0.07
Cu	mg/L	0.11 ± 0.04	0.18 ± 0.01	0.11 ± 0.02
Hg	mg/L	0.01 ± 0.01	0.01 ± 0.04	0.01 ± 0.02
Li	mg/L	BDL	BDL	BDL
Mo	mg/L	0.08 ± 0.01	0.09 ± 0.01	0.08 ± 0.06
Ni	mg/L	1.87 ± 0.02	0.97 ± 0.03	1.12 ± 0.07
P	mg/L	0.35 ± 0.08	0.20 ± 0.01	0.001 ± 0.03
Pb	mg/L	0.02 ± 0.05	0.04 ± 0.03	0.16 ± 0.01
Sb	mg/L	0.02 ± 0.02	0.02 ± 0.02	0.02 ± 0.03
Sr	mg/L	0.36 ± 0.01	0.38 ± 0.09	0.84 ± 0.05
Th	mg/L	0.02 ± 0.01	0.001 ± 0.03	0.01 ± 0.01
Ti	mg/L	0.10 ± 0.04	0.10 ± 0.07	0.1 ± 0.05
V	mg/L	0.11 ± 0.04	0.12 ± 0.01	0.22 ± 0.09
Y	mg/L	2.34 ± 0.04	1.07 ± 0.08	1.91 ± 0.06
Zr	mg/L	0.01 ± 0.02	BDL	0.01 ± 0.03

Where: BDL=Below Detection Limit; ND=not Determined

Table 3-1 revealed that the Field AMD samples (K, T, and P) contain diverse major, minor and trace metals. The major metals include Fe, Ca, Mg, Al, and Mn, with Fe, Ca and Al being predominant, while minor metals include Na, Si and Zn. A diverse range of trace metals were detected, but only Y, Ni and Co are present in concentration > 1 mg/L. Sulphate is the most prominent anion in the sampled AMD, with nitrate and chloride being present in minor quantities.

3.1.1.2 Sodium borohydride solution

Solutions of sodium borohydride at concentrations of 0.1-0.6 M were prepared by dissolving reagent grade sodium borohydride powder in deionised water. Sodium borohydride is a reductant that can be used to prepare nano iron from AMD and ferric chloride solutions.

3.1.1.3 Plant extracts

As a proof-of-concept study, extracts from three different plants were used to prepare green reductants as potentially suitable alternatives to chemical reductants to produce ZVNF, namely *Camellia Sinensis* (green tea), *Aspalathus linearis* (green rooibos tea), and *Aspalathus linearis* (rooibos tea).

After the collection of the polyphenolic containing part of the tea plants, the content was extracted using the method of Sharma and Lall (2014) with some modification. Tea leaves (60 g) were weighed and mechanically ground. The powdered tea was then soaked in 120 mL of deionized water and 30 mL of aqueous ethanol (25%). Thereafter, the tea mixture was agitated using a magnetic stirrer at a speed of 300 rpm for 1 hour at 60°C. After the set time had expired, the mixture was then allowed to cool. Subsequently, the ethanolic content in the resulting tea mixture was evaporated using a roto vapor set at 65°C where after the water content was removed by freeze drying, to obtain an amorphous powder. The obtained powder (product) was then stored in an airtight bottle at 20°C. These extracts were analysed for their free radical scavenging activity (DPPH) and ferric reducing (FRAP) using the analytical methods outlined in Sections 3.2.3.

Field AMD sample (P) was used to produce stable green zero-valent nano iron particles using green tea extract. Solutions of tea extract were prepared by dissolving their different respective masses (0.1, 0.2, 0.3, 0.4 or 0.5 g) in 50 mL of deionized water that corresponded to tea dosages of 2, 4, 6, 8, and 10 g/L. The solutions were centrifuged at 5000 rpm for 3 minutes. The respective collected supernatants (50 mL) were then filtered, characterized (using pH, EC, or ORP) and used to extract stable zerovalent nano-iron particles from field AMD P (50 mL).

3.1.2 Preparation of nano iron products from AMD

3.1.2.1 Chemical synthesis of nano iron products

Sodium borohydride was used as a chemical reductant for the extraction of nano iron from the collected field AMD samples (K, T and P). Sodium borohydride was chosen as reductant for the baseline experiment because it is a strong reducing agent of iron. Thus, 100 mL of sodium borohydride solution with concentrations varying from 0.2 M to 0.6 M was prepared by dissolving their respective masses (0.3787, 0.7574, 1.1360, 1.5148, 1.8935, or 2.2721 g) in deionized water. The prepared solutions were then used to precipitate zerovalent nano-iron particles from Field AMD samples (K, T, or P). Thereafter, in each case, the precipitate was filtered and washed with deionized water prior to sonication for 10 minutes to prevent agglomeration. The sonicated nano-iron particles were then filtered, washed, and dried under an inert environment. Subsequently, the obtained nano-iron particles from AMD were subjected to characterization. Characterization techniques used included: XRD, SEM/EDS and Image J for particle size analysis, FTIR, STEM. In this line of investigation, the generated supernatant after the removal of iron from AMD was further analysed using IC and ICP-OES.

3.1.2.2 Green synthesis of zero-valent nano iron

Green tea was used as a green reductant for the extraction of iron nano particles from Field AMD P samples. Green tea was selected as a choice of green reductant due to its high antioxidant properties and its capacity as a reducing agent. 40 mL of green tea solution was prepared by dissolving the respective masses of green tea extract (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 g) in deionized water. The prepared solution was then used to precipitate green zero-valent nano iron particles from Field AMD P for 24 hours at 35°C. Thereafter, in each case, the precipitate was filtered followed by washing with deionized water. The obtained nano-iron particles were dried under an inert environment prior to characterization. Characterization techniques used included: XRD, SEM/EDS and Image J for particle size analysis, FTIR, STEM. In this line of investigation, the generated

supernatant after the removal of iron from AMD was further analysed using IC and ICP-OES prior to neutralisation using lime.

Different synthesis parameters such as temperature (30, 35, 40, 45 or 50°C) and time (4, 8, 12, 16, 20 or 24 hours) were further considered for the nano iron synthesis optimisation process.

3.1.3 Neutralisation of AMD

AMD neutralisation tests were conducted using slaked lime on field AMD solutions to determine the effect of lime dosage and pH on the compositions of the treated effluent and generated sludge.

Industrial grade hydrated lime (slaked lime) 90% pure was used as neutralising agent for the neutralisation of the AMD sample P using the jar test method.

3.1.3.1 *Direct neutralisation of AMD*

Two different masses of lime ($\text{Ca}(\text{OH})_2$) were used to treat 500 mL of acid mine drainage (AMD) water sample. The masses of lime used were 5.5 g and 6.0 g. The AMD and lime were steadily mixed at 200 to 250 rpm. The pH and EC values were measured after every 10 minutes up to 120 minutes. Supernatants and solid residues were collected after 120 minutes. The treated effluent was submitted for ion chromatography and ICP-OES analysis for anion and element concentrations, respectively. The sludge samples were dried in the oven at 70°C overnight and submitted for XRF and quantitative XRD, to identify solid phases.

3.1.3.2 *Neutralisation of AMD pre-treated with sodium borohydride*

The supernatant obtained after the reduction of zero-valent nano iron from AMD using sodium borohydride (Section 3.1.1.3) was subsequently subjected to the neutralisation process. Two different masses of lime ($\text{Ca}(\text{OH})_2$) of 1.5 and 2 g were used to treat 250 mL of the supernatant sample. This follows the same procedure as described in the aforementioned – direct neutralisation of AMD.

3.1.3.3 *Neutralisation of AMD pre-treated with green tea extract*

The supernatant obtained after the reduction of zero-valent nano iron from AMD using green tea as reductant (Section 3.1.2.2) was subsequently subjected to the neutralisation process. Three different masses of lime ($\text{Ca}(\text{OH})_2$) were used to treat 500 mL of Acid mine drainage (AMD) water sample. The masses of lime used were 2.5, 3.5, 4.5, and 5.5 g. The AMD and lime were steadily mixed at 200 to 250 rpm. The pH and redox values were measured after every 10 minutes, up to 120 minutes. Supernatants and solid residues were collected after 10, 30, 60, 90, and 120 minutes. The treated effluent was submitted for ion chromatography and ICP-OES analysis for anion and element concentrations, respectively. The sludge samples were dried in an oven at 50°C overnight and submitted for qualitative XRD, to identify solid phases.

3.1.4 Analytical methods

Physical and chemical characterization was carried out on the plant extracts, the nano iron products, treated and untreated AMD solutions and neutralisation sludge samples. Analytical techniques are detailed in Sections 3.1.4.1-3.1.4.10.

3.1.4.1 *pH, electrical conductivity, and total dissolved solids measurements: AMD and supernatant solutions*

The pH, electrical conductivity (EC) and TDS of AMD and supernatant solutions were measured using HI 991 301 pH meter with portable pH/EC/TDS/DO/Temperature probe.

3.1.4.2 Ion chromatography (IC): AMD and supernatant solutions

Ion chromatography (IC) is an analytical technique for the analysis of anions in solution. This technique was used to analyse AMD samples and supernatant generated after extraction of nano iron. A small volume of the sample (mobile phase) is pumped through a column of packed particles (stationary phase) and the time it takes for the ion to pass through is recorded as the retention time. The retention time of the ion depends on how it interacts with the column both physically and chemically. Known standard concentrations are used to estimate sample concentrations. In the current study the IC was applied to analyse the concentration of anions such as sulphate and nitrate in the raw and treated wastewater. A stock solution was prepared by dissolving 1.6485 g NaCl in 1000 mL deionised and degassed water to make a chloride solution equivalent to 1000 mg/L. The calibration standards were also made (1 mg/L to 10 mg/L). A single standard was prepared for SO₄-S and NO₃-N as well as the triplicate calibration standards.

3.1.4.3 Inductive coupled plasma-Optical emission spectroscopy (ICP-OES): AMD and supernatant solutions

Samples were submitted for Inductive Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) analysis of dissolved metal concentrations (Fe, Al, Mg, Ca, Na, K, Mn) in the feed and treated AMD samples. Sludge samples were digested by means of aqua regia prior to ICP-OES analysis.

3.1.4.4 DPPH Antioxidant Assay: plant extracts

The radical scavenging activity of the plant extracts was determined against the stable free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH). The assay involves the reaction of DPPH with hydrogen donating antioxidant compounds in a reduction process that can be monitored by means of a spectrophotometer at a wavelength 517 nm as the DPPH colour changes from deep violet to light yellow (Brand-Williams et al., 1995). A 200 mg/L stock solution of the plant extracts was prepared by dissolving 10 mg of the dry extract in 50 mL of methanol. Further dilutions were made from the stock to prepare lower concentrations of the extract (such as 100, 50, 25, 12.5 mg/L until 0.4 mg/L). Stock solutions of ascorbic acid (standard reference) were also made and serially diluted to lower concentrations. Blank solutions were prepared from 100 µL of diluted extract solution and 50 µL methanol, while the negative control was prepared using 100 µL DPPH and 50 µL methanol. Then, 50 µL each of 150 mg/L DPPH in methanol was added to 100 µL solution of extract in a micro plate which was kept in the dark for 30 minutes. The absorbance of the serially diluted extracts, ascorbic acid, blanks, and controls were then measured using a Biotek Power-wave XS Multi Well reader (Analytical and Diagnostic Products, Johannesburg, South Africa). The experiments were run in triplicate and the values were converted into the percentage inhibition using the formula in equation 3.1. The 50% inhibitory concentration (IC₅₀) values were then calculated by linear regression of the plots using Graph Pad Prism version 5.

$$\% \text{ Inhibition} = \frac{(\text{Abs. Blank} - \text{Abs. Sample}) \times 100}{\text{Abs. Blank}} \dots\dots\dots 3.1$$

3.1.4.5 Ferric Reducing Antioxidant Power (FRAP) Assay: plant extracts

FRAP activity was measured according to the method developed by Benzie and Strain (1996) with some modification. An acetate buffer (300 mM, pH 3.6) was mixed with a solution of 10 mM TPTZ (2,4,6-tripyridyl-s-triazine) in 0.1 M HCl and FeCl₃·6H₂O (20 mM) in a ratio of 10 :1:1, to obtain the working FRAP reagent. Then, 2 mg/L each of ascorbic acid (standard) and plant extract were carefully prepared and subjected to agitation for 5 minutes with a vortex mixer (Dragon LAB MX-S), followed by centrifugation (Eppendorf centrifuge 5810R) at 1000 rpm for another 5 minutes to allow for formation of clear solutions of the test samples. 100 mL of tea leaf extracts was mixed separately with 300 mL of the prepared FRAP reagent. The sample absorbance was measured at 593 nm with the aid of 'Multiskan' spectrum (Thermo Electro Corporation). Methanol solutions of FeSO₄·7H₂O ranging from 100 to 2000 µM were prepared and used for creating the calibration curve of known Fe²⁺ concentration. The parameter equivalent concentration is defined as the concentration of antioxidant having a Ferric-TPTZ reducing ability equivalent to that of 1 mM FeSO₄·7H₂O.

3.1.4.6 X-Ray Fluorescence Spectroscopy (XRF): Nano iron intermediate products

The elemental composition of the sludge samples and nano iron products from the reduction of AMD was determined using X-ray fluorescence (XRF) analysis, with a Philips 1404 Wavelength Dispersive spectrometer set up for operational use at 40 mA and 50 kV. The synthesised samples from AMD and milled sludge were oven-dried at 50°C for 12 hours before being mixed with a certain amount of binder (composed of 10% of C-wax and 90% EMU powder). The mixture was then milled and moulded into pellets prior to placing the pellets in the sample holder compartment of the machine. The XRF technique reports concentration as % oxides for major elements and mg/L (mg/kg) for minor and trace elements. The elements reported as mass % oxides were converted to mg/L of the elements using element conversion software downloaded at www.marscigrp.org/elconv.html.

3.1.4.7 X-ray Diffraction (XRD): Neutralisation/HDS sludge and nano iron products

X-ray Diffraction (XRD) analysis was used to determine the mineralogical phases of the sludge and nano iron samples. Each sample (after being ground to a fine powder) was placed in the sample holder and the crystalline phases characterised using a Philips X-ray diffractometer with Cu-K α radiation.

The phase identification was performed by searching and matching obtained spectra with the powder diffraction file data base originating from JCPDS (Joint committee of powder diffraction standards) files for inorganic compounds. Table 3-2 details instrumental set up for Phillip X-pert pro MPD X-ray diffractometer.

Table 3-2 Phillip X-pert pro MPD XRD operation parameter settings

Parameter	Settings
X-ray detector	Vantec 1
Generator voltage	40 kV
Generator current	40 mA
Scanning range angle	10°-80°
Scanning type	Locked couple
Scan speed per step	2 θ /min and step size of 0.02 θ Theta
Scan time	0.5 sec per step
Scan size	0.03°
Synchronous rotation	Copper K α (alpha) at 1.540598

3.1.4.8 High Resolution Scanning Electron Microscopy (HRSEM): Nano iron products

High Resolution Scanning Electron Microscopy (HRSEM) characterises the surface morphology of powdered samples. In this study, SEM was used to determine the surface morphology of nano iron particles and green zero-valent nano particles synthesized from AMD. The morphology of the samples was investigated using an Auriga high resolution scanning electron microscope (HRSEM) equipped with a CDU-lead detector. Synthesised nano particles were oven-dried at 105°C for 12 hours in preparation for the analysis. The dried samples were then sprinkled on a carbon adhesive tape attached onto an aluminium stub. Since the samples that were to be analysed are poor electromagnetic conductors, the aluminium stubs were carbon coated using argon gas on Sputter Coater S150B. The carbon coating was carried out under vacuum. Each sample was then mounted into specimen holders and the morphology (texture), and elemental analysis of the samples were analysed from backscattered electron as well as secondary electron images. Table 3-3 details instrumental set up for the Auriga HSREM.

Table 3-3 Auriga high resolution scanning electron microscope (HRSEM)

Parameter	Settings
Accelerating voltage	30 kV
Current	10 nA
Emitter	Thermal field emission type
Aperture	0.4 mm
Resolution	1 nm
Standard detector	ESB with filtering grid
Magnification	900K

3.1.4.9 High Resolution Transmission Electron Microscopy (HRTEM): Nano iron products

High Resolution Transmission Electron Microscopy (HRTEM) was used to analyse the morphology, crystallinity, and particle size of recovered nano iron particles from AMD. Table 3-4 details instrumental set up for the TECNAI instrument that was used to conduct HRTEM analyses.

Table 3-4 RTEM (TECNAI G2 F20 X Twin Mat FEG) operation parameter settings condition

Parameter	Settings
High tension	200 kV
Extraction voltage	3950 V
FEG emission current	54 μ A
Condenser aperture	3 mm
Objective aperture	2 mm
Gun lens	1 nm
Spot size	3 nm

3.1.4.10 Fourier Transforms Infrared Spectroscopy (FTIR): nano iron products

Fourier Transform Infrared Spectroscopy (FTIR) provides information about the chemical bonding, molecular structure and functional groups present in a substance that can absorb the infrared light. This analytical technique was used to identify functional groups within the nano iron products. A Perkin Elmer 1600 FTIR analyser will be used at a scanning wavelength of between 4000-400 cm^{-1} .

3.2 Thermodynamic modelling of the AMD neutralisation process

This study explored the use of three different models to simulate the distribution and attenuation of chemical species during lime neutralisation of AMD solutions, namely VISUAL MINTEQ, PHREEQ and OLI. Three different systems have been modelled in this study, namely the chemical speciation modelling of typical AMD and NMD solutions (Section 3.2.1), the simulated lime neutralisation of typical acidic and neutral mine drainage

solutions from the Mpumalanga coalfields (Section 3.2.2) and modelling of laboratory-scale neutralisation experiments before and after treatment with reductants (Section 3.2.3).

3.2.1 Chemical speciation modelling of typical AMD and NMD solutions

Apart from the AMD solutions K, T and P collected from the Mpumalanga Coalfields, data was also received from the eMalahleni Water Reclamation Plant (EWRP). The typical chemical compositions of the reported data for the period January 2009 to February 2020 is presented in Table 3-5.

Table 3-5 Compositions of neutral mine drainage (NMD) and acid mine drainage (AMD) streams in the Mpumalanga coalfields

Parameter	Unit	Neutral mine drainage (NMD) streams				Acid mine drainage (AMD) streams					
		1	2	3	4	5	6	7	8	9	10
pH at 25°C	-	7.20	7.15	7.26	3.00	2.67	2.76	3.00	2.29	2.53	2.53
Conductivity	mS/m	400	316	330	257	915	335	447	892	549	ND
Alkalinity as CaCO ₃	mg/L	71	126	227	0.00	0.00	0.00	0.00	0.00	0.00	ND
Acidity as CaCO ₃	mg/L	7.75	7.40	11.30	544	7070	656	1600	3470	2680	ND
Na	mg/L	45.8	88.8	231	26.3	99.9	33.7	40.0	32.8	12.3	52.3
Ca	mg/L	469	468	365	362	475	320	435	318	283	518
Mg	mg/L	444	194	207	48.7	368	155	173	201	279	205
K	mg/L	22.3	10.8	18.4	3.42	42.0	6.30	8.00	1.27	4.80	ND
Mn	mg/L	1.40	0.20	0.04	5.20	4.00	14.7	10.0	43.1	113	34.3
Al	mg/L	0.10	7.60	0.05	79.0	277	43.3	91.0	208	316	15.7
Total Fe	mg/L	0.20	10.2	0.54	16.5	2157	108	442	573	344	445
Cl	mg/L	9.12	26.0	19.8	7.48	7.60	7.95	11.0	n/a	0.10	ND
Sulphate as SO ₄ ²⁻	mg/L	2850	1920	1980	1600	8840	2060	2950	4040	4490	2301
Nitrates & Nitrites as N	mg/L	1.38	0.24	2.22	0.01	0.10	0.10	0.10	0.44	0.10	0.24
F	mg/L	0.78	0.71	1.52	0.20	0.20	0.20	0.20	0.20	0.20	ND

In general, the NMD streams appear to contain slightly higher levels of alkali (Na and K) and alkali earth (Ca and Mg) metals, as well as anions Cl, F, and nitrates, than the AMD streams.

The *Visual MINTEQ* chemical speciation model was used to identify the distribution of chemical species in selected AMD and NMD field samples, namely the collected AMD solutions K, T, P (Table 3-1) and the reported AMD streams 1,5 and 10 (Table 3-5).

Visual MINTEQ was used to be a freeware chemical equilibrium model for the calculation of metal speciation, solubility equilibria and other geochemical properties of natural waters. Version 3.1 was compiled in Visual Basic on 26 November 2020 by Jon Peter Gustafsson, KTH, SEED, Stockholm and was downloaded in December 2020 at <https://vminteq.lwr.kth.se/download>.

3.2.2 Simulated lime neutralisation of typical AMD and NMD solutions.

Two models, PHREEQC (version 3.6.2-15100, USGS-USA) and OLI Studio 10.0 Stream Analyser™, were used to identify the formation of chemical species during the neutralisation of typical AMD and NMD solutions under various simulated conditions.

3.2.2.1 Phreeq Model description

The speciation, saturation indices calculations and batch neutralisation of AMD stream 5 and NMD stream 1 was simulated using PHREEQC (version 3.6.2-15100, USGS-USA) to determine potential pH profiles, and to identify predominant aqueous species and likely precipitate formation as a function of pH. Trace elements were excluded from the simulation. It was assumed that CO₂ present in the air would equilibrate with the solution since the treatment plant is operated as an open system. Hence the solutions were allowed to equilibrate with atmospheric CO₂. Temperature was set at 25°C and the pe at values ranging from 4.0 to 15.0, creating different redox conditions. The treatment of the mine water streams was carried out using Ca(OH)₂ solution to increase the pH from 0-12. The program was coded to add moles of Ca(OH)₂ solution to 1 kg of the AMD solution in several steps. The Ca²⁺ ions from the alkaline agent were considered in the simulated precipitation reactions. Based on the compositions of the solutions (Table 3-5) and the likely chemical behaviour, aqueous species and solid precipitates were selected as potential outputs from the neutralisation of AMD streams and NMD streams and profiled against the pH values (Table 3-6).

Table 3-6 Aqueous species and precipitates modelled for the AMD and NMD systems

Stream	Element	Aqueous Species	Precipitates
AMD and NMD solutions	Ca	Ca ²⁺ , Ca(OH) ⁺ , CaHCO ₃ ⁺ , CaCO ₃ (aq), CaSO ₄ (aq)	Gypsum (CaSO ₄ ·2H ₂ O), calcite (CaCO ₃), aragonite (CaCO ₃), dolomite (CaMg(CO ₃) ₂)
	Mg	Mg ²⁺ , Mg(OH) ⁺ , MgHCO ₃ ⁺ , MgCO ₃ (aq), MgSO ₄ (aq)	Dolomite (CaMg(CO ₃) ₂), Magnesite (Mg(OH) ₂)
	K	K ⁺ , KSO ₄ ⁻	-
	Na	Na ⁺ , NaSO ₄ ⁻	-
AMD solutions only	Fe(II)	Fe ²⁺ , FeOH ⁺ , Fe(OH) ₂ (aq), Fe(OH) ₃ ⁻ , FeHSO ₄ ⁺ (aq), FeSO ₄ (aq), FeHCO ₃ ⁺ , FeCO ₃ (aq), FeCl ⁺	Fe(OH) ₂ , siderite (FeCO ₃)
	Fe(III)	Fe ³⁺ , FeOH ²⁺ , Fe(OH) ₂ ⁺ (aq), Fe(OH) ₃ (aq), Fe(OH) ₄ ⁻ , FeHSO ₄ ²⁺ (aq), FeSO ₄ ⁺ , Fe ₂ (SO ₄) ₃ (aq), FeHCO ₃ ²⁺ , FeCO ₃ ⁺ (aq),	Ferric hydroxide (Fe(OH) ₃), goethite (FeOOH), K-jarosite (KFe ₃ (OH) ₆ (SO ₄) ₂), Na-jarosite (KFe ₃ (OH) ₆ (SO ₄) ₂)
	Al(III)	Al ³⁺ , AlOH ²⁺ , Al(OH) ₂ ⁺ (aq), Al(OH) ₃ (aq), Al(OH) ₄ ⁻ , AlHSO ₄ ²⁺ (aq), AlSO ₄ ⁺ (aq), Fe ₂ (SO ₄) ₃ (aq)	Aluminium hydroxide (Al(OH) ₃), Gibbsite (AlOOH), Alunite (KAl ₃ (OH) ₆ (SO ₄) ₂), Ettringite (Al ₄ SO ₄ (OH) ₁₀ ·4H ₂ O)
	Mn(II)	Mn ²⁺ , MnOH ⁺ , Mn(OH) ₂ (aq), Mn(OH) ₃ ⁻ , MnHSO ₄ ⁺ (aq), MnSO ₄ (aq), MnHCO ₃ ⁺ , MnCO ₃ (aq), FeCl ⁺	Rhodochrosite (MnCO ₃), Manganese hydroxide (Mn(OH) ₂)
	Mn (III) and (IV) oxides	-	Mn(II,III) oxide (Mn ₃ O ₄), Mn(III)oxide (Mn ₂ O ₃), Manganese(IV) oxide (MnO ₂)

In the modelled neutralisation of the NMD streams, 0.004 moles of $\text{Ca}(\text{OH})_2$ were added per kg of solution in 50 steps, resulting in a pH of approximately 11.5. The redox was set at a default value of $\text{pe}=4$. In the case of the AMD streams, various AMD neutralisation scenarios were postulated to simulate different pH (>10) and redox potential regimes ($\text{pe} = 12\text{-}15$), corresponding to different $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios:

- Fe^{3+} (82%) ($3.220\text{E-}02$ molality)/ Fe^{2+} (18%) ($6.904\text{E-}03$ molality), $\text{pe}= 12$, 0.09 moles $\text{Ca}(\text{OH})_2$ added per kg of solution, to bring the pH to a maximum value of 9.
- Fe^{3+} (99.9%) ($3.909\text{E-}02$ molality)/ Fe^{2+} (0.1%) ($8.415\text{E-}06$ molality), $\text{pe}= 15$, 0.08 moles $\text{Ca}(\text{OH})_2$ added per kg of solution.
- Fe^{3+} (82%) ($3.220\text{E-}02$ molality)/ Fe^{2+} (18%) ($6.904\text{E-}03$ molality), $\text{pe}= 12$, 0.4 moles $\text{Ca}(\text{OH})_2$ added per kg of solution allowed, to bring the final pH to values >10.

In each case, special attention was placed on the level of precipitate saturation, as well as the aqueous speciation of the different constituents as a function of pH.

3.2.2.2 *Oli model description*

The OLI Studio 10.0 Stream Analyser™ software model was used to simulate lime neutralisation of AMD stream 10 in both the absence and presence of air, to explore the effect of CO_2 on the predominant aqueous species and likely precipitates.

This model uses thermodynamic equations to predict, over almost any conceivable pH, temperature, pressure and concentration of interest, parameters of interest in the three known phases of matter. The predictions were carried out using the data banks under the aqueous thermodynamic framework survey chemistry model option with redox chemistry and phases selected. As in the case of other thermodynamic models, OLI has some limitations related to its inability to predict kinetic behaviour (which is important for fast reactions such as precipitation) and hence the metastable phases, that form under process conditions, may not always be predicted. Within the OLI stream analyser, the water analysis function was used to reconcile the charges and generate the feed stream which was then modelled. The output was plotted focusing on how the dominant species, within the aqueous and solid phases, changed with pH.

3.2.3 **Thermodynamic modelling of laboratory-scale AMD neutralisation reactions.**

Visual MINTEQ was used to simulate formation of aqueous and solid species under the conditions observed during laboratory-scale neutralisation of the AMD solution P (Section 3.1.3), both before and after treatment with sodium borohydride and green tea extract. In each case carbonate is added to the solutions at various concentrations to simulate the effect of CO_2 entrainment and dissolution during rigorous agitation of the solutions under ambient air conditions. The likely chemical behaviour, aqueous species and solid precipitates selected as potential outputs from the neutralisation of the relevant AMD solutions are outlined in Table 3-6, Section 3.2.2.1.

CHAPTER 4: SYNTHESIS OF NANO IRON FROM AMD

As indicated in Chapter 2, zero-valent iron (ZVI) in the nanoparticle size range (<100 nm) has been found to offer several advantages over micrometric particles for wastewater treatment, with nanotechnology being one of the fastest growing sectors of the high-tech economies. This study builds on previous work at the University of the Western Cape (Alegbe et al., 2018) which established the feasibility of recovering zerovalent nano iron (ZVNF) from ferric chloride and ferric sulphate solutions using sodium borohydride and phenolic plant extracts. A particular focus of this study was on the effect on feed variability and reductant types (chemical and plant extracts) and dosage on the extent of iron extraction and on the properties of nano iron by-products and effluent water quality. Studies were also conducted on the production of nano iron from the HDS process (i.e. indirect production).

4.1 Background: Description and synthesis of nano iron

4.1.1 Structure and properties of nano iron

Zero-valent nano iron takes on a simple core shell structure, with zero valent iron at the core and a shell of Fe oxides on the outside (Figure 4-1). The oxide formation on the $n\text{Fe}^0$ particle is a protective shell to prevent the pure iron from undergoing further oxidation. The outer shell provides the necessary sites for chemical reactions (Li et al., 2003 and 2006; Theron et al., 2008; Zhang, 2003). The core consists mainly of zero-valent iron (Fe^0) which provides the reducing power for the reaction with environmental pollutants while the shell is mainly composed of the oxides/hydroxides obtained from the oxidation of zero-valent iron (Fe^0), according to reaction 4.1-4.3

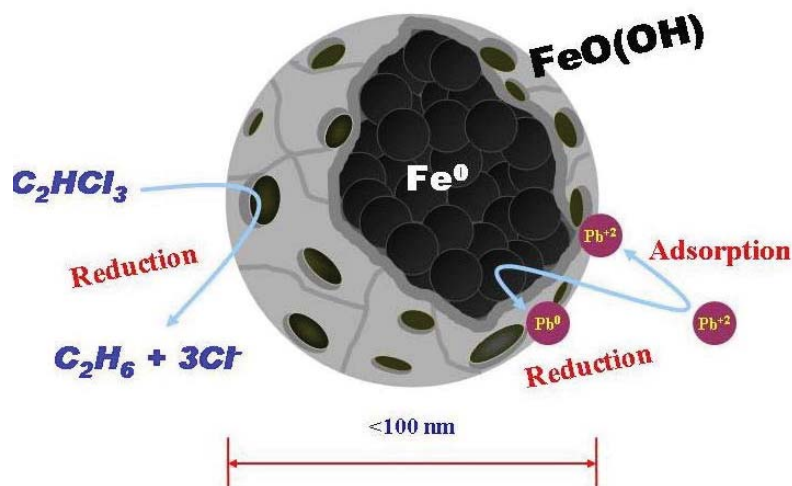


Figure 4-1 A zero-valent nano iron particle and reaction pathways (Cooke, 2009)



Nano sized zero-valent iron particles are characterised by their small size, large surface area, magnetism, and oxidation state. One of the differences between nanoparticles and larger colloids or bulk materials is their extremely high surface area. This property alone makes iron nanoparticles particularly interesting; however, the reactivity of nanoparticles is not entirely due to surface area. A large quantity of energy is stored in nanoparticles as surface-free energy, and this added energy can mean added reactivity, or altered magnetic properties (Li et al., 2006).

The surface atoms of nanoparticles are in a vastly different environment to the atoms in a bulk material, and even compared to atoms in a thin-film material (Cao et al., 2005). This induces a great deal of catalytic activity which is believed to be focused at defect sites of crystals. Due to their extreme curvature, nanoparticles have a high concentration of defect sites (Hube, 2005). This is a simple explanation for the common observation that nanoscale catalysts have a greater reactivity than can be accounted for by their high surface areas alone.

Confinement effects and surfaces that can be viewed as defective also have an impact on the electronic structures of the nanoparticles (Link and El-Sayed, 2000). In the case of iron, most of the interest is on the effect this has on another property resulting from electronic interactions: magnetism. The small number of magnetic spins in an iron nanoparticle leads to vastly different magnetic properties from bulk materials (Huber, 2005). Nanoparticles that are made of a ferro-material and are below a certain size (generally 10-20 nm), can exhibit a unique form of magnetism called superparamagnetism where the spins of unpaired electrons undergo spontaneous magnetisation, where their energy is lowered by aligning with spins in neighbouring atoms.

The reactivity of ZVNF depends on factors such as the source and nature of the iron material, manufacturing method, morphologies, nature of crystals, age of the ZVNF and the presence of impurities (Pullin et al., 2017). Usually, the produced nano iron has the propensity for high activity because of its larger surface area and intrinsic magnetic interaction. However, it is very unstable and rapidly reacts in air and moisture to give a nonhomogeneous nano iron (Pullin et al., 2017). Despite its numerous applications and current commercial status, the universal acceptability of ZVNF is hindered by its instability in moist environments. Apparently, the achievement of stability without compromising the reactivity of the ZVNF and cost of production is a big challenge (Dong et al., 2016; Bulovsky, 2016; Suponik et al., 2016) but simultaneous reduction and stabilization with organic components from tea extracts are proposed in this study.

4.1.2 Synthesis of nano-iron

Synthesis of ZVNF can be achieved through the physical, physio-chemical, or chemical reduction/modification of a higher oxidation state of iron (see Table 4-1). The physical method, which is a bottom-up approach, includes nucleation from homogeneous solution, annealing at elevated temperature and separation of phases (Li et al., 2009). Meanwhile, physio-chemical methods such as reduction of goethite (α -FeOOH) or hematite (α -Fe₂O₃) at an elevated temperature or the use of an ultrasonicator may also be involved in synthesis of ZVNF (Jamei and Khosravi, 2013). The products from these methods usually have a very high surface energy and, consequently, high agglomeration tendency (Mukherjee et al., 2016). Consequently, chemical synthesis is gaining popularity (Bae et al., 2016). It is a simple method which includes reduction of higher oxidation state of iron with active reducing agents such as sodium borohydride (Yuvakkumar et al., 2011). However, the high cost of chemical reducing agents, additional processes of separation, and large quantities of effluents are the limitations associated with industrial application of chemical synthesis. The ultimate method of synthesis must be cost effective, environmentally friendly and result in the production of ZVNF with extensive application (Fazlzadeh et al., 2016; Wang et al., 2017).

Table 4-1 Methods of nano iron synthesis

Process	Principle	Benefits	Disadvantages	References
Precision milling	Physical synthesis	Effective, easy to control, uses no chemical, no toxic effluent, possibility of large-scale production, uniform particle size and high specific surface area.	Irregular shaped ZVNF, agglomeration, energy intensive and needs specific equipment	Li et al., 2009
Carbothermal reduction	High temperature (>500°C) endothermic reaction in presence of gaseous reducing agent	Inexpensive raw materials, waste material can be used for low cost environmentally friendly production.	Cost of energy is high, Irregular shaped nZVI, agglomeration, likely generation of toxic gas (carbon monoxide)	Fowler, 2010
Ultrasound	Physio-chemical synthesis	Small, uniform, and equal-axes grains of iron are produced	Low yield due to simultaneous oxidation of iron	Mir Roozbeh Jamei, 2013
Electro-chemical	Uses $\text{Fe}^{2+}/\text{Fe}^{3+}$ salt electrodes and electrical current	Less expensive, simple, and fast	Agglomeration is common	Yoo et al., 2007
Green synthesis	Plant containing polyphenolic group are used	Needs no expensive chemical, pressure, and additional energy	Destruction of plants and plant parts, incomplete synthesis, and large iron impurity	Kozma et al., 2016
Thermal decomposition	Decomposition of organo-metallic molecule containing iron, i.e. $\text{Fe}(\text{CO})_5$.	Extremely small nZVI and excellent homogeneity	The process is energy intensive; $\text{Fe}(\text{CO})_5$ is very toxic, unstable, and difficult to handle. Generation of carbon monoxide	Hai-Jiao et al., 2016)
Chemical reduction	$\text{Fe}^{2+}/\text{Fe}^{3+}$ salt reduction with sodium borohydride	The most common method. Good for laboratory experiments. Production of homogenous and relatively small size ZVNF.	Quick corrosion and agglomeration of nZVI. Iron III chloride is hydroscopic and acidic. Production of excess sludge	Stefaniuk et al., 2016

Various methods are already developed to ensure the synthesis of stable and effective ZVNF for the purpose of environmental remediation and wastewater treatment (Sections 4.1.2.1-4.1.2.4)

4.1.2.1 *Surfactant modifiers*

These are amphiphilic organic compounds which prevent agglomeration by steric or electrostatic repulsion. Surfactants are used for surface modification to improve solubilisation, desorption, transportation, and reduction of agglomeration in an unstable nanoparticle (Gomes et al., 2014). The common examples are cationic surfactants such as cetylpyridinium chloride (CPC) and hexadecyl trimethyl ammonium (HDTMA) bromide or anionic surfactants such as sodium dodecyl sulphate (SDS) and sodium dodecyl benzene sulphonate (SDBS) as well as non-ionic surfactants such as polyoxyethylene alcohol ether, polyethylene, Saponin, Tween 80 and glycol octylphenol ether (Triton X-100). The use of these types of modifiers is limited

because of their high cost of production, as well as the inhibition of the activity of ZVNF and the reversible nature of its surface.

4.1.2.2 *Polymer modifiers*

Surface modification with negatively charged non-organic polymers is possible due to the large molecular weight and high density of their charged functional group. It can enhance the dispersion of ZVNF, increase its stability as well as aid in reduction of its particle size. This type of modifier also has low/no environmental toxicity (He et al., 2007). The common examples are polyacrylamide (PAM), carboxymethyl cellulose (CMC), polyacrylic acid (PAA), polyethylene glycol (PEG), polyvinyl pyrrolidone (PVP) and poly styrene sulphonate (PSS). They are also expensive, and cause reduction in stability of ZVNF and consequently loss of efficiency.

4.1.2.3 *Biopolymer modifiers*

Like conventional polymers, naturally occurring, large molecular weight and high-density substances can be used for surface modification of ZVNF. The surface adsorption of biopolymer results in steric repulsion and increased viscosity of the suspension, and slow aggregation. The common examples are starch, guar gum (GG) and xanthan gum (XG). They are neutral, nontoxic, hydrophilic, stable, cost effective and biodegradable. The concentration of biopolymer must be determined before application as an excessive concentration may hinder the function of ZVNF in a subsurface environment (He and Zhao, 2005). Optimisation of ZVNF is a subject of current intense research with significant achievements in the use of hydrophilic biopolymers (Jiao et al., 2015), carboxymethyl cellulose (Wang et al., 2010; He et al., 2007), chitosan (Geng et al., 2009), polyelectrolytes (Singh and Misra, 2015), amphiphilic substances (Bishop et al., 2010) and various oil-based micro-emulsions (Berger et al., 2006).

4.1.2.4 *Polyphenolic plant extract*

Currently, green synthesis remains the most outstanding method to produce stable ZVNF (Huang et al., 2014; Pattanayak and Nayak, 2013). It involves the use of polyphenolic compounds from green plants (green tea, lemon, grape, balm, bran, sorghum, etc.) for chemical or physical synthesis of ZVNF (Zaleska-Medynska et al., 2016). The priorities enjoyed by the polyphenolic containing green plants in the production of stable ZVNF may be due to their achievement of greater stability and effectiveness compared to the other methods (Mahmoud et al., 2016; Markova et al., 2014; Yew et al., 2016). However, the interaction between high oxidation state iron and polyphenolic plant extract cannot be clearly explained by a simple reduction reaction (Huang et al., 2014; Oakes, 2013; Pattanayak and Nayak, 2013; Yew et al., 2016). There are also many misconceptions about green chemistry and the nature of the association of polyphenolic constituents of green plants in the reduction of iron metal. The ideal capping agent for the efficient use of ZVNF in environmental applications must be biodegradable to prevent further site contamination. It must not inhibit diffusion or adsorption of substrate to the active surface site. It must also be effective, stable, and cost effective. The stated properties of an ideal capping agent can also be found in some specific polyphenolic plant extracts which have been demonstrated to be capable of performing dual roles of reducing agent and capping agent in the production of ZVNF (Mystrioti et al., 2014; Shahwan et al., 2011). Several plant extracts from green tea, lemon balm, sorghum bran and weeds are widely reported to be rich sources of polyphenols (Oakes, 2013). The choice of a polyphenolic plant candidate should be based on its abundance, biodegradability, solubility at room temperature and low market value of such plants.

4.2 Sodium borohydride treatment of AMD field samples

In accordance with the method outlined in Chapter 3, 200 mL aliquots of the three AMD field samples (K, P and T) were titrated with 100 mL aliquots of sodium borohydride solution of different concentrations, namely 0.1 M, 0.2 M, 0.3 M, 0.4 M, 0.5 M and 0.6 M, corresponding to sodium borohydride dosages of 3.78 g/L, 7.57 g/L, 11.35 g/L, 15.13 g/L, 18.92 g/L and 22.07 g/L respectively. These experiments were all conducted at contact times of 80 minutes and a temperature of 25°C. Initial experiments were designed to determine the

effect of sodium borohydride dosage on the extraction of Fe from solution (Section 4.2.1). Treated AMD solutions were also analysed for Al, to determine whether co-extraction would occur. Based on these results, the supernatant (treated AMD) and the solid product (nano iron) derived from the experiment using 0.6 M sodium borohydride (dosage rate of 22.07 grams per litre of AMD) was subjected to further analysis and characterisation. The results of these experiments are presented and discussed in Sections 4.2.1-4.2.3. The results of the subsequent test work on the lime neutralisation of the treated AMD solutions are presented in Chapter 5.

4.2.1 Effect of reductant on the extraction of Fe and Al

The results of the experiments using 0.3 M, 0.4 M, 0.5 M and 0.6 M sodium borohydride are summarised in Table 4-2 and presented graphically in Figure 4-2. Application of the sodium borohydride solutions with initial concentrations of 0.1 M and 0.2 M (corresponding to dosages of 3.78 and 15.13 g/L respectively) resulted in negligible solid formation.

The results indicate that for each of the solutions, the extraction of Fe increases as the dosage of borohydride increases, with more than 99% extraction occurring at a dosage of 22.07 grams of sodium borohydride per litre of AMD (corresponding to an initial concentration of sodium borohydride concentration of 0.6 M). At this dosage, the concentration of Fe in the treated solutions varied between 0.11 and 0.23 mg/L. The results also indicated that Al was co-extracted, with residual Al in solution varying between 0.44 and 1.21 mg/L.

Table 4-2 Extraction of nano iron from AMD solutions: Effect of initial sodium borohydride concentration on the extraction of Fe and Al (contact time 80 minutes)

Parameter	Initial Concentration (mg/L)	Final concentrations as a function of initial concentration of sodium borohydride solution (mg/L)				Extraction as a function of initial concentration of sodium borohydride solution (% of feed)			
		0.3 M	0.4 M	0.5 M	0.6 M	0.3 M	0.4 M	0.5 M	0.6 M
<u>AMD stream K</u>									
Fe	4600	856	301	185	0.23	72.0	90.0	93.0	99.9
Al	472	0.12	0.06	0.02	0.93	99.9	99.9	99.9	99.9
<u>AMD stream P</u>									
Fe	4140	339	0.03	0.07	0.11	79.0	92.0	99.0	99.9
Al	384	0.06	1.37	0.58	0.44	99.9	99.9	99.6	99.9
<u>AMD stream T</u>									
Fe	1950	278	221	0.12	0.12	87.0	9.0	99.0	99.9
Al	243	0.16	0.77	0.08	1.21	99.9	99.6	99.9	99.5

Where ND = not determined

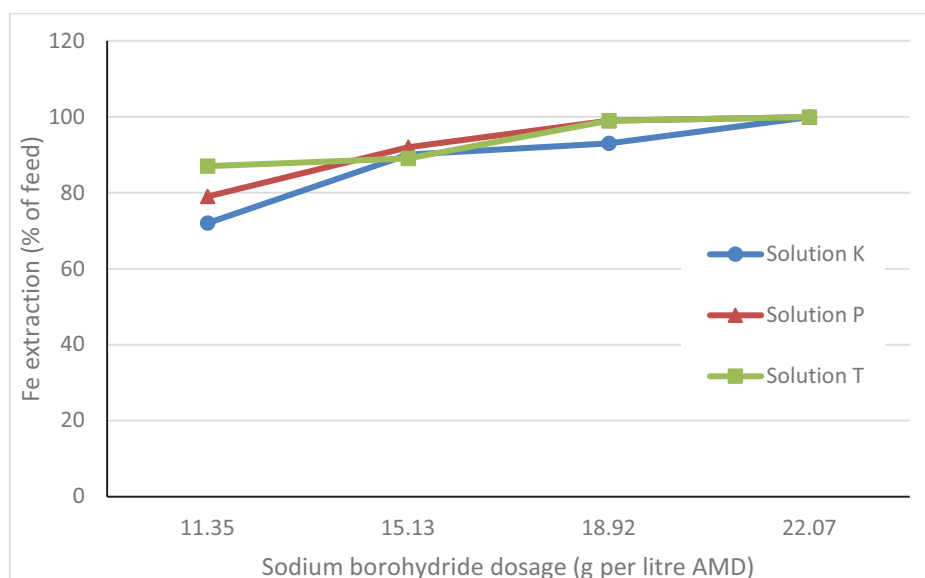


Figure 4-2 Extraction of nano iron from AMD solutions: Effect of sodium borohydride dosage on extent of Fe extraction

4.2.2 Characterisation of treated AMD Solution

Results from the analysis of the supernatant obtained through the treatment of the AMD solutions with a sodium borohydride solution of 0.6 M (corresponding to a dosage of 22.07 g/L) are summarised in Table 4-3.

Table 4-3 Extraction of nano iron from AMD solutions with 0.6 M sodium borohydride solution. Characteristics of the solutions before and after treatment

Elements	K Initial	K Final	P initial	P Final	T Initial	T Final
pH	2.08	5.82	2.14	7.89	2.20	8.92
Al	472	1.21	384	0.93	243	0.44
Fe	4594	0.23	4134	0.11	1950	0.12
Na	BDL	2007	ND	1590	0.06	1090
Mg	422	743	376	427	320	121
Ca	413	913	446	117	428	114
Zn	10.8	0.03	7.35	0.03	3.5	0.04
Mn	110	89.7	79.1	34.6	44.9	7.38
Sr	0.83	0.09	1.05	0.10	0.50	0.012
Co	1.73	0.09	1.03	0.10	0.39	0.012
Ni	1.68	0.03	0.89	0.05	0.71	0.06
Cu	0.29	ND	ND	ND	ND	ND
Mo	0.04	0.09	0.03	0.10	0.03	0.12
Si	ND	6.38	0.21	1.88	ND	6.42
Y	2.34	ND	1.91	ND	1.09	ND
B	2082	3973.85	937.87	2805.43	1269.9	1947.03

Where ND=not determined and BDL= below detection limit

The results in Table 4-3 indicate that, apart from Fe and Al, the treated streams contain reduced levels of metals such as Zn, Co, Ni, Mo, Sr, and Mn. This is indicative of metal co-precipitation during the reductive extraction of iron. The reduction process also results in a significant increase in the pH of the solutions, particularly in the case of solution T, which had a final pH of approximately 9.

4.2.3 Characterisation of nano iron particles

The nano iron particles synthesised from AMD using 0.6 M sodium borohydride as a reductant were characterised using the analytical techniques such as XRD, SEM/EDS, STEM and FTIR, respectively. The input and output samples are assigned codes KNI, TNI and PNI, corresponding to the feed AMD solutions K, T and P respectively.

4.2.3.1 Mineralogy of synthesized nano iron particle

The mineralogy of the synthesized nano iron particles from Solutions K (KNI), T(TNI) and PNI acid mine drainage using sodium borohydride as a reductant was analysed by XRD analysis. Figure 4-3 presents the XRD results of the synthesised nano iron from different AMD sources.

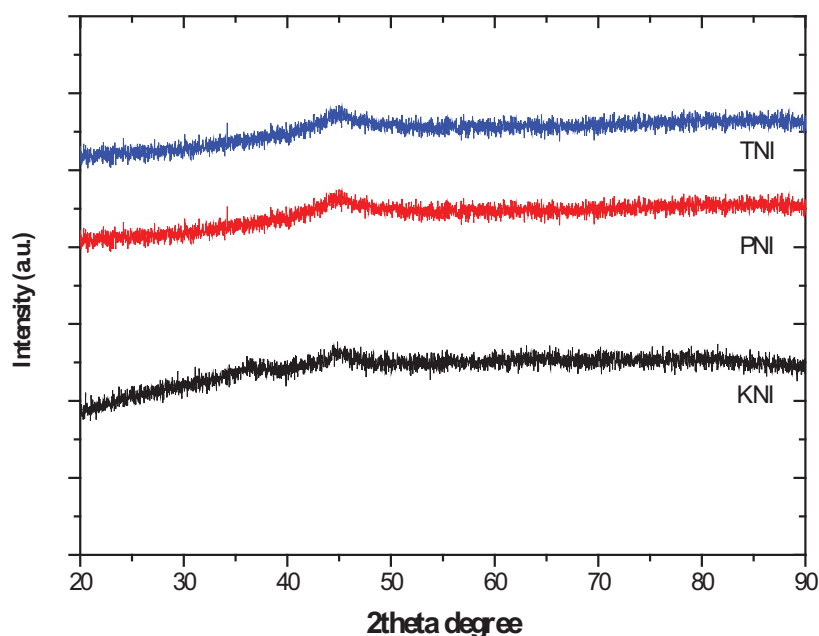


Figure 4-3 Extraction of nano iron from AMD solutions with 0.6 M sodium borohydride solution. XRD pattern of nano iron particles

The XRD patterns in Figure 4-3 show that the AMD-based synthesized nano iron particles have similar XRD diffraction patterns for all feed solutions with identical peak match from 2θ 20° to 90°). The broad diffraction peaks noticed at 44.8° and 36.9° 2θ for TNI confirms the presence of iron oxide (FeO) and pure iron nanoparticles (α -Fe). The broad XRD peaks representing zerovalent iron nanoparticles correspond to a previous study as reported by Singh et al. (2011).

4.2.3.2 SEM Morphology, size distribution and elemental composition (EDS) of nano iron particles synthesized from field AMD samples

The morphology of nano iron synthesized from field AMD samples TNI, PNI, or KNI using sodium borohydride are presented in this section. The elemental composition of the synthesized nano iron particles was analysed using the EDS technique.

SEM micrograph for the nano particles derived from solution TNI, PNI and KNI are presented in Figure 4-4. In accordance with these micrographs, the generated nano iron particles yielded nano range spherical bead-like structure tied to one another in a threadlike manner. Similar nano iron shapes have been reported by Lin et al. (2008). Whilst the solids synthesized from the different solutions have similar morphologies, their particle size distribution appeared to vary, with the KNI nano iron sample having larger particles than the TNI and PNI nano iron samples.

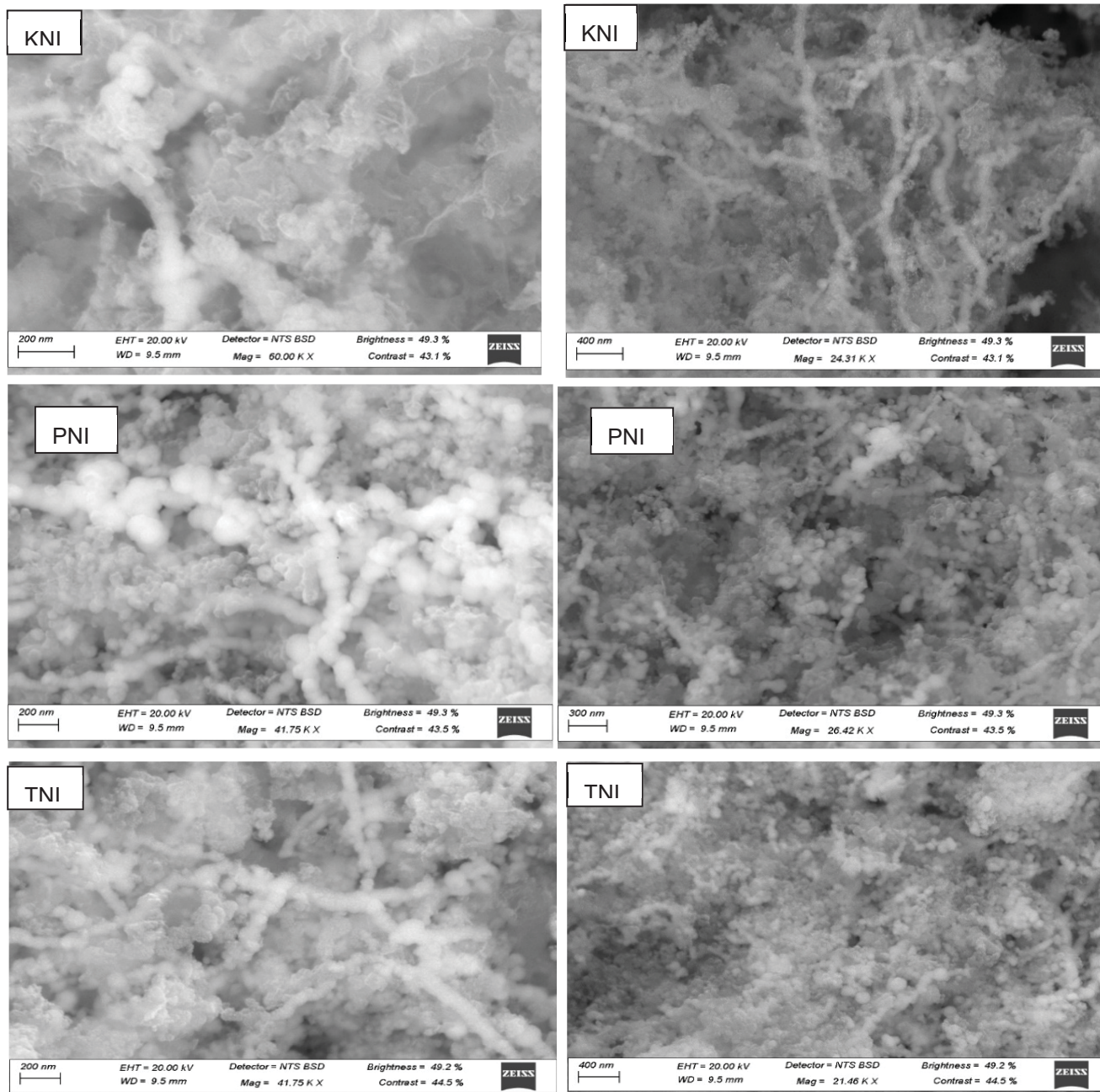


Figure 4-4 Extraction of nano iron from AMD solutions with 0.6 M sodium borohydride solution. SEM micrographs of nano iron particles synthesised from KNI, PNI and TNI AMD solutions

To corroborate the SEM results, a corresponding STEM image was used for particle size measurement alongside Image J software as presented in Figure 4-5.

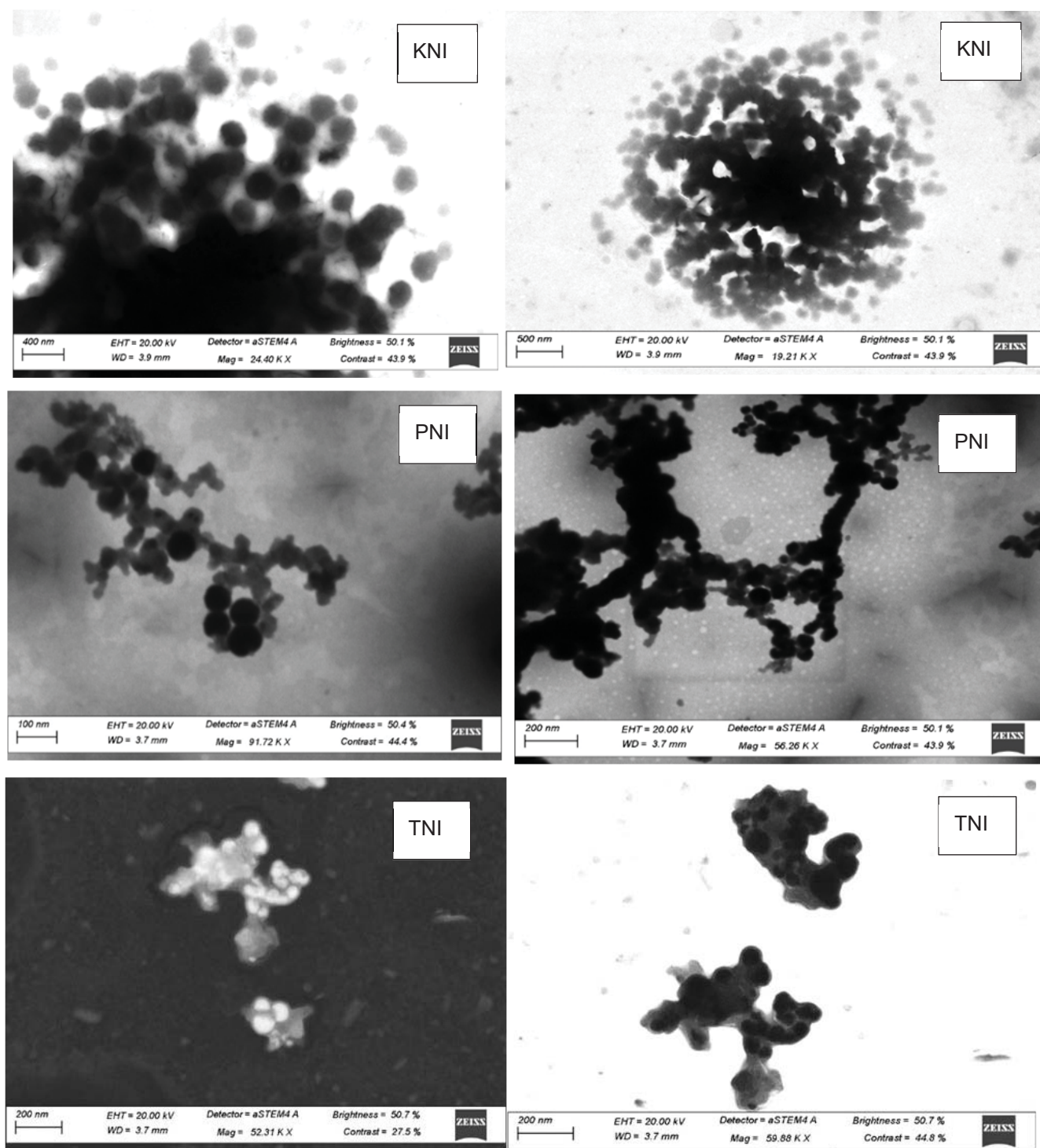


Figure 4-5 Extraction of nano iron from AMD solutions with 0.6 M sodium borohydride solution. STEM micrographs of nano iron particles synthesised from KNI, PNI and TNI AMD solutions

The STEM morphology in Figure 4-5 revealed a spherical shaped nano iron that is connected in the form of a chainlike structure synthesised from field AMD (TNI, PNI or KNI). These results confirm the morphological structure observed in Figure 4-3 by SEM analysis and is consistent with literature reports (Alegbe et al., 2019; Yuvakkumar et al., 2011). According to Alegbe et al. (2019), the spherical shape of the synthesized nano iron particles is characteristic of nano iron particles synthesized by precipitation. The STEM results of TNI, PNI,

and KNI also showed evidence of agglomeration, and this could be attributed to the drying process during sample preparation for STEM or due to the particles' high surface energy.

A graphical representation of the size distribution of nano iron prepared from field AMD with sodium borohydride can be seen in Figure 4-6. The particle size distribution of the nano iron derived for the TNI sample was between 20 nm and 160 nm, with an average of 66.8 nm; in the case of the PNI sample the particle size ranged from 20 nm to 100 nm, with an average particle size of 53.90 nm; whilst for the KNI sample, the particle size ranged between 100 and 250 nm, with an average particle size of 161 nm. These results confirm the variation in particle sizes for the products prepared from the different AMD solutions as observed in the SEM and STEM micrographs. The particle size of the KNI nano iron product exceeded the 100 nm target due to intense agglomeration and formation of large clusters prior to STEM particle size measurement using the Image J software tool.

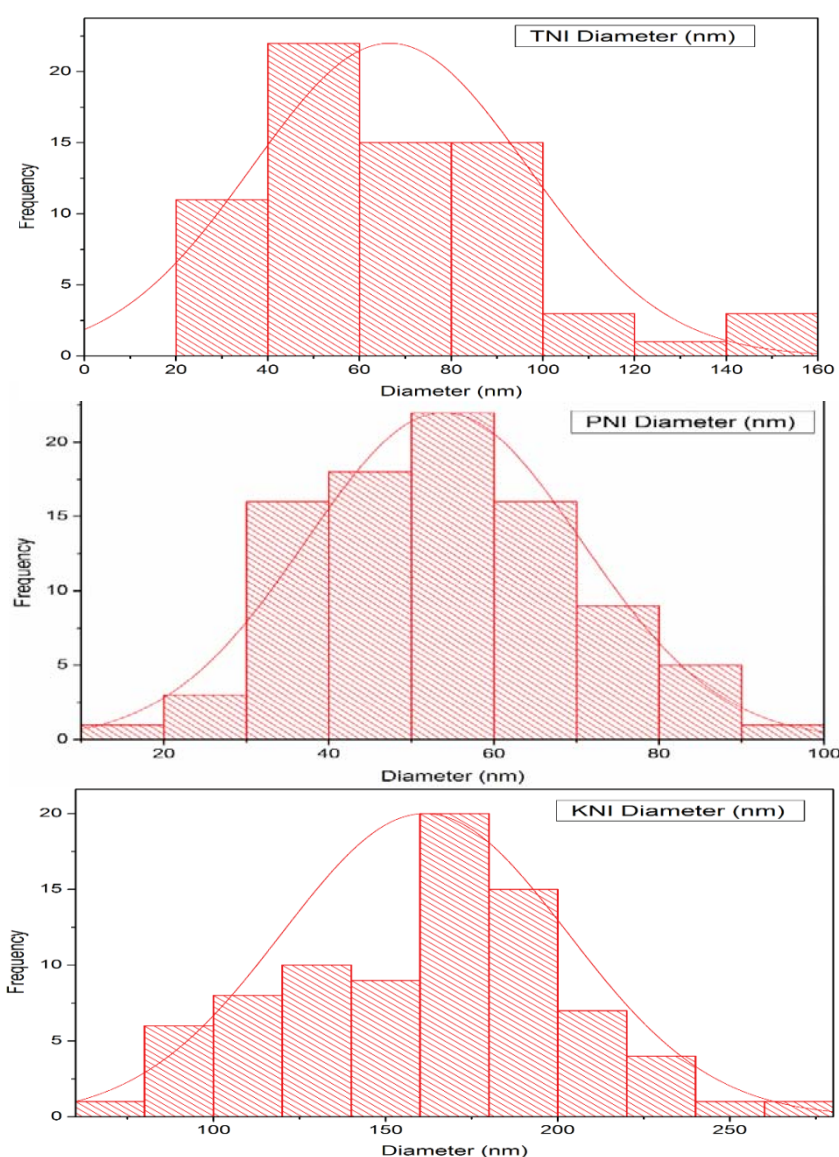


Figure 4-6 Extraction of nano iron from AMD solutions with 0.6 M sodium borohydride solution. Crystal size distribution of nano iron particles synthesised from TNI, PNI and KNI AMD solutions

The EDS spectra of the nano iron products are presented in Figure 4-7, and the quantitative results presented in Table 4-3.

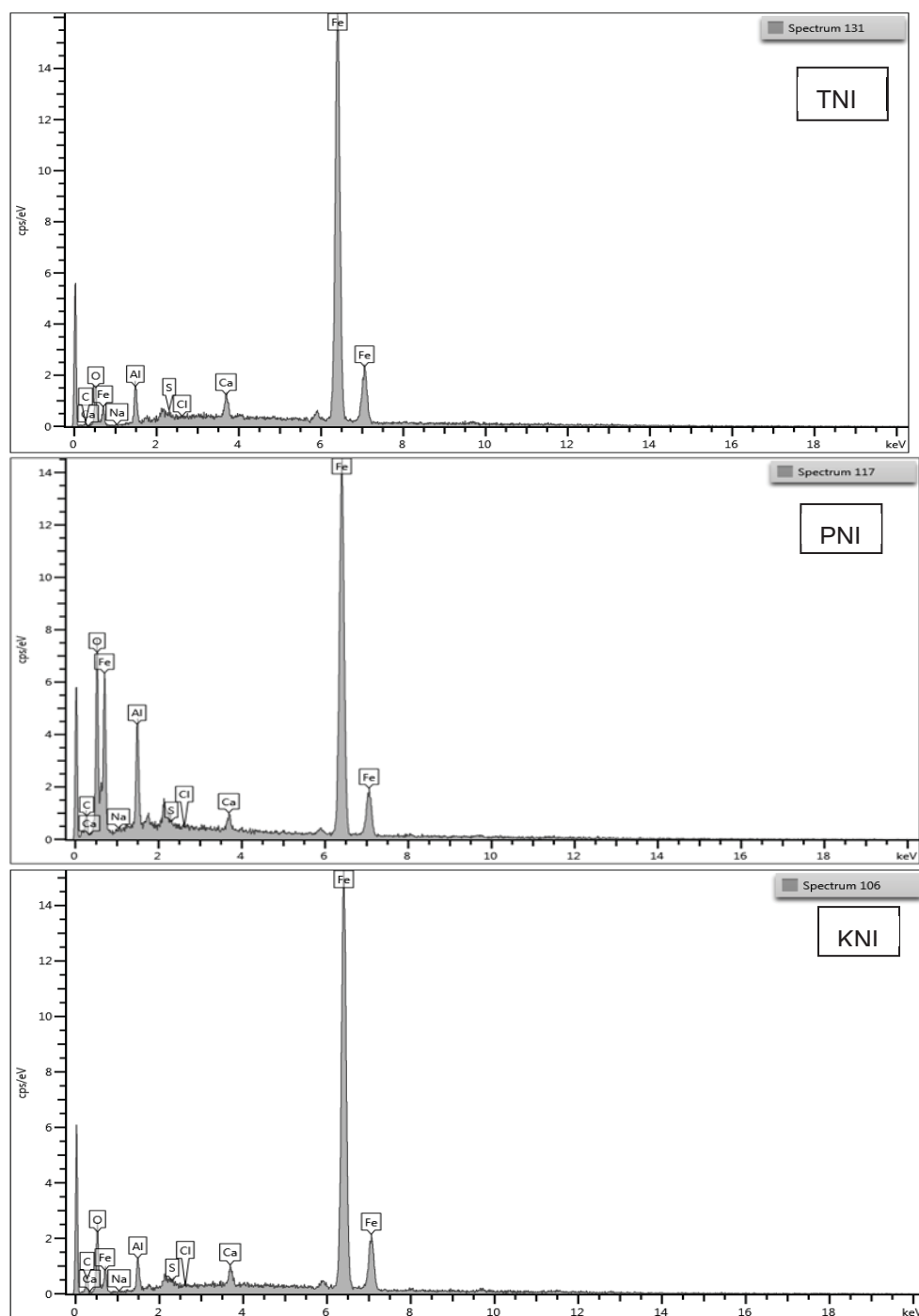


Figure 4-7 Extraction of nano iron from AMD solutions with 0.6 M sodium borohydride solution. EDS spectra of nano iron particles synthesised from TNI, PNI and KNI AMD solutions

The EDS results confirm that the synthesized nano iron particles are comprised mainly of Fe metal and its compounds (81.5-92.5 atomic wt. %), with minor amounts of Al (4.8-6.7 atomic weight %) and Ca (1.1-1.3 atomic weight %), as well as traces of Na, Mg, Si and S. These results are consistent with the compositions of the treated AMD solutions which indicated significant co-extraction of Al, as well as other metals.

Table 4-4 Extraction of nano iron from AMD solutions with 0.6 M sodium borohydride solution: EDS results of nano iron particles synthesised from TNI, PNI and KNI AMD solutions

Elements	TNI (% atomic wt.)	PNI (% atomic wt.)	KNI (% atomic wt.)
C	3.08±2.01	3.67±0.45	4.84±1.34
O	8.50±4.71	8.03±1.74	3.51±1.16
Na	0.06±0.08	0.22±0.24	0.26±0.09
Mg	0.08±0.06	0.10±0.13	0.27±0.15
Al	5.00±1.33	4.79±0.61	6.71±0.38
Si	0.42±0.14	0.33±0.04	0.48±0.04
S	0.03±0.06	ND	0.33±0.08
Cl	0.04±0.06	0.03±0.02	0.02±0.04
Ca	1.34±0.26	1.24±0.12	1.11±0.17
Fe	81.5±0.91	81.6±2.84	92.5±2.08
Total	100	100	100.

4.2.3.3 FTIR Spectra of synthesized nano iron particles from Field AMD

As indicated in Chapter 3, Fourier Transform Infrared Spectroscopy (FTIR) was conducted on the nano iron products to provide information on the chemical bonding, molecular structure, and functional groups. The FTIR spectra of the synthesised nano products are presented in Figure 4-8.

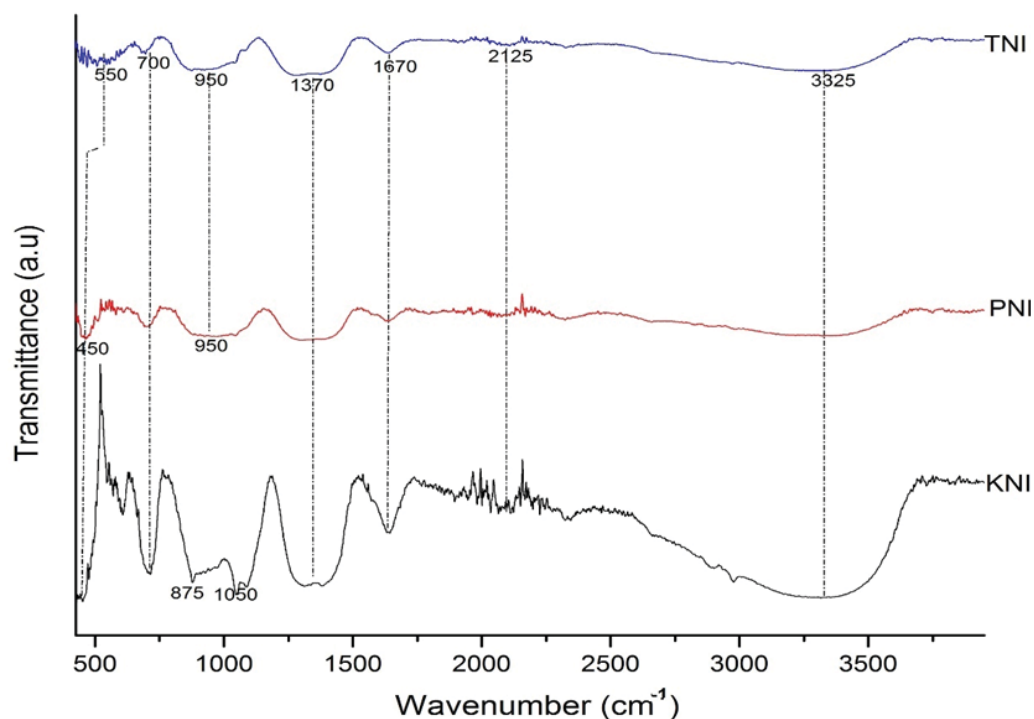


Figure 4-8 Extraction of nano iron from AMD solutions with 0.6 M sodium borohydride solution: FTIR Transmittance spectra of nano iron particles synthesised from TNI, PNI and KNI AMD solutions

Table 4-4 summarizes identified structural vibrations noticed in the synthesised nano iron samples.

Table 4-5 Extraction of nano iron from AMD solutions with 0.6 M sodium borohydride solution: Structural vibrational bands for TNI, PNI and KNI nano iron particles

Samples Name			
Vibration Band	TNI	PNI	KNI
450 cm ⁻¹		Fe-O bending	Fe-O bending
550 cm ⁻¹	Fe-O bending		
600 cm ⁻¹			Fe-O stretch
700 cm ⁻¹	Fe-O stretch	Fe-O stretch	Fe-O stretch
875 cm ⁻¹			Fe-O stretch
950 cm ⁻¹	Fe-O stretch	Fe-O stretch	
1050 cm ⁻¹			Fe-O stretch
1370 cm ⁻¹	C-O stretch	C-O stretch	C-O stretch
1670 cm ⁻¹	O-H bending	O-H bending	O-H bending
2125 cm ⁻¹	C=O stretch	C=O stretch	C=O stretch
2300 cm ⁻¹	C-H stretch	C-H stretch	C-H stretch
3325 cm ⁻¹	O-H stretch	O-H stretch	O-H stretch

The results in Table 4-4 show that the vibrational bend of Fe-O shifted from 450 cm⁻¹ for PNI and KNI, to 550 cm⁻¹ for TNI. It has been reported that the bending and stretching vibrational band between 360 and 570 cm⁻¹ corresponds to Fe-O bending and stretching vibrations that are characteristic of magnetite crystalline lattice. The FTIR data also shows that the Fe was partially in oxide form, and was not fully zero valent, indicating core-shell formation. In this line of investigation, the KNI sample shows strong transmittance peaks between 450 to 600 cm⁻¹ which fall within the range for magnetite transmittance.

4.3 Treatment of AMD with green reductants

4.3.1 Preparation and characterization of polyphenolic tea extracts

In accordance with the method described in Chapter 3, 60 g of ground tea leaves (green tea, green rooibos tea or rooibos tea) were soaked in 120 mL of deionized water and 30 mL of 25% ethanol. The mixture was then agitated at a speed of 300 rpm for 1 hour at a temperature of 60°C. Thereafter, the mixture was left to cool, prior to the evaporation of ethanol using a rotovapor system. Lastly, the remaining tea mixture was freeze dried to obtain an amorphous powder.

The powdered samples of the plant extracts were analysed using Ferric Reducing Antioxidant Property (FRAP), 2,2-diphenyl-1-picrylhydrazyl (DPPH), Fourier transform infrared (FTIR), pH, EC, and Oxidation Reduction Potential (ORP) analytical techniques.

4.3.1.1 Characterization of tea extracts by Ferric Reducing Antioxidant Property (FRAP)

The antioxidant activity of the tea extracts was measured using automated Ferric reducing capability of plasma (FRAP) testing. The ferric ion was reduced to ferrous ion by the polyphenolic substances in the tea extracts. This process occurred at a low pH with the formation of a coloured compound (ferrous-tripyridyltriaz). FRAP values were then recorded by comparing the change in absorbance at 593 nm in the test reaction mixtures with those containing ferrous ions per dry weight of the tested sample as displayed in Table 4-5.

Table 4-6 Antioxidant power of polyphenolic compounds extracted from different tea species as recorded from ferric reducing antioxidant (FRAP) assay

Plant and Chemical reductants	FRAP per dry weight of sample ($\mu\text{mol FeII/g}$)	COV (%) for triplicate measurement
Green Tea extract	888	1.89
Green Rooibos Tea extract	804	2.41
Rooibos Tea extract	756	2.39
Sodium borohydride	6010	2.72

From Table 4-5, it could be noticed that the FRAP values of the aqueous-ethanolic extracts of green tea, green rooibos tea, rooibos tea and sodium borohydride were 804.57, 887.68, 756.00 and 6013.94 $\mu\text{mol/g}$, respectively. The sodium borohydride FRAP test value shown in Table 4-5 was for comparative purposes with that of the tea extracts' antioxidant strength. Even though sodium borohydride had the highest FRAP value, the antioxidant values of the tea reductants were comparable (see Table 4-5). Altogether, the aqueous-ethanolic polyphenolic tea extracts did not show large discrepancies in their FRAP values. Therefore, all the tea extracts had a similar reducing capability of iron. It was further noticed that green rooibos tea had the highest FRAP value (see Table 4-5) among the tea extract reductants. This was an indication that green rooibos tea had a greater capacity to reduce iron from a higher oxidation state to a lower oxidation state. The FRAP test findings are in accordance with the findings by (Oakes, 2013) that tea extracts contain high amounts of polyphenolic compounds with the potential to act as a reducing agent. On this note, it was expected that compounds that donate electrons for the reduction of Fe^{3+} to Fe^{2+} can also quench free radicals. In this line of investigation, the radical scavenging activity of the tea extracts were determined against the stable free radical DPPH antioxidant activities.

4.3.1.2 Characterisation of tea extracts by 2,2-diphenyl-1-picrylhydrazyl (DPPH)

Following the extraction of polyphenols from tea extracts (green tea, green rooibos tea, and rooibos tea), the scavenging activity of the tea extracts were investigated against the stable free radical 2, 2-diphenyl-1-picrylhydrazyl (DPPH). Table 4-6 presents the DPPH results of the tea extracts using ascorbic acid as a reference reductant against DPPH.

Table 4-7 Antioxidant activities of aqueous-ethanolic extracts of tea as recorded by 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay (T=tea)

Antioxidant (mg/L)	% Inhibition			
	Ascorbic acid	Green T	Green Rooibos T	Rooibos T
3.12	25.3 $\pm$ 0.23	2.71 $\pm$ 0.91	4.63 $\pm$ 1.21	1.57 $\pm$ 0.02
6.25	41.8 $\pm$ 1.48	3.16 $\pm$ 0.06	7.12 $\pm$ 1.42	2.86 $\pm$ 1.11
12.5	66.8 $\pm$ 2.67	17.4 $\pm$ 0.21	11.4 $\pm$ 0.98	1.31 $\pm$ 0.71
25	96.5 $\pm$ 0.98	24.5 $\pm$ 0.9	19.4 $\pm$ 1.42	8.94 $\pm$ 1.71
50	97.0 $\pm$ 1.21	40.9 $\pm$ 1.1	40.1 $\pm$ 2.41	17.8 $\pm$ 2.11
100	97.0 $\pm$ 0.72	71.9 $\pm$ 1.4	65.7 $\pm$ 3.1	34.4 $\pm$ 1.98

The tea extracts (green tea, green rooibos tea and rooibos tea) showed a high percentage of inhibition at 100 mg/L on DPPH (see Table 4-6). However, ascorbic acid as a reference standard (reductant) proves to have a significantly higher percentage inhibition that is greater than 97% at 100 mg/L for DPPH (see Table 4-6). The percentage inhibition of ascorbic acid as a reference reductant was close to 100%, but the percentage inhibition values of the tea extracts were somewhat lower compared to that of ascorbic acid as a

reference reductant. These results are in line with the finding by (Badmus et al., 2018). Consequently, green tea, green rooibos tea, and rooibos tea extracts can inhibit oxidative processes by significantly reacting in a biological matrix (Nawwar et al., 2011). In this line of investigation, the structural vibrations of polyphenolic compounds were also analysed.

4.3.1.3 Fourier Transform Infrared Spectroscopy (FTIR)

The purpose of the FTIR analysis was to investigate the structural properties of the various tea extracts. The FTIR results of the tea extracts are presented in Figure 4-9.

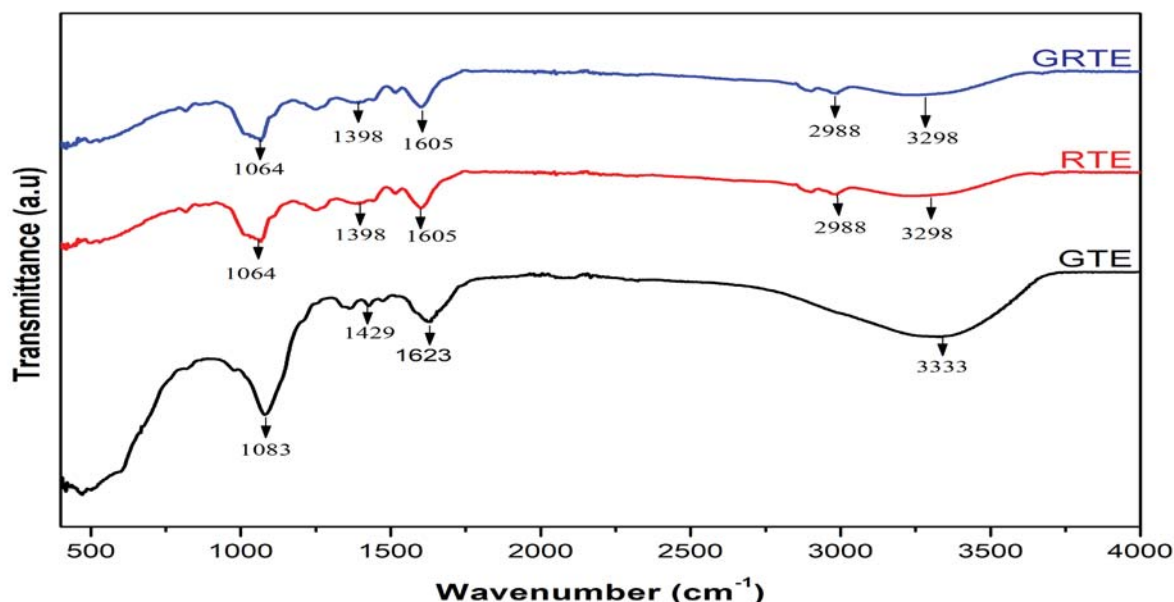


Figure 4-9 FT-IR transmittance spectrum of green tea (GTE), green rooibos tea (GRTE) and rooibos tea (RTE)

From FT-IR data presented in Figure 4-9, the stretching vibrations of the polyphenolic compounds could be noticed. The stretching vibration at 3298 cm^{-1} for green rooibos tea (GRTE) and rooibos tea (RTE) and at 3333 cm^{-1} for green tea could be assigned to O-H stretching (Suresh et al., 2014). The intense O-H vibration of green tea extract (GTE) could be attributed to the high contribution of benzylic OH from its polyphenol, which is greater than that observed in green rooibos tea and rooibos tea (Badmus et al., 2018). The apparent peak found on GRTE, RTE and GTE at 1605 , and 1623 cm^{-1} respectively could be assigned to C=C aromatic skeletal vibrations (J. Lin et al., 2017). The presence of this peak confirms the presence of aromatic compounds in the polyphenolic extracts of tea. Its broad intensity in GTE among others confirms a high concentration of the compound. The symmetric, asymmetric, and carbonyl peaks for GRTE and RTE are found at 1206 , 1398 , and 1064 cm^{-1} while the symmetric, asymmetric and carbonyl peaks shifted to a higher wavelength for green tea extract (GTE) to 1400 , 1429 , and 1083 cm^{-1} . It was also noticed that C-H vibrations were present in GRTE and RTE but absent in the GTE extract. Thereafter, characterization of the polyphenolic extracts from various tea extracts was also done using pH, EC, and ORP analytical techniques.

4.3.1.4 Measurement of pH, electronic conductivity, Oxidation Reduction Potential of tea extracts

The pH, electronic conductivity, Oxidation Reduction Potential measurements were done to assess the quality of green tea extract prior to dosing of AMD for zero valent nano iron recovery. The pH measurement was firstly done, followed by electronic conductivity (EC) and Oxidation Reduction Potential (ORP). The pH results are presented in Table 4-7.

Table 4-8 Measurement of pH values of green tea solutions

Green tea extract (g)	pH	EC	ORP (mV)
0.1	5.42	800	224
0.2	5.39	675	213
0.3	5.34	550	208
0.4	5.33	300	195
0.5	5.33	175	179
0.6	5.32	98	136
0.7	5.31	50	125

Table 4-7 presents pH values of the green tea solutions. The pH values indicated that the solutions were acidic. It could also be noticed that the pH values did not vary much even as the mass of green tea in solution increased from 0.1-0.5 g. After the addition of 0.4 and 0.5 g of green tea powder in solution, a constant pH of 5.33 was measured. Figure 4-10 presents the EC and ORP results of the green tea samples.

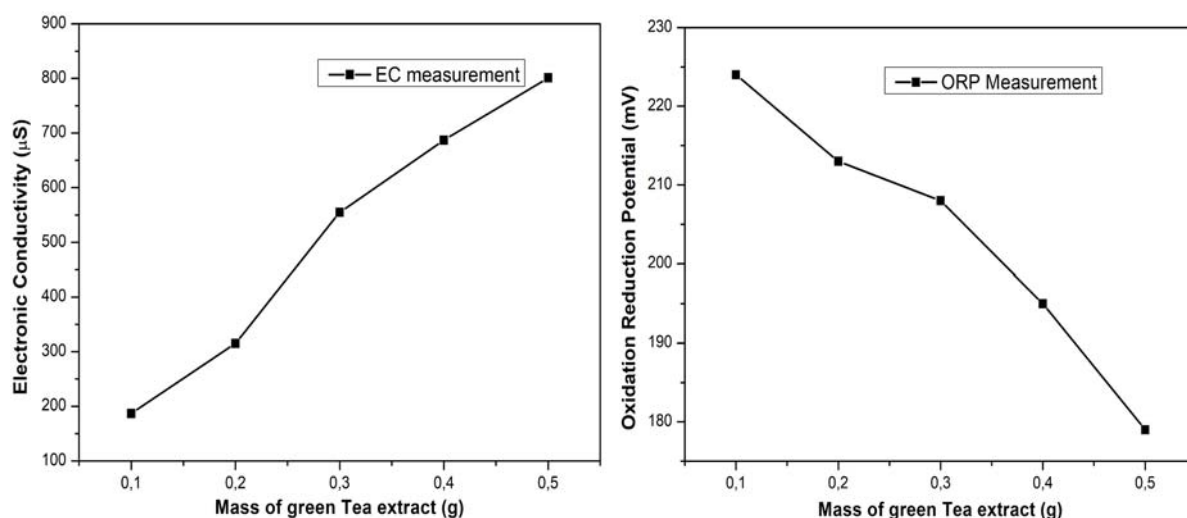


Figure 4-10 (a) EC and (b) ORP of green tea solutions containing different masses of green tea extract

From Figure 4-10, it was noticed that as the amount of green tea extract increased in solution, the electronic conductivity (EC) of the solution increased from 180 μS to 800 μS while its Oxidation Reduction Potential (ORP) decreases from 223 to 170 mV. In summary, the EC values were inversely proportional to the ORP values, indicating that the green tea solutions were acting as a reducing agent by donating electrons to reduce iron from solution. From this investigation, green tea extract was selected as a choice of reductant due to its higher FRAP and DPPH values as compared to green rooibos tea and rooibos tea extract.

4.3.1.5 *Elemental composition of green tea extract reductant*

The elemental analysis of green tea extract was done to assess the concentration of elements in the green reductant prior to dosing AMD for nano iron production. The elemental composition results of green tea extract are presented in Table 4-8.

Table 4-9 Elemental Composition of the green tea extract solutions

Parameter	Unit	Concentration
<u>Elements</u>		
Al	mg/L	12.0
Mn	mg/L	9.01
Fe	mg/L	0.90
Ni	mg/L	0.15
Cu	mg/L	0.12
Zn	mg/L	0.29
Sr	mg/L	0.02
Ba	mg/L	0.04
Ca	mg/L	4.32
Na	mg/L	1.44
P	mg/L	62.0
Si	mg/L	2.41
K	mg/L	281
Co	mg/L	0.008
Ba	mg/L	0.04
Sr	mg/L	0.03
Zn	mg/L	0.3
Cu	mg/L	0.1
Ni	mg/L	0.1
Se	mg/L	0.001

These results indicate that the extract contained elevated levels of K (281 mg/L), minor quantities of P (62 mg/L), as well as traces of Al (12 mg/L), Mn (9 mg/L) and Ca (4 mg/L) and Si (2.4 mg/L)

4.4 Characterisation of treated AMD solution P

In accordance with the characteristics of the tea extracts, green tea extract was selected as a reductant for the treatment of AMD field solution P. The results of the experiments on the treatment of AMD with green tea extract are presented and discussed in this section.

4.4.1 Effect of green tea extract dosage on metal and sulphate removal from AMD

The results in Table 4-9 show the composition of AMD solution P before and after treatment with green tea extract.

Table 4-10 Extraction of nano iron from AMD solution P: Effect of initial green tea extract dosage on the composition of the AMD solutions (AMD volume = 50 ml; contact time= 24 hours)

Parameter	Initial concentration (mg/L)	Final concentration of elements (mg/L) in AMD as a function of initial concentration of green tea extract						
		0.1 g	0.2 g	0.3 g	0.4 g	0.5 g	0.6 g	0.7 g
Fe	40002	1750	1284	894	678	450	451	453
Al	367	263	219	190	146	120	120	116
Ca	503	275	253	239	196	178	176	174
Mn	85	41	32	28	18	13	13	11
Mg	376	257	226	190	152	142	141	133
Si	28	19	16	14	11	10	10	9.0
Cu	0.1	0.06	0.06	0.06	0.05	0.05	0.04	0.04
Zn	9.8	3.6	3.0	2.0	1.6	1.3	1.0	0.4
Mo	0.1	0.01	0.01	0.03	0.03	0.04	0.05	0.05
Ni	1.2	0.3	0.4	0.4	0.3	0.3	0.4	0.3
Co	1.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sr	0.84	0.2	0.2	0.2	0.1	0.08	0.08	0.08
K	ND	127	142	187	243	259	352	360
Se	ND	0.1	0.2	0.3	0.3	0.3	0.3	0.4
P	ND	0.5	0.7	0.9	1.0	1.2	1.3	1.5
Na	33.1	27	26	24	22	19	18	18
Sulphate	11500	7995	7990	7650	7694	7817	8175	8201

ND=not determined

The results indicated that apart from Fe, the treatment of AMD with green tea extracts also results in a reduction in the concentrations of other metals, including Al, Ca, Mg, Mn, Zn, Na, Si, Ni, Sr, and Co, as well as sulphate. The concentrations of potassium and phosphorous, on the other hand, increase. The change in metal and sulphate concentrations as a function of green tea extract dosage is shown in Figure 4-11.

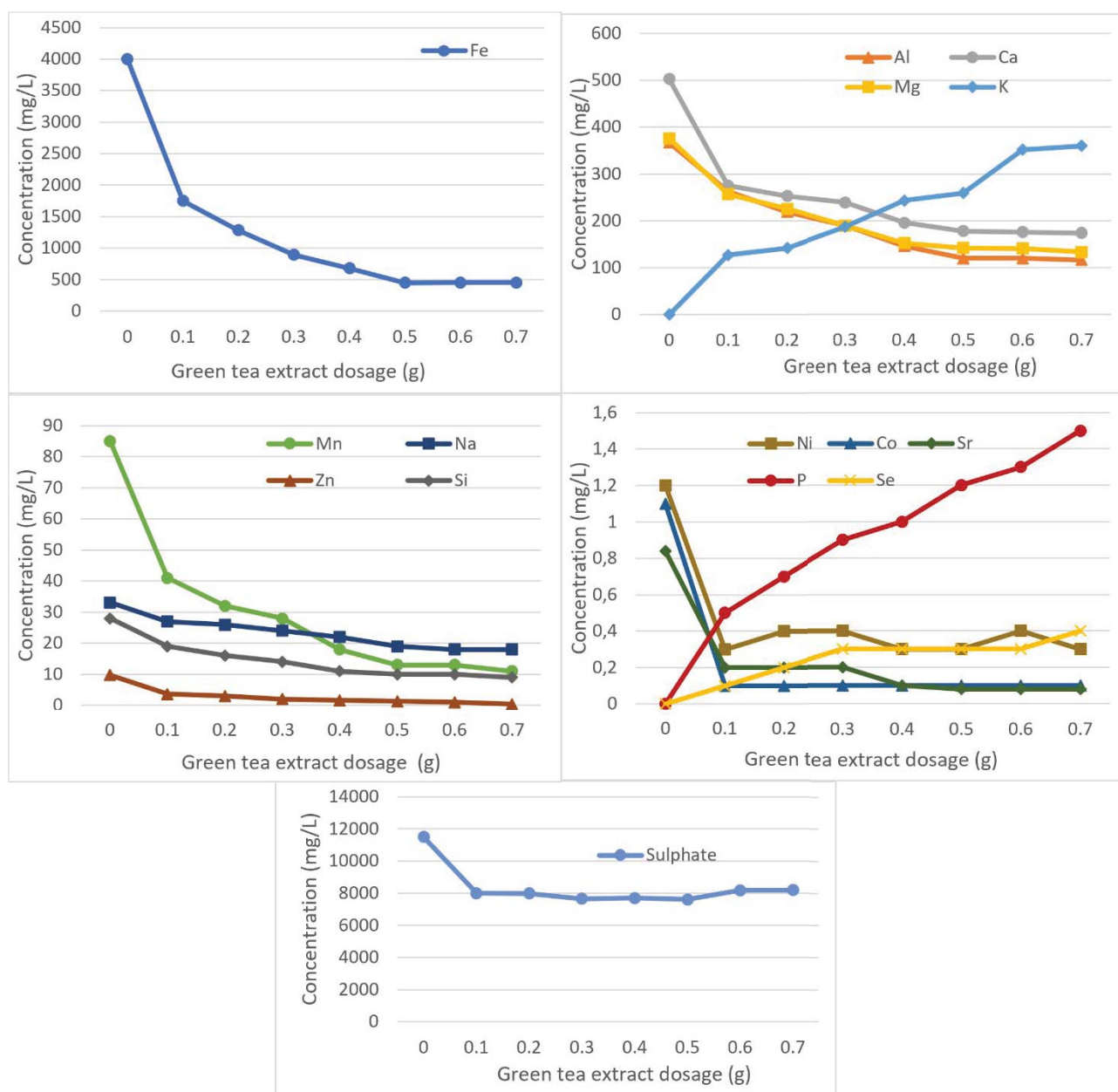


Figure 4-11 Concentration of metals and sulphate in AMD solution P as a function of green tea reductant dosage. Reaction temp = 35°C, Time = 24 hours, Agitation speed=200 rpm, Vol of green tea extract = 40 mL, and Vol. of AMD = 50 mL

The results in Figure 4-11 indicate that in most cases, a dosage of 0.1 g/50 mL of green tea extract results in a significant decrease in element concentration. Except for K and Se, metal concentrations declined steadily upon the addition of additional green tea extract up to a dosage of 0.5 g/50 mL, with further additions of green tea extract appearing to have a negligible effect on metal concentration levels. In contrast, the concentrations of K, P and, to a lesser extent Se, in the treated AMD increase as the dosage of green tea extract increases, indicating the presence of these elements in the extract from the green tea. The sulphate in the treated AMD decreases to approximately 8000 mg/L on addition of 0.1 g of green tea extract and then remains relatively constant upon further increases in green tea extract.

The results showing the effect of using 0.1 g, 0.2 g, 0.3 g, 0.4 g, 0.5 g, 0.6 g, and 0.7 g green tea reductant on the extent of extraction are summarised in Table 4-10 and presented graphically in Figure 4-12.

Table 4-11 The effect of green tea extract dosage on the percentage removal of elements from AMD field solution P

Parameter	Initial concentration (mg/L)	% Extraction of elements from AMD as a function of initial concentration of green tea						
		0.1 g	0.2 g	0.3 g	0.4 g	0.5 g	0.6 g	0.7 g
Fe	4000	55	67	77	83	89	89	89
Al	367	29	40	48	60	67	67	68
Ca	503	45	49	52	61	64	65	65
Mn	85	52	62	67	78	84	84	85
Mg	376	31	39	49	59	62	62	64
Si	28	33	42	50	60	64	64	68
Cu	0.1	42	40	40	50	50	60	60
Zn	9.8	63	69	79	83	86	89	96
Mo	0.1	87	87	62	62	50	37	37
Ni	1.2	73	64	64	73	73	64	73
Co	1.1	90	90	90	90	90	90	90
Sr	0.84	76	76	76	88	90	90	90
K	0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Se	0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
P	0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Na	33.1	18	21	27	33	42	45	45
Sulphate	11500	30	30	33	33	32	28	29

Where: n.a. is not applicable

The results in Table 4-10 indicate that the percentage extraction of the major metal Fe and minor metals Al, Ca, Mg, Mn, Si, Zn and Na increases as the dosage of green tea extract increases from 0.1 g (2 g/L) to 0.5 g (10 g/L). In most cases, the optimum dosage of green tea extract for the extraction of these metals is 0.5 g (10 g/L). This is because, as the dosage of green tea extract increases from 0.5 g to 0.6 and 0.7 g, the percentage removal of metals remains relatively constant. A slightly different trend is observed for the trace metals Ni, Co, and Sr, with the initial dosage of only 0.1 g of green tea extract (2 g/L) resulting in relatively high levels of extraction in comparison with the minor and major metals, but with further additions of extract having a negligible effect of metal extraction. Similarly, increasing the addition of green tea extract above 0.1 g, has negligible effect on the extent of extraction.

At optimum dosage of green tea extract, the maximum extent of removal of the targeted metal, Fe, is 89%. A similar maximum extraction was achieved for divalent minor metals Mn (86%) and Zn (96%) and the trace metals Co (90%) and Sr (90%). The trace element Ni (73%) and other minor metals Al (68%), Ca (65%), Mg (64%), Si (68%) show similar, but lower, extractions under optimum green tea extract dosages. A maximum extraction of only 45% was achieved for the monovalent Na metal, and in the order of 30% for sulphate.

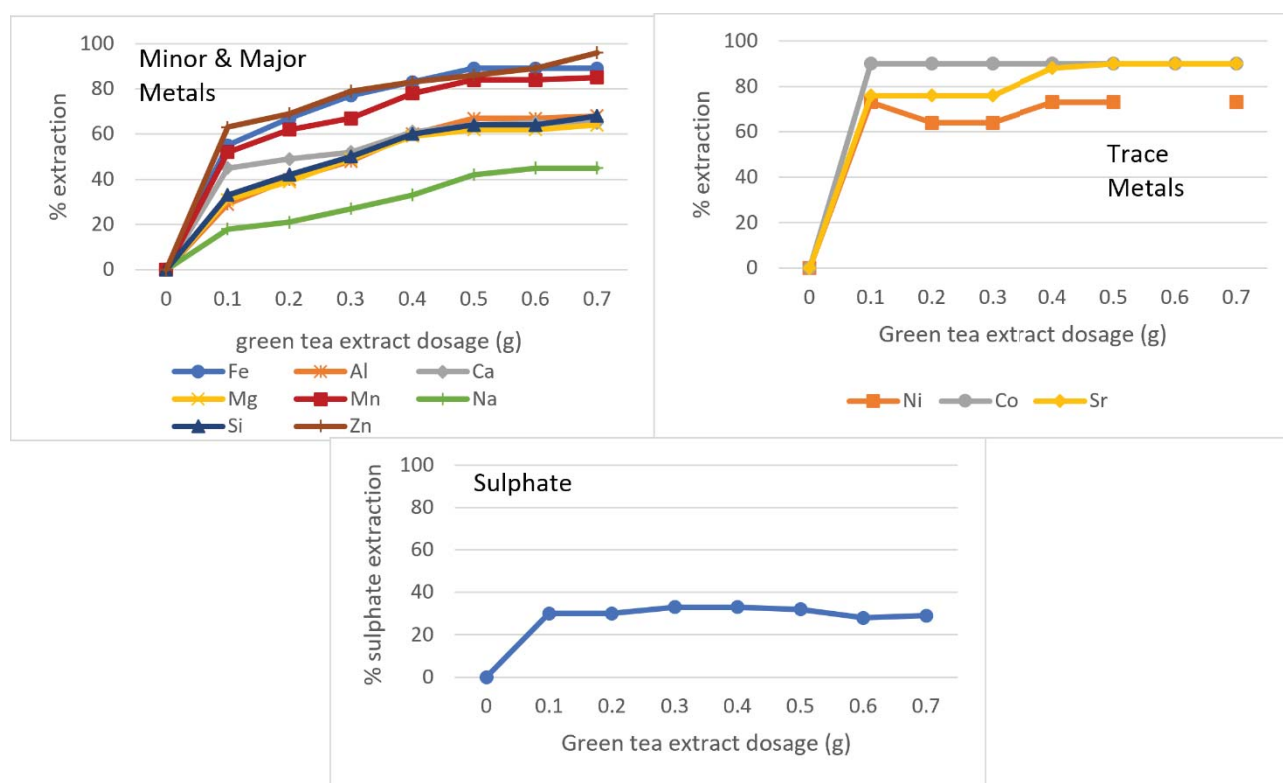


Figure 4-12 The effect of green tea extract dosage on the extent of element extraction. Experimental conditions: Vol of AMD = 50 mL, Time = 24 hours, Reaction Temp = 35°C, (n = 3).

4.4.2 Effect of temperature on metal and sulphate removal from AMD solution

The green tea extract treatment of AMD solution P was conducted at temperatures of 30°C to 50°C at an extract dosage of 0.5 g/50 mL AMD, to explore the effect of reaction temperature on the removal of metal and sulphate from solution. This is because at 25°C, all Fe was still in solution and no precipitate of Fe was formed. The effect of temperature on the concentration of metals and sulphate in the AMD solution P treated with 0.5 g of green tea extract is presented in Table 4-11 and Figure 4-13.

The results in Table 4-11 and Figure 4-13 indicate that in the case of the metals Fe, Ca, Al and, to a lesser extent, Na, an increase in the temperature from 30°C to 45°C results in a decline in the supernatant concentration, with a further increase in temperature to 50°C having a negligible effect on concentration. In the case of Mn, the supernatant concentration declines on increasing the temperature from 30°C to 35°C, with the concentration remaining constant over the temperature range 35°C to 50°C. The temperature-concentration relationship is different for K and Mg, with the concentrations increasing slightly as the temperature increases from 30°C to 45°C, before declining on a further increase in temperature to 50°C. Similarly, an increase in temperature from 30°C to 35°C results in an increase in sulphate concentration with the concentration then declining at a temperature of 50°C.

Table 4-12 Extraction of nano iron from AMD solution P: Effect of temperature on the composition of the supernatants from treatment with green tea extract (Green tea extract dosage = 0.5 g/50 ml of AMD; time = 24 hours)

Component	Feed (mg/L)	Final concentration (mg/L) as a function of temperature				
		30°C	35°C	40°C	45°C	50°C
Fe	4002	500	450	400	378	379
Al	367	131	120	99	90	94
Ca	503	230	182	168	168	152
Mn	85	18	14	14	25	14
Mg	376	139	142	150	160	132
Si	28	10	10	10.5	11	10.5
Cu	0.1	0.06	0.05	0.05	0.05	0.04
Zn	9.8	1.9	1.4	1.8	1.6	1.7
Mo	0.1	ND	0.05	ND	ND	ND
Ni	1.2	0.28	0.33	0.30	0.28	0.28
Co	1.1	0.1	0.07	0.2	0.1	0.1
Sr	0.8	0.08	0.08	0.08	0.07	0.1
K	ND	261	259	272	285	242
Na	33	22	20	20	19	19
Sulphate	11500	7400	7750	7700	7700	7500

Where: ND = not determined

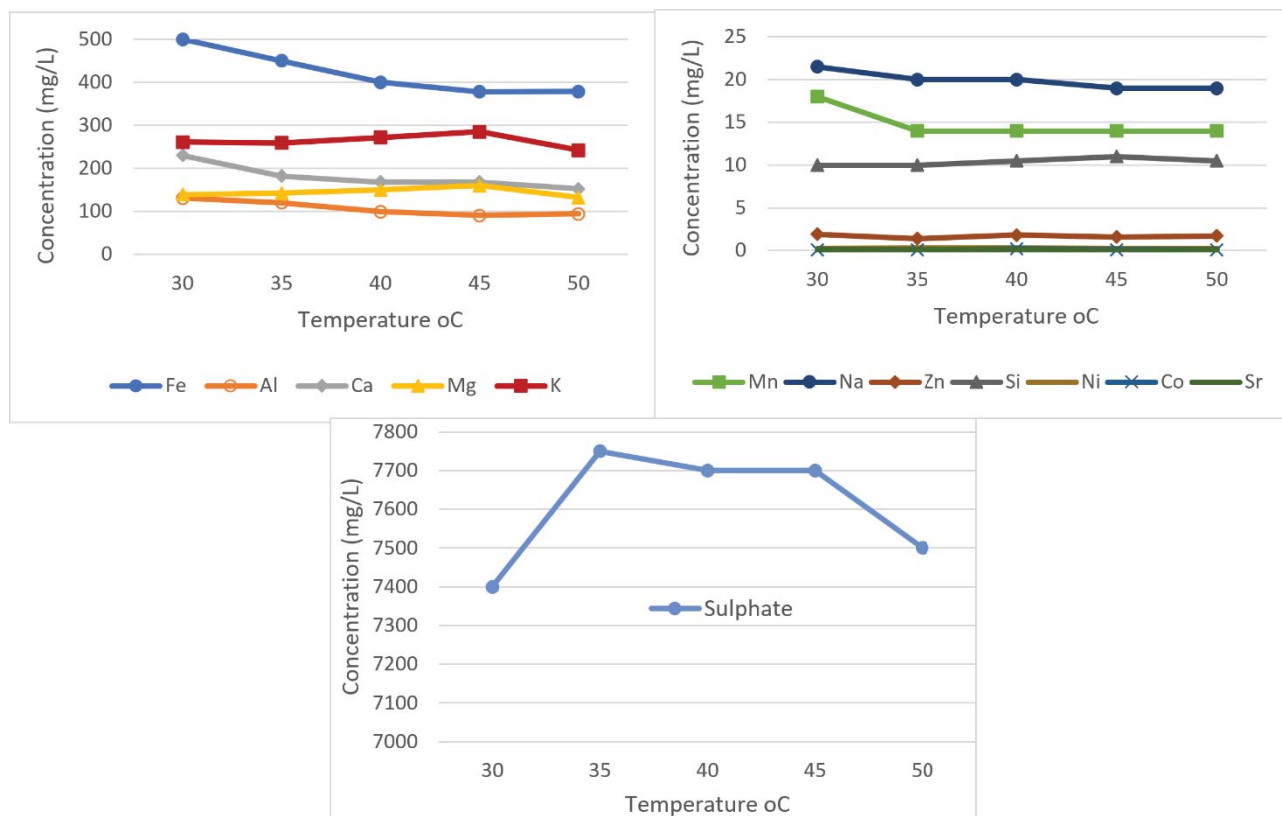


Figure 4-13 Effect of temperature on composition of the supernatant arising from the treatment of AMD Solution P with green tea extract. Dosage of green tea extract 0.5 g/ 50 ml of AMD solution, Time = 24 hours, Agitation speed=200 rpm.

Figure 4-14 shows that the effect of temperature on the extent of extraction of metals and sulphate at a dosage of 0.5 g green tea extract is relatively small, particularly in the case of minor and trace elements. An increase in treatment temperature from 30°C to 50°C results in a slight increase in the extents of extraction of Fe, Mn, Al, Ca, and Na, but a slight decrease in the case of Mg.

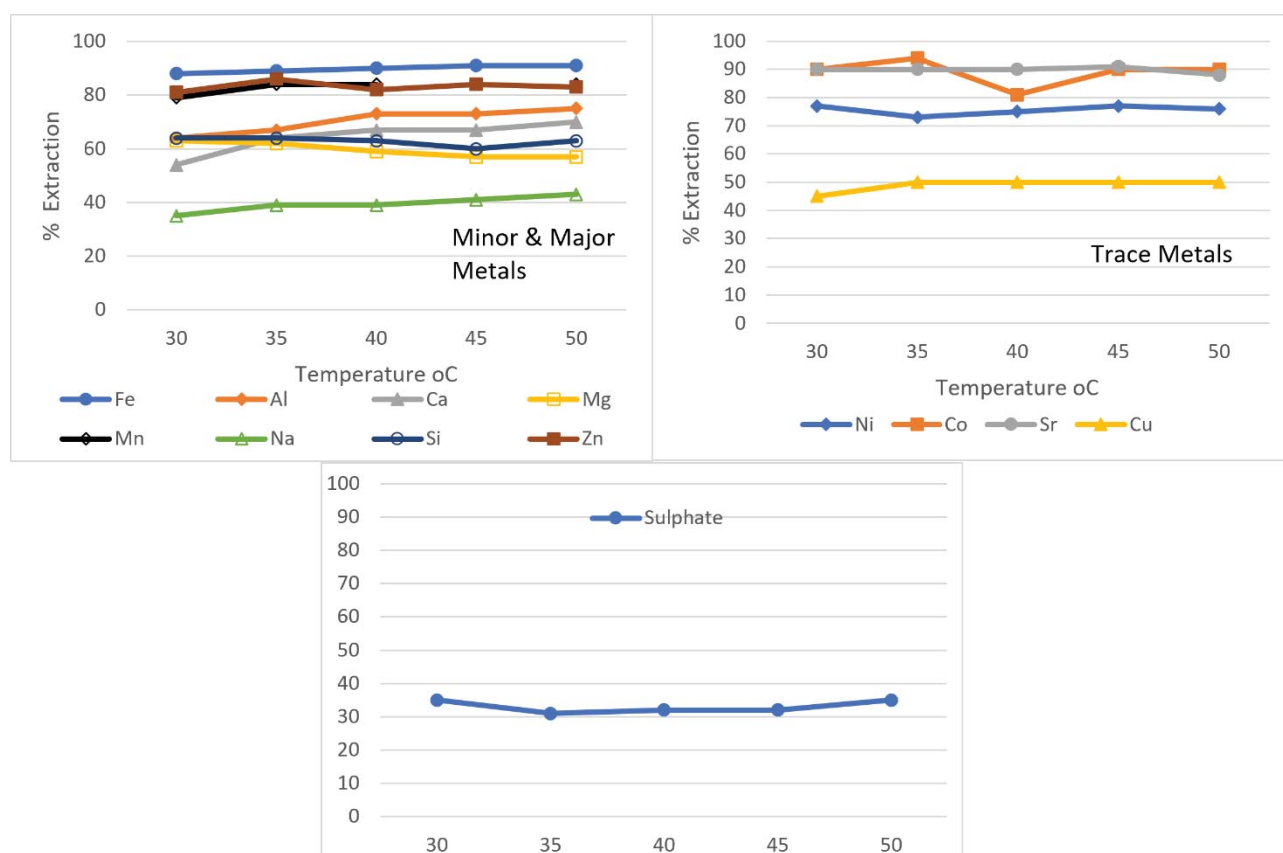


Figure 4-14 Effect of temperature on extent of extraction during treatment of AMD solution P with green tea extract. Dosage of green tea extract 0.5 g/ 50 ml of AMD solution, Time = 24 hours, Agitation speed=200 rpm.

4.4.3 Effect of contact time on metal and sulphate removal from AMD

The effect of changing contact time from 4 hour to 24 hours on the removal of metals and sulphate from AMD solution P was investigated at a green tea extract dosage of 0.5 g / 50 mL. The effect of temperature on the concentration of metals and sulphate in the AMD solution P treated with 0.5 g of green tea extract is presented in Table 4-12 and Figure 4-15.

The results show that the soluble concentrations of most metals, including Fe, Ca, Mg, Al, Mg, Si, Zn and Mn decrease on increasing the retention time from 4 hours to 12 hours, with longer retention times having a negligible effect on the concentrations in the treatment supernatants. Exceptions are Na, the concentration of which continues to increase as the retention time increases in the range 4 hours to 24 hours, and for K, the concentrations of which appears to increase. As in the case of potassium the concentration of sulphate increases from 6489 mg/L to 7329 mg/L on increasing the retention time from 4 hours to 24 hours.

Table 4-13 Effect of retention period on the composition of supernatants from the treatment of AMD solution P with green tea extract (Green tea extract dosage = 0.5 g/50 mL of AMD; Temperature = 35°C)

Parameter	Feed (mg/L)	Concentration of elements (mg/L) from AMD as a function of time					
		4 hrs	8 hrs	12 hrs	16 hrs	20 hrs	24 hrs
Fe	4002	450	375	375	375	375	375
Al	367	183	170	125	120	120	120
Ca	503	230	193	178	178	178	178
Mn	85	34	26	13	13	13	13
Mg	376	207	164	152	148	146	146
Si	28	14	11	11	11	11	11
Cu	0.1	0.07	0.06	0.06	0.05	0.05	0.05
Zn	9.8	4.0	2.0	1.0	1.0	1.0	1.2
Mo	0.1	0.05	0.04	0.04	0.04	0.04	0.04
Ni	1.2	0.5	0.4	0.3	0.3	0.3	0.3
Co	1.1	0.5	0.4	0.3	0.3	0.3	0.3
Sr	0.84	0.3	0.18	0.1	0.09	0.08	0.08
K	ND	236	240	245	245	265	280
Na	33.1	27	27	25	23	20	20
Sulphate	11500	6849	6714	7527	6981	7028	7239

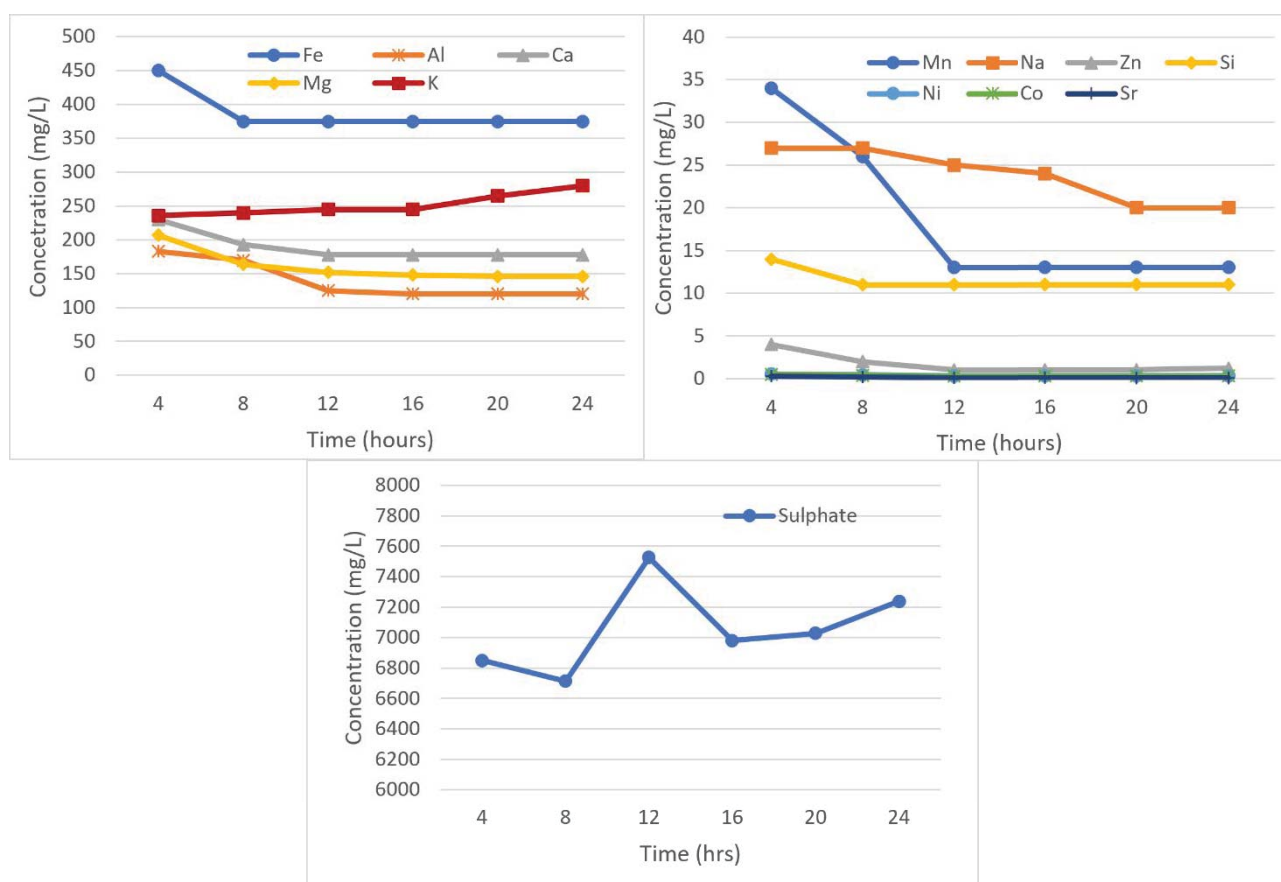


Figure 4-15 Effect of retention time on the composition of the supernatant arising from the treatment of AMD Solution P with green tea extract. Dosage of green tea extract 0.5 g/ 50 mL of AMD solution, Temperature = 35°C, Agitation speed=200 rpm (n = 3).

The effect of retention time on the extent of metal and sulphate extraction when treated with green tea extract at a dosage of 0.5 g / 50 mL is shown in Figure 4-16.

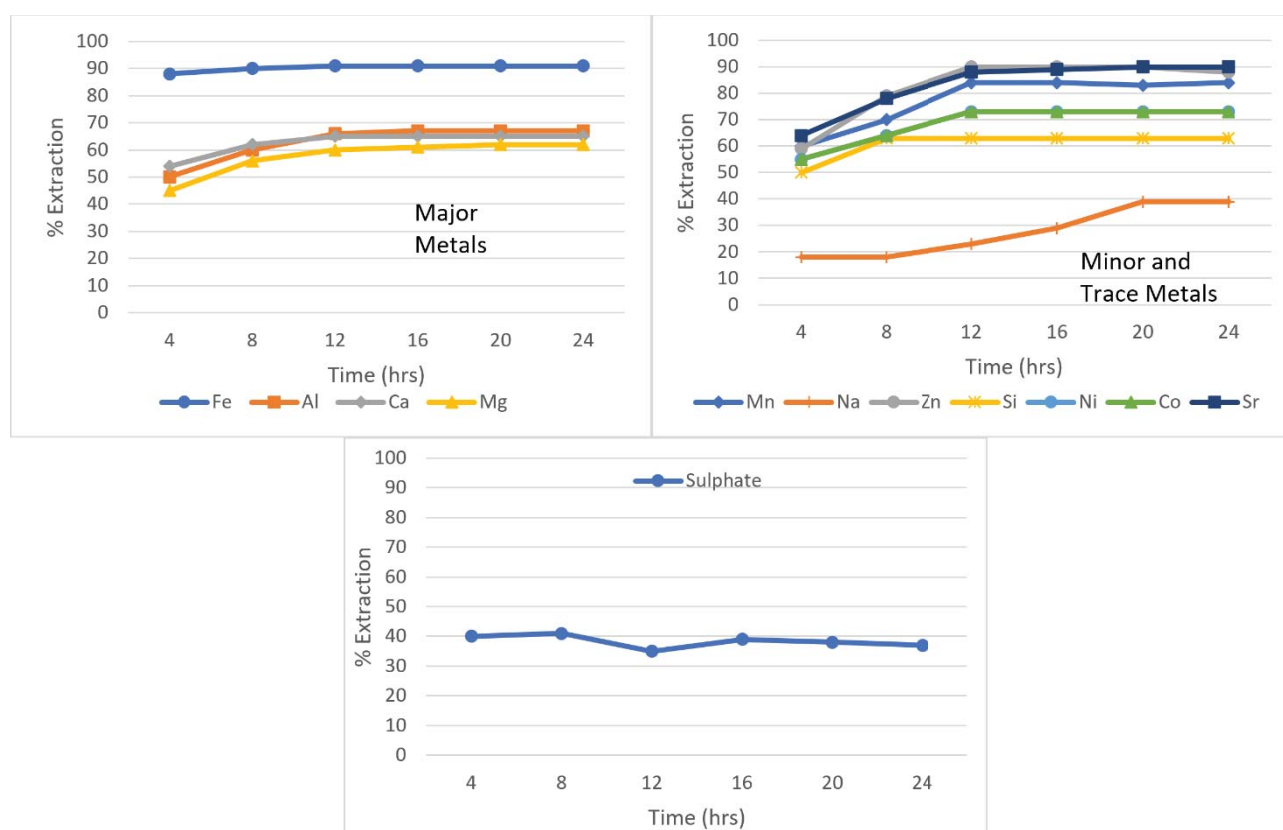


Figure 4-16 Effect of retention time on extent of extraction during treatment of AMD solution P with green tea extract. Dosage of green tea extract 0.5 g/ 50 ml of AMD solution, Temperature = 35°C, Agitation speed=200 rpm.

Consistent with the concentration trends, the results in Figure 4-16 show that in most cases the extraction of metals increases as the retention time increases from 4 hours to 12 hours, with a further increase in the retention period from 12 hours to 24 hours having a negligible effect. An exception is Na, the extraction of which appears to continue to increase over the period 4 to 20 hours. The extraction of Fe, furthermore, appears to be less affected by retention time than other metals, with extraction remaining at 89-91% over the entire time period investigated. This indicates that a purer iron product may be obtained by using shorter retention periods. Similarly, the extraction of sulphate remains relatively constant over the entire time period investigated, with the extent of sulphate extraction varying between 37% and 41%.

4.4.4 Characterisation of nano-iron particles

Green nano-iron particles synthesized from field AMD solution P using 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 g of green tea solutions that corresponds to green tea dosages of 2, 4, 6, 8, 10, 12 and 14 g/L were characterized using ICP-MS, IC, XRD, SEM/EDS, STEM, image J and FTIR analytical techniques.

4.4.4.1 Qualitative X-Ray Diffraction analysis of synthesized nano iron particle

The mineralogy of zerovalent nano-iron particles synthesized from acid mine drainage (AMD P) using green tea as a reductant was characterized by the X-Ray Diffraction technique (XRD) and the results are shown in Figure 4.17. The obtained products were assigned code names (GTNI1, GTNI2, GTNI3, GTNI4, and GTNI5, which are related to the green nano-iron particles synthesized from field AMD P using 0.1, 0.2, 0.3, 0.4 and 0.5 g of green tea solutions, respectively) upon characterization.

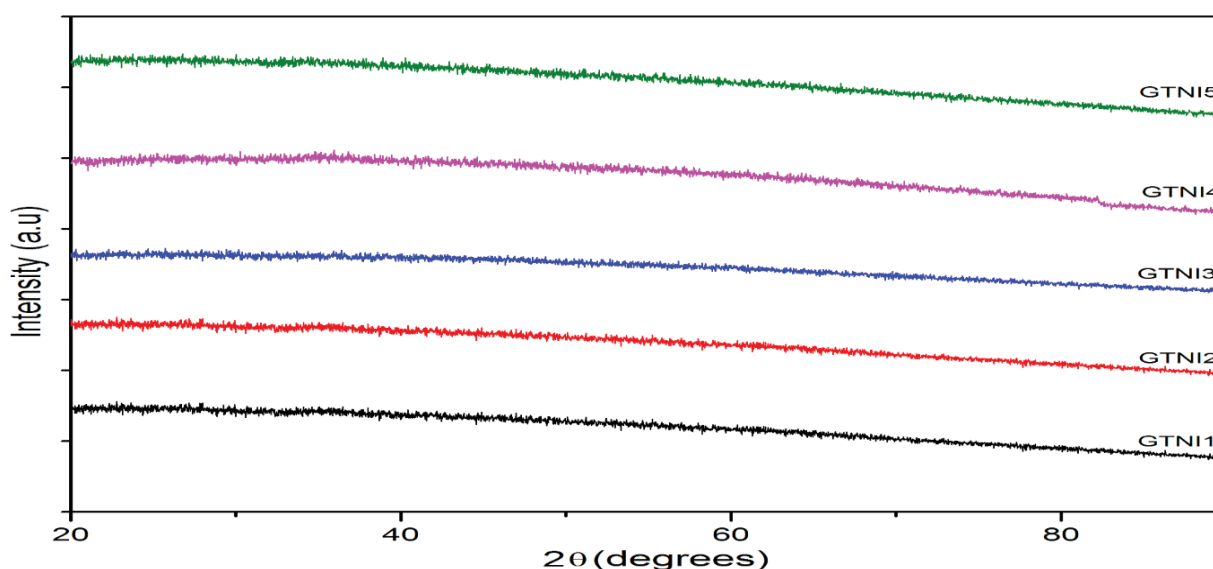


Figure 4-17 Powder X-Ray Diffraction pattern of GTNI1, GTNI2, GTNI3, GTNI4, and GTNI5 of nano-iron particles synthesized from AMD P and GRTE

Figure 4-17 shows the diffraction pattern of nano-iron particles synthesized from AMD P using different dosages of aqueous green tea extract. The crystalline as prepared nano-iron samples obtained from AMD show similar diffraction patterns. No definite diffraction peaks were noticed on the XRD spectra. This indicated that the synthesized AMD based nano-iron particles were so small that peak broadening occurred to the point where they no long-range order could be detected by XRD, giving the appearance of being entirely amorphous. Thus, the synthesized nano-iron particles showed no long-range metallic order, which is typical for very small nanoparticles with high surface to bulk properties. This investigation can be corroborated by the SEM results in Figure 4-4. The insignificant broad hump noticed at $35^\circ 2\theta$ can be ascribed to crystalline FeO mineral phases (Li and Zhang, 2006, K.-S. Lin et al., 2008; Lu et al., 2007, Sun et al., 2006)

4.4.4.2 Fourier Transform infrared spectroscopy (FTIR)

The structural analysis of the synthesized nano-iron particles from AMD P with assigned code names GTNI, GTNI2, GTNI3, GTNI4, and GTNI5 are presented in Figure 4-18.

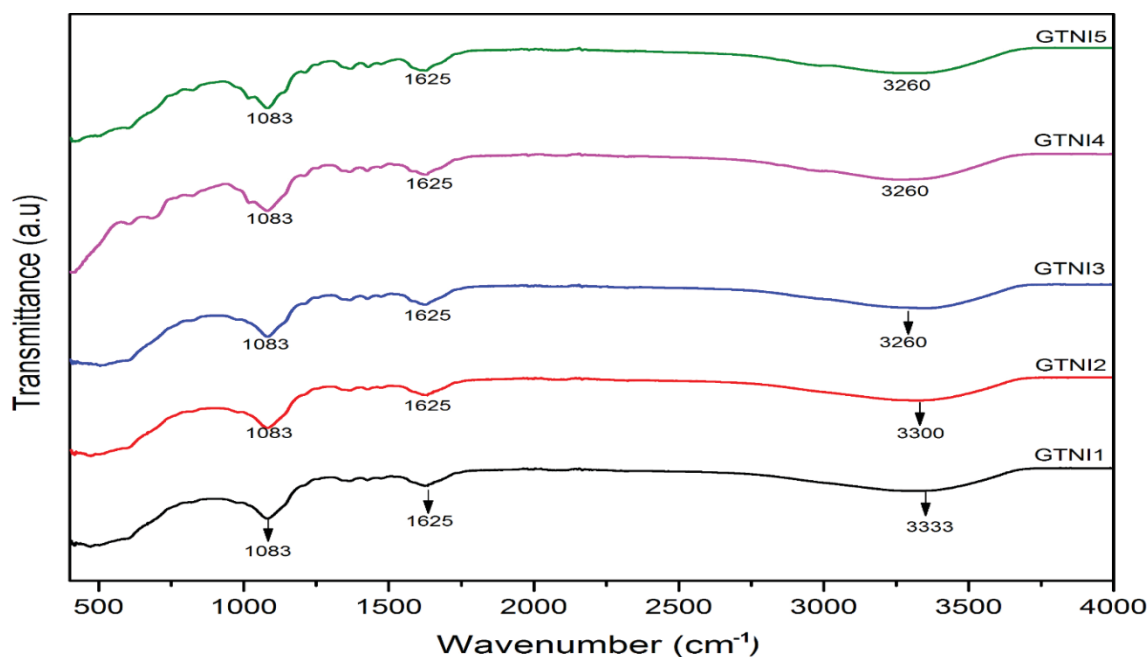


Figure 4-18 FTIR transmittance spectra of synthesized nano-iron particles from AMD P with assigned code names GTNI1, GTNI2, GTNI3, GTNI4,

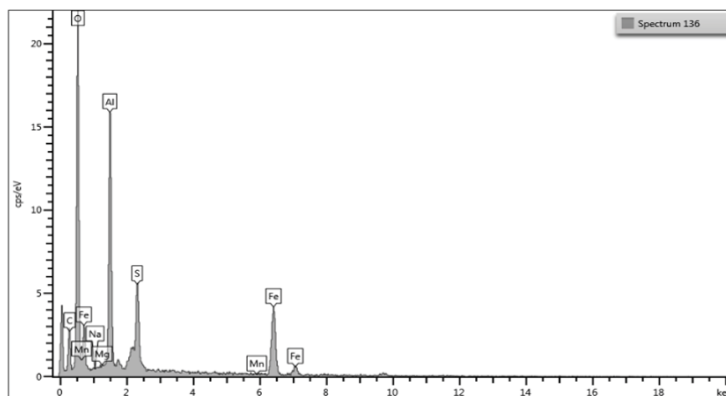
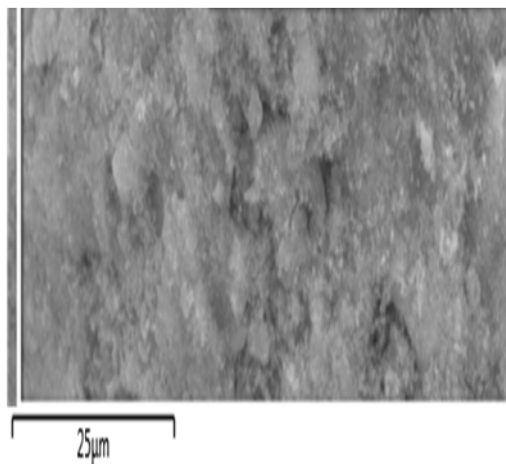
Vibrations of polyphenolic compounds were noticed across all the spectra. The OH stretching vibration were noticed at 3000 to 3333 cm^{-1} on all the samples. The broad OH spectrum indicates the contribution of benzylic OH from the polyphenolic content of the plant extract (Ashokkumar and Ramaswamy, 2014) Liu & Zhang, 2014). The less prominent peak on the spectra indicates the vibrations of aromatics and moisture from air. The second most pronounced peak at 1625 cm^{-1} on the sample's spectra could be assigned to aromatic skeletal vibrations. This indicates the binding of polyphenolic compounds to the active surfaces of the AMD based nano-iron particles and suggested the presence of aromatic compounds (Badmus et al., 2018). Its intensity confirms the presence of Fe-O complex as previously reported by (Sathishkumar et al., 2018, Z. Wang, 2013). In this line of investigation, the asymmetric, symmetric and C-O stretching peaks noticed at 1200, 1392, and 1082 respectively were present on all the coded samples. The carbonyl sugar base of the tea extract acts as a surface modifier of the synthesized nano-iron particles that prevents agglomeration and in its right proportion enhances the catalytic activity of the nano-iron.

4.4.4.3 Scanning Electronic Microscope (SEM) morphological analysis of precipitates generated using green tea extract

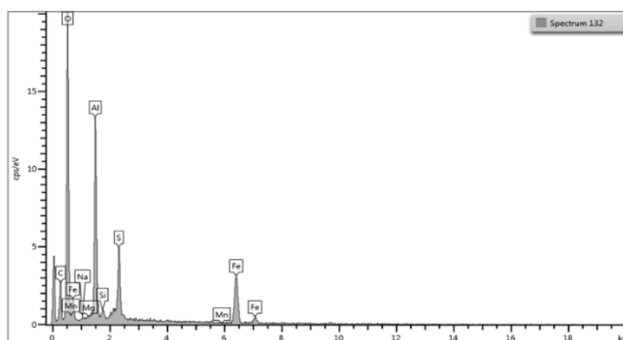
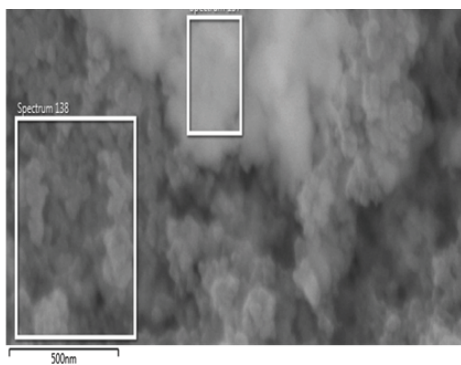
This section presents and discusses the morphology of the precipitates formed because of the reaction between green tea extract and AMD P. It also presents the elemental composition of the formed precipitates.

The surface morphology and elemental composition of GTNI1, GTNI2, GTNI3, GTNI4, and GTNI5 generated from AMD P using various green tea dosages are presented in Figure 4-19 and Table 4-13. It could be noticed that the nano-iron particles generated from different green tea dosages, yielded amorphous shaped particles. These particles differ in their average particle sizes as corroborated by their corresponding TEM images and particle size measurement. The amorphous structure of the nano-iron particles generated in this study is due to the phenolic extracts that coated the iron particulates and are in line with the morphology of nano-iron particles synthesized using tea extract.

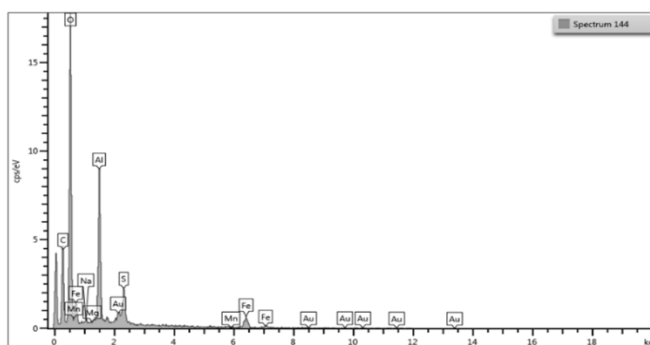
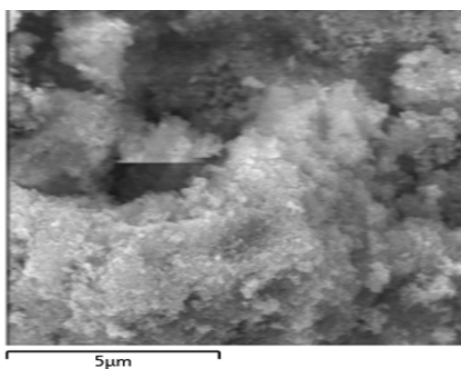
The elemental composition conducted on GTNI1-GTNI5 showed that the optimum recovery of nano-iron from AMD P was recorded at a dosage of 0.4 g of green tea extract where 36.39 weight % of nano-iron was recorded. IC and ICP analysis will support this result



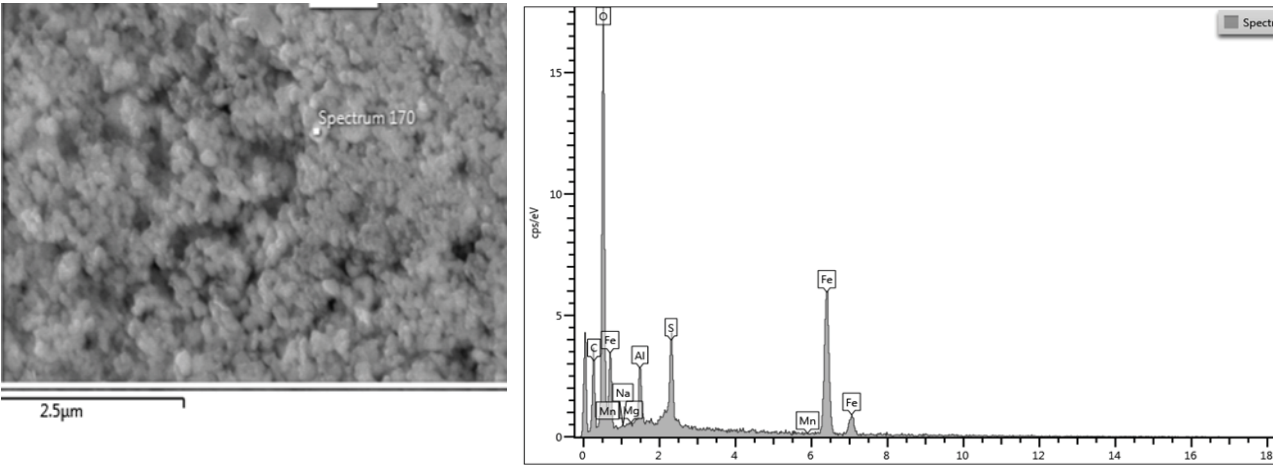
GTNI 1



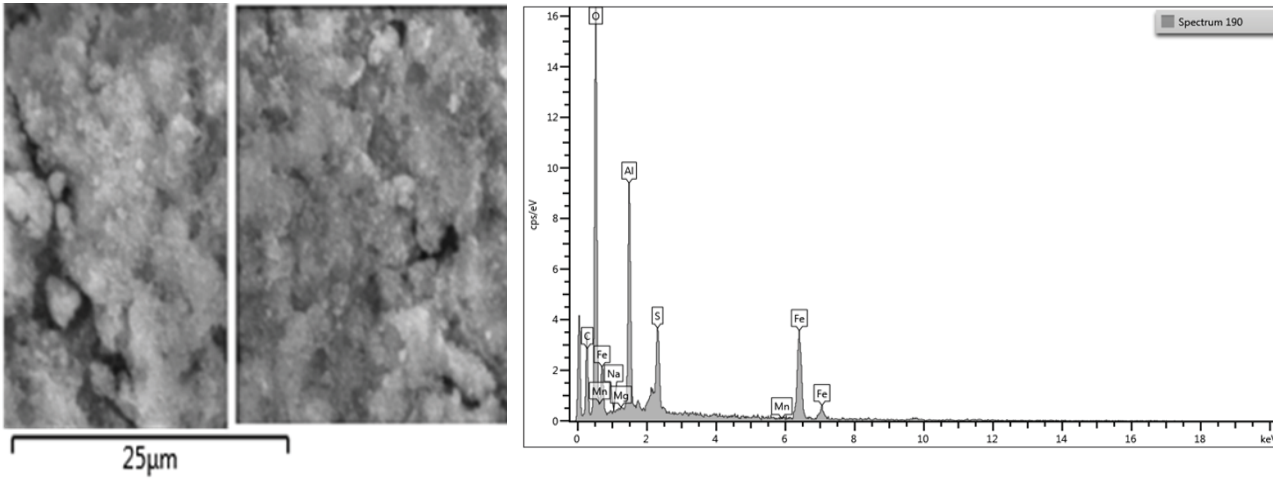
GTNI 2



GTNI 3



GTNI 4



GTNI 5

Figure 4-19 SEM micrographs and EDS spectra of GTNI 1-5

Table 4-14 EDS analysis of nano-iron particles (GTNI 1-5) synthesized from AMD using green tea extract (varying dosages)

Element	% Atomic wt.	Std Dev	Element	% Atomic wt.	Std Dev
C	17.5	1.07	C	16.5	1.07
O	53.4	2.58	O	50.4	2.58
Al	15.1	1.74	Al	12.39	1.74
Si	0.37	0.03	Si	0.43	0.03
S	3.38	0.08	S	0.38	0.08
Fe	9.32	0.89	Fe	15.2	0.89
GTNI 1			GTNI 2		
Element	% Atomic wt.	Std Dev	Element	% Atomic wt.	Std Dev
C	49.6	1.61	C	16.4	0.21
O	8.43	1.61	O	40.0	0.47
Al	6.43	0.51	Al	2.63	0.07
Si	0.20	0.32	S	4.49	0.21
S	2.10	0.13	Fe	36.4	1.07
Fe	14.9	0.60	GTNI 4		
GTNI 3			Element	% Atomic wt.	Std Dev
Element	% Atomic wt.	Std Dev	C	20.0	2.98
C	20.0	2.98	O	47.4	2.91
O	47.4	2.91	Al	8.02	1.55
Al	8.02	1.55	Si	0.11	0.14
Si	0.11	0.14	P	0.21	28
P	0.21	28	S	3.45	0.75
S	3.45	0.75	Ca	0.12	0.12
Ca	0.12	0.12	Fe	20.8	2.23
Fe	20.8	2.23	GTNI 5		
GTNI 5					

4.4.4.4 *Transmission Electron Microscopy (TEM) morphological analysis of nano-iron particles generated using green tea extract.*

The particle size, morphology and crystallinity of the synthesized AMD based nano-iron particles were further confirmed using STEM analysis and the results at various dosages of green tea extract are presented in Figure 4-20.

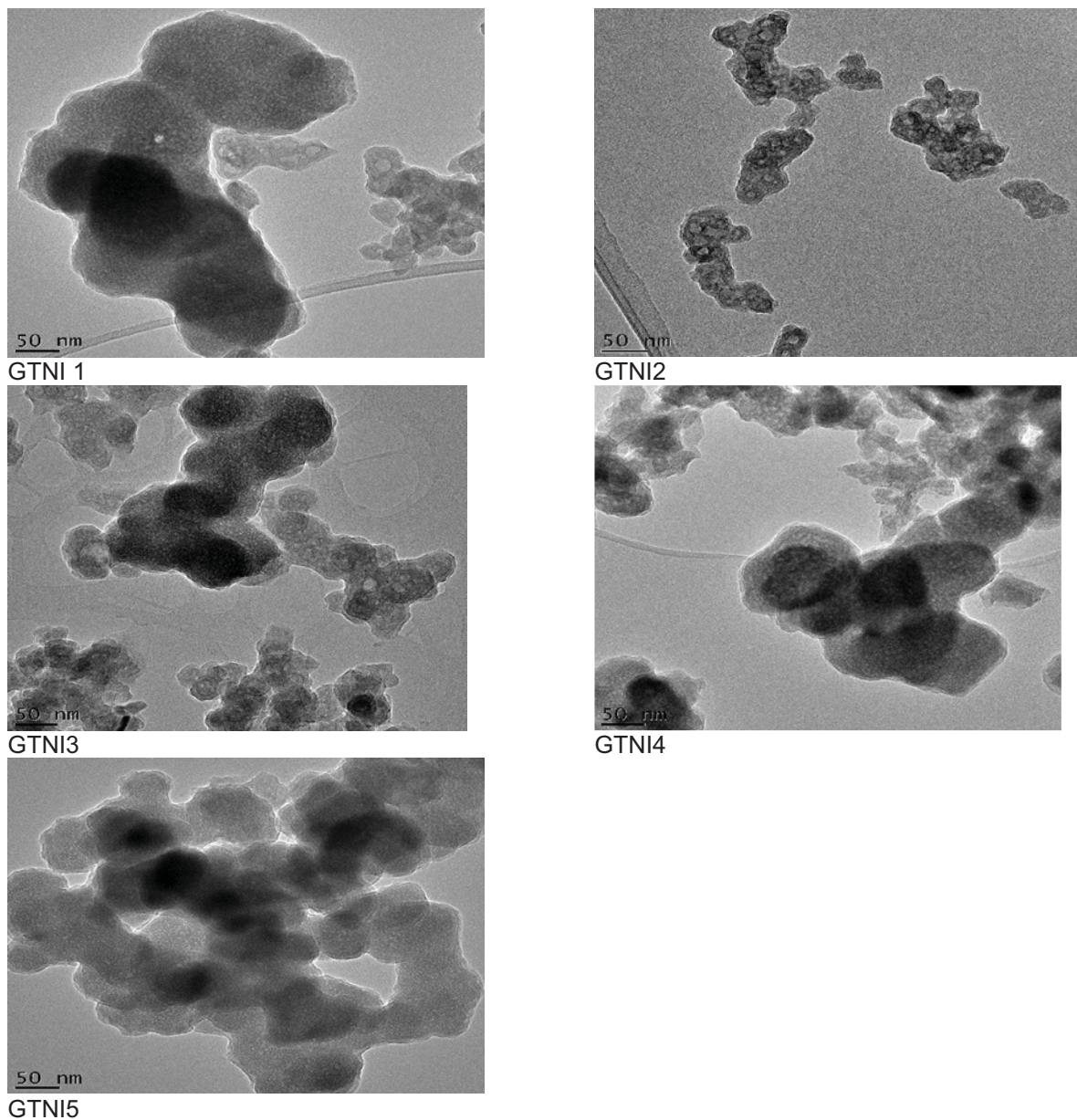


Figure 4-20 TEM micrographs (GTNI) of GTNI1, GTNI2, GTNI3, GTNI4, or GTNI5 nano-iron particles synthesized from AMD using green tea extract (varying dosages) .

Thereafter, the particles sizes of the nano-iron were measured from each STEM image, and a corresponding histogram plot was constructed for each STEM data. This was to determine their particle size distribution and average particle size (Figure 4-21).

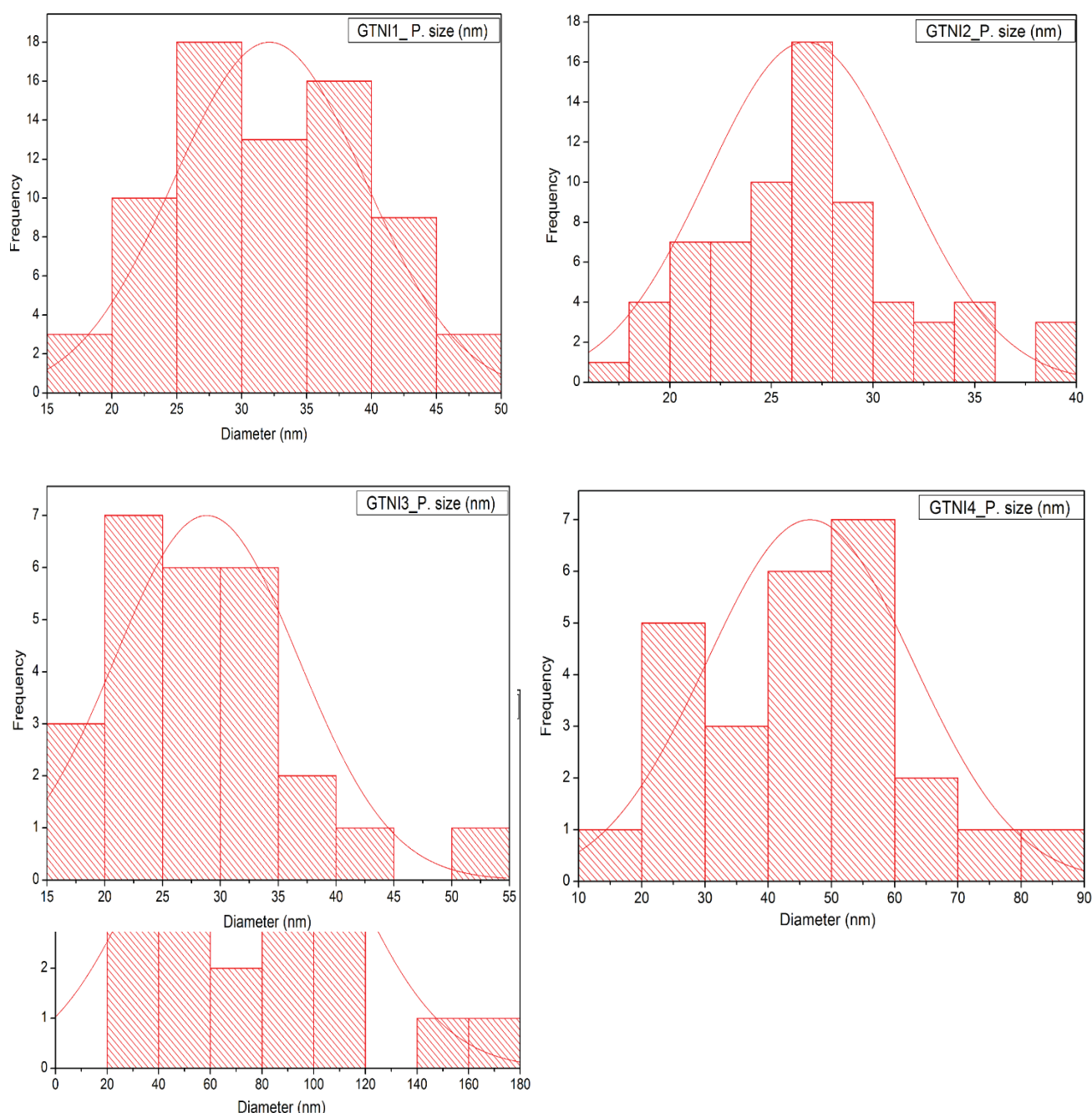


Figure 4-21 Crystal size distribution of nano-iron particles (GTNI1, GTNI2, GTNI3, GTNI4, and GTNI5) synthesised from AMD sample P with green tea

Graphical representation of the size distribution of nano-iron particles from field AMD could be seen in Figure 4-21. It was noticed that the average particle sizes for GTNI1, GTNI2, GTNI3, GTNI4 and GTNI5 were approximately 32 nm, 27 nm, 39 nm, 45 nm, and 55 nm, respectively. Their average particle size increased with an increase in green tea dosage during synthesis except for GTNI2 that decreased with an increase in green tea dosage from 0.1 to 0.2 g.

4.5 Summary

The comparison of the nano iron particles prepared from sodium borohydride with the nano iron particles prepared with tea extracts shows that the sodium borohydride chemical reductant is a straightforward way to

extract the iron from the AMD solutions and form nanoparticles. Its FRAP strength was considerably higher than the tea extracts making it much more effective for preparing the nano iron particles. However, the particle sizes were larger than those prepared with the tea extracts, with borohydride reduced nanoparticles being up to 160 nm whereas the tea extract nanoparticle sizes were in the range of 27-55 nm. This size difference was evident from the XRD spectra as well, with the borohydride displaying some bulk metal long range crystallite ordering whereas the nanoparticles made from the tea had no long-range metal ordering and appeared amorphous. The EDS results showed that nano iron particles prepared using borohydride had a high Fe content between 81-92 wt. % but other elements present in AMD were co-precipitated with the iron. Whereas when the tea extracts were used, the nanoparticles were coated by the polyphenols as could be deduced from the high carbon content shown by EDS and the relatively lower iron content which ranged from 9-36 weight % depending on the extract dosage applied. The FTIR results confirmed that the borohydride reduced nano iron was not fully in a zero valent form, whereas in the case of the plant extracts, the spectral bands from the polyphenols were evident, acting as a surface modifier of the synthesized nano-iron particles that prevents agglomeration.

CHAPTER 5: NEUTRALISATION OF AMD

Neutralisation tests were conducted on field AMD sample P, both before and after pre-treatment with sodium borohydride and green tea extract, using hydrated lime to assess the effect of lime dosage and pH on the removal of metals and salts and the characteristics of the sludges formed.

5.1 Lime neutralisation of AMD solution P before treatment

This section represents the results of the lime neutralisation of the Raw AMD solution P.

5.1.1 pH and redox potential profile

The effect of the 11 and 12 g/L of lime upon pH and redox potential trends in the neutralisation of AMD over time is presented in Figure 5-1.

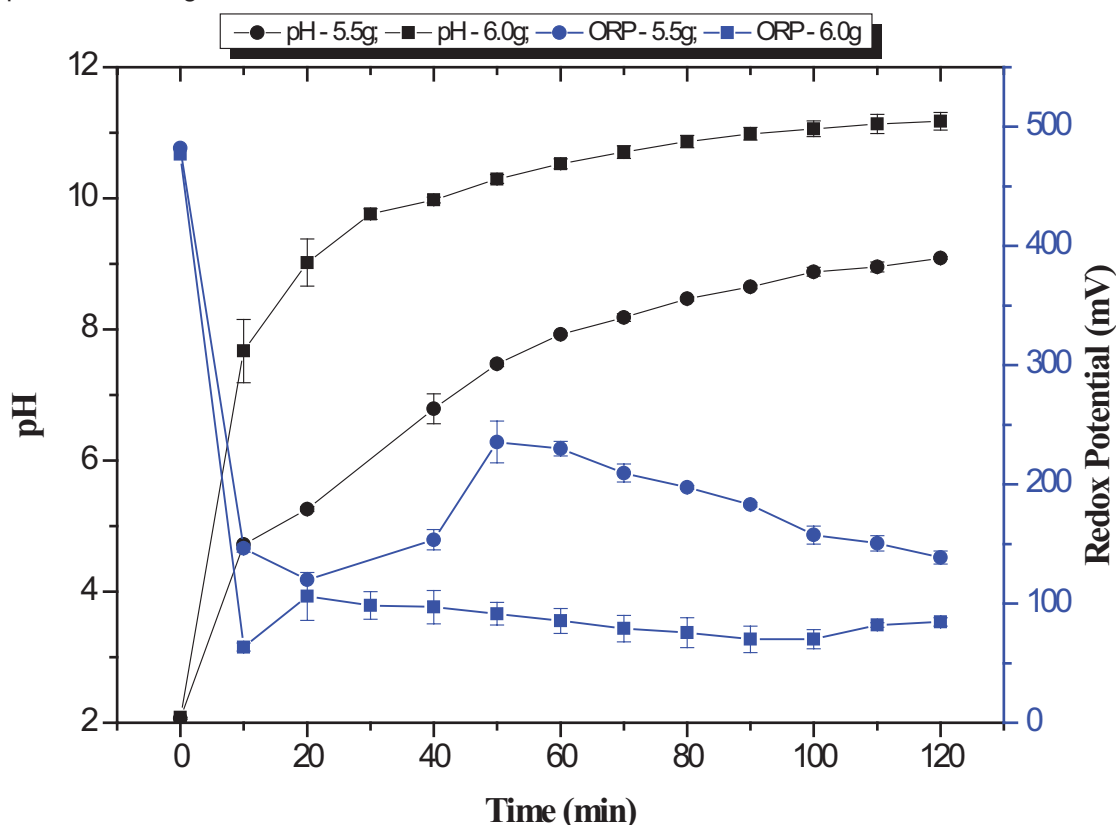


Figure 5-1 pH and redox potential (ORP) of untreated AMD solution P after neutralisation with 11 g/L (■) and 12 g/L (●) of lime

The trends in Figure 5-1 show that pH increases rapidly from the initial value of 2.1 in the first 30 minutes and then more gradually from 30 to 120 minutes. A maximum average pH of 9.1 and 11.2 was obtained after 120 minutes at lime additions of 5.5 g (11 g/L) and 6 g (12 g/L) respectively. The redox potential shows a significant decline from an average of 483 and 477 mV to 147 and 64 mV after 10 minutes of treatment of 500 mL AMD with 5.5 g and 6 g of lime respectively. The redox potential continued to fluctuate before settling at values of 146 mV and 85 mV after 120 minutes at lime additions of 5.5 g and 6 g respectively.

5.1.2 Composition of the neutralisation effluents

The compositions of the effluent obtained from the neutralisation of 500 ml of AMD solution P with 5.5 g (11 g/l) and 6 g (12 g/l) lime are presented in Table 5-1, and the extent of removal of selected components through precipitation presented in Figure 5-2.

Table 5-1 Composition of effluent from the neutralisation of untreated AMD solution P with lime to pH 9.1 (11 g/L lime) and pH 11.2 (12 g/L lime). t= 120 minutes

Parameters	Units	Raw AMD	Neutralisation effluent concentrations as a function of lime dosage (mg/L)	
			11 g/L lime	12 g/L lime
<u>Anions</u>				
Sulphate	mg/L	1150	2790	1730
Nitrate	mg/L	2.13	ND	ND
Chloride	mg/L	10.2	ND	ND
<u>Major Metals</u>				
Fe	mg/L	4003	0.02	0.04
Ca	mg/L	495	560	580
Mg	mg/L	433	226	1.14
Al	mg/L	388	0.48	2.23
Mn	mg/L	83.2	0.30	0.04
K	mg/L	0.98	2.20	2.82
<u>Minor metals</u>				
Na	mg/L	48.8	47.5	54.6
Si	mg/L	46.6	0.40	0.30
Zn	mg/L	9.50	BDL	BDL
<u>Trace elements</u>				
As	mg/L	0.03	BDL	BDL
B	mg/L	0.40	BDL	BDL
Ba	mg/L	0.16	0.00	0.00
Cd	mg/L	0.01	0.00	0.00
Co	mg/L	1.07	BDL	BDL
Cr	mg/L	0.05	BDL	BDL
Cu	mg/L	0.08	BDL	BDL
Hg	mg/L	0.00	BDL	BDL
Mo	mg/L	0.00	BDL	BDL
Ni	mg/L	1.07	BDL	BDL
Pb	mg/L	0.02	BDL	BDL
Sb	mg/L	0.00	0.00	0.00
Sr	mg/L	0.64	0.69	0.63
Se	mg/L	0.00	BDL	BDL
Sn	mg/L	0.00	0.00	0.00
V	mg/L	0.04	BDL	BDL

Where: ND = not determined; BDL = below detection limits

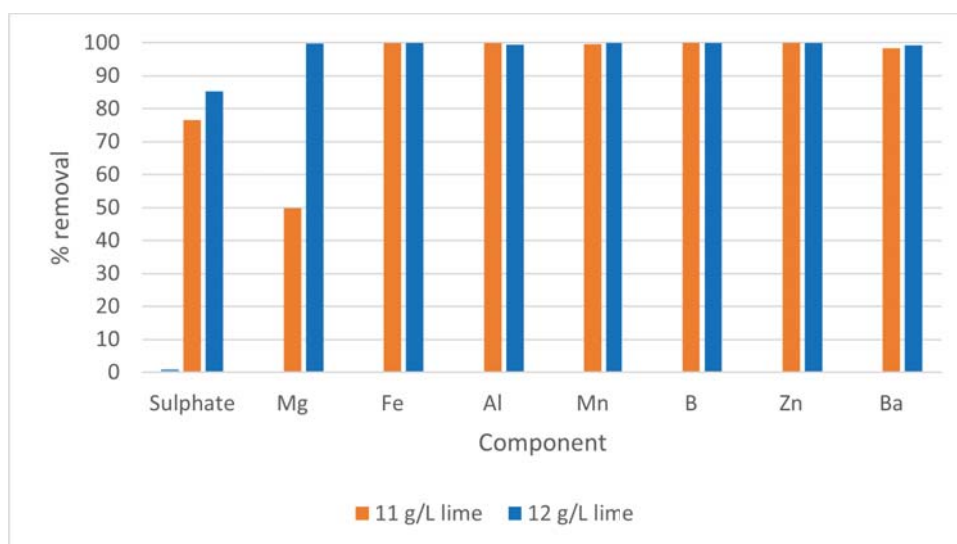


Figure 5-2 Extent of removal of components from untreated AMD solution P after treatment with lime to pH 9.1 (11 g/L lime) and pH 11.2 (12 g/L lime)

The results indicate that neutralisation with lime to pH 9.1 (11 g/l lime dosage), resulted in >99% removal of metals Fe, Al, Mn, and Ba, but only partial removal of Mg (50%) and sulphate (77%) and negligible removal of Na. The effluent solution comprised mainly of residual sulphate (2788 mg/l), Ca (560 mg/l), Mg (226 mg/l) and Na (48 mg/l), with traces of K (2.2 mg/l) and < 0.5 mg/l Al, Mn, and Si. The addition of further lime (12 g/L) to increase the pH to 11.2 enhanced the removal of Mg to >99% and sulphate removal to 85%, resulting in corresponding effluent concentrations of 1.14 mg/l and 1728 mg/l respectively. Raising the pH also resulted in slightly lower effluent Mn concentrations (0.04 mg/l) but higher soluble Al concentrations (2.82 mg/l). In both cases, neutralisation with lime resulted in an increase in the concentration of soluble K (2-3 mg/l) in comparison to the feed AMD (1 mg/l). This increase can be attributed to the presence of K in the hydrated lime (≤ 500 ppm). Both effluents also contained slightly higher concentrations of Ca (560-580 mg/l) than the feed AMD solution (~ 500 mg/l). Mass balances calculations indicated that between 90% and 91% of the total initial Ca (including the Ca added as lime and the Ca in the AMD feed) was removed in the form of precipitates during neutralisation.

5.1.3 Composition of the neutralisation residues

Neutralisation of 500 ml AMD solution P with 5.5 g and 6 g lime resulted in the formation of 14.2 g (28.4 g/L) and 14.9 g (29.8 g/L) of total precipitate formation respectively. The compositions of the residues obtained from the neutralisation of 500 ml of AMD solution P with 5.5 g (11 g/L) and 6 g (12 g/L) lime are presented in Table 5-2.

The results in Table 5-2 indicate that the residues at both pH values are comprised predominantly of sulphate ($\sim 38\%$), calcium (16-17%) and iron (11-13%), with lesser amounts of Al (1.3%), Mg (0.9-1.4%) and traces of Si (0.1-0.3%), Mn (0.2-0.3%) and Na (0.1-0.2%). Qualitative XRD analysis of neutralisation residues prepared over a range of lime additions and pH values show the predominance of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). In residues prepared at pH >5, with evidence of the iron oxyhydroxide, goethite (FeOOH), and, at pH values ≥ 12 , ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$). If all the precipitated sulphate in the two residues presented in Table 5-2 is present as gypsum and the iron as amorphous ferric hydroxide ($\text{Fe}(\text{OH})_3$), this would equate to concentrations of approximately 67% gypsum and 22-24% ferric hydroxide. Parity calculations indicate that the remaining 9-11% of the residue is likely to be made up of hydroxides of Al ($\text{Al}(\text{OH})_3$, at approximately 3.7%), Mg ($\text{Mg}(\text{OH})_2$, at approximately 3.5% and 4.3% at 11 g/L and 12 g/L lime addition respectively), and possibly calcite (CaCO_3),

at approximately 1.4% and 3.7% at 11 g/L and 12 g/L lime addition respectively. The residue is also likely to contain traces of $\text{Mn}(\text{OH})_2$ (~ 0.4%) and amorphous SiO_2 (0.4-0.5%).

Table 5-2 Composition of residue from the neutralisation of untreated AMD solution P with lime to pH 9.1 (11 g/L lime) and pH 11.2 (12 g/L lime). $t=120$ minutes

Component	Residue concentration (%)	
	11 g/L lime (pH 9.1)	12 g/L lime (pH 11.2)
Sulphate	37.9	37.7
Ca	16.3	17.1
Fe	12.5	11.2
Al	1.31	1.30
Mn	0.26	0.23
Mg	0.85	1.40
Si	0.12	0.25
K	0.00	0.00
Na	0.20	0.14

5.2 Lime neutralisation of AMD solutions after nano iron removal using sodium borohydride

This section presents and discusses the neutralisation of AMD after the extraction of iron using sodium borohydride.

5.2.1 pH and redox potential profile

Figure 5-3 shows the pH and redox potential profiles reading of the neutralisation of the supernatant obtained after treatment of AMD solution P with sodium borohydride.

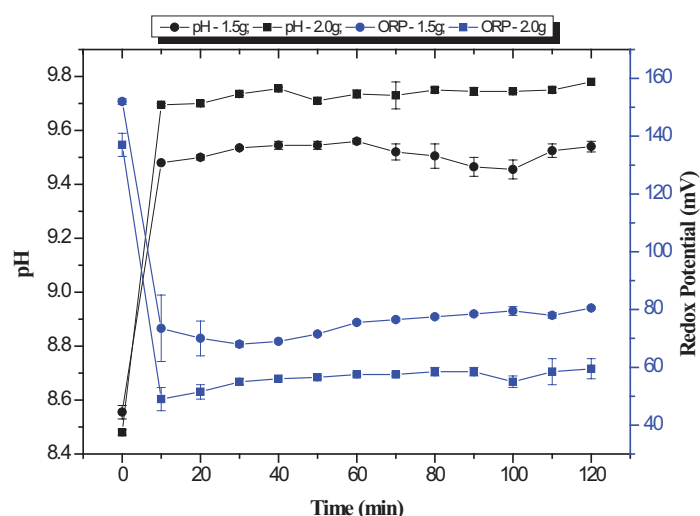


Figure 5-3 pH and redox potential (ORP) of 250 mL supernatant (obtained after treatment with sodium borohydride) after neutralisation with 6 g/L (●) and 8 g/L (■) of lime, respectively.

The results in Figure 5-3 show that upon the addition of 1.5 g (6 g/L) lime to the supernatant, the initial pH of 8.6 increase to 9.5 within the first 10 minutes and remain relatively stable over the entire 120-minute period. A similar trend is observed for the addition of 2 g (8 g/L) lime, with the pH increasing to a value of 9.7 within 10 minutes, and then gradually increasing to 9.8 over the 2 hour retention period. .

In the case of 1.5 g (6 g/L) lime addition, redox potentials drop from initial values of 152 mV to 74 mV in the first 10 minutes, with the redox potential gradually increasing to between 81 mV over the 120 minute retention period. Similar trends were observed at 2 g (8 g/L) lime addition with the redox potential dropping from an initial value of 137 mV to 49 mV, before gradually increasing to 60 mV.

5.2.2 Composition of the neutralisation effluents

The compositions of the effluent obtained from the neutralisation of 250 ml of supernatant, pre-treated with sodium borohydride, with 1.5 g (6 g/L) and 2 g (8 g/L) lime are presented in Table 5-3, and the extent of removal of selected components through precipitation presented in Figure 5-4.

Consistent with previous tests (See Chapter 4), treatment of the raw AMD solution with sodium borohydride results in > 99% removal of Fe along with Al, Zn and Ba, as well as partial removal of Mn (72%), Ca (37%) and Mg (22%). Sodium borohydride treatment also results in 9.5% sulphate removal from solution. The supernatant from the sodium borohydride treatment has a pH of 8.5 and contains major quantities of sulphate (10.4 g/L), Na (5 g/L) and B (2 g/L), minor quantities of Ca (313 mg/L), Mg (338 mg/L) and Mn (24 mg/L), as well as trace quantities of K (6 mg/L), Si (4 mg/L) and Al (0.5 mg/L).

As indicated in Figure 5-4, subsequent neutralisation of the pre-treated supernatant results in further removal of Fe (35% and 100% at 1.5 g and 2 g lime respectively), Al (24% and 69% at 1.5 g and 2 g lime addition respectively), Mn (52% and 75% at 1.5 g and 2 g lime respectively), Mg (0.2% and 35% at 1.5 g and 2 g lime respectively), sulphate (7% and 13% at 6 g/L and 8 g/L lime respectively), as well as partial removal of B (26% and 42% at 6 g/L and 8 g/L lime respectively). In all cases, the extent of removal increases on increasing the lime dosage from 6 g/L to 8 g/L, with corresponding lower concentrations in the treated effluent. Nevertheless, the effluent solutions still contains elevated concentrations of sulphate (10.7 g/L and 10.8 g/L at 1.5 g and 2 g lime respectively), Na (5.9 g/L and 5.2 g/L at 6 g/L and 8 g/L lime respectively), B (1.7 g/L and 1.3 g/L at 1.5 g and 2 g lime respectively) and Ca (1.3 g/L and 1.1 g/L at 6 g/L and 8 g/L lime respectively), as well as minor quantities of Mg (347 mg/L and 280 mg/L at 6 g/L and 8 g/L lime respectively) and Mn (11.3 mg/L and 5.8 mg/L at 6 g/L and 8 g/L lime respectively). Neutralisation of the supernatant from sodium borohydride treatment results in an increase in both the calcium and potassium concentrations relative to the feed supernatant, with mass balance calculations indicating that approximately 63% and 86% of the total initial Ca (including the Ca added as lime and the Ca in the pre-treated supernatant) is removed in the form of precipitates during neutralisation at 6 g/L and 8 g/L lime addition respectively. The relatively high concentration of Ca in solution could possibly be due to the formation of the calcium borate ion $[\text{CaB}(\text{OH})_4]^+$ which is reported to form in alkaline solutions of Ca and B (Tsai and Lo, 2015). Complex formation stabilises ions in solution, retarding precipitate formation.

Table 5-3 Neutralisation of AMD pre-treated with sodium borohydride solution to pH 9.2 (6 g/L lime) and 9.8 (8 g/L lime): Composition of neutralisation effluent (t=120 minutes)

Parameters	Units	Raw AMD	Treatment Supernatant	Neutralisation effluent concentration as a function of lime dosage	
				6 g/L lime	8 g/L lime
<u>Anions</u>					
Sulphate	mg/L	11500	10400	10700	10800
Nitrate	mg/L	2.13	ND	ND	ND
Chloride	mg/L	10.2	ND	ND	NA
<u>Major Metals</u>					
Fe	mg/L	4003	0.06	0.04	BDL
Ca	mg/L	495	313	1254	1144
Mg	mg/L	433	338	347	280
Al	mg/L	388	0.53	0.41	0.16
Mn	mg/L	83.2	23.6	11.5	5.76
K	mg/L	0.98	5.93	8.55	7.33
<u>Minor metals</u>					
Na	mg/L	48.8	5005	5805	5177
Si	mg/L	46.6	4.03	0.78	0.28
Zn	mg/L	9.47	0.00	0.01	0.00
<u>Trace elements</u>					
As	mg/L	0.03	0.00	0.00	0.00
B	mg/L	0.40	2194	1664	1262.25
Ba	mg/L	0.16	0.00	0.00	0.00
Cd	mg/L	0.01	BDL	BDL	BDL
Co	mg/L	1.07	BDL	BDL	BDL
Cr	mg/L	0.05	BDL	0.01	0.02
Cu	mg/L	0.08	BDL	0.01	BDL
Hg	mg/L	0.00	0.00	0.00	0.00
Mo	mg/L	0.00	BDL	0.02	0.00
Ni	mg/L	1.07	0.01	0.14	0.00
Pb	mg/L	0.02	BDL	BDL	BDL
Sb	mg/L	0.00	0.00	0.00	0.00
Sr	mg/L	0.64	0.37	0.53	0.47
Se	mg/L	0.00	0.00	0.00	0.00
Sn	mg/L	0.00	BDL	BDL	BDL
V	mg/L	0.04	0.00	0.00	0.00

Where ND=not determined and BDL=below detection limit

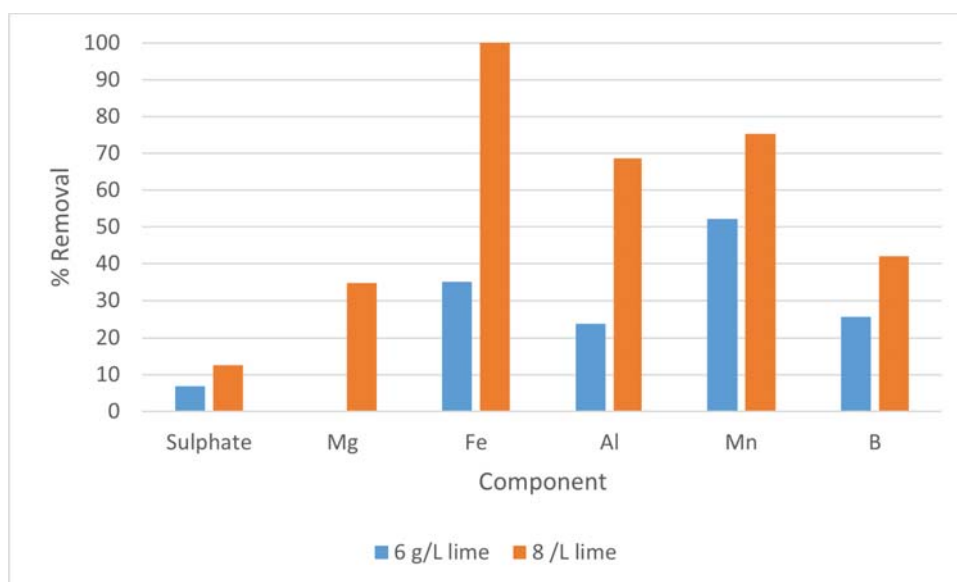


Figure 5-4 Extent of removal of components during neutralisation of pre-treated (sodium borohydride) AMD solution P with lime to pH 9.2 (6 g/L lime) and pH 9.8 (8 g/L lime). $t = 120$ minutes

The net removal of elements from the raw AMD solution P through sodium borohydride and subsequent neutralisation with lime is presented in Figure 5-5.

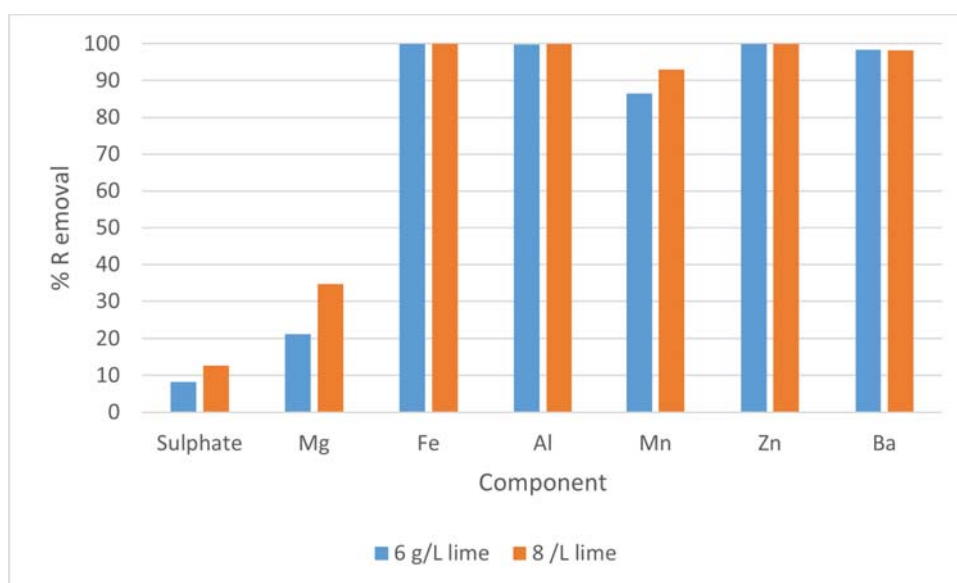


Figure 5-5 Overall extent of removal of components during sodium borohydride pre-treatment and subsequent neutralisation of 250 ml AMD solution P with lime to pH 9.2 (6 g/L lime) and pH 9.8 (8 g/L lime). $t = 120$ minutes

Overall, treatment of the AMD solution P with sodium borohydride and lime (to pH values < 10) results in > 99.9% removal of Fe, Al, and Zn, as well as significant removal of Ba (>98%) and Mn (86% and 93% at lime addition of 6 g/L and 8 g/L respectively). However, removal of Mg (21% and 35% at 1.5 g and 2 g lime respectively) and sulphate (8% and 13% at 1.5 g and 2 g lime respectively) is only partial, whilst Na, Ca, B and K concentrations in the treated solution are higher than in the raw feed (see Table 5-3).

5.2.3 Composition of the neutralisation residues

Neutralisation of 250 ml supernatant after sodium borohydride treatment with 1.5 g (6 g/L) and 2 g (8 g/L) lime resulted in the formation of 2.2 g (8.8 g/L) and 3.6 g (14.4 g/L) of total precipitate formation respectively. The compositions of the residues are presented in Table 5-4.

Table 5-4 Composition of residue from the neutralisation of 250 ml pre-treated (with sodium borohydride) AMD solution P with lime to pH 9.2 (6 g/L lime) and pH 9.8 (8 g/L lime). t=120 minutes

	Residue concentration (%)	
	6 g/L lime (pH 9.2)	8 g/L lime (pH 9.8)
Sulphate	8.3	9.2
Ca	20.2	22.5
Fe	0.50	0.02
Al	0.31	0.00
Mn	0.31	0.29
Mg	1.20	1.40
Si	3.15	0.24
K	0.04	0.04
Na	1.01	0.76

The results in Table 5-4 indicate that the residues at both pH values are comprised mainly of calcium (20-23%) with sulphate (8-9% and ~ 38%) and lesser amounts of Si (0.2-3%), Na (0.8-1%), Mg (1.2-1.4%) and Mn (0.3%). In contrast to the results from the neutralisation of raw AMD, the residues contain relatively low quantities of sulphate, corresponding to gypsum contents of only 15-17% and accounting for only 17-18% of the Ca content in the residues. Whilst boron is reported to form several stable calcium borate precipitates upon neutralisation with lime (Remy et al., 2005; Tsai and Lo, 2015; Yilmaz et al., 2012), the relatively high residual concentrations in the neutralisation effluent indicate that the boron concentrations in the residues would have been relatively low. It is possible that most of the calcium in the precipitate was present as the relatively insoluble calcite (CaCO_3), with the dissolved carbonate having been formed through the entrainment of air during rigorous agitation of the relatively small volume of supernatant used in the neutralisation experiment. Whilst the presence of this species still needs to be confirmed, mass balance calculations indicate that the residues may contain 42% and 46% calcite in the case of 6 g/L and 8 g/L lime dosage respectively. Calcite has a lower solubility than gypsum and hence will form preferentially in the presence of carbonate ions.

5.3 Lime neutralisation of AMD solutions after nano iron removal using green tea extract

This section summarises the results of the neutralisation tests performed on the AMD solution P after pre-treatment with green tea extract.

5.3.1 pH and redox potential profile

The effect of the dosage of lime upon the pH and redox trends over time is shown in Figure 5-6.

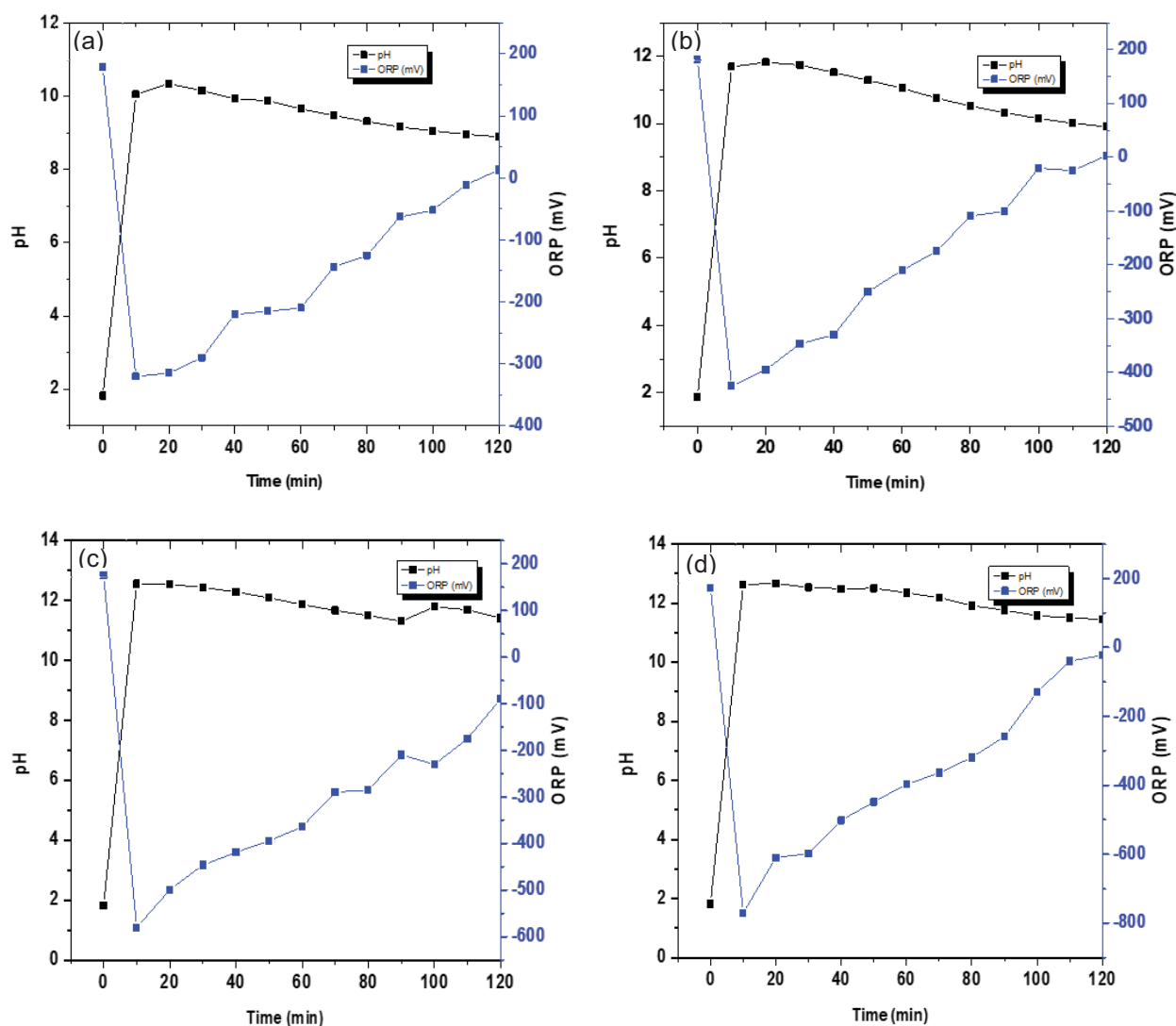


Figure 5-6 pH and redox potential of 500 mL supernatant solution P (from the pre-treatment of AMD with green tea extract) after dosage with 5 g/L lime (a), 7 g/L lime (b), 9 g/L lime (c) and 11 g/L lime (d).

The results in Figure 5-6 show that, even though the pH of the supernatant is more acidic (1.81) than that of the raw AMD (2.14), the pH of the supernatant increases significantly in the first 10 minutes of liming (pH=10.1, 11.7, 12.6 and 12.6 corresponding to lime dosages of 5 g/L, 7 g/L, 9 g/L, and 11 g/L) respectively. In all cases, this is followed by a gradual decrease in pH over the subsequent 100-minute retention period. Similarly, the redox potentials of the solutions drop rapidly from an initial value of 177 mV within the first 10 minutes after lime addition (-320 mV, -425 mV, -580 mV, -770 mV at 5 g/L, 7 g/L, 9 g/L, and 11 g/L lime addition respectively), but then increase over the period 10 minutes to 120 minutes.

5.3.2 Composition of the neutralisation effluents

The compositions of the effluent obtained from the neutralisation of 500 ml of supernatant, pre-treated with 0.5 g green tea extract, with 2.5 g (5 g/L) and 3.5 g (7 g/L), 4.5 g (9 g/L) and 5.5 g (11 g/L) lime are presented in Table 5-5, and the extent of removal of selected components through precipitation presented in Figure 5-7.

Table 5-5 Neutralisation of pre-treated (green tea extract) AMD to pH 8.9 (5.0 g/L lime), pH 9.9 (7 g/L lime), pH 11.4 (9.0 g/L lime) and pH 11.5 (11 g/L lime). t =120 minutes

Parameters	Units	Raw AMD	Supernatant	Neutralisation effluent concentrations as a function of lime dosage (mg/L)			
				5.0 g/L lime	7 g/L lime	9 g/L lime	11 g/L lime
pH		2.1	1.8	8.89	9.91	11.42	11.45
Electrical conductivity (EC)	mS/cm	2900					
Redox potential	mV	448	177	13	3	-90	-22
<u>Anions</u>							
Sulphate	mg/L	11500	7820	2914	2027	3249	3070
Nitrate	mg/L	2.13	1.4	0.20	0.76	1.50	0.24
Chloride	mg/L	10.2	11.2	16.5	16.9	16.3	16.1
<u>Major Metals</u>							
Fe	mg/L	4002	420	0.08	0.54	9.70	13.7
Ca	mg/L	494	178	1067	1264	1339	1288
Mg	mg/L	432	142	48.4	9.60	1.10	1.00
Al	mg/L	388	120	1.05	3.8	0.69	0.22
Mn	mg/L	83.2	13.0	0.44	0.06	0.22	1.56
<u>Minor metals</u>							
Na	mg/L	48.81	19.0	29.7	32.3	29.7	31.8
Si	mg/L	46.56	10.0	0.30	0.20	0.70	1.30
Zn	mg/L	9.47	1.30	0.09	0.04	0.01	0.01
<u>Trace elements</u>							
As	mg/L	0.03	BDL	BDL	BDL	BDL	BDL
Be	mg/L	BDL	BDL	BDL	BDL	BDL	BDL
Cd	mg/L	0.01	BDL	BDL	BDL	BDL	BDL
Cr	mg/L	0.05	BDL	BDL	BDL	BDL	BDL
Cu	mg/L	0.08	0.05	0.01	0.02	0.02	0.03
Li	mg/L	0.03	BDL	BDL	BDL	BDL	BDL
Mo	mg/L	0.03	0.04	BDL	BDL	BDL	BDL
Ni	mg/L	1.07	0.3	0.16	0.13	0.11	0.18
P	mg/L	BDL	1.20	0.30	0.60	0.60	0.60
Pb	mg/L	0.01	BDL	BDL	BDL	BDL	BDL
Si	mg/L	46.6	10.0	0.30	0.20	0.70	1.30
Sr	mg/L	0.57	0.08	0.63	0.67	0.99	1.36
Th	mg/L	BDL	BDL	BDL	BDL	BDL	BDL
Ti	mg/L	0.01	BDL	BDL	BDL	BDL	BDL
Y	mg/L	BDL	BDL	BDL	BDL	BDL	BDL
Zr	mg/L	0.01	BDL	BDL	BDL	BDL	BDL

BDL = Below detection limit

Consistent with previous tests (See Chapter 4), treatment of the raw AMD solution with green tea extract was found to result in approximately 89% Fe removal, 86% Zn removal and 84% Mn removal, along with substantial amounts of Si (78%), Al (69%), Mg (67%), Ca (64%) and Na (64%). Green tea extract removal also results in removal of 32% of the soluble sulphate. The supernatant from the green tea extract treatment had an acidic pH of 1.8 and still contained significant quantities of sulphate, along with major quantities of Fe (420 mg/L), Ca

(178 mg/L), Mg (142 mg/L), Al (120 mg/L), and minor-trace quantities of Mn (13 mg/L), Si (10 mg/L), Na (19 mg/L), P (1.2 mg/L) and Zn (1.3 mg/L). As indicated in Figure 5-7, subsequent neutralisation of the pre-treated supernatant results in further precipitation of Fe (>99% in all cases), Al (>99% in all cases), Zn (93% to > 99%), Mn (88% to >99%), Mg (66% to > 99%), Si (87-93%), and partial removal from solution of sulphate (58-74%). An increase in the final pH from 8.9 (5 g/L lime) to 9.9 (7 g/L lime) results in an increase in the extent of removal of Mg from solution significantly (from 66% to 93%), whilst also increasing the extents of Mn and Zn precipitation from 96% and 93% respectively, to > 99%. Additional lime dosage to a pH value of 12.5 (9 g/L lime), further increases the extent of Mg removal to >99%. A lime dosage of 11 g/L, corresponding to a final pH of 11.5, results in a slight decrease in the extent of precipitation of some metals including Mn, Si and, to a lesser extent, Fe. This increase can probably be attributed to the formation of stable oxanion species at the elevated pH values. The major components in the effluents treated with 7 g/L and 9 g/L lime are sulphate (2.9-3.3 g/l) and Ca (1.3 g/L), with minor amounts of Na (30-32 mg/L), and traces of Fe (0.54-9.7 mg/L), Mg (9.6-1.1 mg/L), Al (0.7-4 mg/L), Mn (0.06-0.2 mg/L), Si (<1 mg/L), Zn (<0.05 mg/L), Ni (0.1 mg/L) and Sr (0.7-1 mg/L). Neutralisation results in an increase in the calcium concentration relative to the feed supernatant, with mass balance calculations indicating that approximately 61% and 78% of the total initial Ca (including the Ca added as lime and the Ca in the pre-treated supernatant) is removed in the form of precipitates during neutralisation.

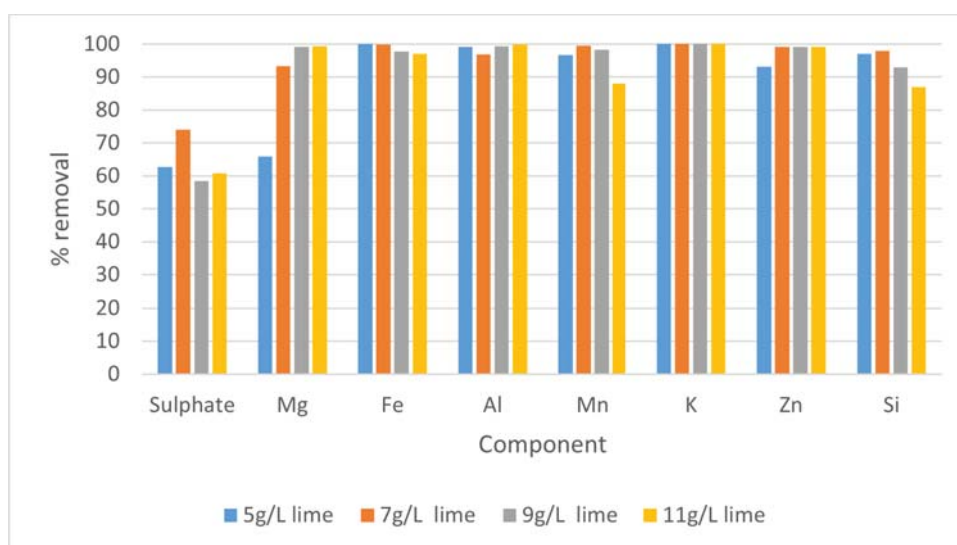


Figure 5-7 Extent of removal of components during lime neutralisation of AMD solution P after pre-treatment with green tea extract. Effluent pH 8.9 (5 g/L lime), pH 9.9 (7 g/L lime), pH 11.4 (9 g/L lime) and pH 11.5 (11 g/L lime); $t = 120$ minutes

The net removal of elements from the raw AMD solution P through green tea extract treatment and subsequent neutralisation with lime is presented in Figure 5-8.

Overall, treatment of the AMD solution P with green tea extract and lime (to pH values > 10) results in effective removal (>99.9%) of Fe, Al, Zn, Mn, Si and Mg, as well as significant removal of sulphate (72-82%) and, to a lesser extent, Na (42-44%). However, removal of Mg is dependent on the pH of the neutralisation with relatively high pH values (>11) and lime dosages (9 g/L) being required to achieve > 99% Mg removal from solution (equivalent to a residual concentration of ≤ 1 mg/L).

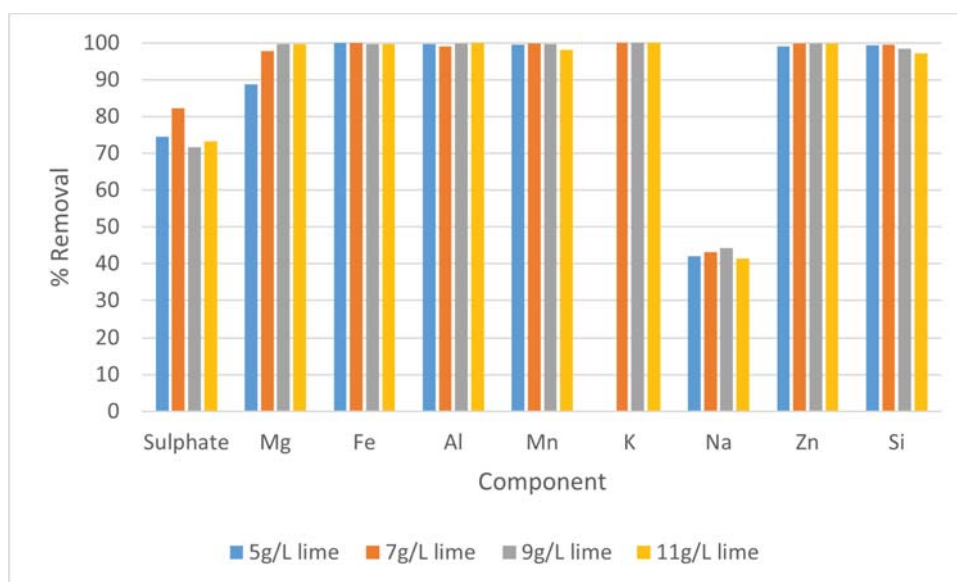


Figure 5-8 Overall extent of removal of components during green tea extract pre-treatment and subsequent neutralisation of 500 ml AMD solution P with lime to pH 8.9 (5 g/L lime), pH 9.9 (7 g/L lime), pH 11.4 (9 g/L lime) and pH 11.5 (11 g/L lime). $t = 120$ minutes

5.3.3 Composition of the neutralisation residues

Neutralisation of the pre-treated AMD solution P with 5 g/L, 7 g/L, 9 g/L and 11 g/L lime resulted in the formation of 6.2 g/L, 7.6 g/L, 9.5 g/L and 11.3 g/L of total precipitate formation respectively, approximately 21-31% of that obtained from raw AMD. The compositions of the neutralization residues obtained are presented in Table 5-6.

Table 5-6 Composition of residue from the neutralisation of pre-treated (green teas extract) AMD solution P with lime. $t = 120$ minutes

Component	Residue concentration (%)			
	5 g/L lime	7 /L lime	9 g/L lime	11 g/L lime
Sulphate	25.6	24.5	22.2	19.5
Ca	21.4	22.9	25.9	29.1
Fe	2.78	3.00	2.75	2.60
Al	1.11	0.76	0.98	0.80
Mn	0.11	0.12	0.32	0.36
Mg	0.30	1.60	1.42	1.29
Si	0.11	0.10	0.14	0.15
K	0.02	0.01	<0.01	0.02
Na	0.12	0.03	0.13	0.15

The results in Table 5-6 indicate that the residues at all pH values are comprised predominantly of sulphate (~ 320-26%) and calcium (21-29%), with lesser amounts of Fe (2.6-3.0%), Al (0.8-1.1%), Mg (0.3-1.3%) and traces of Si (0.1-0.15%), Mn (0.1-0.4%) and Na (0.1-0.2%). The sulphate content decreases (from 26% to 20%) and the calcium concentrations increases (from 21% to 29%) on increasing the lime dosage from 5 g/L

to 11 g/L. Parity calculations based on the sulphate contents indicates a gypsum content of 44-46%, 40-44%, 34-40% and 28-34% at lime additions of 5 g/L, 7 g/L, 9 g/L and 11 g/L respectively, depending on whether Al is present as aluminium hydroxide or ettringite. Calculations indicate furthermore that gypsum formation only accounts for only 47%, 40%, 32% and 23% of the Ca in the residue at lime dosages of 5 g/L, 7 g/L, 9 g/L and 11 g/L respectively. As in the case of the residues from the neutralisation of solutions pre-treated with sodium borohydride, it is possible that the remaining Ca was present in the form of calcite (CaCO_3) formed through the entrainment of CO_2 , with calculations showing possible calcite concentrations of 27-28%, 32-34%, 41-44%, and 52-56% at lime dosages of 5 g/L, 7 g/L, 9 g/L and 11 g/L respectively. The increase in gypsum content and decrease in calcite content as the lime dosage increases from 5 g/L to 11 g/L is consistent with the sulphate and calcium content trends. Iron contents are consistent with ferric hydroxide contents of between 4.9 and 5.3% in all cases. Solid Al compounds amount to 2.4% to 5.7%, depending on whether these exist as aluminium hydroxide ($\text{Al}(\text{OH})_3$) or ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$). (And amorphous SiO_2 (0.4-0.5%).

5.4 Summary

A comparison of lime dosage (Table 5-6) indicates that the pre-removal of iron through treatment with the AMD solutions reduces the amount of lime required to achieve any specific pH value.

Table 5-7 pH as a function of lime addition during the neutralisation of AMD samples before and after pre-treatment to recovery nano iron

Lime Addition (g/L)	pH
<u>Raw AMD</u>	
11	9.1
12	11.2
<u>AMD pre-treated with NaBH_4</u>	
6	9.2
8	9.8
<u>AMD pre-treated with green tea extract</u>	
5	8.9
7	9.9
9	11.4
11	11.5

In all cases, neutralisation to pH values > 9 results in effective removal (> 99%) of Fe, Al, Mn, Ba, and Zn. Although Mg removal at pH values < 11 is only partial ($\leq 50\%$), this increases to > 99% at pH values > 11. However, whilst between 72% and 85% precipitation of sulphate occurs during neutralisation of the raw AMD and AMD pre-treated with green tea extract, neutralisation of the AMD solution after NaBH_4 treatment results in only 7-13% sulphate precipitation. The effluent from the neutralisation of AMD pre-treated with NaBH_4 not only still contains elevated levels of sulphate, but also high levels of residual sodium and boron which may adversely affect the subsequent ultrafiltration and reverse osmosis treatment processes (Figure 5-9).

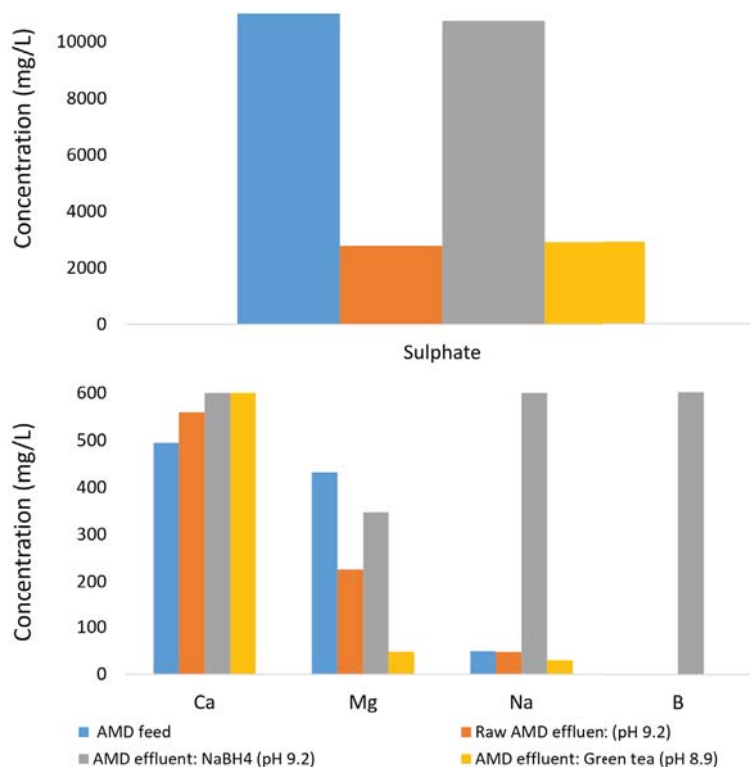


Figure 5-9 Comparison of the concentrations of key components in the AMD feed and neutralisation effluents with pH values of 8.9-9.2 ($t = 120$ minutes)

A comparison of the contents of the key components in the neutralisation residues derived from AMD solution P, both before and after pre-treatment is shown in Table 5-8. Whilst the pre-treatment of the AMD results in a considerable decrease in the Fe content of the neutralisation residues, pre-treatment did not give rise to residues with higher gypsum content, as reflected by the lower sulphate contents. This could possibly be attributed to the preferential formation of calcite due to carbonate formation as a result of CO_2 entrainment during the laboratory-scale neutralisation tests. Mass balance calculations show that the calcite content increases as the lime dosage (and hence the final pH) increases for any given feed solution, with calcite formation being more prevalent during the neutralisation of AMD solutions pre-treated with sodium borohydride. The factors influencing CO_2 entrainment and/or carbonate formation could include chemical factors such as alkalinity as well as physical factors such as agitation speed and/or volume of solution. The effect of these factors would require further investigation.

Table 5-8 Concentrations of key components in the residues derived from the neutralisation of AMD solution P before and after pre-treatment ($t = 120$ minutes)

Component	Content in the neutralisation residue as a function of final pH (%)						
	Raw AMD		AMD treated with NaBH_4		AMD treated with green tea extract		
	pH 9.1	pH 11.2	pH 9.2	pH 9.8	pH 8.9	pH 9.9	pH 11.4
Fe	12.5	11.2	0.5	0.02	2.8	3.0	2.8
Ca	16.3	17.1	20.2	22.5	21.4	22.9	25.9
Sulphate	37.9	37.7	8.3	9.2	25.6	24.5	22.2
Gypsum ¹	67.9	67.5	14.9	16.5	45.8	44.0	39.8
Calcite ¹	1.4	3.7	42.0	46.6	26.7	31.8	41.7

1. Calculated, assuming that all sulphate is present as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and the remaining calcium is present as calcite (CaCO_3)

CHAPTER 6: THERMODYNAMIC MODELLING OF AMD NEUTRALISATION

Theoretical predictions of elemental distribution behaviours in mineral resource-based process systems can be conducted using equilibrium speciation models, which are designed to generate information and data on the equilibrium distribution of phases, as well as the chemical compositions of interfacing fluid-solid systems, based on fundamental thermodynamic principles. Examples of commercially available thermodynamic models (also termed equilibrium speciation models or aqueous geochemical models) for aqueous systems include MINTEQA2 version 3.0 (Allison et al., 1990) and version 4.0 (US EPA CREAM, 2005); OLI (OLI Systems Inc., 1991); PHREEQE (Parkhurst, 1995); WATEQF4 (Ball and Nordstrom, 1991); ORCHESTRA (Meeussen, 2003); and HSC Chemistry® for Windows (Outokumpu, 2002), have been developed to simulate various chemical equilibrium processes which includes, acid/base reactions, oxidation/reduction, adsorption/desorption and dissolution/precipitation processes based on equilibrium constants. Although equilibrium thermodynamic models do not consider factors such as reaction kinetics and non-idealities (e.g. formation of mixed or non-stoichiometric precipitates), they can provide useful and versatile information in terms of the most likely stable forms and major distribution pathways of elements in these process systems.

This is particularly the case for lime neutralisation of metal and salt rich AMD solutions, as most of the precipitation/dissolution and/or adsorption/desorption reaction mechanisms controlling the extent to which constituents are removed from solution are relatively rapid, equilibrium-controlled reactions. Thermodynamic models can thus play a valuable role in understanding the effect of neutralisation parameters, such as pH, neutralising reagents, and feed solution compositions, on the reaction mechanisms controlling the removal of metals and salts from solution and the compositions of the sludges. This in turn can serve to inform R&D campaigns to optimise the neutralisation process in terms of desirable properties of output streams, as well as assist in the effective operation of an operating neutralisation operation by enabling the potential effects of variability in the compositions of input streams (AMD feed and neutralising reagents).

This study explored the use of three different models to simulate the distribution and attenuation of chemical species before and during lime neutralisation of AMD solutions, namely VISUAL MINTEQ, PHREEQE and OLI, each of which have different advantages and disadvantages. This section of the report presents the results of the thermodynamic modelling of the chemical species existing in the raw AMD and NMD solutions (Section 6.1), simulated lime neutralisation of typical acid mine drainage (AMD) and neutral mine drainage (NMD) solutions from the Mpumalanga coalfields (Section 6.2) and modelling of laboratory-scale neutralisation experiments (Section 6.3).

6.1 Simulated neutralisation of typical NMD and AMD solutions

Thermodynamic modelling has been conducted to determine to identify chemical species existing in the raw AMD and NMD field solutions (Section 6.1.1) and formed during neutralisation of these solutions (Section 6.1.2 and Section 6.1.3).

6.1.1 Visual MINTEQ chemical speciation modelling of typical AMD and NMD solutions

Visual MINTEQ is a freeware chemical equilibrium model for the calculation of metal speciation, solubility equilibria and other geochemical properties of natural waters. Version 3.1 was compiled in Visual Basic on 26 November 2020 by Jon Peter Gustafsson, KTH, SEED, Stockholm and was downloaded in December 2020 at <https://vminteq.lwr.kth.se/download>. This model was used to identify the distribution of chemical species in selected AMD and NMD field samples, namely solutions K, T, P (collected and analysed under the auspices

of this project) and streams 1,5 and 10 (reported as typical feed streams received at the eMalahleni Water reclamation plant, EWRP). The analytical compositions of these field samples are presented in Table 6-1.

Table 6-1 Compositions of modelled NMD and AMD solutions

Parameter	Unit	NMD (stream 1)	AMD (stream 5)	AMD (stream 10)	Field AMD K	Field AMD T	Field AMD P
pH at 25°C	-	7.20	2.67	2.53	2.08	2.20	2.14
Redox potential	mV	ND	ND	ND	458	425	448
Conductivity	mS/m	400	915	ND	ND	ND	ND
Alkalinity as CaCO ₃	mg/L	70.08	0.00	0.00	ND	ND	ND
Acidity as CaCO ₃	mg/L	7.75	7070	2779	ND	ND	ND
Na	mg/L	45.8	99.9	52.3	33.5	64.2	48.8
Ca	mg/L	469	475	518	527	508	494
Mg	mg/L	444	368	205	575	414	432
K	mg/L	22.3	42.0	ND	ND	ND	39.1
Mn	mg/L	1.40	4.00	34.3	126	48.3	83.2
Al	mg/L	0.10	277	15.7	460	246	388
Total Fe	mg/L	0.20	2160	445	4420	1927	4002
Zn	mg/L	ND	ND	ND	13.1	6.10	9.47
B	mg/L	ND	ND	ND	0.11	0.17	0.10
Cl	mg/L	9.12	7.60	ND	15.3	10.1	10.2
Sulphate as SO ₄ ²⁻	mg/L	2850	8840	2301	13200	9910	11500
Nitrates & nitrites	mg/L	6.21	0.44	0.24	3.89	2.20	2.13
F	mg/L	0.78	0.20	<0.20	ND	ND	ND

Where ND = Not Determined.

As indicated in Table 6-1, the NMD solution contains 2853 mg/L sulphate, and has Ca and Mg as major metals (468.5 and 443.5 respectively) with Na and K as minor metals (45.80 and 22.30 mg/L respectively). The NMD solution (pH 7.2) contained negligible Fe (0.20 mg/L) and Al (0.10 mg/L), and only trace quantities of Mn. In contrast, in addition to Ca (398-527 mg/L), Mg (231-575 mg/L), Na (33-100 mg/L) and K (3-42 mg/L), the AMD field samples (pH 2.0-2.7) contain elevated sulphate (2301-13200 mg/L), Fe (455-4420 mg/L) and Al (16-460 mg/L). Despite a pH of 2.45, AMD stream 10 has a significantly lower concentration of sulphate (2301 mg/L) and metals, particularly Fe (455 mg/L).

Despite the differences in compositions, thermodynamic modelling indicates similar distribution of chemical species in the AMD field solutions (Figure 6-1). Modelling shows that the major and minor metals are present mainly as free cations (M²⁺) and aqueous M(II)SO₄ complexes, with Ca being present as Ca²⁺ (51-57%) and aqueous CaSO₄ (43-51%), Fe as the Fe(II) species Fe²⁺ (48-55%) and aqueous FeSO₄ (45-52%), and Mg as Mg²⁺ (47-61%) and aqueous MgSO₄ (38-45%). Sulphate is mainly present as divalent sulphate ions (SO₄²⁻ at 31-48%) and aqueous FeSO₄ (18-28%), with lesser amounts of bisulphate (HSO₄⁻ at 4-10%), Al(III) sulphate complexes (Al(SO₄)₂⁻ at 8-12% and AlSO₄⁺ at 5-8%), aqueous MgSO₄ (6-8%) and aqueous CaSO₄ (4-9%). Whilst the distribution of metal species in the NMD solutions is like that of the AMD solutions, the relatively low concentration of Fe and Al and the higher pH values results in very low concentrations of Fe(II) and Al(III) sulphate complexes and bisulphate ion. Sulphate is thus largely present in Stream 1 as the divalent sulphate ion (SO₄²⁻ at 62%), aqueous MgSO₄ (21%) and aqueous CaSO₄ (16%). Modelling also showed that all the AMD solutions except Stream 10 with a relatively low sulphate concentration are saturated with respect to gypsum. The NMD solution, on the other hand, is saturated with respect to the Fe(III) hydroxide species, Fe(OH)₃, and the Al hydroxysulphate species, alunite (KAl₃(OH)₆(SO₄)₂).

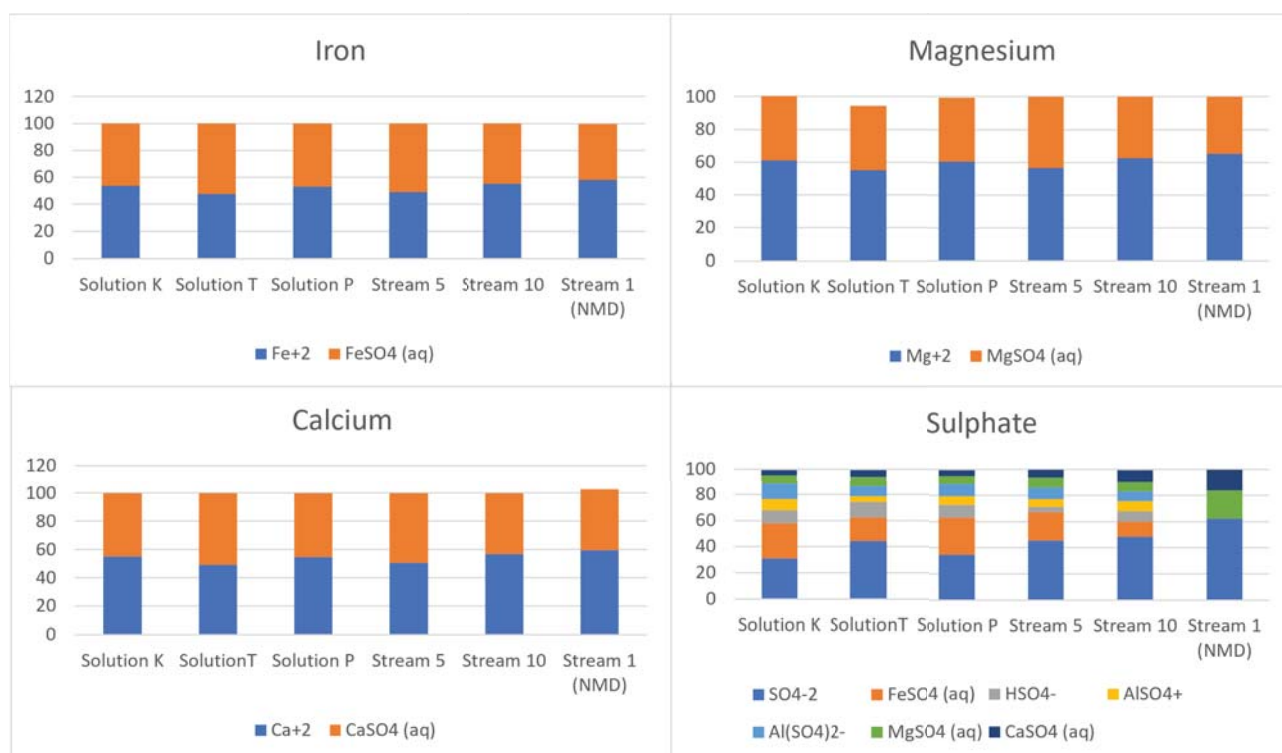


Figure 6-1 Distribution of Fe, Mg, Ca, and sulphate species in Field AMD and NMD samples (Visual MINTEQ model results)

6.1.2 PHREEQC modelling of NMD and AMD neutralisation profiles

PHREEQC (version 3.6.2-15100, USGS-USA) has been used to model pH profiles, and to identify predominant aqueous species and likely precipitate formation as a function of pH. Two solutions were selected for this initial modelling work, namely the NMD stream 1 and AMD stream 5.

6.1.2.1 PHREEQC modelling of NMD Stream 1

PHREEQC modelling of NMD solutions was carried out by adding 0.004 moles per kg of solution in steps until a pH of approximately 11.5 under ambient conditions ($p_e = 4$). Fractionation (% of total) of aqueous species i for component M was calculated in accordance with equation 6.1

$$\text{Fraction (\%)} = C_{i,M} / C_{T,M} \dots\dots\dots 6.1$$

Where $C_{i,M}$ is the concentration of species i , and $C_{T,M}$ is the total dissolved concentration of component M .

The results for the simulated neutralisation of NMD stream 1 are summarized for in Figures 6-2 and 6-3.

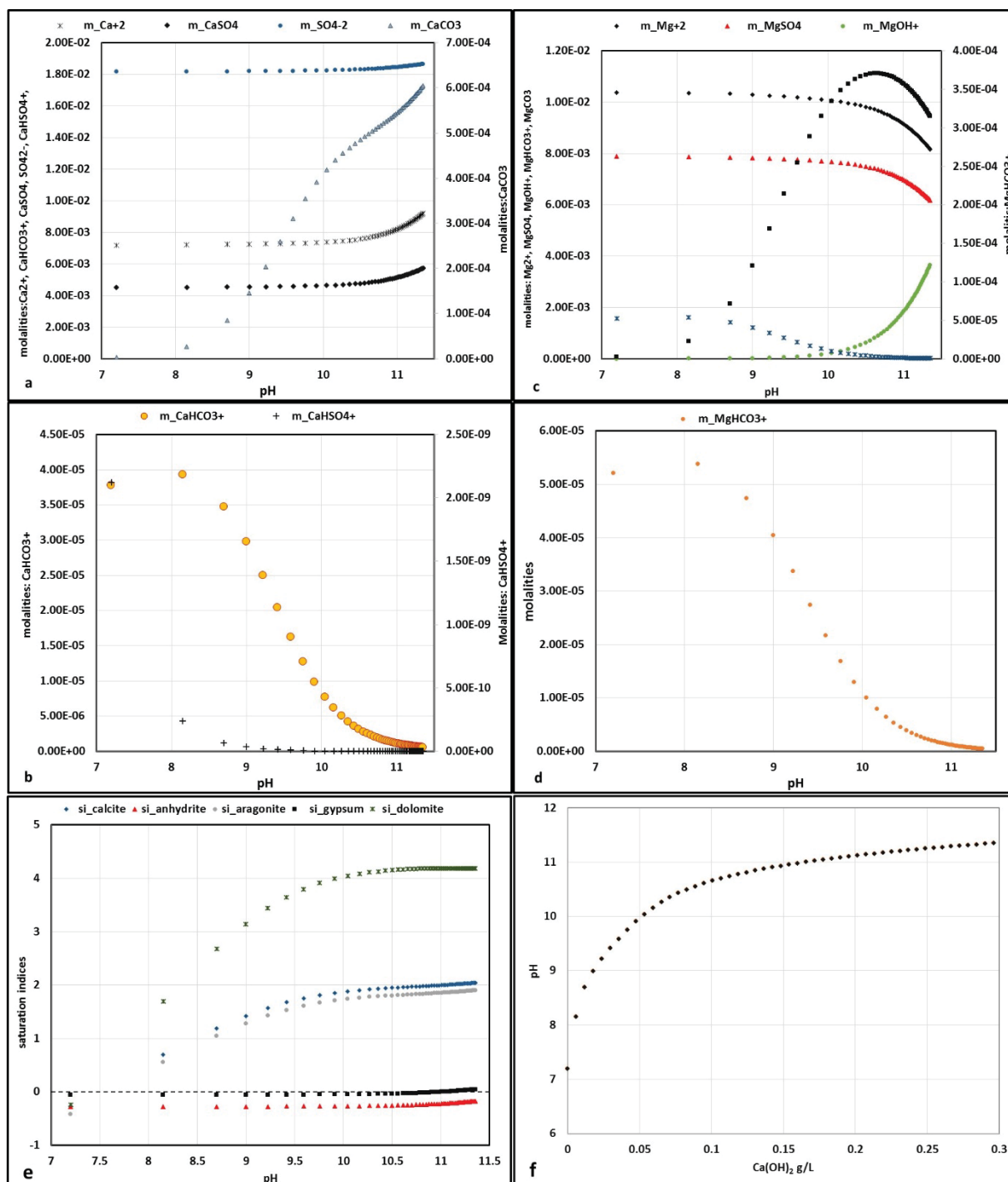


Figure 6-2 Results of the PHREEQC modelling of the simulated neutralisation of NMD solution 1; a-d: aqueous species concentrations, e: saturation indices of solid precipitates; f: pH profile as a function of Ca(OH)_2 dosage.

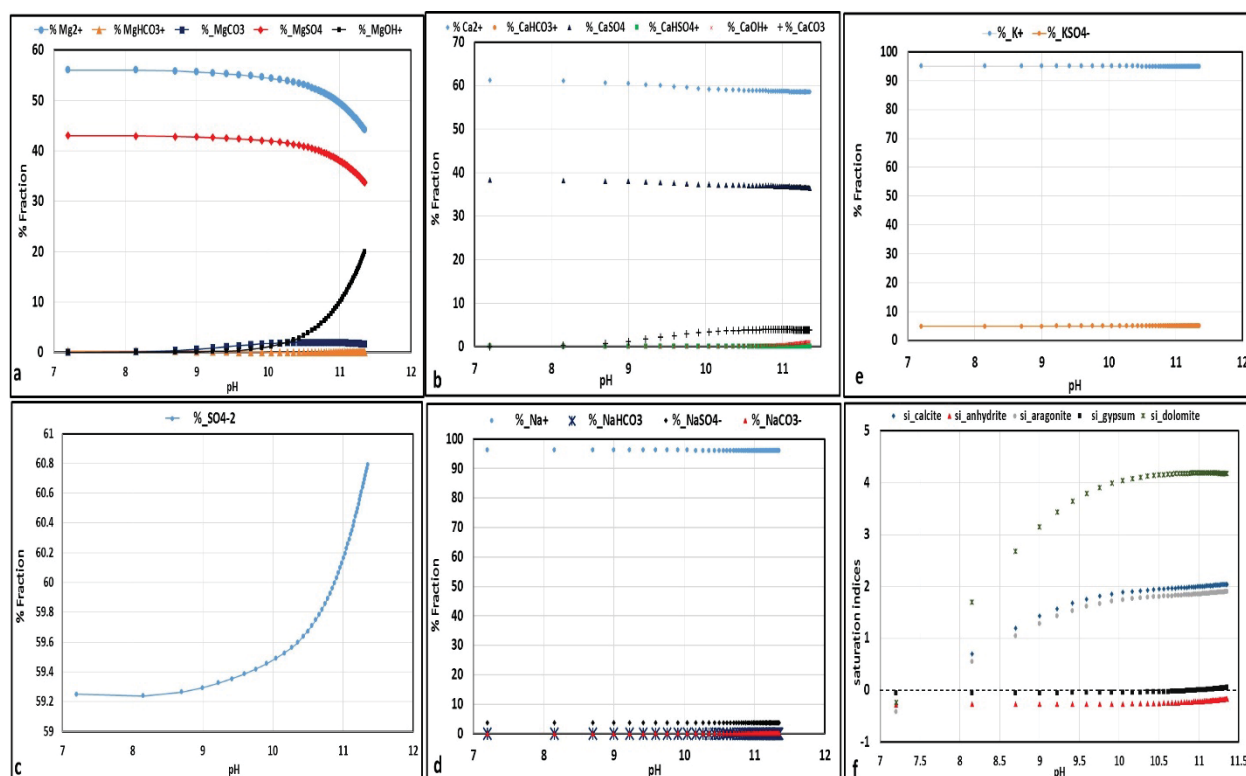
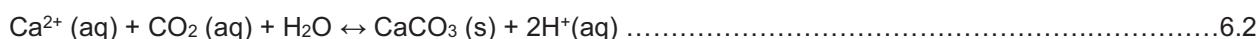


Figure 6-3 Results of the PHREEQC modelling of the simulated neutralisation of NMD solution 1; a-d: fractionation of Mg, Ca, K, S and Na; e: saturation indices for selected mineral phases.

The model outputs (Figure 6-2f) indicate that the pH increases rapidly from a value of 7.2 to pH 10 at a dosage of 0.05 g $\text{Ca}(\text{OH})_2$ per litre. The pH continues to rise, albeit more gradually, on further increases in lime dosage, with a pH of approximately 11.3 being achieved at a dosage of 0.3 g/L. As in the case of the NMD feed solutions (see MINTEQA modelling results in Section 6.1.1), the results (Figure 6-2a) indicate that soluble Mg and Ca is dominated by the free M^{2+} ions and the $\text{MSO}_4(\text{aq})$ complex over the entire pH range, whilst both soluble Na (Figure 6-2c) and K (Figure 6-2d) are dominated by the free Na^+ and K^+ ions. The saturation indices as a function of pH (Figure 6-3e) show that the solution is slightly below or near saturation across all pH in the case of gypsum, indicating that gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is unlikely to form under neutralisation conditions. However, the solutions become saturated with respect to dolomite, $\text{CaMg}(\text{CO}_3)_2$, and the calcium carbonate CaCO_3 precipitates, calcite, and aragonite, at pH values > 8. This can be attributed to the formation of aqueous carbonate species in solutions saturated with respect to air. At pH values > 8, the free carbonate ions, CO_3^{2-} , become the dominant aqueous carbonate species, with subsequent formation of insoluble Ca and/or Ca, Mg carbonates in accordance with reactions in Equations 6.2 and 6.3 respectively.



The formation of carbonate precipitates accounts for the pH buffering effect at pH values greater than 9-10, with both the formation of Ca and Mg carbonates resulting in the generation of acid. However, although dolomite is thermodynamically, more stable than the carbonates of Ca or Mg, dolomite cannot be precipitated formed directly from solution under ambient conditions (Pina and Pimentel, 2017). Rather CO_2 exposure of solutions of salts of Ca and Mg results in the formation of a calcium carbonate with low Mg content, instead of dolomite. Furthermore, the formation of crystalline forms of calcium carbonate (e.g. calcite, aragonite and vaterite) is preceded by the formation of amorphous phases of calcium carbonate ($\text{CaCO}_3 \cdot x\text{H}_2\text{O}$).

6.1.2.2 PHREEQC modelling of AMD Stream 5

PHREEQC modelling of AMD solutions was carried out by adding 0.009 moles per kg of solution in steps until a pH of approximately 9 under ambient conditions. In this scenario the pe (redox potential) was adjusted to 12.00 to simulate oxidized AMD such that greater than 82% of total Fe was in the form of Fe^{3+} . Graphs showing the pH profiles as a function of lime dosage, and the fractionation of aqueous species are shown in Figures 6-4 (Al, Fe(II), Fe(III), Mn and sulphate) and 6-5 (Mg, Ca, Na and K). Saturation indices for the solid species as a function of pH are presented in Figure 6-6.

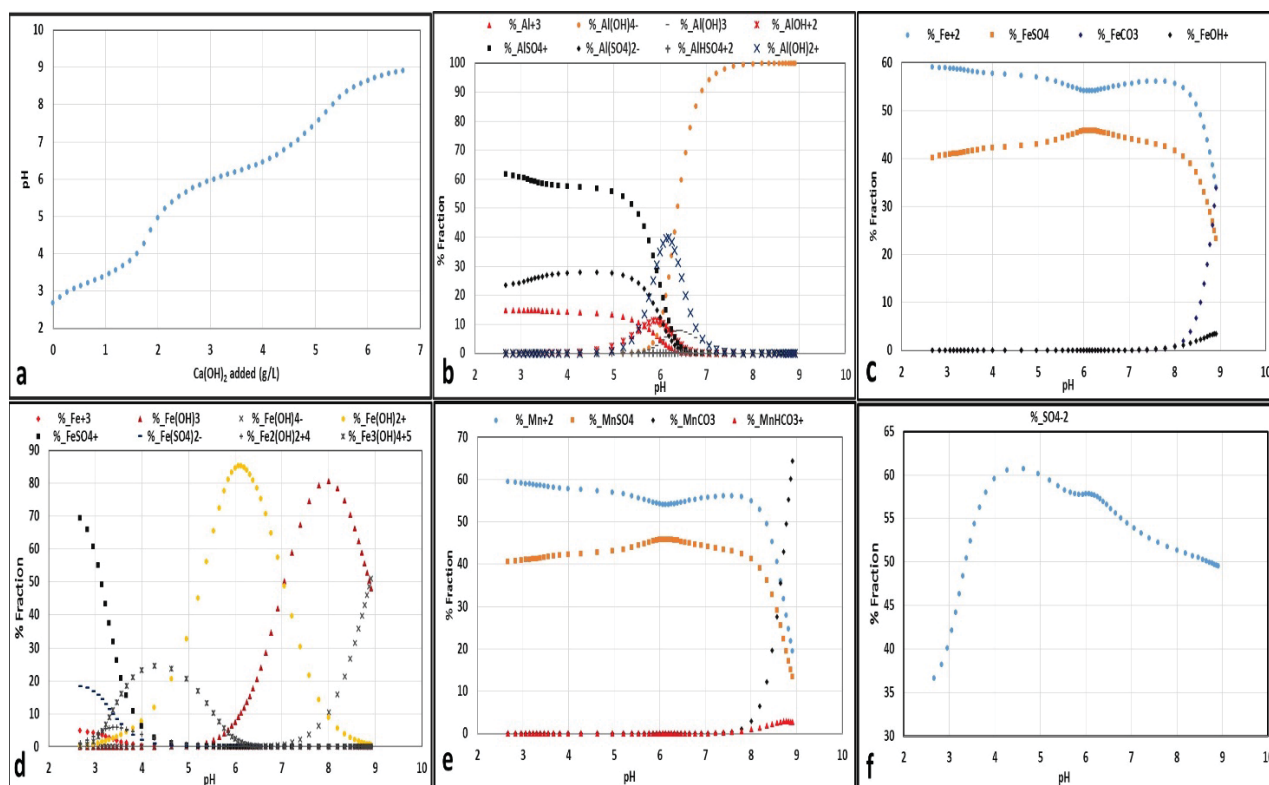


Figure 6-4 Results of the PHREEQC modelling of the simulated neutralisation of AMD solution 5; a: pH profiles as a function of $\text{Ca}(\text{OH})_2$ dosage; b-f: fractionation of soluble Al, Fe(II), Fe(III), Mn(II) and sulphate.

The graphs in Figures 6-4 and 6-5 reflect the complexity of the chemistry of the neutralisation of AMD solutions. In contrast to the pH profiles for the neutralisation of NMD, the pH profiles in the case of AMD show pH 3 buffer zones, in the pH ranges 3-4.5; 5.5-6.5 and $\text{pH} \approx 9$. A pH value of approximately 9 was achieved at a lime dosage of 6.8 g/L. The aqueous chemistry of Al(III) and Fe(III) (Figure 6-4b and d) is dominated by sulphate complexes at lower pH values and hydroxy complexes at higher pH values. More specifically, the Al(III) sulphate complexes AlSO_4^+ and $\text{Al}(\text{SO}_4)_2^-$ and the free Al^{3+} ion dominate at pH values < 6 , and the hydroxy complexes $\text{Al}(\text{OH})_4^-$ and $\text{Al}(\text{OH})_2^+$ dominate at higher pH values. In the case of Fe(III), FeSO_4^+ dominates at $\text{pH} < 3.5$, whilst at higher pH values the Fe(III) hydroxy complexes, $\text{Fe}_3(\text{OH})_4^{5+}$ ($\text{pH} 3.5\text{--}4.5$), $\text{Fe}(\text{OH})_2^+$ ($\text{pH} 4.5\text{--}7.0$), $\text{Fe}(\text{OH})_3$ (aq) ($\text{pH} 7\text{--}9$) and $\text{Fe}(\text{OH})_4^-$ ($\text{pH} > 9$) dominate. The divalent ions Fe(II) and Mn(II) (Figure 6-4c and e) are dominated by the free ions (Fe^{2+} and Mn^{2+}) and the monosulphate complexes (FeSO_4 (aq) and MnSO_4 (aq)) at acidic, neutral, and weakly alkaline pH values. At pH values $> 8.5\text{--}9.0$, the monocarbonate complexes FeCO_3 (aq) and MnCO_3 (aq) become dominate.

In the case of the alkaline earth metals Mg (Figure 6-5b) and Ca (Figure 6-5c), aqueous chemistry is dominated by the free ions (Mg^{2+} and Ca^{2+}) and the monosulphate complexes (MgSO_4 (aq) and CaSO_4 (aq)) over the entire pH range investigated. The alkali metals Na (Figure 6-5e) and K (Figure 6-5f) are dominated by the free ions Na^+ and K^+ .

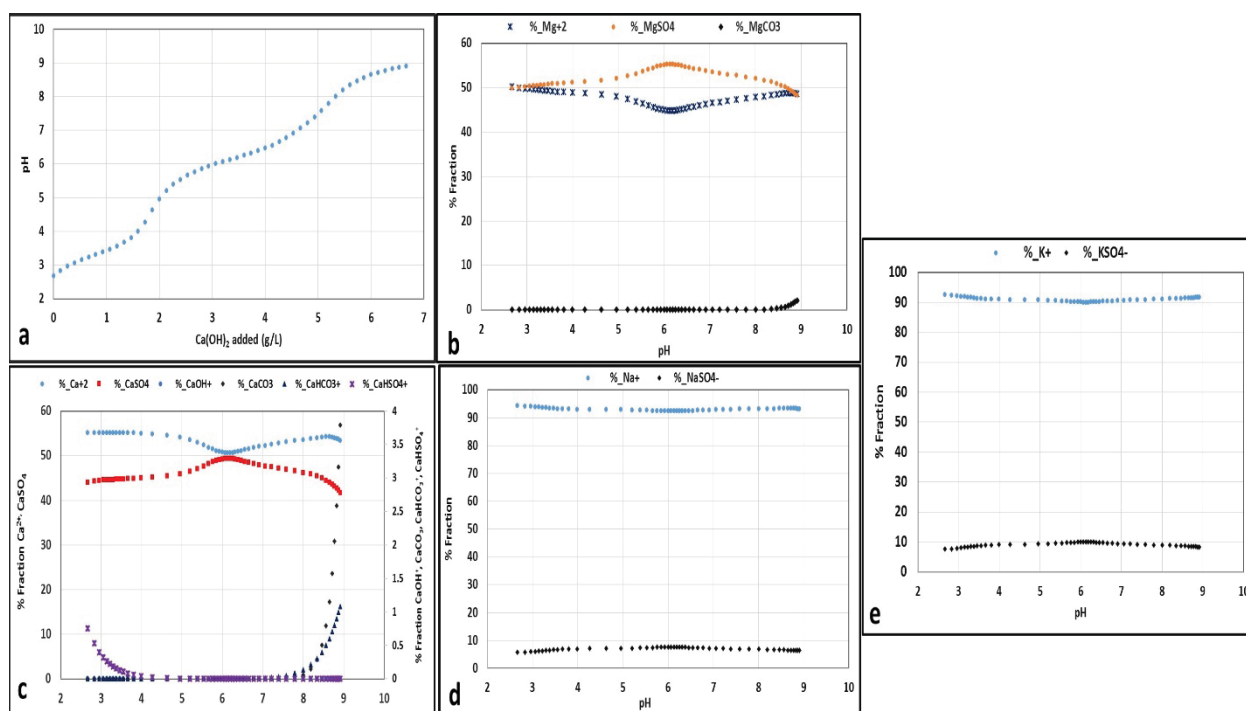


Figure 6-5 Results of the PHREEQC modelling of the simulated neutralisation of AMD solution 5; a: pH profiles as a function of Ca(OH)_2 dosage; b-e: fractionation of soluble Mg, Ca, Na and K.

Saturation indices for solid Al(III) species (Figure 6-6a), show that the solution will be supersaturated with respect to several oxyhydroxide and hydroxysulphate precipitates over the pH range investigated. Whilst many of these have been identified as secondary minerals in nature, not all of these are likely to form under ambient conditions within the timeframes of the neutralisation process. These include crystalline forms of AlOOH , gibbsite and boehmite. Al(III) precipitates which are most likely to form under neutralisation conditions include the hydroxysulphates jurbanite ($\text{AlSO}_4\text{OH} \cdot 5\text{H}_2\text{O}$), alunite ($\text{KAl}_3(\text{OH})_6(\text{SO}_4)_2$) and basaluminite ($\text{Al}_4\text{SO}_4(\text{OH})_{10} \cdot 4\text{H}_2\text{O}$), predicted to form at pH values 3-9, as well as amorphous Al(OH)_3 , predicted to form at pH values 5-9. In accordance with the saturation indices, solid forms of Al(II) will be dominated by alunite and basaluminite, with an optimum stability at pH 6. The model did not predict saturation with respect to ettringite, ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3\text{OH}_{12} \cdot 26\text{H}_2\text{O}$), a hydrated basic sulphate of calcium and aluminium which has been reported to form in high pH environments ($\text{pH} > 10$) under oxidizing conditions where sufficient dissolved calcium, aluminium, and sulphate are present. The formation and stability of ettringite is dependent on several factors, particularly concentration of the constituents and pH.

Similarly, the Fe(III) oxides and oxyhydroxides, haematite (Fe_2O_3) and crystalline goethite (FeOOH) are unlikely to form under ambient AMD neutralisation conditions. The AMD solution is, however, likely to be saturated with respect to amorphous Fe(III) hydroxide, Fe(OH)_3 , over the pH range 3-9 (Figure 6-6b). This compound is predicted to be the dominant Fe(III) precipitate. The saturation indices also show that the solution will be saturated with respect to the Fe(II) carbonate siderite, FeCO_3 , at pH values > 7 (Figure 6.6b), and with respect to the Mn(II) carbonate rhodochrosite, MnCO_3 , at pH > 7.5 (Figure 6-6d). The saturation indices also indicate that the solution will be saturated with respect to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) at pH values > 2.5 (Figure 6-6c).

The formation of the Al(III) precipitates, alunite, basaluminite and amorphous Al(OH)_3 , amorphous Fe(OH)_3 , the carbonates siderite and rhodochrosite, as well as gypsum, are presented in Equations 6.4-6.10



Amorphous $\text{Al}(\text{OH})_3$: $\text{Al}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \text{Al}(\text{OH})_3 + 3\text{H}^+$	6.6
Amorphous $\text{Fe}(\text{OH})_3$: $\text{Fe}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})_3 + 3\text{H}^+$	6.7
Siderite: $\text{Fe}^{2+}(\text{aq}) + \text{CO}_2(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{FeCO}_3(\text{s}) + 2\text{H}^+(\text{aq})$	6.8
Rhodochrosite: $\text{Mn}^{2+}(\text{aq}) + \text{CO}_2(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{MnCO}_3(\text{s}) + 2\text{H}^+(\text{aq})$	6.9
Gypsum: $\text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \leftrightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	6.10

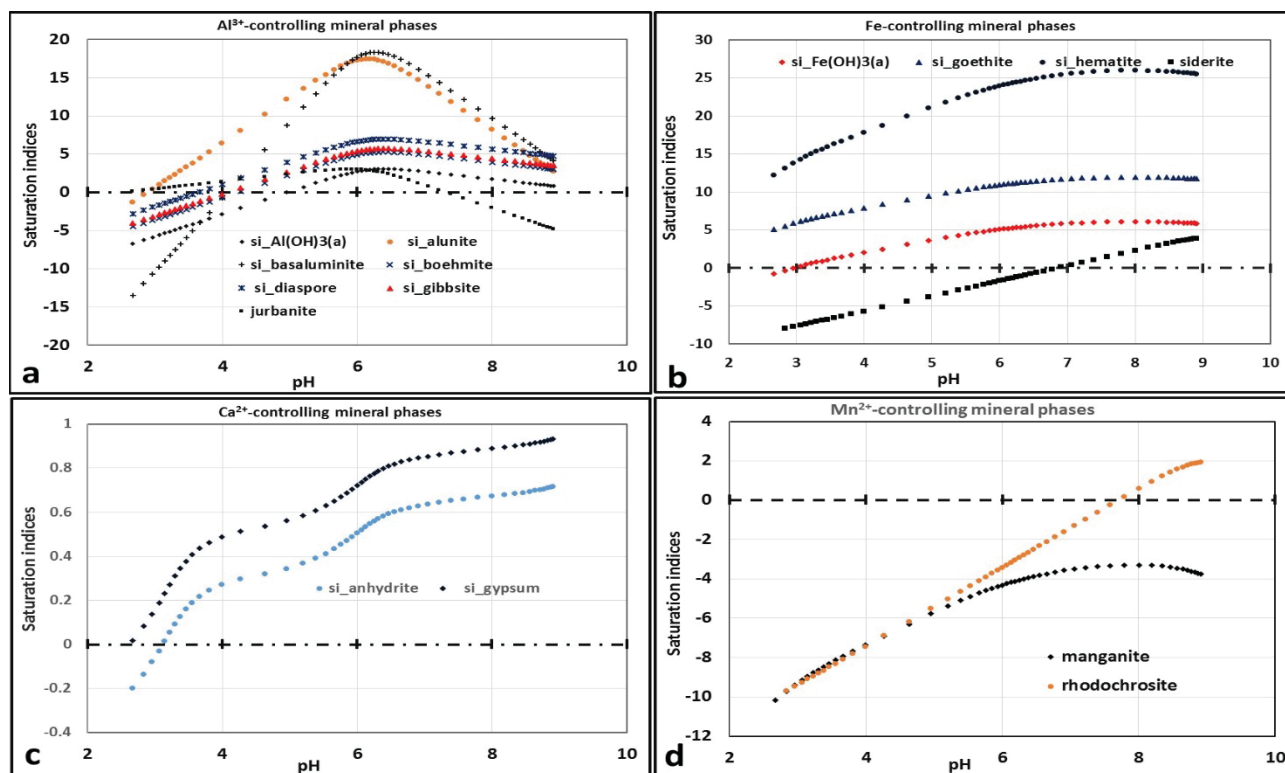


Figure 6-6 Results of the PHREEQC modelling of the simulated neutralisation of AMD solution 5; a-d saturation indices of Al(III), Fe(III), Ca(II) and Mn(II) solid species.

Equations 6.4 to 6.10 indicate that the formation of Al, Fe and Mn precipitates all entail generation of acid, and are thus likely to be linked to the observed pH buffer zones.

6.1.3 OLI modelling of AMD neutralisation profiles

Phreeq modelling (Section 6.1.2) showed that when the AMD and NMD solutions are allowed to equilibrate with atmospheric CO_2 , carbonate precipitates of Fe(II), Mn(II) and, at low sulphate concentrations associated with NMD solutions, Mg(II) and Ca(II) may be formed. To investigate the effect of CO_2 in air on the further OLI modelling of AMD stream 10 was conducted to identify predominant aqueous species and likely precipitate formation as a function of pH under two scenarios: one with no addition of air (0 CO_2) and one with air (CO_2 at a fixed concentration).

6.1.3.1 Without air (anoxic conditions)

The formation of precipitates and species concentrations as a function of lime addition and associated pH in the absence of air are presented in Figure 6-7 and Figure 6-8 respectively.

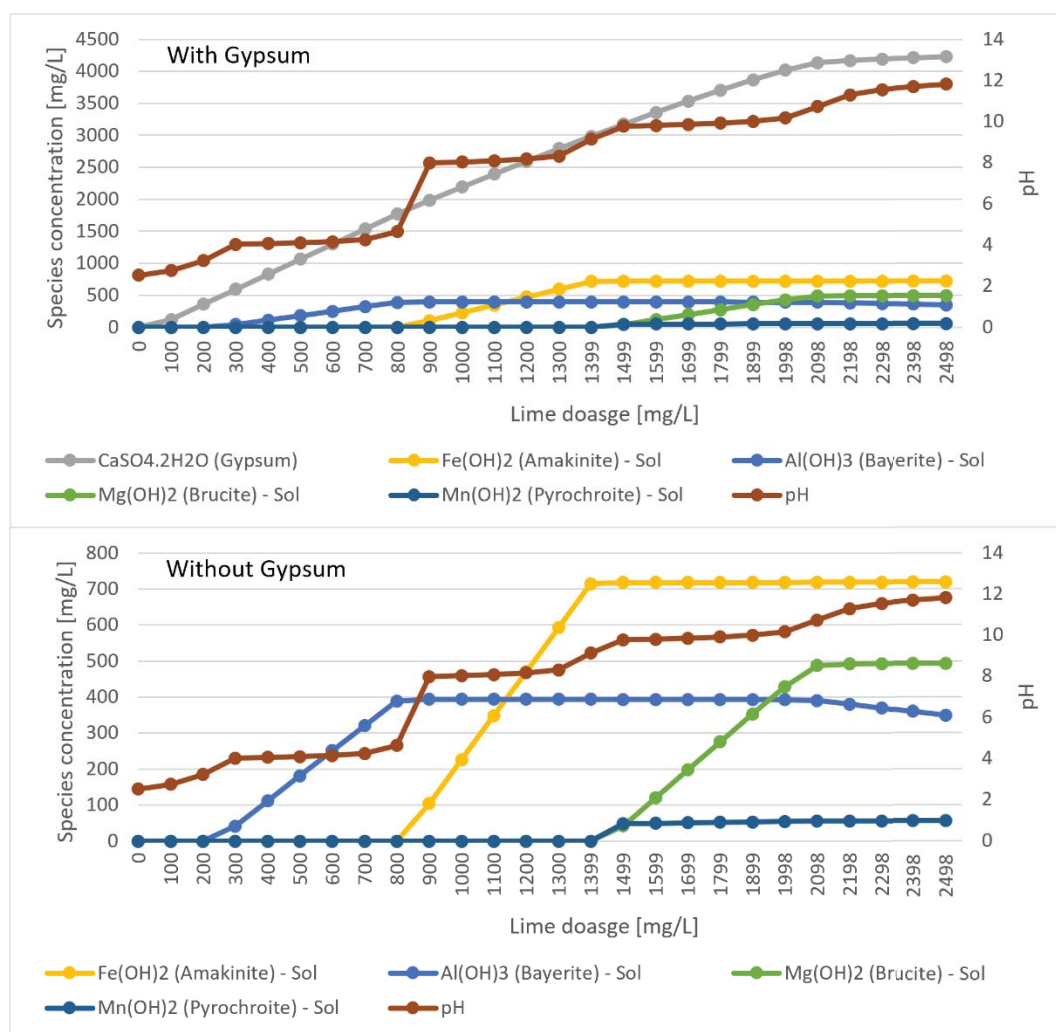


Figure 6-7 OLI modelling of the simulated neutralisation of AMD stream 10: Precipitate formation and pH for different $\text{Ca}(\text{OH})_2$ dosages with no air present.

Consistent with the Phreeq modelling results, gypsum is the dominant solid phase formed (in accordance with Equation 6.10), with the extent of formation increasing as the lime, and hence Ca, dosage increases until the solubility limit of gypsum is reached at a sulphate concentration of 830 mg/L (Figure 6-8) and a total lime addition of approximately 2.5 g/L, corresponding to a pH of 11.8. Aluminium precipitates out as $\text{Al}(\text{OH})_3$ over the pH range 4.0 to 4.6 (in accordance with Equation 6.7) resulting in buffering of the pH at corresponding values. Due to the anoxic conditions, iron remains in the divalent state and is precipitated from solution as $\text{Fe}(\text{OH})_2$ over the pH range 8.0 to 8.3 resulting in a buffering of the pH in the corresponding range. At a pH of 9.8, soluble Mg starts to precipitate as $\text{Mg}(\text{OH})_2$, with the extent of precipitate formation increasing to pH 10.7, resulting in a third pH zone in this range. The final precipitate at optimum sulphate and metal removal comprises mainly gypsum (72%), together with 12% $\text{Fe}(\text{OH})_2$, 8% $\text{Mg}(\text{OH})_2$, 6% $\text{Al}(\text{OH})_3$ and <1% $\text{Mn}(\text{OH})_2$.

The concentrations of soluble species in solution as a function of lime addition (Figure 6-8a) and pH (Figure 6-8b) are consistent with the formation of soluble species, with the final solution at pH 11.8 comprising mainly soluble SO_4^{2-} and Ca^{2+} at 831 mg/L and 769 mg/L respectively.

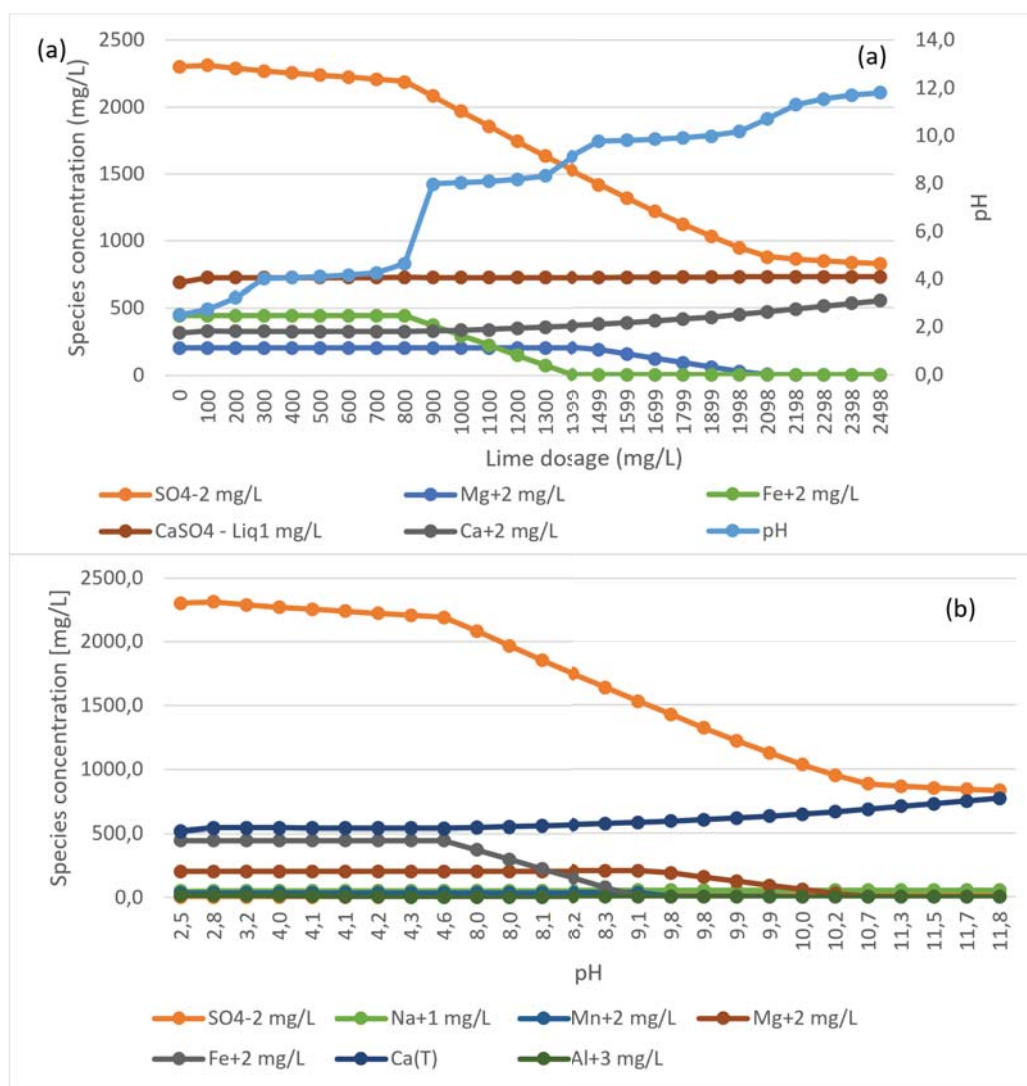


Figure 6-8 OLI modelling of the simulated modelling of AMD stream: concentration of soluble species as a function of (a) lime dosage and (b) pH in the absence of air.

6.1.3.1 With air

The formation of precipitates and species concentrations as a function of lime addition and associated pH in the presence of air are presented in Figure 6-9 and 6-10 respectively. In this scenario, Fe(II) oxidises to Fe(III) and CO₂ is added at a fixed concentration to form carbonate species.

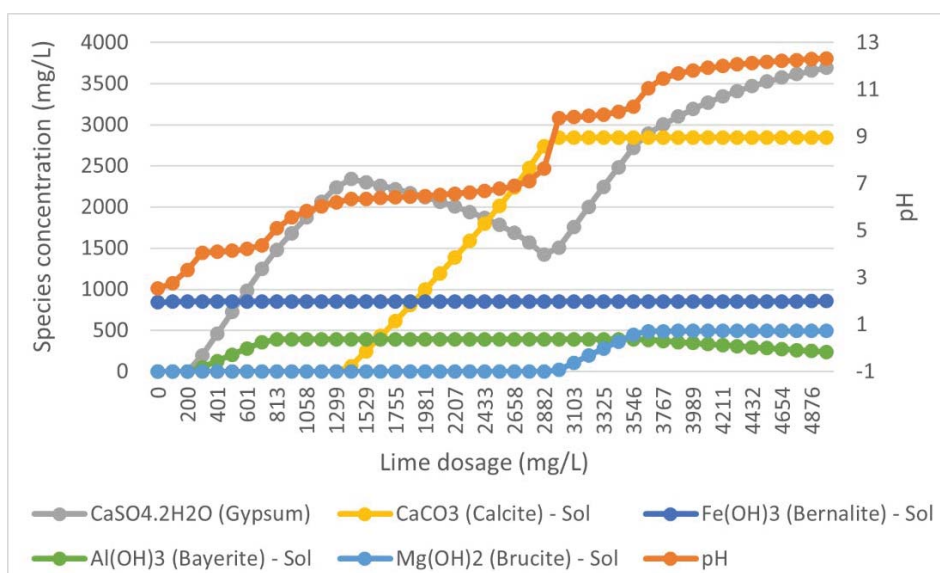


Figure 6-9 OLI modelling of the simulated neutralisation of AMD stream 10: Precipitate formation and pH for different $\text{Ca}(\text{OH})_2$ dosages under aeration conditions.

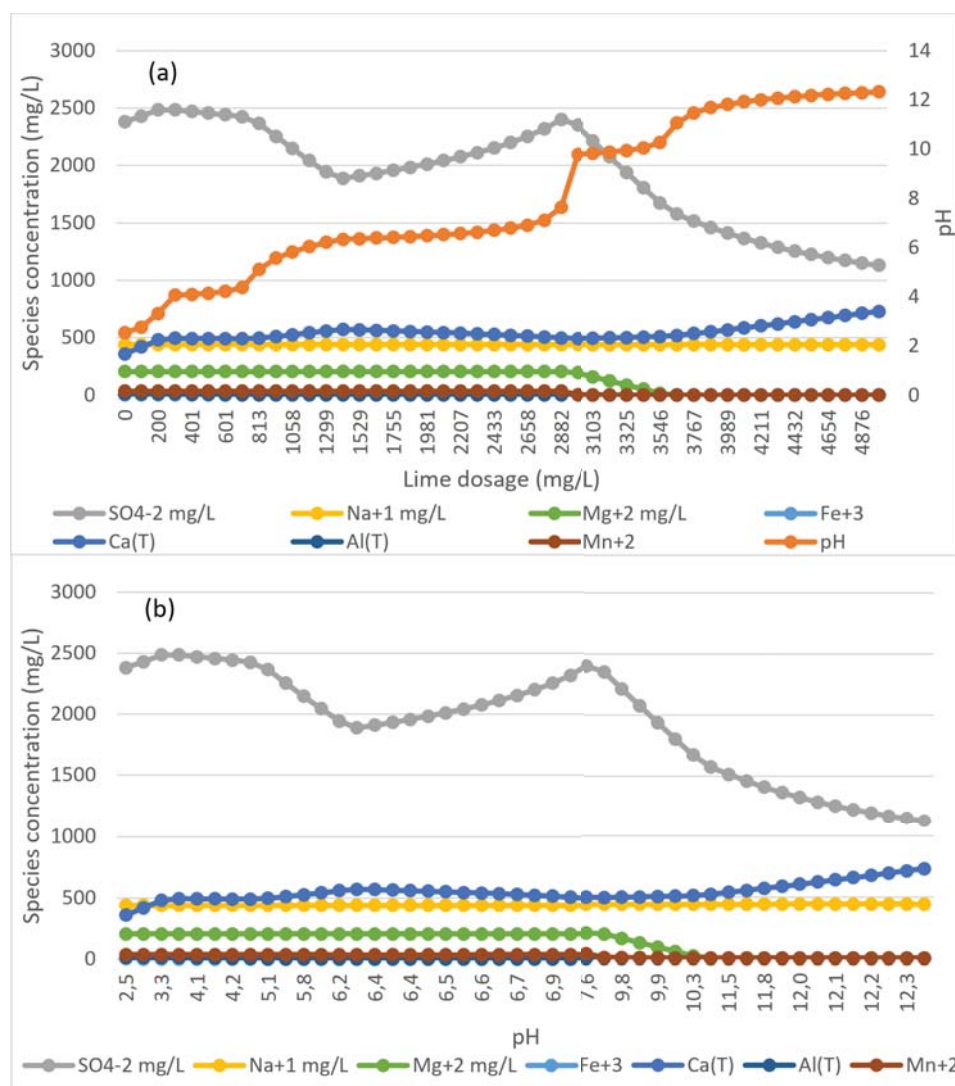


Figure 6-10 OLI modelling of the simulated modelling of AMD stream: concentration of soluble species as a function of (a) lime dosage and (b) pH in the absence of air.

In contrast to the anoxic scenario, the formation of aqueous carbonate and consequently solid calcium carbonate is associated with considerable pH buffering in the range 5.5-7.1, ultimately resulting in significantly higher lime consumption for effective soluble sulphate and metal removal. As indicated in Figure 6-10, a total lime dosage of 5 g/L, corresponding to a pH of 12.3, is required to reduce sulphate levels to 1131 mg/L, with a similar residual sulphate concentration being achieved at a lime dosage of 1.8 g/L and a corresponding pH of 9.9 in the anoxic scenario. The final neutralisation residue obtained at pH 12.3 also has a significantly lower gypsum content (45%), with calcite (35%) and the hydroxides of Fe ($\text{Fe}(\text{OH})_3$ at 10%), Al ($\text{Al}(\text{OH})_3$ at 3%) and Mg ($\text{Mg}(\text{OH})_2$ at 6%) accounting for the remaining mass of precipitate.

6.2 Thermodynamic modelling of laboratory neutralisation experiments before and after treatment with reductants.

Visual MINTEQ was used to simulate formation of aqueous and solid species under the conditions observed during laboratory-scale neutralisation of the AMD solution P, both before (Section 6.2.1) and after treatment with chemical (Section 6.2.2) and green (Section 6.2.3) reductants. In each case carbonate is added to the solutions at various concentrations to simulate the effect of CO_2 entrainment and dissolution during rigorous agitation of the solutions under ambient air conditions.

6.2.1 Lime neutralisation of AMD solution P before treatment

As indicated in Chapter 5, neutralisation of the raw AMD solution P was carried out at lime dosages of 10 g/L and 12 g/L and agitation continued for a period of 120 minutes, resulting in final pH values of 9.2 and 11.2 and residue masses of approximately 28 g/L and 30 g/L, respectively.

As shown in Figure 6-11, thermodynamic simulation of the effect of the addition of lime and corresponding pH adjustment predicts that the increase in pH from 9.2 to 11.2 (corresponding to lime dosages of 10 g/L and 12 g/L respectively) will result in an increase in the extent of removal of sulphate (from 87% to 91%), Al (from 91% to 99%), Mn (from 83% to 100%) and, in particular, Mg (from 0% to 95%). Complete precipitation of Fe occurs at both pH 9.2 and pH 11.2.

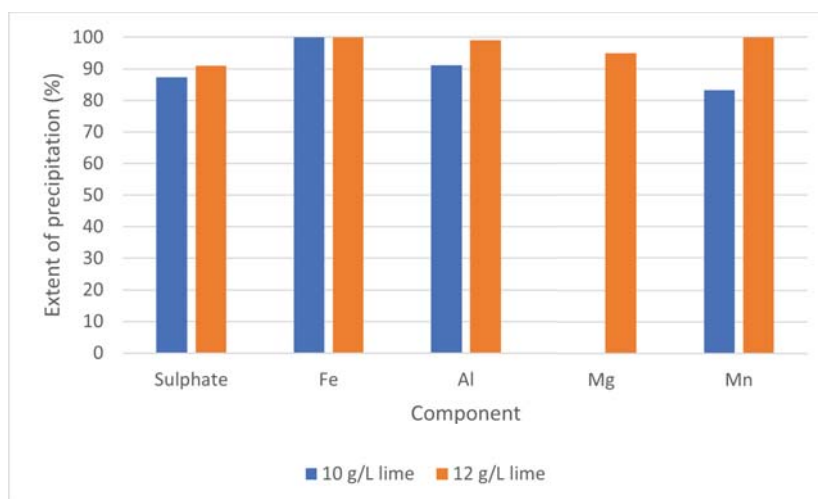


Figure 6-11 Visual MINTEQ simulation of the laboratory-scale neutralisation of AMD solution P: Extent of precipitation as a function of lime addition (0 additional carbonate).

Thermodynamic modelling shows, however, that the extent of sulphate precipitation, as well as the sulphate and calcium concentrations in the final effluent and the compositions of the neutralisation residues, are influenced by the presence of soluble carbonate, which may be formed during the entrainment and dissolution

of atmospheric CO₂ during the neutralisation process. The effect of added carbonate at 10 g/L and 12 g/L lime dosage is explored in Sections 6.2.1.1 and 6.2.1.2 respectively.

6.2.1.1 Lime dosage of 10 g/L

Thermodynamic modelling of raw solution P after addition of calcium to 5135 mg/L (equivalent of 10 g/L lime @ 95% purity) and adjustment of pH to 9.2 and redox potential of 133 mV, shows formation of between 27 g/L and 28 g/L of solid precipitates at soluble carbonate additions of between 0 and 2420 mg/L. This is in good agreement with the experimental value of 28 g/L. Furthermore, gypsum is the predominant solid constituent, accounting for than 50% of the total solid precipitate formation in all cases. As shown in Figure 6-12, the thermodynamic model indicates that the neutralisation residues will all contain gypsum as a major component (>50%), with significant quantities of amorphous ferric hydroxide (Fe(OH)₃) at 27%) as well as amorphous aluminium hydroxide (Al(OH)₃) at approximately 2.5%. The precipitate generated in the absence of additional carbonate also showed formation of minor amounts of ettringite (Ca₆Al₂(SO₄)₃OH₁₂ 26H₂O at 8%). The results in Figure 6-12 also show that the content of gypsum declines slightly from 61% to 55% and the concentration of amorphous calcite increases from 2% to 13% as the concentration of added carbonate increases from 500 mg/L to 2420 mg/L, the conditions at which a good charge balance was achieved. The thermodynamic model also predicts that the residues from the solutions containing additional carbonate will contain traces of MnCO₃ at approximately 0.6%. Consistent with Phreeq and OLI simulation modelling, no precipitation of salts Na, K and Mg is predicted to occur.

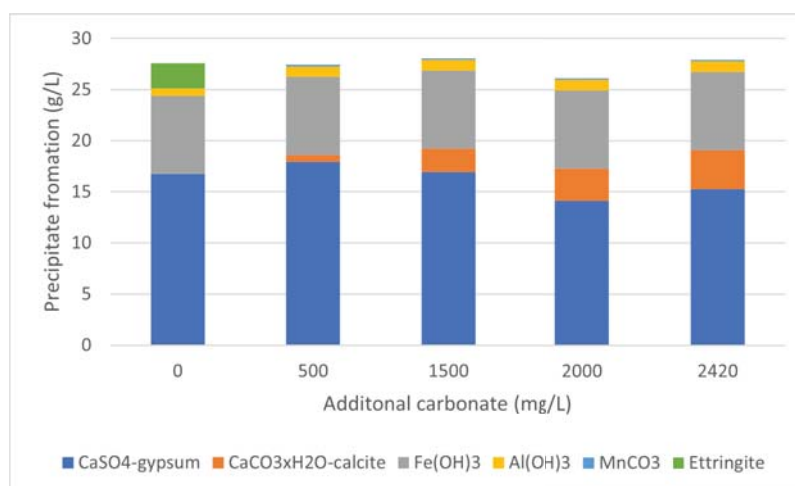


Figure 6-12 Visual MINTEQ simulation of the laboratory-scale neutralisation of AMD solution P at 10 g/L lime dosage: Precipitate content as a function of carbonate addition (pH 9.2, redox potential 133 mV, t=120 minutes).

The predicted concentrations of sulphate and calcium in the neutralisation effluents and nutrients as a function of additional carbonate are presented and compared with experimental results in Figure 6-13. Modelling results show that the sulphate concentrations increase, and the calcium concentrations decrease as the gypsum formation decreases and the calcite formation increases in the presence of increasing concentrations of carbonate. Experimental sulphate and calcium concentrations in the effluent are consistent with the model predictions at carbonate additions of ≥ 2000 mg/L, equivalent to dissolved carbonate concentrations of 30–40 mg/L. Whilst predicted and experimental Ca concentrations in the residue are generally consistent with those predicted on the basis of thermodynamics, the assayed sulphate concentrations (37%) in the laboratory-derived residue are, however, slightly higher than those values predicted (30%) under conditions of ≥ 2000 mg/L carbonate conditions. Furthermore, although the residual iron in the experimental residue is consistent with the theoretically predicted content Fe(OH)₃ content of 27%, analysis of the experimental residue shows a Mg content of 0.8% in contradiction to the model output value of 0%. This is possible due to substitution of Mg²⁺ ions in the calcite precipitate, as reported in the literature (Pina and Pimentel, 2017). Attenuation of metal cations onto the surfaces of ferric hydroxide precipitates is also a commonly reported occurrence.

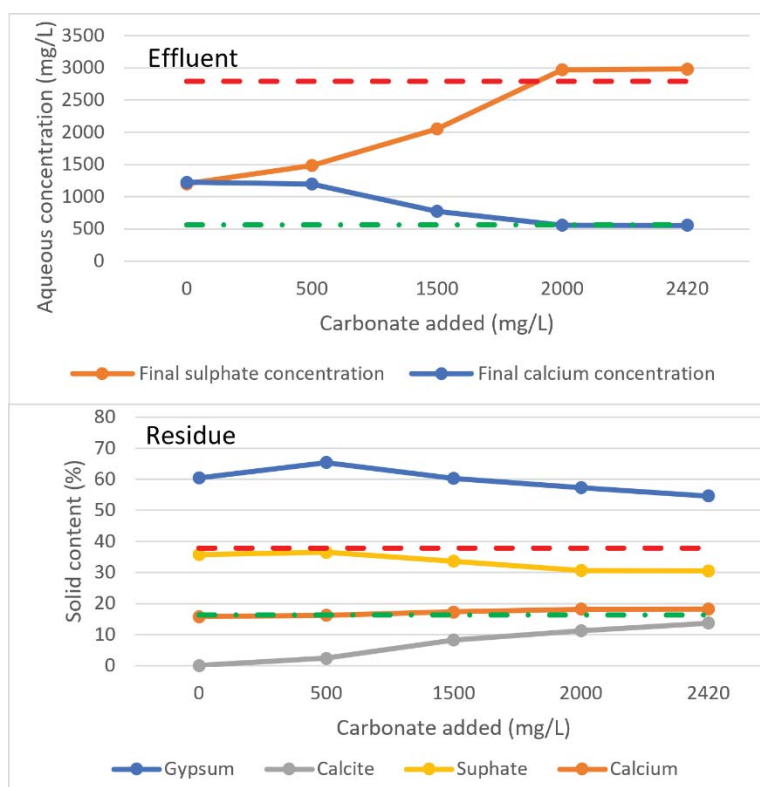


Figure 6-13 Visual MINTEQ simulation of the laboratory-scale neutralisation of AMD solution P at 10 g/L lime dosage: Ca and sulphate concentrations in effluents and residues as a function a function of carbonate addition. Experimental sulphate and calcium values are represented by red and green dashed lines respectively (pH 9.2, redox potential 133 mV, $t=120$ minutes).

6.2.1.2 Lime dosage of 12 g/L

Thermodynamic modelling of raw solution P after addition of calcium to 6162 mg/L (equivalent of 12 g/L lime @ 95% purity) and adjustment of pH to 11.2 and redox potential of 84 mV, shows formation of between 30 g/L and 32 g/L of solid precipitates at soluble carbonate additions of between 0 and 1600 mg/L. As in the case of the lower lime addition, this is in good agreement with the experimental value of 30 g/L. Figure 6-14 shows that, although gypsum is still present as a dominant solid constituent at $\geq 45\%$ of the total solid precipitate formation in all cases, theoretical predictions indicate that the higher pH value favours ettringite formation, which is present in significant quantities (28%) in all neutralisation residues. This precipitate accounts for 100% of the Al in the system, as well as a significant proportion of the net sulphate and calcium precipitated (approximately 21% and 14% respectively). All neutralisation residues are also predicted to contain significant quantities of $\text{Fe}(\text{OH})_3$ (24%), as well as trace quantities of $\text{Mn}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ (approximately 0.4% in both cases). It is noted that $\text{Mg}(\text{OH})_2$ was not predicted to form at the lower lime addition and pH value (see Section 6.2.1.1). Like the trends observed for pH 9.2, thermodynamic modelling predicts that the content of gypsum will decline slightly (from 47% to 45%) and the concentration of amorphous calcite increase (from 1% to 9%) as the concentration of added carbonate increases from 50 mg/L to 1600 mg/L, with a good charge balance being achieved at 1500 ppm total carbonate addition corresponding to a soluble carbonate concentration of 9 mg/L.

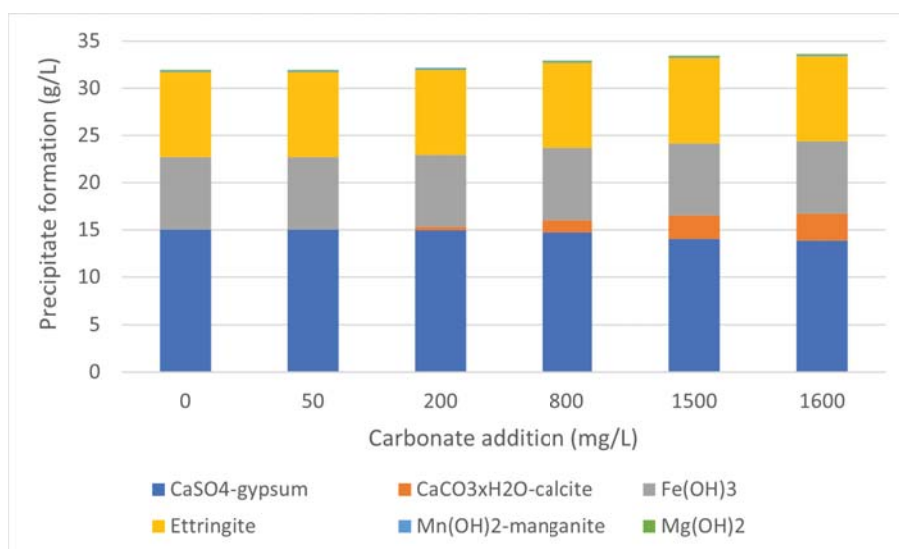


Figure 6-14 Visual MINTEQ simulation of the laboratory-scale neutralisation of AMD solution P at 12 g/L lime dosage: Precipitate content as a function of carbonate addition (pH 11.2, redox potential 84 mV, t=120 minutes).

The predicted concentrations of sulphate and calcium in the neutralisation effluents and nutrients as a function of additional carbonate are presented and compared with experimental results in Figure 6-15.

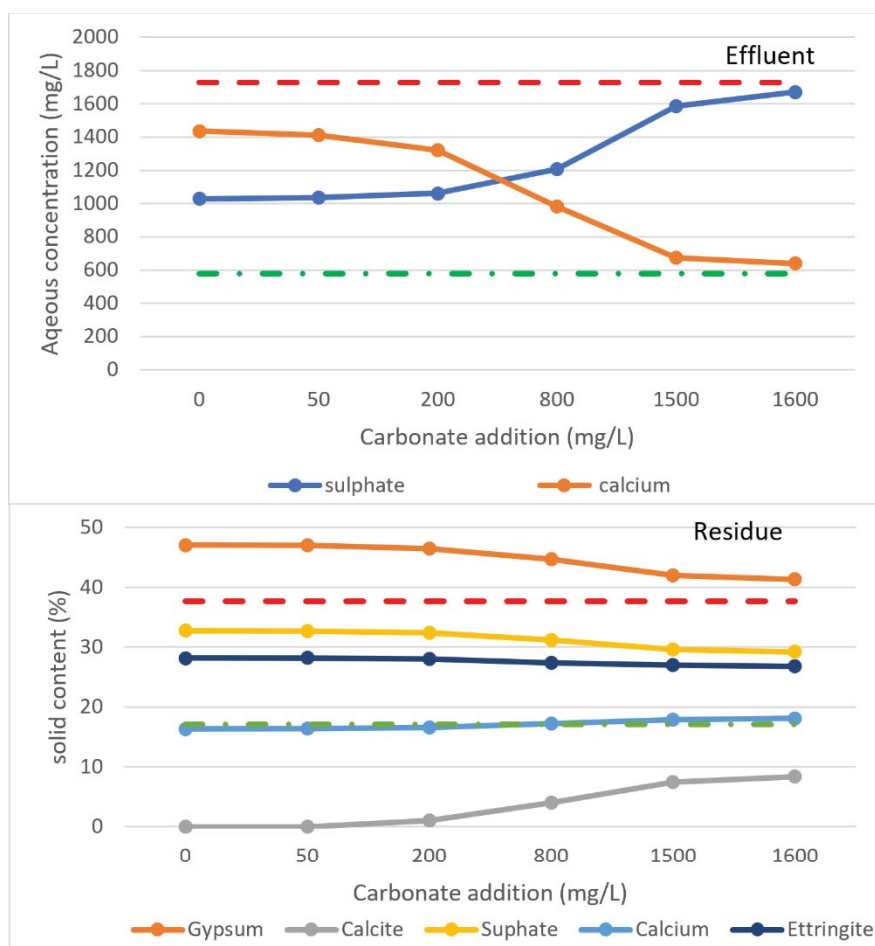


Figure 6-15 Visual MINTEQ simulation of the laboratory-scale neutralisation of AMD solution P at 12 g/L lime dosage: Ca and sulphate concentrations in effluents and residues as a function a function of carbonate addition. Experimental sulphate and calcium values are represented by red and green dashed lines respectively (pH 11.2, redox potential 84 mV, t=120 minutes).

Modelling results once again show that the sulphate concentrations increase, and the calcium concentrations decrease as the gypsum formation decreases and the calcite formation increases in the presence of increasing concentrations of carbonate. Experimental sulphate and calcium concentrations in the effluent are in good agreement with the model predictions at carbonate additions of approximately 1600 mg/L. Once again, the assayed sulphate (38%) and magnesium (1.4%) concentrations in the laboratory-derived residue are slightly higher than those values predicted (29% and 0.12% respectively).

6.2.2 Lime neutralisation of AMD solution P after nano iron removal using sodium borohydride

As indicated in previous chapters, the pre-treatment of AMD solution P with sodium borohydride resulted in a supernatant with a relatively high pH, and containing relatively high concentrations of sulphate, sodium, and boron, but low metal values. Neutralisation of the treated supernatant was conducted at lime dosages of 6 g/L and 8 g/L and agitation continued for a period of 120 minutes, resulting in final pH values of 9.5 and 9.8 and residue masses of approximately 29 g/L and 14 g/L respectively.

Figure 6-16 shows the simulated effect of the addition of lime and corresponding pH adjustment on extent of precipitation of key components during neutralisation. In accordance with thermodynamics, under the experimental neutralisation conditions residual iron will be completely removed from solution, but removal of sulphate and manganese will only be partial – the extent of precipitation increasing from 54% to 69% in the case of sulphate and from 49% to 77% in the case of Mn – as the pH increases from 9.5 to 9.8 (corresponding to lime dosages of 6 g/L and 8 g/L respectively). No precipitation of Al, Mg or boron is predicted to occur under these experimental conditions.

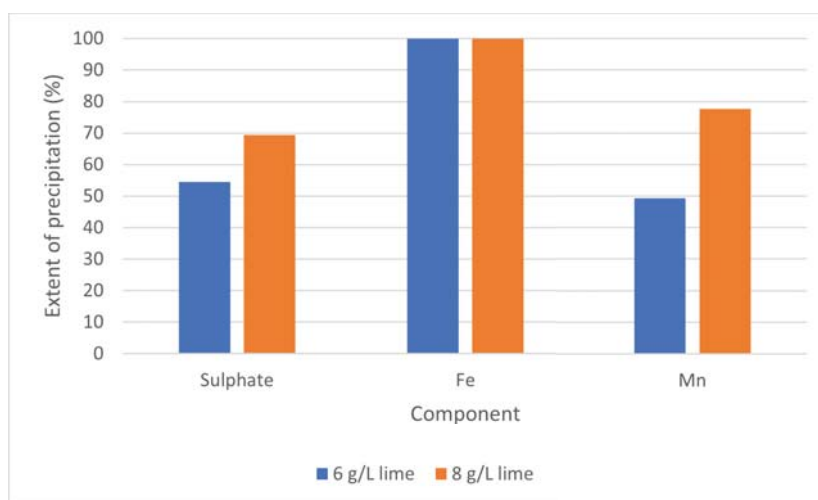


Figure 6-16 Visual MINTEQ simulation of the laboratory-scale neutralisation of sodium borohydride treated AMD solution P: Extent of precipitation as a function of lime addition (0 additional carbonate).

As in the case of the neutralisation of raw AMD, thermodynamic modelling shows that the presence of carbonate will influence the extent of sulphate precipitation, as well as the sulphate and calcium concentrations in the final effluent and the compositions of the neutralisation residues. The effect of carbonate at 6 g/L and 8 g/L lime dosage is discussed in Sections 6.2.2.1 and 6.2.2.2 respectively.

6.2.2.1 Lime dosage of 6 g/L

Thermodynamic modelling of raw solution P after addition of calcium to 3081 mg/L (equivalent of 6 g/L lime @ 95% purity) and adjustment of pH to 9.5 and redox potential of 81 mV, shows that the only significant precipitates that will be formed will be gypsum and calcite depending on the concentration of carbonate. This is consistent with the relatively low levels of metals in the treated supernatant. Whilst thermodynamics indicate that the neutralisation residue will consist primarily of gypsum (99.8%) in the absence of carbonate, the gypsum

content decreases, and the content of calcite increases, until the residue consists primarily of calcite (99.4%) at a carbonate dosage of 5000 mg/L (See Figure 6-17).

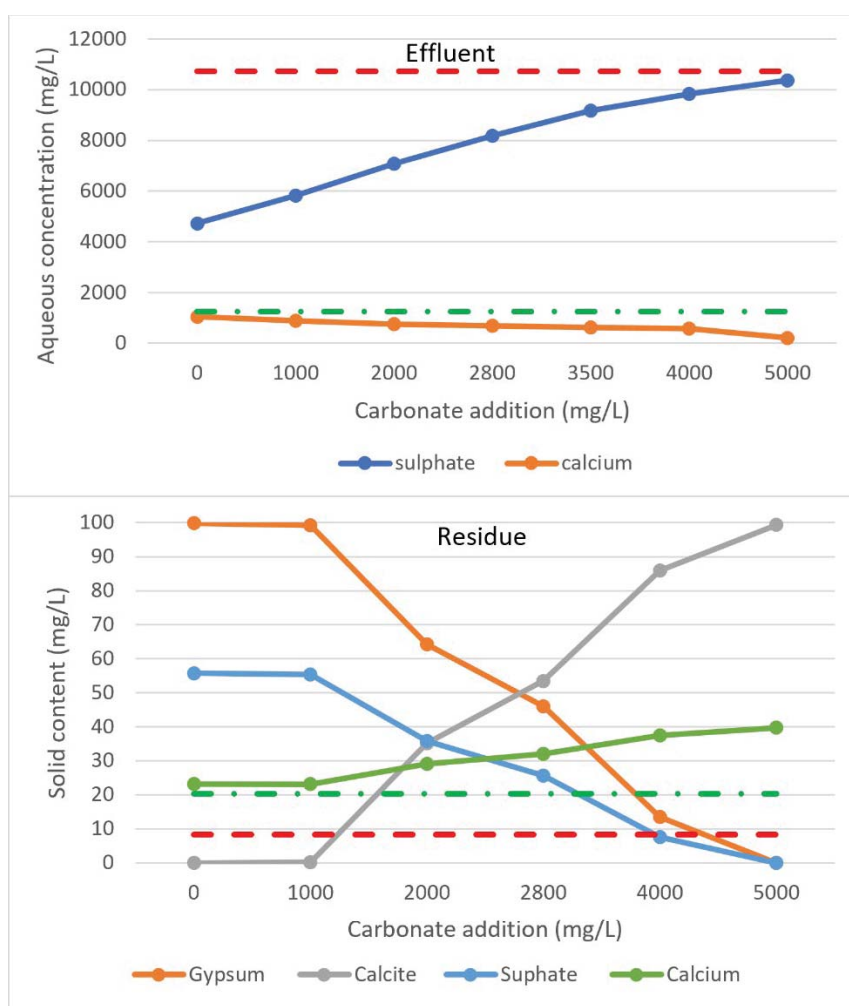


Figure 6-17 Visual MINTEQ simulation of the laboratory-scale neutralisation of sodium borohydride treated AMD solution P at 6 g/L lime dosage: Ca and sulphate concentrations in effluents and residues as a function of carbonate addition. Experimental sulphate and calcium values are represented by red and green dashed lines respectively (pH 9.5, redox potential 81 mV, t=120 minutes).

The decrease in the formation of gypsum corresponds to an increase in soluble sulphate, with negligible removal of sulphate corresponding to an initial carbonate concentration of 5000 mg/L. A comparison with experimental results indicates that the effluent sulphate concentrations correspond to the modelling outputs obtained at 5000 mg/L carbonate addition and negligible gypsum formation. A comparison of experimental and theoretical residue concentrations in the residue indicates that the sulphate content in the laboratory-derived residue (8.3%, corresponding to 15% gypsum) correlates most closely with the theoretical scenario with 4000 mg/L carbonate addition (7.5% sulphate, corresponding to 13% gypsum and 86% calcite). However, the theoretically predicted Ca content (38%-40%) in the residue at high carbonate additions (≥ 4000 mg/L) and calcite content ($\geq 86\%$) is considerably higher than the experimental Ca content (20%). Furthermore, the experimental results indicate that the concentration of boron decreases by approximately 25% during neutralisation, in contrast to the thermodynamic model which does not predict any boron precipitation. In accordance with the literature, boron can form insoluble compounds in the presence of lime, such as dicalcium hexaborate pentahydrate, $2\text{Ca}_3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (Remy et al., 2004). Calculations based on analysed boron concentrations in the neutralisation effluent indicate that formation of this precipitate could be as much as 4 g/L, and as much as 30%-36% of the residue, with concomitantly lower gypsum and calcite contents. It has also been reported that boron co-precipitates with both gypsum and calcite in alkaline solutions. Remy et al.

(2004) postulate that sulphate in gypsum may be substituted for the tetrahedrally-co-ordinated anion $B(OH)_4^-$, which is the stable form of boron at $pH > 9.2$. This alteration could alter the stability of the gypsum, and hence the outputs of the thermodynamic model. Boron precipitation would also impact on the charge balance in the solutions, with the addition of carbonate required to achieve a charge balance possibly being higher than the theoretical value of 2000 mg/L (corresponding to a final soluble carbonate concentration of 52 mg/L) derived at zero boron removal.

6.2.2.2 Lime dosage of 8 g/L

Thermodynamic modelling of raw solution P after addition of calcium to 4019 mg/L (equivalent of 8 g/L lime @ 95% purity) and adjustment of pH to 9.8 and redox potential of 63 mV, shows similar trends in terms of sulphate and calcium deportment as the addition of 6 g/L lime (Figure 6-18).

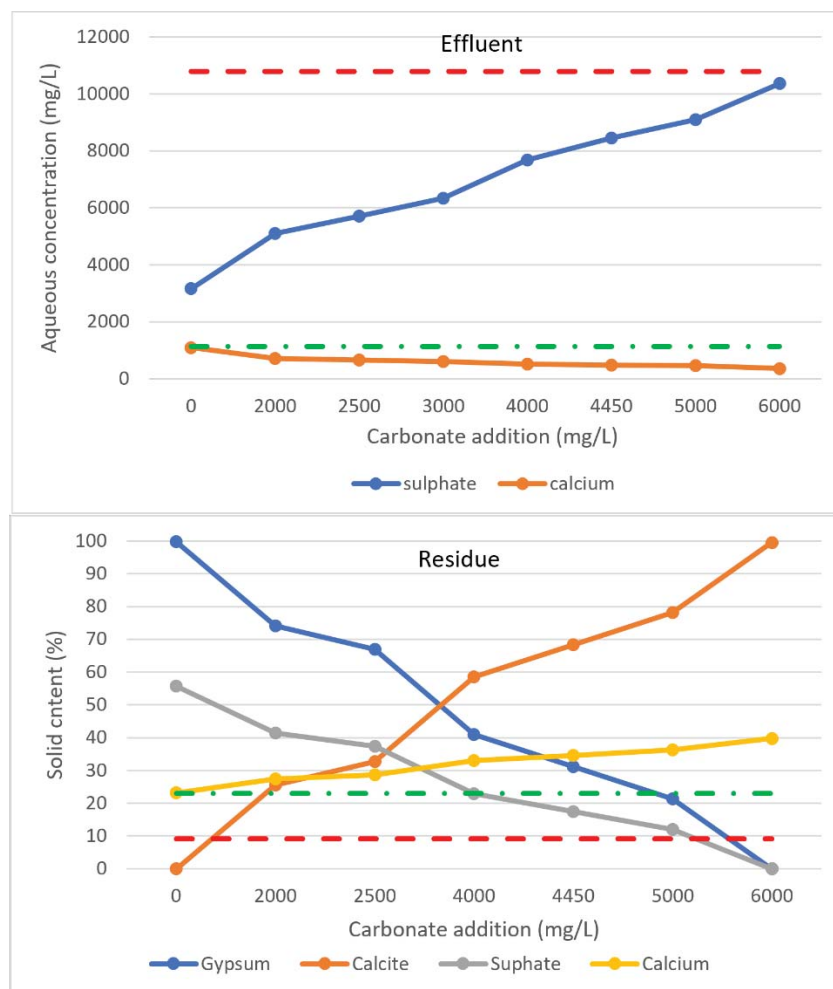


Figure 6-18 Visual MINTEQ simulation of the laboratory-scale neutralisation of sodium borohydride treated AMD solution P at 8 g/L lime dosage: Ca and sulphate concentrations in effluents and residues as a function a function of carbonate addition. Experimental sulphate and calcium values are represented by red and green dashed lines respectively (pH 9.8, redox potential 63 mV, t=120 minutes).

Figure 6-18 shows that negligible gypsum formation and removal of sulphate occurs at a carbonate addition of 6000 mg/L, under which conditions the theoretical concentration of sulphate in the effluent is equivalent to that observed experimentally. A comparison of experimental and theoretical residue concentrations in the residue indicates that the sulphate content in the laboratory-derived residue (9.2%, corresponding to 16.5% gypsum) correlates with a theoretical carbonate addition of between 5000 mg/L and 6000 mg/L added carbonate addition, with corresponding final soluble carbonate concentrations of 50-65 mg/L. As in the case of 6 g/L lime addition, the theoretically predicted Ca content (36%-40%) in the residue at high carbonate

additions (≥ 5000 mg/L) and calcite content ($\geq 78\%$) is considerably higher than the experimental Ca content (22%). The concentration of boron in the experimentally derived effluent indicates a boron removal of 42% (i.e. higher than the 25% obtained at 6 g/L lime dosage), with calculations indicating that formation of this precipitate could be as much as 6.4 g/L, and as much as 34%-38% of the residue. This could have a significant effect on the gypsum and calcite contents, predicted on the basis of thermodynamics.

6.2.3 Lime neutralisation of AMD solution P after nano iron removal using green tea extracts

The pre-treatment of AMD solution P with green tea extract resulted in a supernatant with a low pH (1.8) and containing significant relatively high concentrations of sulphate (~ 8 g/L), as well as residual metals, particularly Fe (420 mg/L) and Al (120 mg/L) and K (259 mg/L). Neutralisation of the treated supernatant was conducted at lime dosages from 5, 7, 9 and 11 g/L giving rise to effluents with pH values of 8.9, 9.9, 11.4 and 11.5 after a retention period of 120 minutes respectively.

Figures 6-19 presents the modelled extents of precipitation under the experimental conditions corresponding to the different lime dosages. Removal of sulphate from the solution increases from 70% to 90% as the lime dosage increases from 5 g/L (effluent pH ~ 9) to 11 g/L (effluent pH 11.5). Effective removal ($>96\%$) of Mg only occurs at the higher lime dosages of 9 g/L and 11 g/L, corresponding to pH values of ~ 11.5 , whilst complete removal of Mn is only predicted to occur at a lime dosage of 11 g/L (effluent pH 11.5). Residual Fe is precipitated at all pH values, whilst $> 99.9\%$ Al precipitation occurs at lime additions ≥ 7 g/L (effluent pH ≥ 10).

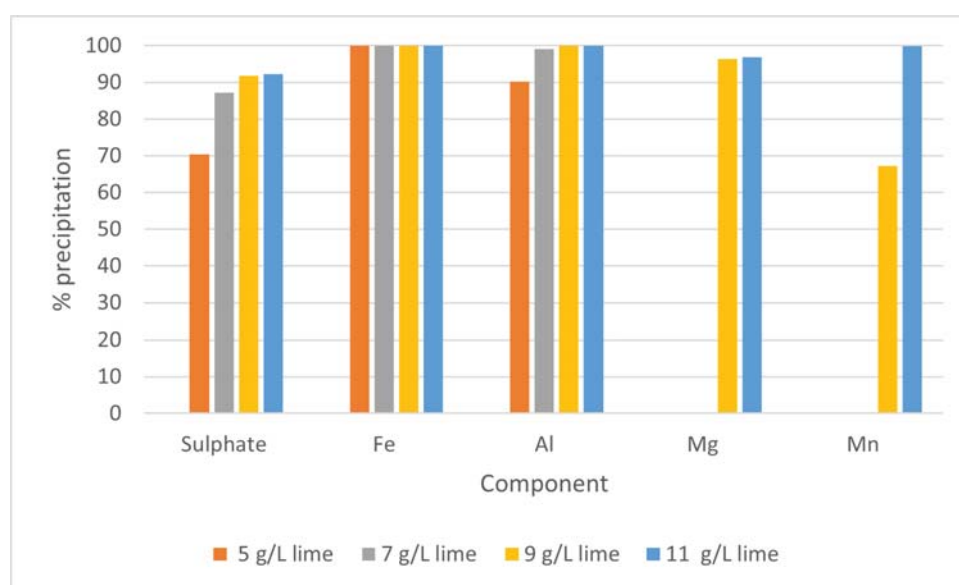


Figure 6-19 Visual MINTEQ simulation of the laboratory-scale neutralisation of AMD solution P after treatment with green tea extract: Extent of precipitation as a function of lime addition (0 additional carbonate).

In the absence of carbonate, thermodynamic simulation indicates that gypsum is the major constituent ($> 75\%$) in the neutralisation residues obtained at all lime additions, with $\text{Fe}(\text{OH})_3$ accounting for 5-7% of all residues (Figure 6-20). The lower gypsum content (75% to 76%) in the precipitates at lime additions ≥ 7 g/L (effluent pH ≥ 10) can be attributed to the formation of ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3\text{OH}_{12} \cdot 26\text{H}_2\text{O}$), which accounts for 17% to 19% of the residues generated under these conditions. At 5 g/L lime addition (corresponding to an effluent pH ~ 9), alunite ($\text{KAl}_3(\text{OH})_6(\text{SO}_4)_2$) is predicted to be the stable form of Al. Alunite accounts for only 5% of the residue with a concomitant higher gypsum content (87%). The residues obtained at lime additions of 9 g/L and 11 g/L also contained minor quantities ($\sim 2\%$) $\text{Mg}(\text{OH})_2$.

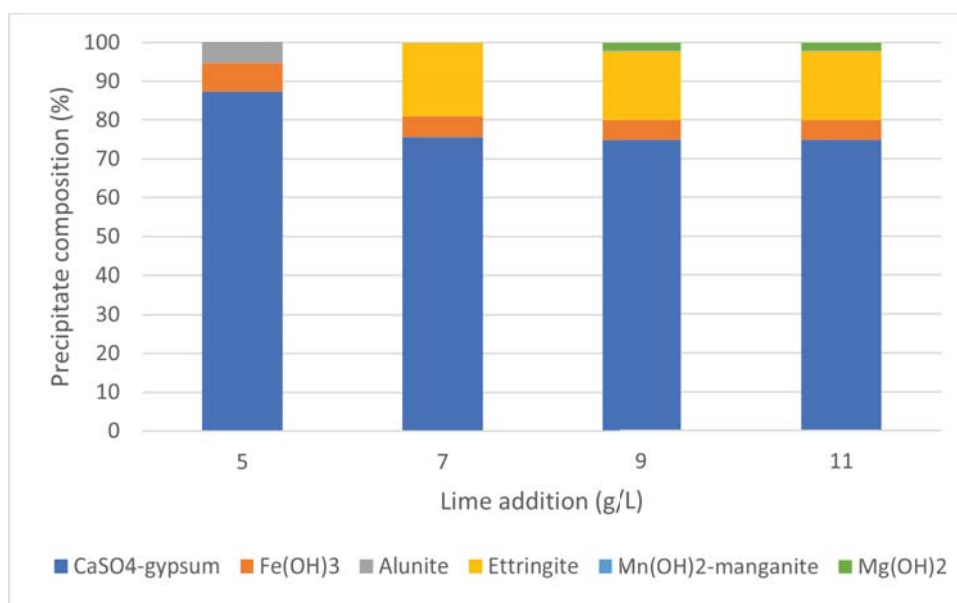


Figure 6-20 Visual MINTEQ simulation of the laboratory-scale neutralisation of AMD solution P after treatment with green tea extract: Precipitate composition as a function of lime addition (0 additional carbonate).

As in the previous cases, thermodynamics predict that the deportment and concentrations of calcium and, to a greater extent, sulphate in the effluent and residue will be highly dependent on the extent of carbonate formation due to CO₂ entrainment and solubilisation. The effect of carbonate addition on the effluent sulphate and calcium concentrations is shown in Figure 6-21.

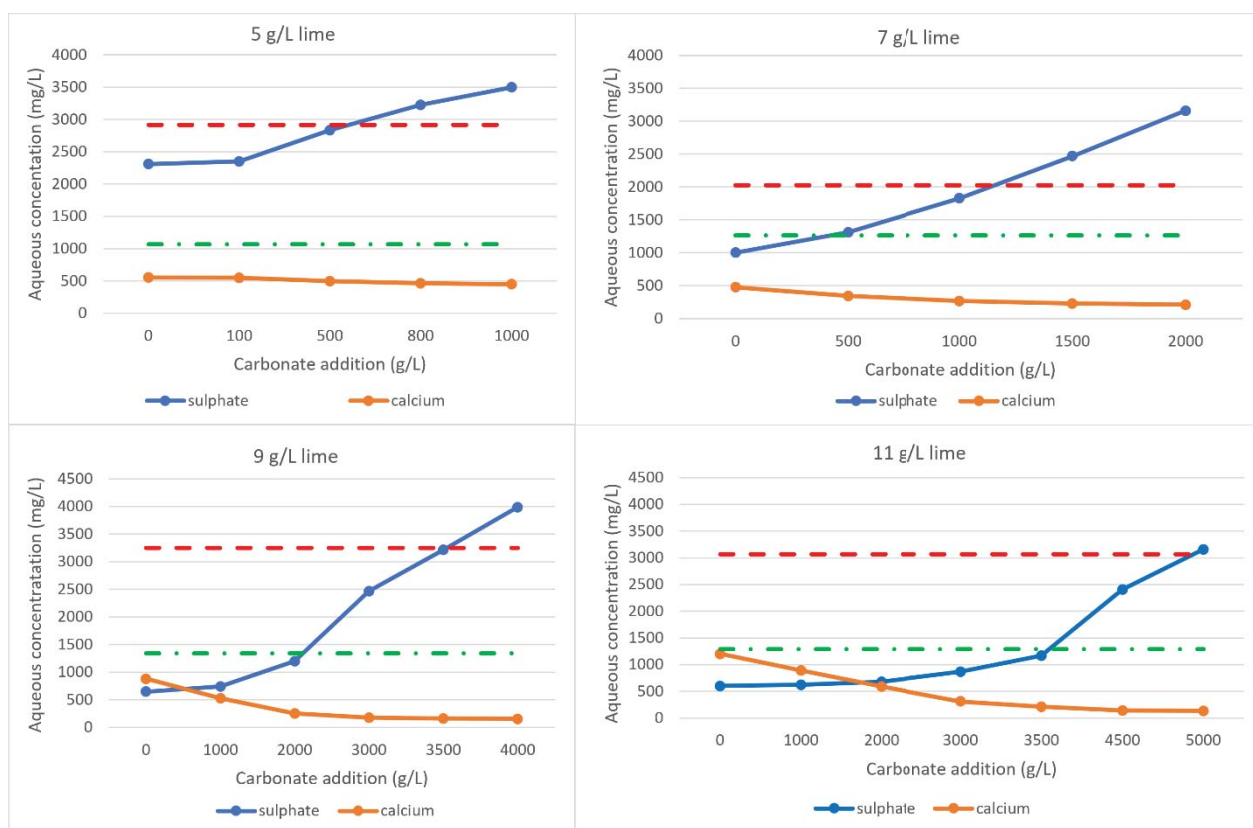


Figure 6-21 Visual MINTEQ simulation of the laboratory-scale neutralisation AMD solution P after treatment with green tea extract. Ca and sulphate concentrations in effluents as a function a function of carbonate addition. Experimental sulphate and calcium values are represented by red and green dashed lines respectively.

These results show that the effluent sulphate concentrations increase significantly as the amount of carbonate added to the solution increases. This can be attributed to a concomitant decrease in the formation of gypsum, as calcium preferentially forms calcite in the presence of soluble carbonate (see Figure 6-22). The increase in carbonate addition also results in a corresponding decrease in effluent calcium concentrations due to the higher stability (lower solubility) of calcite relative to gypsum. A comparison with experimental values indicates that the experimental sulphate concentrations in the effluent solutions (2914, 2030, 3249 and 3070 mg/L at lime additions of 5, 7, 9 and 11 g/L respectively) are significantly higher than those values predicted (2309, 100, 646 and 600 mg/L at lime additions of 5, 7, 9 and 11 g/L respectively) in the absence of carbonate (i.e. based on gypsum and, at pH ≥ 10 , ettringite formation alone), particularly at the higher lime dosages corresponding to pH value of 11.4-11.5. Experimental calcium concentrations are also higher than those predicted based on the theoretical stability of gypsum in the zero-carbonate scenario, particularly at the lower lime dosages. This is potentially due to the fact that the experimentally derived gypsum is less soluble than that predicted on the basis of the solubility product for pure gypsum, which may, in turn, be due to inclusions of other cations such as Mg. The enhanced solubility of gypsum alone is, however, unlikely to account for the discrepancies in soluble sulphate concentrations, particularly at the higher lime dosages. Thermodynamic calculations indicate good correlation between experimental and theoretical sulphate concentrations at initial carbonate additions of approximately 500, 1200, 3500 and 5000 mg/L at lime dosages of 5, 7, 9 and 11 g/L respectively, corresponding to soluble carbonate concentrations in the effluent of 19, 15, 12.5 and 12.3 mg/L at the respective lime dosages. These values correspond to theoretical residues containing 7, 14, 35 and 43% calcite at lime dosages of 5, 7, 9 and 11 g/L respectively (Figure 6-22). Once again, the higher experimental concentrations of soluble Ca in the effluents compared to those predicted theoretically, particularly at the higher carbonate additions, are indicative of the relatively high solubility of the calcite precipitates, possibly due to Mg substitution, as reported in the literature (Pina and Pimentel, 2017). Ettringite concentrations at lime dosages ≥ 7 g/L lime are controlled largely by initial Al concentrations and are relatively independent of carbonate.

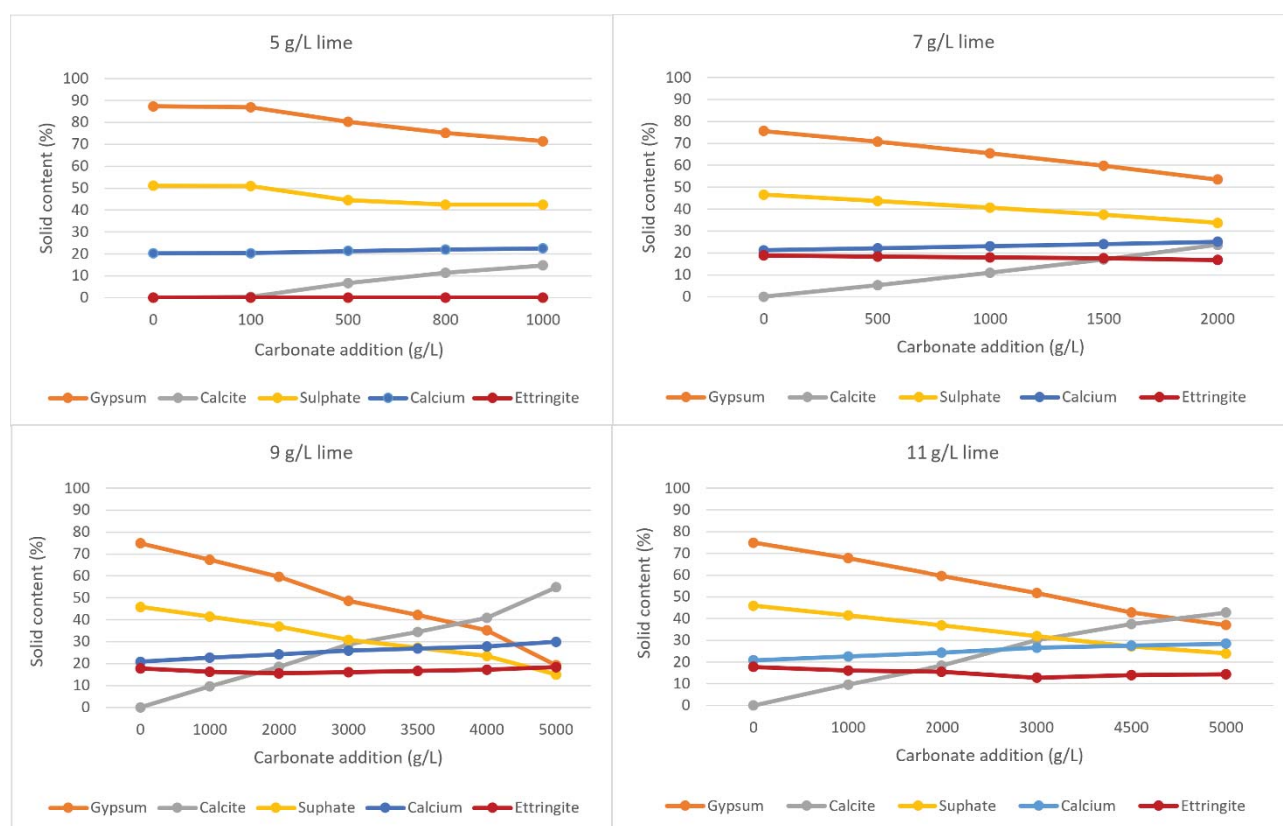


Figure 6-22 Visual MINTEQ simulation of the laboratory-scale neutralisation AMD solution P after treatment with green tea extract. Ca and sulphate species and concentrations in effluents as a function a function of carbonate addition. Experimental sulphate and calcium values are represented by red and green dashed lines respectively.

6.3 Summary

A number of difficulties were experienced in terms of the application of thermodynamic models to accurately simulate empirical neutralisation results. To some extent this could be attributed to the characteristics and configurations of the models themselves. For instance, the OLI model automatically reconciles anion and cations in terms of mass and charge balance before running simulations, which can result in significant discrepancies between simulated and experimental results in cases where input datasets are incomplete, or where there are any irregularities in the data. Furthermore, the operator is unable to adjust the model database or to select possible species that may be formed under ambient neutralisation conditions in an engineered system. The Visual MINTEQU model, on the other hand, allows for more flexibility in terms of manipulating input parameters and the database, but is best suited for simulating batch systems, as opposed to dynamic processes such as titration of AMD solutions with lime. The PHREEQ model appears to address both the shortcomings of the OLI and Visual MINTEQU models but is not as user-friendly. The specific advantages and disadvantages of this model were not investigated in detail in this study. In general, the ability to use thermodynamic models to directly simulate empirical neutralisation results is limited due to the fact that these models do not consider non-idealities, such as the formation of mixed or non-stoichiometric precipitates due to inclusion and substitution mechanisms. Nevertheless, equilibrium thermodynamic models provided valuable information on the possible neutralisation reaction mechanisms and controlling parameters. The key findings from the thermodynamic simulation of laboratory-scale experiments include:

- Modelling confirmed that whilst neutralisation of the AMD solutions results in effective removal of residual metals such as iron and aluminium at pH values of approximately 9-10, higher pH values (>11) are required to remove Mg as $\text{Mg}(\text{OH})_2$. The extent of Mn precipitation also increases on increasing the neutralisation pH above 11.
- The formation of ferric hydroxide and Al hydroxy or hydroxysulphate precipitates during neutralisation of solutions containing residual Fe and Al results in a decrease in the gypsum content of the residues. In particular, the formation of relatively stable ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3\text{OH}_{12} \cdot 26\text{H}_2\text{O}$) which is favoured by an increase in soluble Al and/or pH results in a significant drop in gypsum formation. The predicted mineralogical compositions of the residues prepared under the empirical neutralisation conditions in the absence of CO_2 entrainment (see results in Chapter 5) are summarised in Table 6.2. In accordance with the thermodynamic modelling results, the residues from the neutralisation of AMD pre-treated with NaBH_4 (containing negligible Fe and Al) are predicted to consist of almost pure gypsum. This is compared to a maximum gypsum content of 61% in the residues from the neutralisation of raw AMD containing elevated levels of Al and Fe. The results in Table 6.2 also show that a feed Al concentration of 388 mg/L (raw AMD) the ettringite content in the neutralisation is predicted to increase from 8% to 28% on increasing the pH from 9.2 to 11.2, with a concomitant decrease in gypsum content from 61% to 47%. However, at a feed Al concentration of 120 mg/L, ettringite formation only occurs at a pH ~ 10, with a corresponding decrease in the gypsum content from 87% to 75%.

Table 6-2 Thermodynamic predictions of the compositions of the residues obtained during neutralisation of AMD solution P before and after treatment with NaBH₄ and green tea extract (0 carbonate formation)

	Feed solutions concentrations (mg/L)		Effluent pH	Predicted mineral composition of neutralisation residue (%)				
	Al	Fe		Gypsum	Ettringite	Alunite	Al(OH) ₃	Fe(OH) ₃
Raw AMD	388	4002	9.2	61	8	2.5	2.5	27
			11.2	47	28	0	0	24
AMD after treatment with green tea extract	120	420	8.9	87	0	5.2	0	7
			9.9	76	19	0	0	6
			11.4	75	18	0	0	5
			11.5	75	18	0	0	5
AMD after treatment with NaBH ₄	0.5	<0.1	9.2	99.8	0	0	0	0
			9.8	99.8	0	0	0	0

- Formation of soluble carbonate through entrainment of CO₂ (during rigorous agitation or aeration) can also give rise to calcite (CaCO₃·xH₂O) precipitation with a concomitant decrease in the extent of gypsum (CaSO₄·2H₂O) formation and sulphate removal, and an increase in the amount of lime required to achieve any given pH value. A comparison of predicted effluent sulphate concentrations as a function of simulated carbonate addition, with those obtained experimentally is indicative of calcite formation, with a concomitant decrease in gypsum content, under all experimental conditions (Table 6.3). This is particularly the case during neutralisation of solution pre-treated with NaBH₄, with thermodynamic modelling showing that the high values of effluent sulphate concentration and the low sulphate concentration in the neutralisation residue can be attributed to extensive calcite formation during neutralisation, resulting in significant pH buffering. The high levels of calcite formation could possibly be attributed to the high alkalinity of the solutions, in the form of NaOH, and/or the relatively low volume of feed solution (250 mL), resulting in significant air entrainment under vigorous agitation. A comparison of theoretical and empirical values for effluent sulphate levels during neutralisation of AMD solution P which has been pre-treated with green tea extract shows that calcite formation is likely to increase as the dosage of lime, and hence pH, increases.

Table 6-3 Predicted concentrations of gypsum and calcite in the residues obtained during neutralisation of AMD solution P, with and without carbonate addition.

	Effluent pH	Simulated carbonate addition (mg/L)	Predicted composition of neutralisation residue (%)	
			Gypsum	Calcite
Raw AMD	9.2	0	61	0
		2000	57	11
	11.2	0	47	0
		1600	41	8
AMD after treatment with green tea extract	8.9	0	87	0
		500	80	7
	9.9	0	76	0
		1200	65	14
	11.4	0	75	0
		3500	42	35
AMD after treatment with NaBH ₄	11.5	0	75	0
		5000	37	43
	9.2	0	99.8	0
		4000	13	86
	9.8	0	99.8	0
		5500	10	89

CHAPTER 7: CONCLUSIONS AND RECOMMENDATIONS

The emission of acid mine drainage (AMD) and neutral mine drainage (NMD) from coal mining and processing operations is a major cause of water pollution in the Mpumalanga Province of South Africa. Whilst historically, emphasis has been on the treatment of AMD to comply with local legislative limits for discharge into the environment, current trends are towards recovery of potentially valuable resources, including water and other by-products. This study is concerned largely with the technical feasibility of generating nano iron from AMD, and the effects of this on the downstream neutralisation process parameters and outputs, particularly gypsum which constitutes one of the major wastes from the eMalahleni Mine Water Plant (EWRP).

7.1 Summary of key findings

7.1.1 The potential for value recovery from AMD

Conventional AMD treatment processes, such as High Density Sludge lime neutralisation and Reverse Osmosis, are expensive and generate considerable quantities of sludges and brines, the disposal of which can amount to between 25% and 30% of the total costs of the process. Recovery of by-products from AMD and/or the wastes generated from the treatment of AMD can both reduce costs of waste disposal and offset costs of the treatment process, whilst also being consistent with the principles of sustainable development and related concepts such as resource efficiency, the circular economy and industrial ecology. A preliminary review and assessment of opportunities and processes for the recovery of useful by-products from the AMD treatment sludge has shown that, apart from water, there are several potentially useful, or even valuable, by-products that can be recovered from AMD, including metal, sulphur-based products, and salts. Of relevance to AMD from the Mpumalanga coalfields is the potential recovery of iron and sulphur-based products as these components are typically presented in elevated levels (up to 4 g/L iron and 13 g/L sulphate). One potentially valuable iron product that could be recovered from iron-rich AMD, is zero-valent iron in the nanoparticle size range (<100 nm), also known as zero-valent nano iron (ZVNF). Synthesis of ZVNF can be achieved through the reduction of a higher oxidation state of iron using chemical reductants, such as sodium borohydride, or polyphenolic compounds extracted from green plants such as green tea, lemon, grape, sorghum, etc. The so-called “green” synthesis of ZVNF generates a more stable product at potentially lower cost than chemical synthesis. Whilst zero-valent nano iron offers a number of advantages over micro- and macro-iron in water treatment applications due to its high reactivity, its recovery from AMD remains relatively unexplored.

Prior removal and recovery of iron also provides the opportunity to generate a purer, and potentially more valuable, gypsum product during subsequent lime neutralisation. Gypsum is widely used in a range of applications including use in construction as an additive in cement and floor screed; in the manufacture of building products such as plasterboards, cornices, and other moulded products; and in agriculture, as a soil conditioner or nutrient. Although relatively impure gypsum can be used in agricultural applications ($\geq 70\%$ purity) and in cement production ($\geq 82\%$ purity), a much higher purity ($> 95\%$) gypsum with negligible soluble salts such as P_2O_5 , MgO , F and K_2O is required for the manufacture of gypsum plasterboard. A preliminary assessment of local supply and demand indicates that whilst there is likely to be a local surplus of low-grade gypsum for construction and agricultural applications in the medium to long-term, the market for high-grade plasterboard shows good potential for sustained growth. Alternatively, gypsum can also be processed further into downstream products, such as sulphur, limestone, and magnesite ($MgCO_3$), with potentially higher value and market demand, using Gyp-SLiM or similar technologies. South Africa has historically been a major importer of sulphur for sulphuric acid production, and other mining-intensive countries in Africa are similarly importing large quantities of sulphur at relatively high cost for the manufacture of sulphuric acid. The demand

for limestone in South Africa is also likely to increase significantly with the installation of FGD units at Eskom power stations.

Apart from marketable gypsum or gypsum-derived products, opportunities have also been identified for the niche local applications of the gypsum residues for rehabilitation and remediation of local coal mines, based on the integration of wastes streams across the entire coal deposit-energy mechanistic chain. Such options include combining gypsum-rich AMD neutralisation residues with coal combustion fly-ash and/or coal processing wastes for the generation of fabricated soils, or for mine backfill.

Whilst the potential for recovery of value from the wastes generated within the EWRP has been investigated in previous studies, options explored to date have been limited and relatively few of these opportunities have been applied on a commercial scale, beyond the sale of gypsum for agricultural purposes.

7.1.2 Incorporation of nano-iron extraction into the AMD treatment circuit

Laboratory-scale tests were conducted to investigate the technical feasibility of extracting nano-iron from a typical AMD solution using sodium borohydride and green tea extract, and to assess the effect of this extraction on the compositions of the effluents and residues generated during subsequent lime neutralisation of the iron-depleted supernatant. Thermodynamic simulation modelling of the neutralisation experiments was conducted with a view to generating information on the formation and distribution of possible species, and the controlling chemical reactions.

7.1.2.1 Sodium borohydride as a chemical reductant

Sodium borohydride treatment of AMD solutions containing between 1.9 g/L and 4.6 g/L Fe, resulted in effective and relatively rapid removal of iron ($\geq 99.9\%$ removal in 8 minutes) at a sodium borohydride dosage of 22 g/L. Treatment also resulted in effective removal ($>99\%$) of other metals such as Al, Zn, Ba, Ni and Co as well as partial removal of Mn (56-83%), Ca (37%) and Mg (22%). The resulting products had a purity of 82-93% with respect to iron, with minor amounts of Al (5-7%) and Ca (1.1-1.3%) as well as traces of Na, Mg, Si and S. The size distribution of the particles was largely in the desired range of <100 nm, although agglomeration and formation of large clusters resulted in larger particle sizes in some cases. The morphological structure-spherically nano iron that is connected in the form of a chainlike structure was consistent with that reported in the literature for nano-iron prepared from pure ferric chloride solutions. Also consistent with literature reports, the nano-iron product formed from sodium borohydride was highly unstable and oxidised rapidly on exposure to air.

Although depleted in iron, aluminium and other metals, the sodium borohydride treated AMD solution contained significantly higher B (1.2-3.9 g/L) and Na (1-5 g/L) as well as a higher pH value (6-9) than the raw AMD. Contrary to expectations, subsequent lime neutralisation of this solution to pH values of 9.2-9.8 did not result in significant sulphate removal ($< 15\%$), and the final effluent was thus characterised by high levels of sulphate, as well as elevated levels of Na and B relative to the untreated AMD. Thermodynamic modelling confirmed that the low levels of gypsum formation during neutralisation could probably be attributed to the preferential formation of calcite because of CO_2 attenuation and dissolution in the NaOH-bearing supernatant solutions. Chemical analysis also indicated partial deportment of boron (up to 42%) to the neutralisation residue, although it is not currently clear whether this is due to formation of calcium borate precipitates, such as dicalcium hexaborate pentahydrate ($2\text{Ca}_3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), or substitution of sulphate or carbonate ions for the tetrahedrally-co-ordinated anion $\text{B}(\text{OH})_4^-$.

7.1.2.2 Tea extract as a phenolic plant extract (green reductant)

The effectiveness of polyphenolic green tea for the removal of Fe was found to be dependent on the extract dosage, temperature, and retention time, with optimum extraction occurring at an extract dosage of 0.5 g/L of AMD, a temperature of 30°C and a retention time of 12 hours. Consistent with the lower antioxidant activity, green tea extract was not as effective in removing iron as sodium borohydride, giving rise to a maximum Fe

extraction of 89% under optimum conditions. As in the case of sodium borohydride, treatment of the AMD with green tea extract resulted in at least partial co-extraction of other constituents, including Al (~ 67%-69%), Mg (~62%-67%), Ca (~64%), Na (~42-64%), Mn (~84%), Zn (~86%), Co (~90%) and sulphate (~30-32%). Characterisation of the nano-iron product indicated that the nano-iron was present in an amorphous form with active surfaces coated by polyphenolic compound. Due to the high organic content, the iron content of the nano-iron product was considerably lower (9-36 weight %) than that obtained from sodium borohydride. The average particle size of the green tea extract product was also smaller (32-55 nm) than the sodium borohydride product, indicating that the polyphenol complexation prevents particle agglomeration. Although the treated AMD solutions contained lower concentrations of sulphate and most metals than the raw AMD feed, concentration levels of K, P and, to a lesser extent, Se were higher due to the presence of these elements in the tea extract. The treated AMD was also slightly more acidic than the raw AMD solution (pH of 1.8 vs 2.1).

Subsequent lime neutralisation of the treated solution, showed similar extents of sulphate, metals and salts removal to that obtained during neutralisation of raw AMD, but at lower dosages of lime. As in the case of the effluent from the neutralisation of raw AMD, the treated effluent solutions contained low concentrations of metals (generally ≤ 1 mg/L) with sulphate (2-3 g/L) and Ca (1.0-1.3 g/L Ca). Residual Ca concentrations were slightly higher than the values obtained during raw AMD neutralisation, whilst Mg was only effectively removed from solution at relatively high pH values (> 11). Thermodynamic modelling indicated that the gypsum concentration of the pre-treated residue is likely to be higher than that obtained from the neutralisation of raw AMD due to the lower concentrations of residual Fe and Al which precipitate from solution in the form of oxyhydroxides and oxysulphate compounds. Nevertheless, the gypsum content is unlikely to exceed 87% at pH values ≤ 9 , due to the formation of $\text{Fe}(\text{OH})_3$ and alunite $(\text{KAl}_3(\text{OH})_6(\text{SO}_4)_2)$. At pH values ≥ 10 the potential formation of ettringite $(\text{Ca}_6\text{Al}_2(\text{SO}_4)_3\text{OH}_{12} \cdot 26\text{H}_2\text{O})$ decreases the gypsum content even further to a maximum value of 75-76%. Thermodynamic modelling also indicated that the presence of soluble carbonate, formed through the entrainment and solubilisation of CO_2 under atmospheric conditions can result in preferential precipitation of calcite, resulting in further decreases in the gypsum content of the neutralisation residue. Whilst thermodynamic simulation indicates that calcite contents may range between 7% and 37%, this still needs to be confirmed experimentally.

7.1.3 The application of a thermodynamic modelling framework for simulating the AMD neutralisation process

This study explored the use of three different models to simulate the distribution and attenuation of chemical species before and during lime neutralisation of AMD solutions, namely VISUAL MINTEQ, PHREEQC and OLI. Although equilibrium thermodynamic models do not consider reaction kinetics, they can, in principle, be used to simulate relatively rapid, equilibrium-controlled reactions such as the precipitation/dissolution and/or adsorption/desorption reaction mechanisms controlling the extent to which constituents are removed from solution during lime neutralisation. In practice, however, several challenges were experienced in the application of these models for simulation purposes. One of the main disadvantages of predictive thermodynamic models is that they require fairly comprehensive and accurate input data to generate reliable outputs such as an acceptable cation/anion charge balance. Of particular importance is comprehensive list of element concentrations, such that an acceptable (90-110%) charge balance is achieved. In the absence of an acceptable balance between cation and anion concentrations, data outputs become unreliable and/or the models are not able to converge. A second major drawback of using thermodynamic equilibrium models is that they do not consider non-idealities, such as the formation of mixed or non-stoichiometric precipitates due to inclusion and substitution mechanisms. Finally, predictive thermodynamic models presuppose knowledge of all prevailing reaction mechanisms and stable chemical phases, and associated equilibrium constants. Unfortunately, most complex systems remain poorly understood, and the required model input information and data is frequently either unavailable or highly uncertain. This problem is aggravated in cases where the models do not permit the user access to the model database, thus reducing the transparency and adding to the uncertainty of the model predictions.

In terms of challenges associated with specific models in this study, problems were experienced with the application of the OLI model, due to its lack of flexibility in terms of allowing the operator to manipulate the back end of the software. Specifically, OLI automatically reconciles anion and cations in terms of mass and charge balance before running simulations. This can result in significant discrepancies between simulated and experimental results in cases where input datasets are incomplete, or where there are any irregularities in the data. Furthermore, the operator is not able to adjust the model database or to select possible species that may be formed under ambient neutralisation conditions in an engineered system. Utilisation of this model, furthermore, requires a licence. Whilst the freeware Visual MINTEQU model allows for more flexibility in terms of manipulating input parameters and the database, the model is best suited for simulating batch systems, as opposed to dynamic processes such as titration of AMD solutions with lime. Whilst the model PHREEQ appears to address both the shortcomings of the OLI and Visual MINTEQU models, a detailed assessment of the advantages and disadvantages of using this model for simulating the neutralisation of AMD with lime was not carried out in this study.

Despite the above-mentioned limitations and challenges, the study showed that equilibrium thermodynamic models can play a valuable role in understanding the effect of neutralisation parameters, such as pH, neutralising reagents, and feed solution compositions, on the reaction mechanisms controlling the removal of metals and salts from solution and the compositions of the sludges. This in turn can serve to inform R&D campaigns to optimise the neutralisation process in terms of desirable properties of output streams, as well as assist in the effective operation of an operating neutralisation operation by enabling the potential effects of variability in the compositions of input streams (AMD feed and neutralising reagents) to be determined. For example, the thermodynamic modelling in this study showed the potential to form carbonate precipitates, such as calcite, during neutralisation in the presence of air, with concomitant additional lime consumption, elevated sulphate concentrations in the effluent, as well as reduced gypsum content in the residue. Thermodynamics also indicated that the formation of ettringite at elevated pH values may result in a concomitant decrease in the gypsum content.

7.2 Concluding remarks

Whilst this study has demonstrated the technical feasibility of extracting nano iron from AMD, the application of sodium borohydride is likely to be expensive and gives rise to effluents containing elevated levels of sodium and boron with potentially adverse effects on the downstream lime neutralisation and reverse osmosis processes. The application of green reductants such as green tea extract appears to be more affordable and effective, providing a relatively stable nano iron product as well as generating a purer gypsum product during subsequent neutralisation. However, the presence of residual polyphenols in the feed, and the potential effects on the reverse osmosis process requires further investigation, as does the effectiveness of the nano-iron product for downstream water treatment. In addition, the green tea extract used in this study was not as effective as removing iron and other metals as the chemical reductant, sodium borohydride. Incomplete removal of metals such as iron and aluminium by green teas extracts means that the subsequent neutralisation residue, although containing a higher gypsum content than that generated from neutralisation of raw AMD, is unlikely to be sufficiently pure for the manufacture of high-end products such as gypsum board. Nevertheless, the improved purity may render the residue suitable for construction applications (e.g. manufacture of cement or cement bricks), or as feed to the Gyp-SLiM or similar process for the manufacture of higher value sulphur, magnesite, and limestone. These applications, as well as current uncertainties and information gaps will need to be addressed as part of a more comprehensive feasibility study on the different options for the recovery of value from AMD.

7.3 Recommendations

Based on the results and outcomes of this study, the following recommendations are made:

- Additional laboratory-scale test work is conducted to further explore the feasibility of using polyphenolic plant extracts to recover nano iron from AMD. This should include an investigation of the distribution and stability of polyphenols in the treated AMD; the local availability of alternative and potentially more effective green reductants; the feasibility of using the nano iron products for downstream water treatment; and the characteristics of the subsequent neutralisation residue.
- Laboratory-scale test work is also conducted to explore and compare options for a more holistic approach to value recovery from gypsum-rich neutralisation residues which considers the integration of wastes streams across the entire coal deposit-energy mechanistic chain. Such options include the manufacture of higher-end by-products and applications, as well as niche local applications of the gypsum for rehabilitation and remediation of local coal mines.
- Further investigation is carried out to explore the potential for using thermodynamic models such as Visual MINTEQ and PHREEQ for guiding and informing the simulation and optimisation of lime neutralisation process systems.

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APPENDIX A

SPECIFICATIONS FOR GYPSUM PLASTERBOARD

General European specifications (OTM 2009)

NO.	MAIN SPECIFICATIONS	FIGURES	RISKS (for plasterboard manufacturers)
1	Humidity	< 10% (max. 12%)	Drying cost
2	Purity	> 95%	Strength and lighter board
3	pH	5<pH<9 (if possible, 6<pH<8)	Risk of interaction with silicates
4	Particle size	30 µm<d50<80 µm	Water demand
5	No needle (crystalline molecular structure)	L/I>3	High water demand
6	Density	non tapped : >1000 g/L	Powder flow control
	Soluble Salts:		
7	Na ₂ O	<500 mg/L	Bond quality
8	MgO	<1000 mg/L	Flowering, Bond quality
9	Chloride	<100 mg/L	Calcination, Bond quality
	Impurities:		
10	Non soluble salts	<2,5%	Purity
11	Quartz	<1%	Wear of material
12	Al ₂ O ₃	<0.3%	
13	Fe ₂ O ₃	<0.15%	Colour
14	CaCO ₃ +MgCO ₃	<2.5%	Purity
15	Sulphites	<0.5%	
	Other Specifications:		
16	Heavy metals		Environment
	As	0-3 mg/L	
	Cu	1-10 mg/L	
	Zn	0-50 mg/L	
	Pb	0-33 mg/L	
	Cd	0-3 mg/L	
	Ni	0-3 mg/L	
	V	1-4 mg/L	
	Cr	1-7 mg/L	
	Mn	8-13 mg/L	
	Ti	100-400 mg/L	
17	Free carbon	<0.05%	Foam stability
18	Colour	Cream or white	
19	Odour	Neutral	
20	Organic matter	No additives which could affect the plaster behaviour	
	Radioactivity:		
21	Europe Radioactivity Index I <0.5	This is the radioactivity of plasterboards	

Lafarge Gypsum Specifications (and statistics) for FGD Gypsum Worldwide as of October 2008 (OTM 2009)

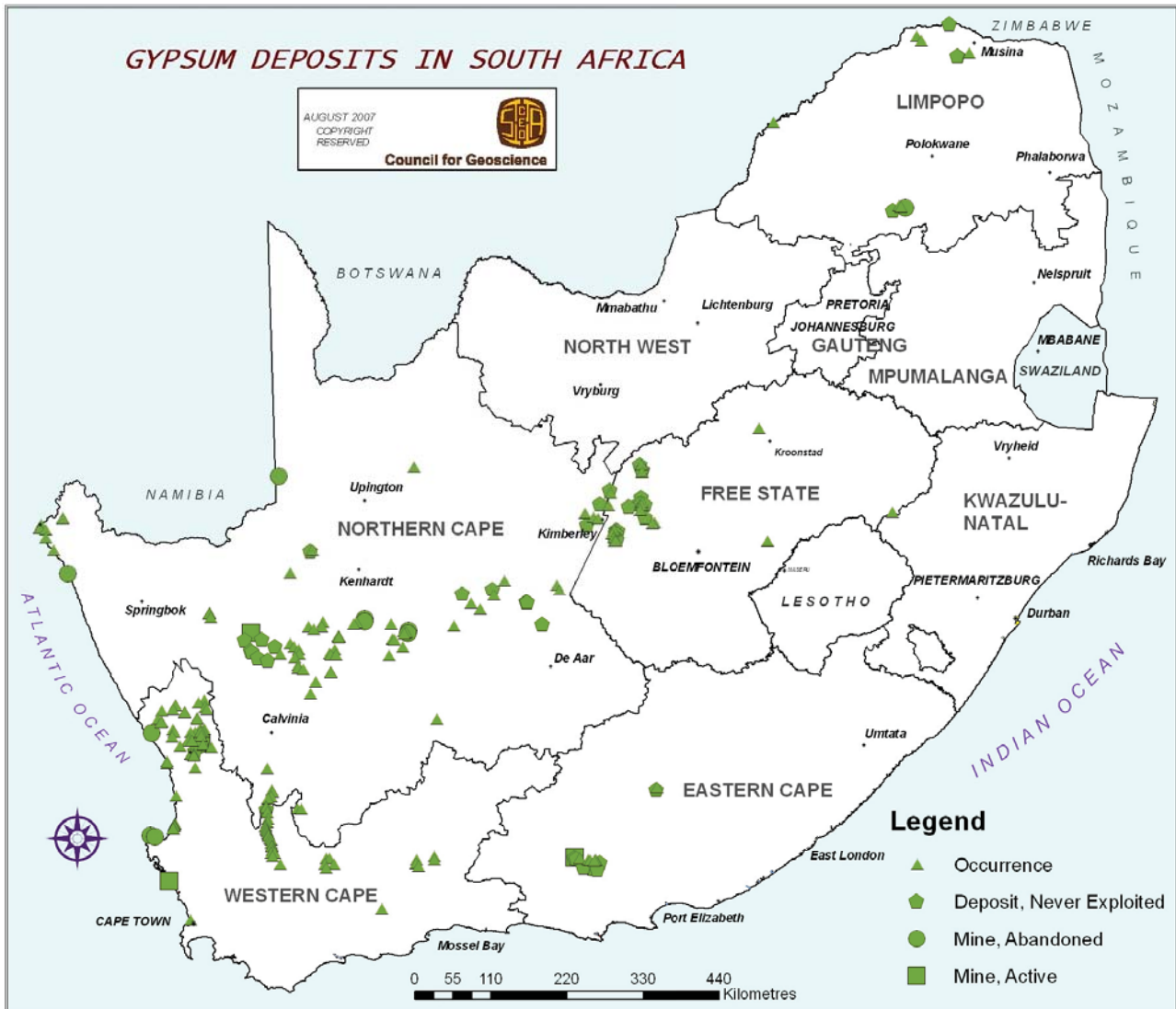
NO.	CHARACTERISTIC	LAFARGE SPECIFICATIONS	Actual values observed		
			Ave.	Min.	Max.
1	Humidity	< 10%	9.2	6.0	13.0
2	Purity	> 95%	95.0	89.0	99.0
3	pH	5<pH<9	8.1	6.3	9.6
4	Particle size	30 µm<d50<80 µm	56	16	134
5	No needle	L/I>3	80% of measures compliant		
6	Density	non tapped : >950 g/L	1.04	0.49	1.26
	Soluble Salts:				
7	Na ₂ O	<500 mg/L	46	4	275
8	MgO	<600 mg/L	305	8	2866
9	Chloride	<100 mg/L	110	80	200
10	K ₂ O	<600 mg/L	25	4	180
	Impurities:				
11	Sulphites	<0.5%	100% of measures compliant		
12	Metals				
	As	<10 mg/L	Test method being developed		
	Cu	<100 mg/L	42	5	107
	Zn	<200 mg/L	15	3	65
	Pb	<50 mg/L	13	3	23
	Cd	<5 mg/L	100% of measures compliant		
	Ni	<100 mg/L	17	6	33
	V	<100 mg/L	21	3	77
	Cr	<500 mg/L	16	10	23
	Mn	<500 mg/L	48	8	224
	Hg	<5 mg/L	100% of measures compliant		
13	Colour	White	Occasional pigmentation issues		
14	Odour	Neutral	Experienced an exceptional NH ₄ issue in a specific plant		
15	Gypsum must be non-toxic				

Typical European FGD Specifications for Plasterboard as supplied by Gyproc

SPECIFICATION	UNIT	VALUE	THRESHOLD	ACCEPTABLE ERROR
Free moisture	%	10	Maximum	± 0.25
Purity as CaSO ₄ .2H ₂ O	%	95	Maximum	± 0.50
CaCO ₃	%	5	Maximum	± 0.50
CaSO ₄	%	0.5	Maximum	± 0.50
Chloride	mg/L	100	Maximum	± 10
K ₂ O+MgO+Na ₂ O with Na ₂ O % = 0.05 maximum	%	0.1	Maximum	± 0.01
Fe ₂ O ₃	%	0.4	Maximum	± 0.04
pH		6 to 8		± 0.10
Crystal size	µm	75%>16		

APPENDIX B

OCCURRENCE OF NATURAL GYPSUM IN SOUTH AFRICA (2008)



Source: DRME 2009

