

**Extraction of major elements from PGE tailings in view of nanoparticle
synthesis for environmental technological applications**

by

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Abstract

Mining operations associated with the primary production of PGE's in South Africa have generated and continue generating large quantities of mineral waste and by-products, for instance in the form of tailings. Mine tailings (MT) have been identified as a major source of environmental impact for many mining operations and changes in legislation are enforcing more stringent requirements with regards to the management of tailings storage facilities (TSF). Mineral beneficiation of PGE's has become a key focus area in South Africa to ensure sustainable growth of the economy beyond mining. This initiative could potentially be expanded to include associated mineral waste products which could create a suitable platform to minimize the volume of tailings stored in a TSF and reduce associated environmental impact. Magnesium-rich PGE mine tailings have been previously assessed for mineral carbonation technologies, although researched processes were unsuccessful in extracting significant amounts of magnesium. PGE tailings also contain significant amounts of other major elements (e.g. Al, Fe). Therefore, they offer the potential to serve as secondary mineral sources which can be reprocessed and converted into value-added products, provided that a suitable economically-viable technological process can be developed.

This study demonstrated that major elements contained in PGE mine tailings (e.g. Fe, Al, Mg, Cr) can be extracted using a suitable technological process. A multi-stage process was developed, which involved a thermochemical solid-solid treatment using ammonium-based reagents as activators followed by aqueous dissolution. Potential uses for the major elements have been identified, such as the conversion of Fe and Al to nanoparticles, with potential applications in contaminated water remediation.

The variability of the bulk elemental compositions and mineralogy of the tailings was expected to have a direct effect on the elemental extraction efficiency from PGE tailings. The Two Rivers tailings sample, obtained from the eastern limb of the BIC was used as a first case study to establish the experimental design and develop the process. The Two Rivers tailings sample is typically fine-grained and relatively enriched in Fe, Mg, Al, and Cr. The primary minerals present are generally unaltered, comprising of spinel, plagioclase, enstatite and amphibole mineral species. Preliminary studies have qualitatively evaluated the effect of particle size of the tailings and treatment temperature on the thermochemical solid-solid treatment using ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$; AS). Results have shown that the transformation of the mineral phases into metal sulphate-based compounds is dependent on tailings particle size and on treatment temperature. Subjecting the 45-75 μm tailings size fraction to the thermochemical treatment at temperatures below 500 $^{\circ}\text{C}$ favoured the formation of ammonium metal sulphate based compounds. At 550 $^{\circ}\text{C}$ it favoured the formation of metal sulphate based compounds. The reaction product generated at 550 $^{\circ}\text{C}$ was identified by XRD as mikasaite ($\text{Fe}_2(\text{SO}_4)_3$). Morphological examination and elemental analysis indicated that the mikasaite phase was made up of hexagonal structures which contained Fe, Al, Cr and Mg. This suggested that elements such as Fe, Al, Cr and Mg may compete for AS during thermochemical treatment. Since a temperature of 550 $^{\circ}\text{C}$ for the thermochemical treatment of the 45-75 μm fraction favored the formation of metal sulphates rather than ammonium metal sulphates, this temperature was selected for all future experiments.

The efficiency of the thermochemical treatment step could only be evaluated if dissolution step of the process was optimized in terms of temperature, pH and duration of dissolution. Elemental extraction efficiency for all elements in ultra-pure water improved significantly with an increase in temperature from ambient temperature to 80 °C; however under the latter conditions, elemental extraction was hindered by the secondary precipitation of Fe during the dissolution procedure, an observation which had not been made at ambient temperature. The dissolution procedure was further examined in 0.63M HNO₃ in an attempt to prevent the secondary precipitation of Fe. Baseline dissolution experiments at ambient temperature confirmed the absence of secondary precipitation; however elemental extraction efficiencies for Al, Ca, Cr, Fe, and Mg remained relatively low. The effect of dissolution temperature on elemental extraction efficiency in 0.63M HNO₃ was investigated by subjecting the thermochemically-treated MT (MT_{ro}) formed using the selected thermochemical treatment to the dissolution procedure at 80 °C from 30 minutes up to 17 hours. The percentage mass loss endured by MT_{ro} following dissolution indicated that the optimal dissolution probably occurred within 6 hours, after which further dissolution may be negligible. Higher elemental extraction efficiencies were obtained for Al (56 %), Cr (20 %), Fe (24 %), Mg (23 %) and Ca (79 %) within the first 6 hours of dissolution at 80 °C. The effect of dissolution temperature on elemental extraction efficiency was further investigated by subjecting MT_{ro} to the dissolution procedure at 60 °C and 95 °C. Higher elemental extraction efficiencies were achieved for Al (59 %), Cr (27 %) and Fe (35 %) except for Ca (80 %) and Mg (25%) which were similar after dissolution at 95 °C. Dissolution at 60 °C and 80 °C yielded much lower extraction efficiencies for Al (33 – 56 %), Fe (18 - 24 %), Mg (21 – 23 %), Ca (50 – 79 %) and Cr (12 – 20 %). The co-extraction of the major elements Fe, Cr, Al, Mg and Ca demonstrated their competitive chemical affinity for AS during thermochemical treatment, which constrained the preferential extraction of Fe. The optimum dissolution conditions established for maximum elemental extraction efficiency, particularly for Fe, was achieved using 0.6M HNO₃ solution at a temperature of 95 °C for 6 hours.

Using the optimal dissolution parameters, the effect of different ammonium salts (ammonium chloride (NH₄Cl); ammonium nitrate (NH₄NO₃); ammonium bisulphate (NH₄HSO₄), ammonium sulphate (NH₄)₂SO₄) and thermochemical treatment temperature on major elemental extraction efficiency was also investigated. (NH₄)₂SO₄ proved to be the most suitable activator, yielding the highest elemental extraction for Al (59 %), Fe (35 %), Cr (27 %), Ca (79 %) and Mg (25 %) between 500 °C and 550 °C. NH₄Cl, NH₄NO₃ and NH₄HSO₄ yielded lower elemental extraction efficiencies for all temperatures tested. However, NH₄Cl and NH₄NO₃ were more selective for Ca at a lower thermochemical treatment temperature (450 °C) compared to all other elements yielding up to 79 % Ca extraction which was similarly achieved using (NH₄)₂SO₄.

In an attempt to investigate the effect of Fe:Cr ratio on the elemental extraction efficiency (case study 2), a series of tailings samples with varying mineralogy and Fe:Cr ratios were selected from the Amandelbult, Marico Chrome and Rhovan operations TSF's located along the western limb of the BIC. The mineralogical composition of the different tailings are different and correlate to the local variations in mineralogy observed along the limb which changes from a harzburgitic rock-type in the north to a pyroxenetic rock-type further south and, finally a noritic rock-type further southeast. The tailings comprise of varying proportions of spinel and plagioclase mineral phases, with minor amounts of alteration minerals

(serpentine, talc, chlorite, and calcite). Experimental results indicated that Cr-depleted mine tailings yielded higher Fe (ca. 72 %), Al (ca. 100 %), Ca (ca. 100 %) and Mg (ca. 40 %) extraction efficiencies in comparison to Cr-enriched tailings. The correlation between the elemental Fe:Cr ratio in the starting materials (i.e. MT₄₅₋₇₅) and the one in solution following thermochemical treatment and optimal dissolution was assessed. In the main, the higher the Fe:Cr ratio in the starting material, the higher the Fe:Cr ratio in solution. The correlation followed a linear relationship ($R^2 \approx 1$) with slopes of about 1.5 and 2 for 350°C and 550°C respectively. This linear correlation was unexpected; given the complex mineralogical composition of the samples originating from different tailings generated from varying mineral deposits, and could not be explained at this stage. The result would suggest that Fe and Cr were co-extracted from similar mineral phases. However, Fe and Cr are contained in different types of minerals for the different tailings. A detailed mineralogical investigation is required in order to better understand the extraction of these two elements from tailings. It can however be speculated that following thermochemical treatment, Fe and Cr are present in a number of similar sulphate-based Fe-Cr solid solutions (which may also contain additional substituting (compatible) elements such as Mg and Al), which are then dissolved during the dissolution process.

Results from this study have shown that the multi-stage process under development has the potential to extract major elements from PGE tailings. The best extraction efficiencies obtained for Fe, Al, Ca and Mg were 72 %, 100 %, 100 % and 40 % respectively, although those were not obtained for the same tailings or using the same activator. Further studies will be required to further enhance the elemental extraction efficiency of Fe and Al.

Academic Output

Conferences:

Mohamed, S., Doucet, F.J., van der Merwe, E.M., Altermann, W. (2015). Thermochemical treatment of PGE mine tailings using ammonium sulphate as chemical agent. ThermSA – Applications in Thermal Analysis, 2015, 17-18 August 2015, Stellenbosch, South Africa, poster presentation.

Castleman, B.A., Doucet, F.J., **Mohamed, S.**, and van der Merwe, E.M. (2014). A thermal study on the solid-state reaction between diamond mine tailings and ammonium sulphate. Analitika 2014, 7-11 September 2014, Parys, South Africa, poster presentation.

Mohamed, S., Doucet, F.J., Atanasova, M., van der Merwe, E.M., Altermann, W., Yibas, B. (2014). Mechanisms of thermal decomposition for the reaction between ammonium sulphate and metal oxides from PGE mine tailings. Analitika 2014, 7 -11 September 2014, Parys, South Africa, poster presentation.

Doucet, F.J., **Mohamed S.**, Kanyane, K., Nkosi, Z.H., Altermann, W., van der Merwe, E.M., Petrik L. (2013). Mineral carbonation and valorization of platinum and diamond tailings for sustainable CO₂ management. 3rd South African Carbon Capture and Storage Conference, 3 - 4 October, Johannesburg, South Africa.

Mohamed, S., van der Merwe, E.M., Altermann, W., Nkosi, Z.H., Doucet, F.J. (2013). Controlled mineral transformations in mining wastes for valorisation and sustainability - The case of platinum tailings. Mineralogical Association of South Africa (MINSA) Mini Symposium and AGM, 22 August 2013, Pretoria, South Africa.

Mohamed, S., Nkosi, Z.H., Rapholo, K., Altermann, W., Doucet, F.J., & van der Merwe, E.M. (2013). Investigating the CO₂ Sequestration Potential Of Mine Waste Tailings Through Mineral Carbonation. Geological Society of South Africa (GSSA) – Geoforum, 3-5 July 2013, Johannesburg, South Africa.

Peer-reviewed papers:

Mohamed, S., Doucet, F.J., van der Merwe, E.M., Altermann, W. (2015) Processing of PGM mine tailings by thermochemical treatment: Principle and preliminary elemental extraction studies using ammonium sulphate. (in preparation).

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Mohamed, S., Doucet, F.J., van der Merwe, E.M., Altermann, W. (2015) Processing of PGM mine tailings by thermochemical treatment with ammonium sulphate: Effect of mineralogy and chromium content on iron and aluminium extraction. (in preparation).

Mohamed, S., Doucet, F.J., van der Merwe, E.M., Altermann, W. (2015) Processing of PGM mine tailings by thermochemical treatment: Extraction of magnesium in view of CO₂ mineralization. (in preparation).

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List of Acronyms and Abbreviations

AMD – Acid Mine Drainage

ARD – Acid Rock Drainage

ARM – African Rainbow Minerals

AS – Ammonium sulphate; , $(\text{NH}_4)_2\text{SO}_4$

BIC – Bushveld Igneous Complex

BMA - Bulk Mineralogical Analysis

BMS - Base Metal Sulphides

CCMC - Carbon Capture and Mineral Carbonation

CFA – Coal Fly Ash

CRP – Chrome recovery plant

DEA – Department of Environmental Affairs

DMR – Department of Mineral Resources

DWAF – Department of Water Affairs

EC – Electrical Conductivity

FE-SEM – Field Emission Scanning Electron Microscopy

ICP-OES – Inductively Coupled Plasma Optical Emission Spectroscopy

IUGS - International Union of Geological Sciences

L.O.I – loss on ignition

LoM- Life of mine

MT – untreated mine tailings

MT₄₅₋₇₅ – 45 – 75 µm fraction

MT_{ht} - thermally treated MT₄₅₋₇₅

MT_{res} – undissolved residue

MT_{ro} – thermochemically treated mine tailings

NGP – New Growth Plan

n-ZVI - Zero-valent iron nanoparticles

ORP - Oxidation-Reduction Potential

PGE – Platinum Group Elements

PGM – Platinum Group Metals

PMA - Particle Map Analysis

PSD – Particle Size Distribution

REE's – Rare Earth Elements

RLS - Rustenburg Layered Suite

RoM – Run of Mine

SDTA/DTA - Thermo-gravimetric or simultaneously differential thermal analysis

SEM – Scanning Electron Microscopy

SEM-EDS – Scanning Electron Microscopy coupled to Energy Dispersive spectroscopy

SMWMP-national - National Strategic Mine Water Management Programme

TCT – Total Concentration Thresholds

TDS – Total Dissolved Solids

TGA – Thermogravimetric Analysis

TGA-FTIR – Thermogravimetric Analysis coupled to Fourier Transform Infrared spectroscopy

TGA-MS - Thermogravimetric Analysis coupled to a Mass Spectrometer

TSF – Tailings storage facility

XRD – X-Ray Diffraction

XRF – X-Ray Fluorescence

Chapter One – Introduction

Background to the study, problem statement, aims, objectives and research questions are outlined. Research methodology and layout of the thesis are summarised.

South Africa is to a large extent a resource-based economy which is primarily driven by the mining and minerals industry. The sector is vital to the economic and socioeconomic growth of the country resulting in infrastructure development, job creation and foreign exchange earnings. South Africa has an abundance of mineral resources and hosts approximately 96 % of the known global reserves of platinum group elements (PGE's), 74 % chrome (Cr), 26 % manganese (Mn), 25 % vanadium (V) and 11 % gold (Au) reserves (DMR, 2015). In South Africa, PGE's are produced from the Merensky reef, UG2 and Platreef within the Bushveld Igneous Complex (BIC). South African PGE mines have produced 264.2 tonnes out of the 63 000 tonne reserve of PGE's in 2013/2014 (DMR, 2015). The ore is mined by underground and open cut mining, resulting in the production of vast volumes of mine waste, tailings and waste rock which require planning and monitoring to prevent major environmental impacts such as tailings dam failure (Mogalakwena spillage in 2013; Anglo American plc, (2013)) and generation sulphate-rich drainage waters (Mudd, 2012). The over-production and under-utilization of mine tailings is leading to an unsustainable use of the country's mineral resources. There is therefore the opportunity to examine their potential applications as raw materials for the production of value-added products through re-processing technologies.

1.1 Mine wastes and tailings residues

Mine residue stockpiles and deposits were previously regulated under the Minerals and Petroleum Resources Development Act (MPRDA) 28 of 2002 and not subjected to the South African Waste Management Act. However, as of December 2014, changes in legislation dictate that mine residue stockpiles and deposits will be regulated under the National Environmental Management Waste Act (NEMWA) and are subjected to prescribed standards for the management of residue deposits and residue stockpiles (NEMWA, 2014). This indicates that mining companies will be compelled to report the total mine wastes under their control and management. Mine tailings generated from mineral processing used to be considered a by-product however, with the change in legislation (NEMWA, 2014), advancement in technology and gradual depletion in natural resources, it has become a necessity to reuse, recycling and reprocess mine waste residues in order to promote sustainability within the mining industry and decrease the environmental impact and management costs associated with tailings disposal and storage. Valorisation of mine residues plays a vital role within the sustainability of the country's mineral resources. Not only can these residues help reduce the overall costs of waste treatment and disposal, it can be considered as economic leverage in terms of a secondary mineral source. Mine waste and tailings residues such as those from the PGE mining industry contain a significant portion of Al, Fe, Ca, Mg bearing silicates which have the potential to serve as a secondary mineral source and can be reprocessed and converted into value-added products.

1.2 Water resources and remediation technologies

Water resources are scarce in South Africa, with many areas facing a water crisis coupled with deterioration in water quality. Water quality is the primary factor in determining its potential reuse, recyclability and impact on the environment. Irrigation is considered the largest consumers of water supply (60 %), with the balance being for domestic purposes, industry and power stations.

In order to promote sustainability and meet high-water-quality requirements, recycling and treatment of water and wastewaters (including mine water) will be a necessary requirement which will impose higher energy requirements. Recycling of mine wastewater plays an important role in the water-management strategy which includes optimising use of recycled water and improving monitoring and measuring programs (Anglo American plc, 2013).

The extent of water consumption for PGE production is variable for the different metals produced; furthermore, it is constrained by a limited water supply and poorly-developed water infrastructure. Mudd (2012) has found that water consumption at the milling stage ranges between $0.18\text{--}15.6\text{ m}^3\text{ t}^{-1}$ and the average range for unit water consumption per unit PGE produced is $241\text{--}2743\text{ m}^3\text{ kg}^{-1}$ PGE. Water-management initiatives in the PGE industry are becoming increasingly important for the sustainable use of the water resources. Remediation and treatment of wastewater by desalinisation, metal removal and inter-basin water transfers, appear to be the most feasible options (DWA, 2010) which could potentially be applied by the mining industry to reduce water consumption and improve the quality of available water resources.

Nanotechnology, particularly Fe nanoparticles, has received considerable attention for water and wastewater remediation over the last decade (Neyaz *et al.*, 2013; Mohmood *et al.*, 2013; Xu *et al.*, 2012; Hua *et al.*, 2012; Crane *et al.*, 2011; Noubactep and Schöner, 2009). The use of zero valent Fe (n-ZVI) nanoparticles is the most common and attractive technology owing to the relatively low costs associated with synthesis, the high adsorptive efficiencies, high reactivity and environmental compatibility (Crane and Scott, 2012; Brame *et al.*, 2011). n-ZVI are nano-sized particles (1-100 nanometers; nm) which comprise of a zero-valent core (Fe^0) or metallic iron core with an iron oxide (FeO) or iron hydroxide (FeOOH) shell. The Fe^0 core provides the reducing power for reactions with environmental contaminants while the outer shell provides sites for absorption and/or chemisorption (Crane and Scott, 2012; Brame *et al.*, 2011).

Commercial grade reagents have been the major source of Fe required for the synthesis of Fe-nanoparticles. Their high costs limiting the application as a water and wastewater treatment option on a large scale as required in South Africa. This could however be overcome by the synthesis of n-ZVI from low-cost, locally available iron-bearing wastes in order to consider nanotechnology for sustainable water management (Brame *et al.*, 2011). For instance, iron nanoparticles have recently been synthesised using iron extracted from coal fly ash and acid mine drainage (AMD) (Alegbe, 2015). PGE tailings may represent a more concentrated source of iron for the synthesis of n-ZVI. The extraction of Fe and other major elements from PGE tailings was the main focus of this study.

1.3 Problem Statement

The mining and metallurgical industry is inundated with tonnes of solid and liquid wastes, residues and stock piles which require monitoring, treatment, and secure disposal in order to meet legislative requirements. A large volume of tailings is discharged into engineered storage facilities (tailings storage facility; TSF) which may present risks of failure due to geotechnical problems and poor management of the stored tailings (Wang *et al.*, 2014). Major environmental problems induced by mining activities and stockpiling of e.g. gold mine tailings typically involve the production of AMD which occurs via oxidation of metal sulphides upon exposure to oxygen and water. AMD results in a toxic environment which is characterised by a very low pH (< 2), a high oxidation-reduction potential (ORP), a high concentration of total dissolved solids (TDS) comprising of sulphates, nitrates, phosphates, ammonium, and major and trace elements such as Al, Fe, Mn and As, Be, Cr, V, (Klimkova *et al.*, 2011). Minerals present in the waste, especially clays, tend to absorb water into its crystal structure resulting in swelling which not only increases the volume of discharged material but results in poor water recovery and increases the ecological footprint of the TSF. Remediation of acid mine drainage (AMD) and other contaminated waters remains a top priority for the South African mining industry, with the overall objective to design and implement mitigating measures that minimise the residual impact of mining (Akcil and Koldas, 2006).

1.4 Rationale and motivation of the study

South Africa has a competitive advantage for developing downstream beneficiation owing to its wealth in mineral resources and developing value-addition infrastructure within the mineral processing and manufacturing industries (DMR, 2011). The New Growth Plan (NGP) adopted by the South African government seeks to create a more inclusive economic growth by encouraging more labour absorptive economic activities. Mineral beneficiation (e.g. PGE's) has been identified as a priority growth node for job creation. The PGE industry could potentially benefit in extending its value chain by reprocessing and reusing the residue and stockpiles generated from mining products. The major player in the PGE industry, Anglo American Platinum Ltd has reported 849 895 kilotonnes of mineral waste which have accumulated in active and inactive tailings dams during the 2012-2013 reporting period (Anglo American plc, 2013). PGE mine tailings represent an abundant and unexploited source of valuable metals and minerals, in many cases already ground to fine particle size (Cole and Ferron, 2002). The tailings contain a considerable amount of iron (Fe), chromium (Cr), aluminium (Al), magnesium (Mg), calcium (Ca), silicon (Si) which could be utilised in the manufacture of useful materials and/or products. This may include carbonate-based compounds for carbon capture and mineral carbonation (CCMC) technology, iron oxide concentrates for the steel, iron and alloys industries, Al and Fe nano-oxides for water remediation, chromium oxide for pigments and refractory bricks. The valorisation of these tailings will ensure development of the country's mineral value chain and promote sustainable use of mineral resources.

1.5 Research approach

An integrated research approach in this thesis included an in-depth literature review on the extraction of metal cations from silicate ores, stockpiles and mine residues using ammonium salts. PGE mine tailings from different South African mines were characterised using a variety of analytical techniques, which included particle size analysis (PSD), X-ray diffraction (XRD), and X-ray fluorescence (XRF) in order to determine their physico-chemical properties and to identify the mineral phases which host the economic and valuable metals. Samples of interest were further analysed using scanning electron microscopy (SEM) techniques, reflected light microscopy and Raman spectroscopy as complementary techniques. Tailings were subjected to a thermochemical treatment using ammonium salts, followed by controlled aqueous dissolution. Complementary techniques such as thermogravimetric analysis (TGA) and thermogravimetric analysis coupled to Fourier Transform Infrared spectroscopy (TGA-FTIR) were utilised to better understand the reaction mechanisms of the thermochemical treatment and to confirm the identity of the resulting products. The efficiency of the thermochemical treatment was determined by the dissolution step which was quantified using ICP-OES. PGE mine tailings material from the Two Rivers mine was used for preliminary testing and for optimisation of the dissolution step of the process, whilst other PGE tailings with varying chemical and mineralogical compositions were used to study the effect of Fe:Cr ratio on elemental extraction efficiency.

1.6 Aims and Objectives

The aim of this study was to demonstrate that PGE mine tailings could be used as a secondary source of major elements (e.g. Fe, Al) for various applications. A multi-step process for the extraction of major elements from silicate-rich PGE mine tailings was developed, which combines a thermochemical solid-solid treatment using ammonium-based reagents with subsequent aqueous dissolution. The main objectives of this study were to (1) characterise PGE mine tailings in order to identify its potential for additional resource recovery and (2) investigate and optimise a number of process parameters that promote maximum elemental extraction. Specific focus was given on the extraction of Fe for prospective applications in nanoparticle synthesis and contaminated water remediation.

1.7 Research hypotheses

- PGE mine tailings are enriched in valuable elements which can be extracted for subsequent conversion into value-added products
- Ammonium-based salts are suitable reagents for the extraction of major elements from PGE tailings via thermochemical solid-solid treatment
- Chemical competition of major elements present in PGE tailings with ammonium-based salts may prevent the preferential extraction of specific elements.

1.8 Scope and delimitations of this study

The scope of this study is limited to the extraction of major elements from PGE mine tailings, with emphasis on Fe which could then be utilized for environmental technological applications. The main focus was to test the suitability of ammonium salt reagents for major elements extraction from PGE mine tailings using the combination of a thermochemical solid-solid treatment with subsequent dissolution. The influence of a number of process parameters which has a direct effect on elemental extraction efficiency was investigated and the dissolution step was optimised. No attempt was made to link the extraction results to the mineralogy due to the complexity of the mineralogy of the different tailings, which in some cases represent a mixture of tailings generated during mining of different reefs (e.g. Merensky and UG2). This will be part of a future project which will characterise the tailings in greater details and assess whether a link between the mineralogy and the elemental extraction efficiencies can be drawn. The synthesis of iron nanoparticles was also not investigated in this study.

1.9 Structure of the thesis

This thesis is organised into six chapters which are summarised below. The study has been sub-divided into two case studies, (1) Two Rivers PGE mine tailings and (2) Other PGE tailings, whereby the process development and experimental design is established under case study 1 and further evaluated using case study 2.

Chapter One: Introduction - provides an introduction and background into this study, the research approach taken, rationale and motivation, hypotheses, scope and delimitations of this study.

Chapter Two: Literature Review - examines the physicochemical characteristics of mine residues with particular emphasis on PGE mine tailings. Different technological processes which have been developed for the extraction of elements from primary and secondary resources are presented. A brief theoretical background of the analytical techniques used in this study is provided.

Chapter Three: Materials and methods - provides a brief geological overview of the area from which the tailings were sampled, discusses the PGE mine tailings used in this study, the process under development, experimental design and analytical techniques used to achieve the specific objectives of this study.

Chapter Four: Characterisation of PGE tailings - presents a chemical and mineralogical characterisation of the different PGE mine tailings which were used as raw material for the thermochemical and dissolution experiments.

Chapter Five: Results and Discussion - presents and discusses the results from the thermochemical treatment and subsequent dissolution experiments.

Chapter Six: Conclusion and recommendations - concludes the study and lists recommendations for future work.

References – Provides a list off all the literature cited in the study.

Appendix - contains all supplementary material associated to this study. This includes standard test methods, waste guidelines, and additional SEM image analysis.

Chapter Two – Literature Review

This chapter focuses on the physicochemical characteristics of mine waste and residues with particular focus on PGE mine tailings. Different technological processes which have been developed for the extraction of elements from primary and secondary resources are presented.

2.1 Introduction

Conservation and preservation of natural resources have become increasingly important and changes in legislation of mine waste which has been integrated into the National Environmental Management Waste Act in September 2014 (NEMWA, 2014), emphasise the need to reuse, recycle and reprocess mining and industrial residual waste and process residues (hereafter called 'waste'). Landfills and tailing storage facilities (TSF) are increasingly becoming an important secondary mineral and metallic resource which can provide a sustainable alternative to the intensive use of natural resources. Environmental remediation is also becoming a primary concern due to surface and/or subsurface contamination, and human/ecosystem health associated with the potential risks of acid mine drainage (AMD) and acid rock drainage (ARD). Understanding the chemical and mineralogical composition of mine 'wastes' is an important step which determines the potential for waste processing and resource recovery.

2.2 Definition and classification of waste

The definition and classification of 'wastes' is typically interpreted differently depending on the country where they are generated and the field of application. In the context of this study, all definitions will be considered in view of mining and mineral applications. The term "mine waste" is a general term given to the solid, liquid or gaseous by-products produced through mining, mineral processing, and metallurgical extraction which has no current economic value resulting in accumulation (Hudson-Edwards *et al.*, 2011). In general, mine wastes are classified according to their physicochemical properties and source. *Mine waste* comprises of waste rock, mine water and drainage sludge collected and accumulated through the removal of material for access to the mine and/or ore and dewatering prior to extraction of economic commodities. *Processing wastes* are mainly composed of mine tailings which can be described as a heterogenous mixture of solids (crushed rock) which are suspended in process waters which are contaminated with soluble species resulting from the removal of the economic metals and minerals from the mined resource. *Metallurgical wastes* comprise of low grade leached residues or smelted ores which do not favour further treatment economically (Wang *et al.*, 2014a; Hudson-Edwards *et al.*, 2011). However, mining and industrial residual waste and process residues are not classified in an identical way in South Africa. It is beyond the scope of this dissertation to discuss this in detail. However, since this study focuses on reprocessing PGM tailings, it is important to note that South African mine tailings are considered as stock piles and are now regulated by the South African Waste Management Act.

2.3 Current approaches towards waste management with regards to tailings disposal

The management and disposal of mine tailings has become increasingly important due to the drive towards sustainability, the increase in exploration of metals from lower grade deposits, pressures from government and environmental health and safety issues. In South Africa, mining and construction companies are subjected to international standards for planning, design, construction, operation and closure of mine residue storage facilities. Mine waste disposal is independently regulated by the Department of Mineral Resources (DMR), Water Affairs (DWAF) and Environmental Affairs (DEA) and closure certificates are only issued if the long-term objectives of stabilising the geochemical and geotechnical conditions of the disturbed mining area are met in order to prevent on-going environmental degradation. Legislation also requires that rehabilitation of a mining area is a component of the life of mine (LoM) and includes the disposal of tailings within a TSF which is safe, large enough to accommodate the estimated volume of tailings for the LoM, allow for the construction and operation of pollution control facilities and decommissioning thereof (Scheurenberg and Grant-Stuart, 2008, 2012; Wills, 2006).

Many mining companies have taken the stance to reduce, re-use and recycle (three 'R's) the waste produced in order to comply with legislation and promote sustainability. Lottermoser (2011) has applied definitions to the three R's which highlights the key differences between them. *Reuse* entails the new use or application of the total mine waste in its original form for a specific purpose without any reprocessing. *Recycling* entails the extraction of new valuable resources or to use as a feedstock and convert the mine waste into a new valuable product or for an application with some reprocessing. *Reprocessing* entails using the waste material as a feedstock for producing a valuable product such as recovered minerals and metals. The three R's conform to the concept of "zero waste" which ensures total resource utilization whereby all the material mined is utilised and no waste is generated.

The utilisation of mine waste presents an environmentally friendly approach towards mineral beneficiation processes and not only results in the reduction of waste but may also generate income after the run of mine (ROM) has lapsed and rehabilitation of the mine is underway. This has been demonstrated by the recycling process developed by Struthers *et al.* (1997), which entails additional metal recovery from mine tailings, decontamination of material which can be used as backfill and soil remediation (Figure 2.1).

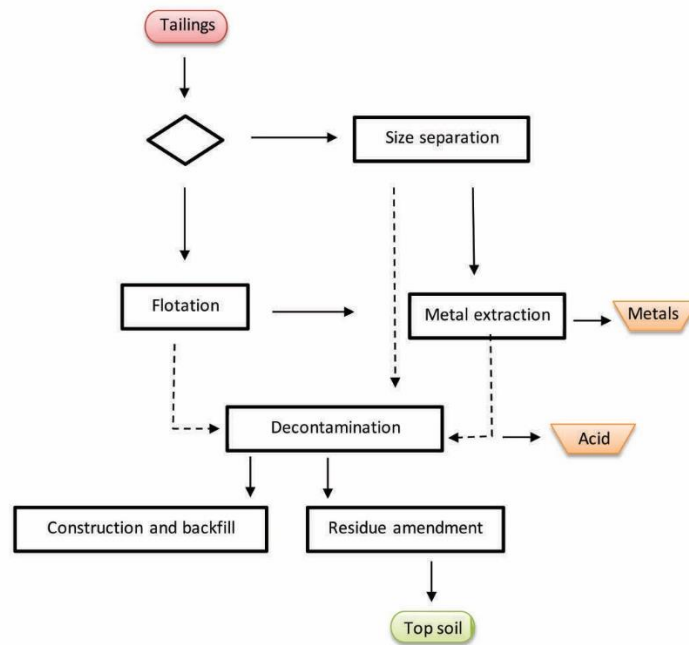


Figure 2.1. Schematic illustration of a tailings recycling process (adapted from Edraki *et al.*, 2014).

2.3.1 Methods of disposal

Traditional methods of tailings disposal included the discharge into streams and rivers and discarding coarse dewatered tailings on to land. However, with the accepted environmental implications of not properly managing mine tailings and with the realisation of profitable applications such as reprocessing to recover additional commodities and reusing the tailings as a secondary product, the disposal in engineered tailings dams has become common practice. Semi-dry and dry disposal techniques are a common and cost-effective approach which requires thickening and dewatering of tailings prior to disposal, resulting in a dense and viscous mixture of water and tailings which do not segregate during transportation (Wills, 2006). This practice has many advantages including the improvement in energy, water and reagent recovery, metal reclamation, and a decrease in tailings volume, thus reducing the risk of dam failure and environmental impact. Thickened tailings are generally treated with lime to neutralise acids and subsequently precipitate heavy metals in the form of soluble hydroxides or used to backfill underground mines. Dewatering ensures water reclamation by removing and reusing free water in TSF that is removed and reused in the mill. However; the reclaimed water tends to recirculate pollutants which affect downstream recovery process. The integration of a detailed mineralogical assessment of TSF into LoM may be useful to obtain a quantitative analysis of potentially valuable economic elements which could be recovered, to monitor physicochemical changes and the release of toxic elements into the surrounding environment over time (Brough *et al.*, 2013). Edraki *et al.* (2014) has identified “points of intervention” located along the beneficiation cycle (Figure 2.2) which need to be considered for improvement in achieving maximum recovery and enhancing the management of TSF. This may create the potential for reuse and recycling of the waste present in TSF and ultimately reduce the ecological footprint on the mine itself.

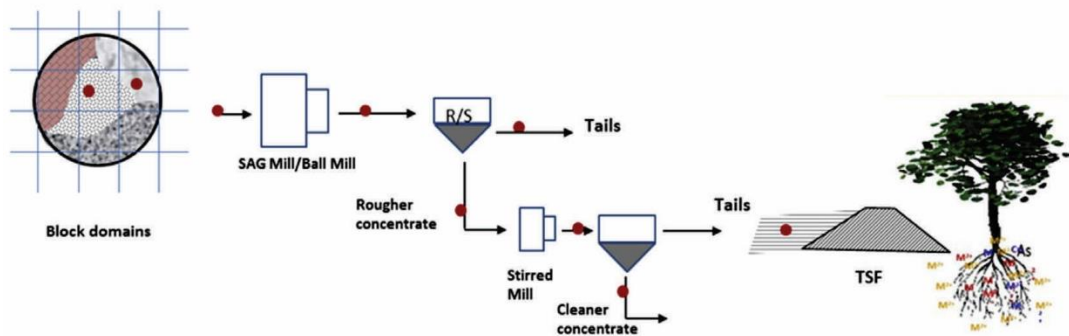


Figure 2.2. Potential points of intervention located along the beneficiation cycle of mineral wastes (adapted from Edraki *et al.*, 2014).

2.3.2 Environmental considerations

The most serious environmental problem which arises from the disposal of tailings is the release of pollutants such as sulphide-bearing minerals disposed as tailings or mineralised waste rocks, polluted water which includes solutes and solids, heavy metals, mill reagents, and sulphur-based compounds, the unsightly visual impact on the environment and weathering and erosion of waste deposits (Wills, 2006).

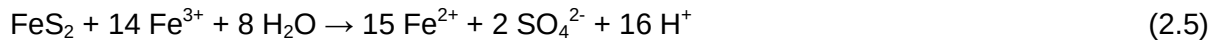
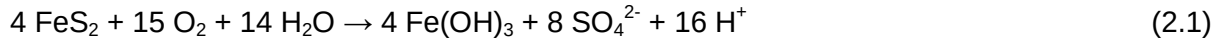
Mine wastes from various industries contain a combination of primary and secondary mineral wastes which are either sulphide bearing or sulphide deficient minerals liberated from the ore and minerals formed by the weathering of primary minerals respectively. Table 2.1 lists common primary and secondary minerals which may interact with water and result in environmental toxicity. A high abundance of alkaline gangue minerals such as carbonates (limestone) provides a natural pollution control and results in the formation of less soluble metals and neutralises oxidation products (Wills, 2006). The fine-grained nature of mine tailings as a result of comminution tend to disaggregate the particles and results in an elevated concentration of acid generating minerals creating a more aggressive effluent being released (Johnson and Hallberg, 2005).

Table 2.1. Primary and secondary minerals present in mine waste (adapted from Jamieson, 2011).

	Mineral	Formula
primary minerals	Pyrite	FeS_2
	Marcasite	FeS_2
	Pyrrhotite	$\text{Fe}(1-x)\text{S}$
	Chalcopyrite	CuFeS_2
	Bornite	Cu_5FeS_4
	Sphalerite	$(\text{Zn},\text{Fe})\text{S}$
	Pentlandite	$(\text{Fe},\text{Ni})_9\text{S}_8$
	Enargite	Cu_3AsS_4
	Galena	PbS
	Molybdenite	MoS_2
	Tetrahedrite–Tennantite	$(\text{Cu},\text{Fe})_{12}\text{Sb}_4\text{S}_{13}$ – $(\text{Cu},\text{Fe})_{12}\text{As}_4\text{S}_{13}$
	Cinnabar	HgS
	Cobaltite	CoAsS
	Stibnite	Sb_2S_3
	Realgar	AsS
	Orpiment	As_2S_3
secondary minerals	<i>Iron oxyhydroxides</i>	
	Goethite	$\alpha\text{-FeO}(\text{OH})$
	Lepidocrocite	$\gamma\text{-FeO}(\text{OH})$
	Ferrihydrite	$\text{Fe}(\text{OH})_3$
	<i>Aluminum oxyhydroxides</i>	
	Gibbsite	$\text{Al}(\text{OH})_3$
	AlO(OH)	$\text{AlO}(\text{OH})$
	<i>Sulfate minerals</i>	
	Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
	Jarosite group minerals	$(\text{K},\text{Na},\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$
	Schwertmannite	$\text{Fe}_{16}\text{O}_{16}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$
	Melanterite	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
	Copiapite	$\text{Fe}^{2+}\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$
	Epsomite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
	Anglesite	PbSO_4

Environmental problems induced by mining activities typically involve the production of AMD, the release of heavy metals, and organic and inorganic pollutants. The generation of AMD and metal release occur simultaneously resulting in a toxic environment which is characterised by a very low pH (< 2), a high oxidation-reduction potential (ORP), a high concentration of total dissolved solids (TDS) comprising of sulphates, nitrates, phosphates, ammonium-based compounds, major and trace elements such as Al, Fe, Mn and As, Be, Cr, V (Jamieson, 2011; Klimkova *et al.*, 2011). AMD has been a major environmental problem in South Africa caused by the historical mining of gold which was left untreated either due to a lack of adequate treatment technologies or overbearing costs. The processes of AMD generation is typically caused by the oxidation of sulphide minerals e.g. pyrite (FeS_2) resulting from exposure to oxygen and water according to the general equation 2.1. However pyrite oxidation is a multistep process and the primary oxidant which participates in the oxidation of pyrite is the ferric iron (Fe^{3+}) rather than the molecular oxygen. Furthermore pyrite oxidation follows an oxygen-independent reaction (Fe^{3+} attack on mineral (pyrite)) and oxygen-dependent reactions (re oxidation of ferrous iron (Fe^{2+}) to Fe^{3+} (Johnson and

Hallberg, 2005). The process of pyrite oxidation can be broken down into four reaction mechanisms which take place over time. The first reaction is the oxidation of sulphide mineral into dissolved iron (Fe), sulphate (SO_4^{2-}) and hydrogen (H^+) (equation 2.2) which represents an increase in total dissolved solids (TDS) and activity of water and a decrease in pH. Further exposure to an oxidising environment (dependent on O_2 concentration, pH and bacterial activity) will result in the oxidation of Fe^{2+} into Fe^{3+} (equation 2.3), followed by its subsequent precipitation as $\text{Fe}(\text{OH})_3$ (equation 2.4). Any residual Fe which has not precipitated from solution in equation 2.4 will oxidize additional pyrite according to equation 2.5 (Akcil and Koldas, 2006; Johnson and Hallberg, 2005).



Ensuring that the mineralogical composition of the tailings disposed in TSF is geochemically inert with little to no sulphides present is crucial to the sustainability of the resource and the surrounding environment. Particular attention needs to be drawn by mineral processing operations in order to mitigate the environmental impact caused by TSF's which should ideally be incorporated into the planning of the LoM.

2.3.3 Application of mine waste products

Research on metal extraction from mine waste and tailings is not new; however, it is gaining momentum with the advent of intensified sustainable development initiatives. The key aspects which determine the viability of reprocessing mine waste is dictated by chemical and geotechnical properties of the waste material as well as the potential environmental impacts (Bian *et al.*, 2012), which have a direct impact on economics. Possible reuse and recycling options of mine waste are presented in Table 2.2 and highlights key applications in which secondary metal extraction can be utilised. Sufficient scope exists to improve the efficiency of metal extraction and separation of mine waste. Appropriate economically-viable technologies need to be developed in order to address the current processing limitations to ensure full extraction of valuable metals from primary and secondary resources and their subsequent conversion into value added products.

Table 2.2. Reuse and recycling alternatives for waste streams produced by the mining industry (adapted from Lottermoser, 2011).

Waste type		Reuse and recycling option
Mining wastes	Waste rocks	• Resource of minerals and metals • Backfill for open voids • Landscaping material • Capping material for waste repositories • Substrate for revegetation at mine sites • Aggregate in embankment, road, pavement, foundation and building construction • Asphalt component • Feedstock for cement and concrete • Sulfidic waste rock as soil additive to neutralize infertile alkaline agricultural soils
	Mine waters	• Dust suppression and mineral processing applications • Recovery of metals from AMD waters • Drinking water • Industrial and agricultural use • Coolant or heating agent • Generation of electricity using fuel cell technology • Engineered solar ponds to capture heat for electricity generation, heating, or desalination and distillation of water
	Mine drainage sludges	• Extraction of hydrous ferric oxides for paint pigments • Extraction of Mn for pottery glaze • Flocculant/adsorbant to remove phosphate from sewage and agricultural effluents
Processing wastes	Tailings	• Reprocessing to extract minerals and metals • Waste reduction through targeted extraction of valuable minerals during processing • Sand-rich tailings mixed with cement used as backfill in underground mines • Clay-rich tailings as an amendment to sandy soils and for the manufacturing of bricks, cement, floor tiles, sanitary ware and porcelains • Mn-rich tailings used in agro-forestry, building and construction materials, coatings, cast resin products, glass, ceramics and glazes • Bauxite tailings as sources of alum • Cu-rich tailings as extenders for paints • Fe-rich tailings mixed with fly ash and sewage sludge as lightweight ceramics • Energy recovery from compost-coal tailings mixtures • Phlogopite-rich tailings for sewage treatment • Phosphate-rich tailings for the extraction of phosphoric acid • Ultramafic tailings for the production of glass and rock wool • Carbon dioxide sequestration in ultramafic tailings and waste rocks
Metallurgical wastes	Bauxite red mud	• Treatment of agricultural and industrial effluents • Raw material for glass, tiles, cements, ceramics, aggregate and bricks • Treatment of AMD waters • Carbon dioxide sequestration
	Historical base metal smelting slags	• Production of concrete and cement • Use as fill, ballast, abrasive and aggregate • Extraction of metals (e.g. Cu, Pb, Zn, Ag, Au)
	Phosphogypsum	• Soil amendment • Building and construction material • Extraction of elements and compounds (e.g. U, Y, REE and calcium sulfate)

2.4 PGE mine tailings

PGE mine tailings is the residue which remains after the liberation of PGM's from the ore, i.e. Platinum (Pt), Rhodium, (Rh), Palladium (Pd), Rhuthenium (Ru), Osmium (Os), and Iridium (Ir). The mineralogy of PGE tailings is generally unaltered by the comminution processes and may be considered as a secondary resource of natural minerals which can be exploited to recover metals of great economic value. PGE ores have been classified into three broad categories,

- (1) **PGE dominant ores** - which include Merensky (layered with disseminated sulphides), Chromitite (stratiform deposits), placer-type (alluvial, eluvial and Alaskan-derived type deposits) and dunite pipes (PGE's are present as Pt-Fe alloys; sperrylite (PtAs₂) and geversite (PtSb₂))

(2) Ni-Cu dominant ores – mines for Ni and Cu. PGE's are recovered as co-existing products

(3) Miscellaneous ores such as porphyry Cu, Cu-Mo, carbonitites, black shales, hydrothermal and supergene Cu ores and Ni laterites in which PGE's are present in solid solution with other minerals as as discreet PGM's (Cole and Ferron, 2002).

Most PGE mine tailings still have high assay values for major elements such as Mg, Fe, Al, Si and trace elements such as V, Ni and Cr. Early stage tailings are more concentrated with valuable elements than later staged tailings due to technological advances and the development of secondary commodity recovery plants. Although the initial costs of infrastructure and technological implementation may appear to be high, secondary beneficiation could be considered as pre-rehabilitation step which may not just decrease the ecological footprint of the tailings dam but also generate income to overcome the additional costs generated (Lottermoser, 2011).

2.4.1 The Bushveld Igneous Complex (BIC)

The Bushveld Igneous Complex is a mafic layered igneous intrusion which underlies an area of approximately 65 000 km² extending from Zeerust to Burgersfort from west to east and Villa Nora to Bethal from north to south. The BIC is subdivided into 5 main units and limbs, whereby the eastern and western limbs are best exposed (Figure 2.3). The BIC is intruded discordantly into the Pretoria Group of the Transvaal Supergroup and the stratigraphy is generally consistent over the intrusion; however, a complete correlation does not exist in all areas.

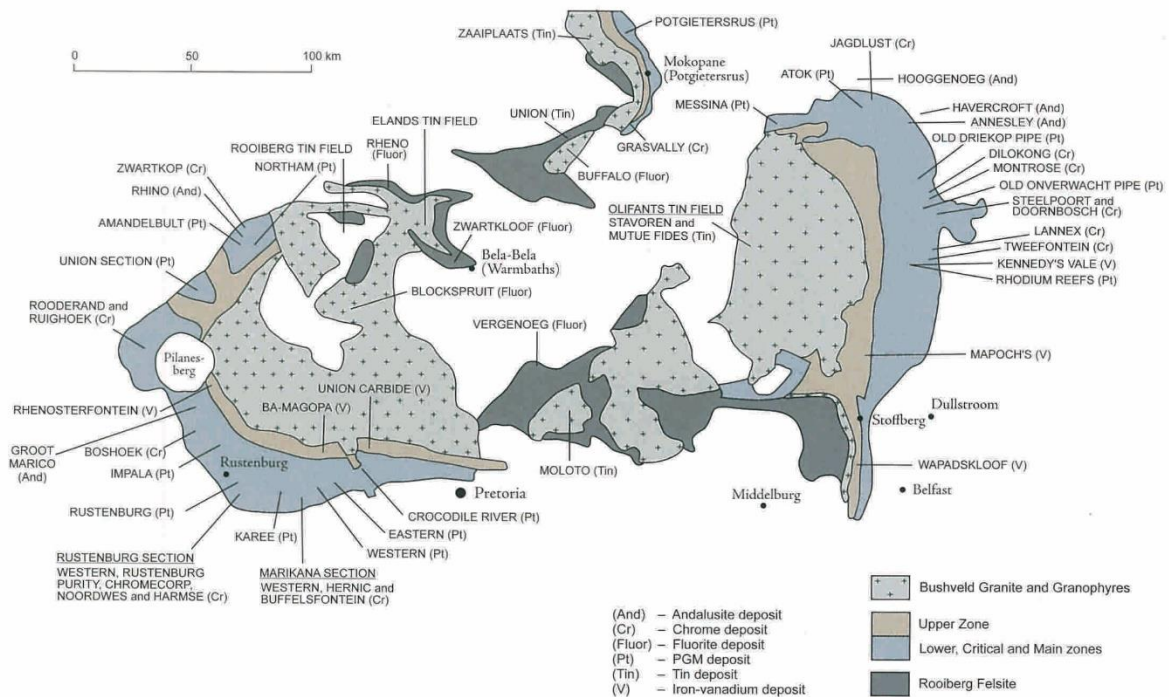


Figure 2.3. Distribution and economic deposits of the Bushveld Igneous Complex (adapted from Eales, 2014).

The BIC comprises the largest ore reserves of Platinum Group Elements (PGE's), chromium (Cr) and vanadium (V) and other mineral deposits which are hosted in the mafic (dark coloured) rocks sequences of the Rustenburg Layered Suite (RLS; Figure 2.3). The stratigraphy of RLS is further subdivided into four different zones namely the lower zone, critical zone, main zone and upper zone, comprising of layered ultramafic and mafic rock sequences which include anorthosites, diorites, dunite, gabbro, norite, and pyroxenites (Figure 2.4). The nomenclature of the different rock types is based on the mineralogical distinctions made by the International Union of Geological Sciences (IUGS) and corresponds to the relative proportions of the various mineral phases they contain (Table 2.4. and Figure 2.5). PGE mineralisation within the BIC is confined to distinct mineral-bearing reefs, i.e. the Merensky Reef, UG2 Reef, Platreef and chromitite layers; however, traditional mining operations have preferentially exploited the Merensky Reef and UG2 reefs which are primarily composed of metal-silicates and other mineral phases (olivine, pyroxene, feldspars, amphiboles, micas, spinels and sulphides). The general formula and description of the various mineral phases is given in Table 2.3.

The Merensky Reef is often referred to as a pegmatoid zone bounded by chromite layers ranging between 2 - 3 mm in thickness. A variation in terms of PGE concentration, base metal sulphides (BMS) and gangue mineralogy is often observed. PGE's occur either as discrete PGM or in a solid solution with Cu, Ni and Fe sulphides. PGE's are present as fine inclusions within BMS or as intergrowths between BMS and gangue mineral contact surfaces, which enables liberation during the grinding process. A coarse grain size i.e. between 75 and 150 μm is commonly chosen for the liberation of PGE's. The UG2 reef is

characterised by a high concentration of chromite (60 – 90 %), orthopyroxene (5 – 25%), plagioclase (5 - 15 %) and trace amounts of BMS. Sulphide minerals occur along the chromite mineral boundaries which are generally between 1 and 30 µm in diameter. Liberation of PGE's from the UG2 by detachment is a common practice which requires the ore to be milled down to the natural chromite grain size i.e. approximately 100 µm in order to expose the BMS surfaces. The PGM may also occur as single grains along chromite grain boundaries or as inclusions within chromite or other silicate gangue minerals (Cole and Ferron, 2002).

Table 2.3. Primary mineral phases present in the Bushveld Igneous Complex (compiled from Eales, 2014).

Mineral group	End-member	Formula	Notes
olivine	fayalite	$\text{Fe}^{2+}_2(\text{SiO}_4)$	
	forsterite	$\text{Mg}_2(\text{SiO}_4)$	
pyroxene	orthopyroxene	$(\text{Mg}, \text{Fe})\text{SiO}_3$	May contain minor amounts of Ca, Al, Cr, Ti, Mn and Na
	clinopyroxene	$\text{Ca}(\text{Mg}, \text{Fe})\text{Si}_2\text{O}_6$	
feldspars	anorthite	$\text{CaAlSi}_2\text{O}_8$	(1) plagioclase feldspar series: albite-anorthite ($\text{NaAlSi}_3\text{O}_8$ to $\text{CaAl}_2\text{Si}_2\text{O}_8$), (2) alkali feldspar series ($\text{NaAlSi}_3\text{O}_8$ to $\text{KAl}_2\text{Si}_2\text{O}_8$)
	albite	$\text{NaAlSi}_3\text{O}_8$	
	orthoclase/microcline	KAlSi_3O_8	
amphiboles	hornblende	$\text{Ca}_2((\text{Fe}^{2+}, \text{Mg}^{2+})_4\text{Al})(\text{Si}_7\text{Al})\text{O}_{22}(\text{OH})_2$	
micas		$\text{KMg}_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$	
	muscovite	$\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$	
spinel	magnetite	$\text{Fe}^{2+}\text{OFe}^{3+}_2\text{O}_3$	General formula AB_2O_4 . $\text{A}=\text{Fe}^{2+}, \text{Mg}^{2+}, \text{Mn}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}$ and $\text{B}=\text{Fe}^{3+}, \text{Al}^{3+}, \text{Cr}^{3+}$ or $(\text{Fe}^{2+}\text{Ti}^{4+})^{6+}$. May contain Ti, V
	chromite	$(\text{Mg}, \text{Fe})\text{O}(\text{Cr}, \text{Al}, \text{Fe})_2\text{O}_3$	
quartz		SiO_2	
apatite		$\text{PCaO}_3(\text{P}_2\text{O}_5)\text{CaF}_2$	
sulphides	pyrite	FeS_2	
	chalcopyrite	CuFeS_2	
	pentlandite	$(\text{Fe}, \text{Ni})_9\text{S}_8$	
	pyrrhotite	Fe_7S_8	

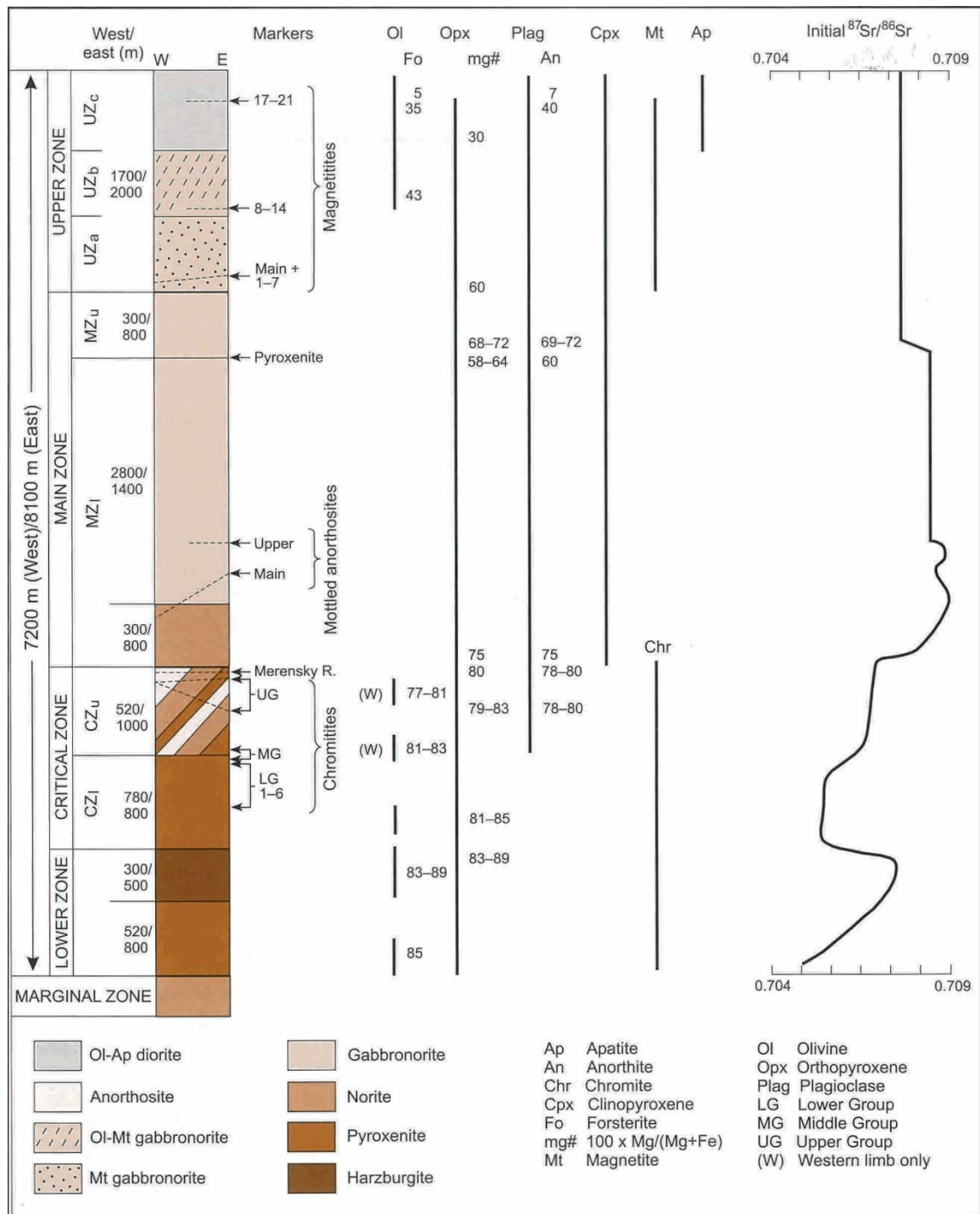


Figure 2.4. Subdivisions of the Rustenberg Layered Suite and associated enrichment of the various mineral phases (adapted from Cawthorn *et al.*, 2006).

Table 2.4. Common rocks and associated mineral phases of the Bushveld Igneous Complex (adapted from Eales, 2014).

Combination of minerals present	Conventional rock name
Olivine only	Dunite
Olivine + orthopyroxene	Hazburgite
Orthopyroxene only	Orthopyroxenite (pyroxenite, bronzite)
Orthopyroxene + plagioclase	Norite
Plagioclase only	Anorthosite
Plagioclase + orthopyroxene+ clinopyroxene	Gabbronorite
Plagioclase + minor pyroxenes	Leuconorite
Plagioclase + clinopyroxene	Gabbronorite
Plagioclase + clinopyroxene+alkali feldspar+quartz	Diorite
Chromite only	Chromitite
Magnetite only	Magnetite

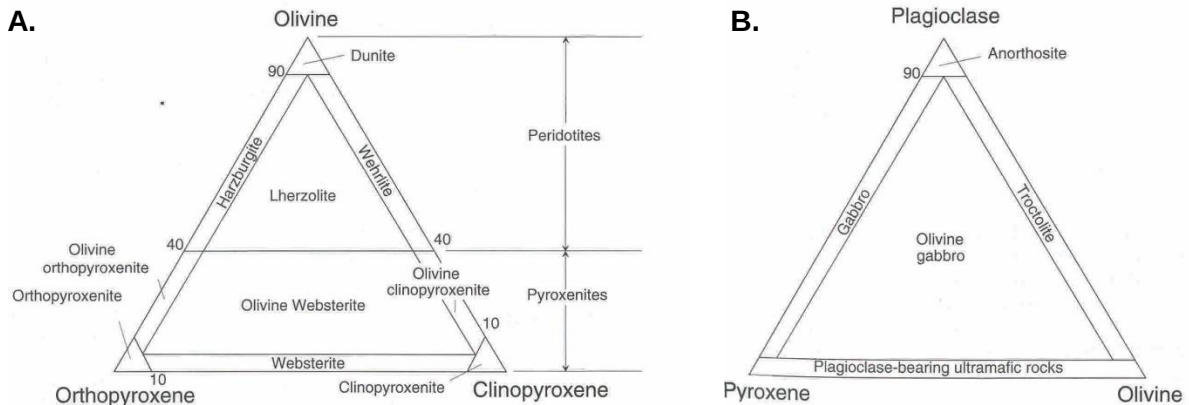


Figure 2.5. Rock classification diagrams for (A.) ultramafic and (B.) Gabbroic rocks defined by the International Union of Geological Sciences (IUGS, adapted from Winter, 2001).

Traditional methods of PGE liberation and transformation

PGE's are recovered through underground and open pit mining and liberated from various mineral phases using mineral processing and extractive metallurgical techniques. The mineralogy of the ore typically dictates the various process routes and therefore differs from one operation to another (Cole and Ferron, 2002). Liberation and floatation are the most important factors for the recovery of PGE's. Liberation is achieved via particle size reduction using comminution processes such as crushing, autogenous and semi-autogenous grinding, rod and ball milling, fine grinding using tower mills, stirred mills and IsaMill™ mills for floatation and concentrate re-grinding. The introduction of IsaMill™ mills has improved the fineness of the tailings thus improving the liberation and recovery of PGE's (Vogeli *et al.*, 2011). Comminution is generally followed by a pre-concentration step which utilises the

physical properties of the ore and gangue minerals and includes the use of spirals, magnetic separators, cones, gravitational techniques. Flotation is the most important separation technique which allows for the selective recovery of valuable elements. The flotation process generally consists of several stages to clean the concentrates and scavenge the valuable minerals from the tailings. This is achieved by utilising the differences in the physicochemical surface properties of the particles after conditioning with reagents. PGE-bearing particles are generally hydrophobic in nature and are retained on the water surface forming a stable froth whereas hydrophilic particles (gangue) remain within the pulp and are discharged into the TSF (Vogeli *et al.*, 2011; Cole and Ferron, 2002).

Physicochemical properties of BIC tailings

The physicochemical properties of mine tailings vary with ore type which is characterised by its bulk chemical composition, mineralogy and grain size (Wang *et al.*, 2014a). Understanding these complexity, variability and inhomogeneity of PGE tailings is crucial to better understand their nature of transformation and to identify their environmental impacts and their potential for the secondary recovery of metals. The physicochemical properties of different tailings samples studied by Amponsah and Reid (2014); Meyer *et al.* (2013); Mohamed (2012) and Vogeli *et al.* (2011) are compared in the following sections, which provide a background of the chemical and mineralogical characteristics and variability along the different limbs along the BIC.

Particle size distribution (PSD) and specific surface area (SSA)

Comparison of the particle size distribution by laser diffraction indicate that overall there is a wide variability between the particle size distribution of the various PGE tailings. This may be attributed to different comminution procedures employed at each operation at different operation times and with depth, due to improvement or technological advances. The BRPM ($D(v,90) = 138 \mu\text{m}$; Vogeli *et al.*, 2011), Northam ($D(v,90) = 238 \mu\text{m}$; Vogeli *et al.*, 2011), Lonmin ($D(v,90) = 293 \mu\text{m}$; Meyer *et al.*, 2013) and Two Rivers ($D(v,90) = 236 \mu\text{m}$; Mohamed, 2012) tailings samples are similarly fine grained compared to Amandelbult, Waterval, Oókiep, Nkomati and Mogalakwena Platreef tailings (Figure 2.6) studied by Amponsah-Dacosta and Reid, (2014). The Impala ($D(v,90) = \sim 400 \mu\text{m}$) and Union ($D(v,90) = \sim 550 \mu\text{m}$) tailings are the coarsest. PGE tailings are generally characterised by low specific surface area values (Amponsah-Dacosta and Reid, 2014; Vogeli *et al.*, 2011). The specific surface area of the Mogalakwena Platreef ($5.2 \text{ m}^2/\text{g}$) tailings is greater than for for BRPM ($1.5 \text{ m}^2/\text{g}$), Northam ($1.3 \text{ m}^2/\text{g}$), Lonmin ($0.917 \text{ m}^2/\text{g}$) and Impala ($0.0454 \text{ m}^2/\text{g}$) tailings.

The PSD of the various tailings confirmed the fine grained nature of PGE tailings and is indicative of a larger mineral surface area per unit mass thus a higher reactivity of the particles. This suggests that no additional sorting or grinding (mechanical activation) would in principle be required during the reprocessing or re-use of the tailings (Doucet, 2011).

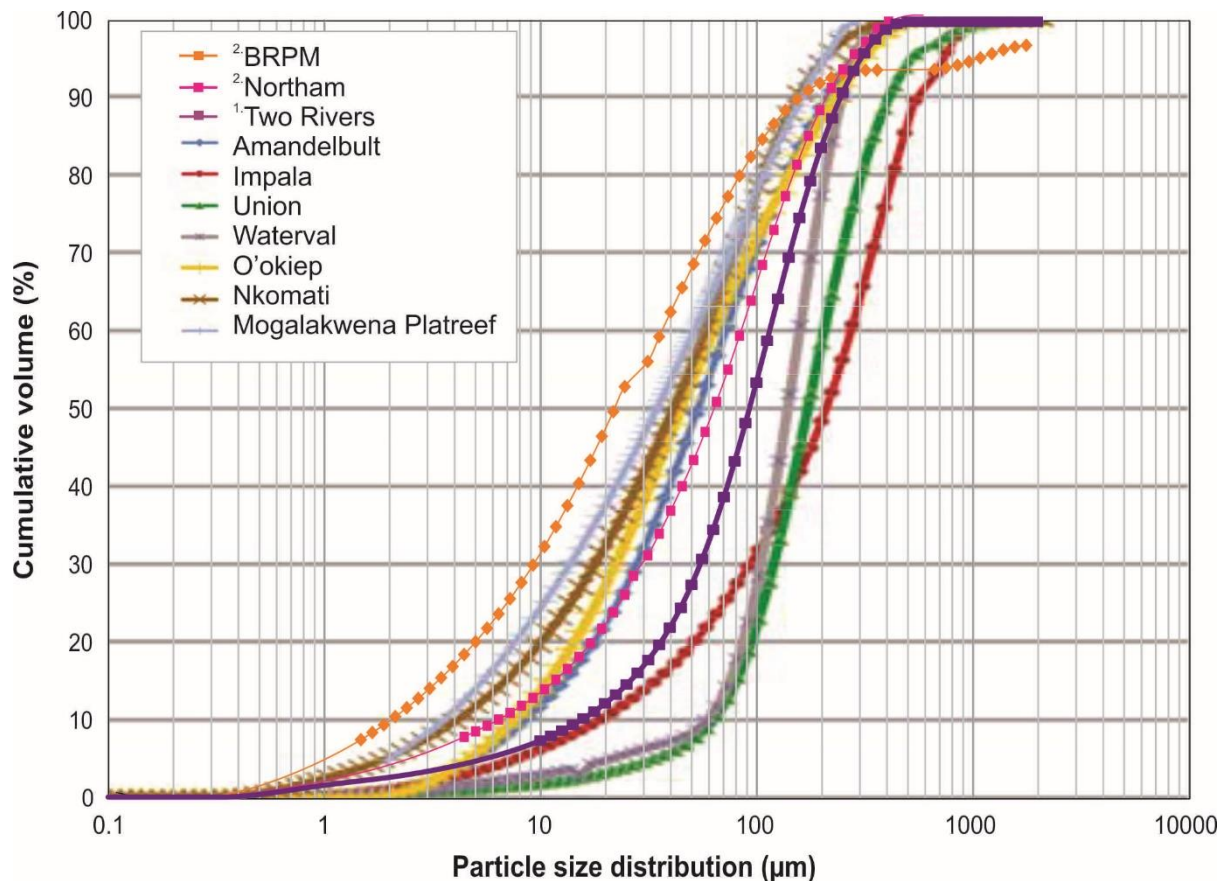


Figure 2.6. Particle size distribution for PGE tailings sampled along the eastern and western limbs of the Bushveld Complex, South Africa (modified from Amponsah-Dacosta and Reid, (2014)). Particle size data for BRPM, Northam and Two Rivers mining operations were sourced from ¹. Mohamed, 2012 and ². Vogeli *et al.*, 2011.

Chemical characteristics of PGE tailings

The chemical composition of the tailings and the minerals that host the potentially economical and valuable elements is the most important link to process characteristics which are used to recover the metals. Table 2.5 presents the bulk chemical compositions of PGE mine tailings samples from different TSF's. The chemical compositions differ quantitatively due to the spatial distributions of the mineral assemblages and/or secondary refining processes which recover chromium. Overall, there is variability in the chemical composition of the different PGE mine tailings. The tailings are relatively enriched in SiO₂ (26.0 – 51.8 wt. %) relative to Al₂O₃ (5.0 – 16.9 wt. %), Fe₂O₃ (8.9 – 20.5 wt. %), MgO (13.3 - 21.9 wt. %), CaO (2.4 – 10.8 wt. %) and Cr₂O₃ (0.4 – 24.4 wt. %). The modal abundance of TiO₂, MnO, Na₂O, K₂O, P₂O₅ and NiO are relatively lower (<1.3 wt. %).

The relative proportions of Fe, Cr, Al, Mg is variable for the different tailings samples and may be attributed to the local variations in mineralogy and the extensive solid-solution which exists between the various mineral phases. The chemical composition confirms the relative abundance of major oxides (Al₂O₃, Cr₂O₃, MgO, Fe₂O₃) in the various PGE tailings which may be reprocessed for metal recovery and/or converted into value added products.

Table 2.5. Chemical composition (in weight percent; wt. %) of PGE tailings from the Bushveld complex. Data was compiled from ¹Amponsah-Dacosta and Reid, (2014), ²Meyer *et al.*, 2013, ³Mohamed, (2012) and ⁴Vogeli *et al.*, (2011).

Major oxide (wt. %)	Mining Operation (tailing storage facility, TSF)								
	Northern limb		Western limb						Eastern limb
	Mogalakwena ¹	Amandelbult ¹	BRPM ⁴	Impala ¹	Northam ⁴	Union ¹	Lonmin ²	Waterval ¹	Two Rivers ³
SiO ₂	48.1	38.2	49.9	35.1	47.8	26.0	51.8	47.2	31.1
TiO ₂	0.2	0.4	0.2	0.7	0.3	0.5	0.3	0.2	0.5
Al ₂ O ₃ **	9.1	12.2	14.4	13.0	7.9	12.2	9.0	16.9	14.5
Fe ₂ O ₃ **	10.8	15.8	8.9	19.4	13.1	20.5	10.9	9.1	16.4
MnO	0.2	0.2	-	0.2	-	0.2	0.2	0.1	0.2
MgO**	19.3	17.1	14.6	16.2	21.9	15.7	19.3	13.3	16.3
CaO	7.5	4.9	8.7	4.3	5.0	2.4	5.8	7.8	3.4
Na ₂ O	1.2	0.9	1.2	0.9	0.8	0.5	0.9	1.3	0.7
K ₂ O	0.4	0.2	-	0.1	-	0.1	0.2	0.2	0.1
P ₂ O ₅	0.1	0.0	-	0.0	-	0.0	0.0	0.0	0.0
Cr ₂ O ₃ **	0.4	10.9	0.9	12.2	2.3	24.4	1.0	3.7	16.2
NiO	0.3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
LOI	2.7	0.3	*	-0.3	*	-0.9	0.2	0.5	*

* Normalised, no loss on ignition (LOI) was done to determine structural water and changes in oxidation state.

** Elements of potential economic value

Mineralogy of PGE mine tailings

The link between mineralogy and process characteristics plays a vital role in the recovery of metals. It is expected that the bulk mineralogy of PGE mine tailings differs spatially in accordance to the different ores being targeted and depicts the parent mineralogy of the ore from which it has been processed. The mineral phases present in the Two Rivers, BRPM, Lonmin and Northam tailings studied by Vogeli *et al.* (2011), Mohamed (2012) and Meyer *et al.* (2013) are predominantly comprised of silicate, aluminosilicates and oxides, minor to trace amounts of alteration minerals (serpentine ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$), talc ($\text{Mg}_3(\text{OH})_2\text{Si}_4\text{O}_{10}$), chlorite ($(\text{Mg}_5\text{Al})(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_8$), calcite ($\text{Ca}(\text{CO}_3)$) and sulphides (Table 2.6).

The absence of sulphide bearing minerals in the Two Rivers samples is characteristic of mining from the UG2 which has a lower sulphide content compared to the BRPM, Lonmin and Northam tailings which originate from the Merensky Reef. This distinction in primary ore is also evident in the spinel (chromite) content which is higher in the Two Rivers compared to BRPM, Lonmin and Northam. The BRPM, Lonmin, Northam and Two Rivers tailings samples contain a significant amount of enstatite ($\text{Mg}_2\text{Si}_2\text{O}_6$) and plagioclase ($(\text{Na},\text{Ca})(\text{Si},\text{Al})_4\text{O}_8$) with minor amounts of clinopyroxene ($(\text{Ca},\text{Na})(\text{Mg},\text{Fe},\text{Al},\text{Ti})(\text{Si},\text{Al})_2\text{O}_6$), amphibole ($\text{Ca}_2[\text{Mg}_4(\text{Al},\text{Fe}^{3+})]\text{Si}_7\text{AlO}_{22}(\text{OH})_2$) and mica ($\text{KFeMg}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$). In terms of alteration minerals, Northam and BRPM tailings samples contain a higher amount of talc and serpentine which is consistent to the higher modal abundance of olivine ($(\text{Mg},\text{Fe})_2(\text{SiO}_4)$) in comparison to Two Rivers tailings sample which has a higher modal abundance of calcite and chlorite.

Quantitative mineralogical results obtained by Vogeli *et al.* (2011) indicated that the various mineral phases tend to concentrate in different size fractions (Figure 2.7). Plagioclase and enstatite tend to concentrate within the coarser size fractions (75 - 1000 μm) whereas amphibole and alteration minerals tend to concentrate within the finer and intermediate size fractions (10 - 38 μm). Olivine and diopside ($\text{CaMgSi}_2\text{O}_6$) appear to be relatively constant in all particle sizes (10 - 1000 μm). Although differences exist in the composition of PGE tailings, the ubiquitous presence of pyroxene, feldspar and spinel minerals was evident.

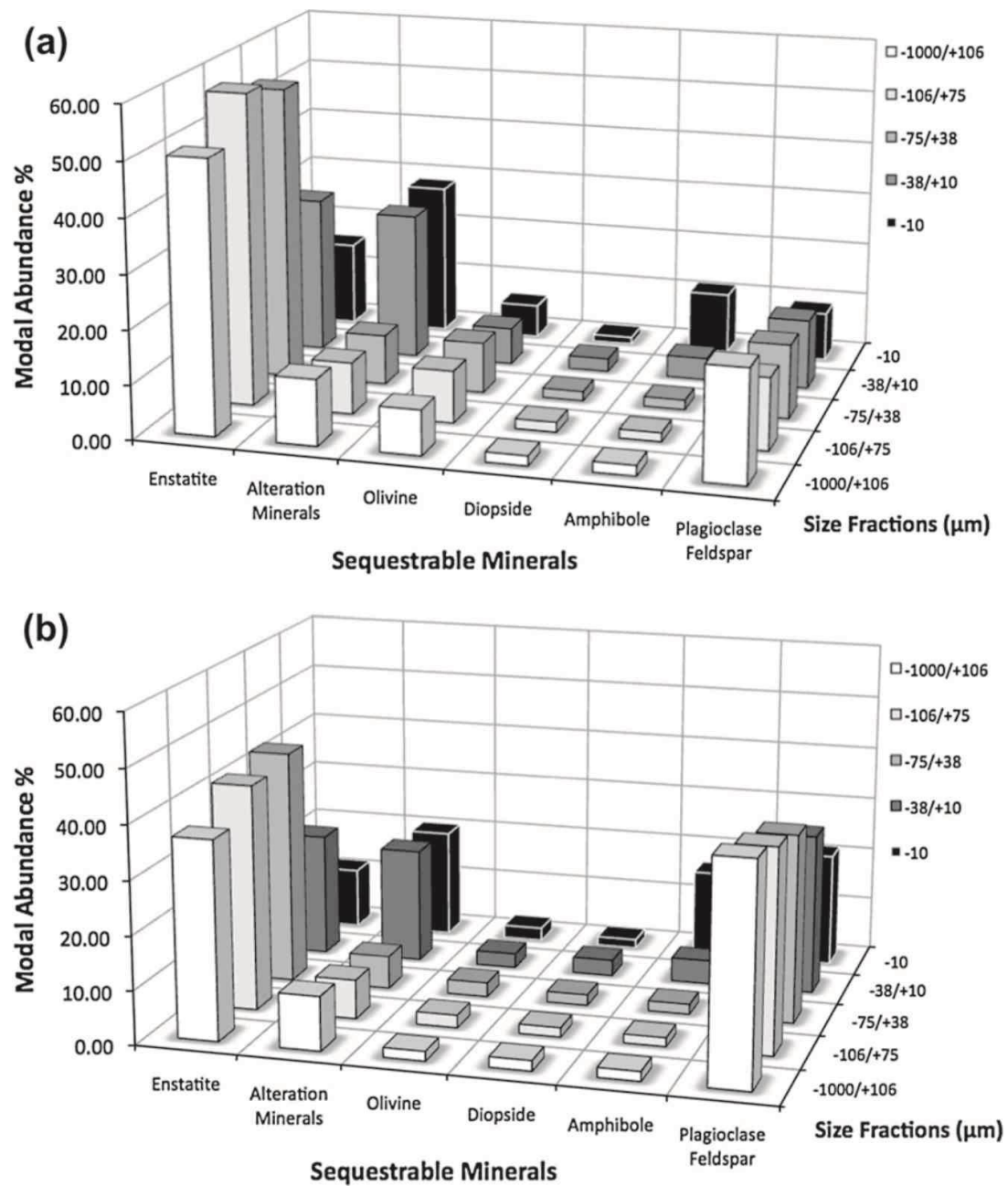


Figure 2.7. Size by size modal abundance of minerals present in the (A.) Northam and (B.) BRPM mine tailings samples (adapted from Vogeli *et al.*, 2011).

Table. 2.6. Summary of mineral phases present in the Bushveld Igneous Complex and identified by XRD for tailings from Northam, BRPM and Two Rivers mining operations, (compiled using data from Eales, 2014; ¹Mohamed 2012; ²Vogeli *et al.*, 2011; ³Meyer *et al.*, 2013).

Mineral group	End-member	Formula	Northam ²	BRPM ²	Two Rivers ¹	Lonmin ³
olivine	fayalite	Fe ²⁺ ₂ (SiO ₄)	8.1	2.4		0.3
	forsterite	Mg ₂ (SiO ₄)				
pyroxene	orthopyroxene	(Mg,Fe)SiO ₃	41.9	30.6	29.9	65.6
	clinopyroxene	Ca(Mg,Fe)Si ₂ O ₆	1.8	2.1	3.1	5.3
feldspars	anorthite	CaAlSi ₂ O ₈	13.6	33.4	20.5	15.8
	albite	NaAlSi ₃ O ₈				
	orthoclase/microcline	KAlSi ₃ O ₈				
amphiboles	hornblende	Ca ₂ ((Fe ²⁺ ,Mg ²⁺) ₄ Al)(Si ₇ Al)O ₂₂ (OH) ₂	3.9	5.5	6.1	2.8
micas		KMg ₃ (AlSi ₃)O ₁₀ (OH) ₂	0.4	0.5	1.1	0.9
	muscovite	KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂				
spinel	magnetite	Fe ²⁺ OFe ³⁺ ₂ O ₃	5.6	1.9	31.1	2.4
	chromite	(Mg, Fe)O(Cr, Al, Fe) ₂ O ₃				
quartz		SiO ₂	0.9	1.3		0.8
apatite		PCaO ₃ (P ₂ O ₅)CaF ₂				
sulphides	pyrite	FeS ₂	0.1	0.1		0.5
	chalcopyrite	CuFeS ₂				
	pentlandite	(Fe, Ni) ₉ S ₈				
	pyrrhotite	Fe ₇ S ₈				
calcite/ dolomite		(Ca,Mg)(CO ₃) ₂	0.1	0.1	2.9	0.2
chlorite		(Mg ₅ Al)(Si,Al) ₄ O ₁₀ (OH) ₈	0.8	1.7	4.4	0.9
talc/ pyrophyllite		Mg ₃ (OH) ₂ Si ₄ O ₁₀	12.4	11.1	0.6	1.0
serpentine	lizardite	Mg ₃ Si ₂ O ₅ (OH) ₄	3.7	3.7	tc*	0.1

*tc : trace

2.5 Extraction of major elements from silicate rocks

Mafic and ultramafic silicate rocks and associated process residues can be considered as potential secondary resources which are present as large scale mineable deposits (Vogeli *et al.*, 2011). To date there have been many attempts of extracting the major elements from silicate-rich materials for economic gain using pyro and hydro-metallurgical processes. This section provides an overview of the various wastes which have been considered for metal recovery and/or conversion into value added products.

2.5.1 Conventional methods of elemental extraction

2.5.1.1 Extraction of aluminium (Al) and silicon (Si) from coal fly ash

Coal Fly Ash (CFA) is a solid incombustible residue that is generated during coal combustion in thermoelectric power stations (Yao *et al.*, 2015). CFA is typically enriched in Al and Si, with lesser amounts of Fe, Mg, trace elements and Rare Earth Elements (REEs). CFA typically comprise of an Al-rich amorphous glass phase and crystalline aluminosilicate phase i.e. mullite - $\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$ ($x \approx 0.4$) which are not identically susceptible to the same methods of extraction; it may therefore require the use of multi-step processing techniques.

CFA has been extensively studied for valuable metal recovery, including REE's, by thermal activation using NaOH or Na_2CO_3 as sintering additives (Guo *et al.*, 2013), hydrothermal methods (Li *et al.*, 2014), aqueous leaching using HCl (Guo *et al.*, 2013) or H_2SO_4 (Shemi *et al.*, 2012), etc. Particle size and leaching parameters (duration, temperature, solid-liquid ratio, sintering additives) play an important role in the extraction of Al and Si, and will affect the extraction efficiency of the process.

Al extraction - Several methods have been developed for the extraction of Al., Those include (i) sintering process using soda and soda lime additives, (ii) acid leaching using H_2SO_4 , and (iii) HiChlor process which entails high temperature chlorination of CFA in the presence of a reductant to form metal chlorides. The sintering process typically entails the use of lime or soda lime as sintering additive, yielding extraction of up to 80 %. Wang *et al.*, (2012) demonstrated that de-silication prior to leaching improves Al extraction to 90 %. More recently, Shemi *et al.*, (2015) adapted an acid leach-sinter-acid leach process in order to manipulate the properties of the amorphous and crystalline phase. The amorphous phase is generally reactive and soluble in inorganic solvent such as H_2SO_4 , whereas mullite is mostly insoluble. CaCO_3 was used a sintering additive and proved successful in transforming mullite into a more reactive crystallite which readily dissolves in the leaching step. Although this technique proved to be successful in extracting Al (ca. 88 %), the inorganic solvent is not fully recyclable due to "contamination" of Fe, Ti and Mg and cannot be re-used between the

two leaching steps. This drawback was also experienced by processes mentioned previously. The acid leach process promotes dissolution of Al with silicon-rich residues being generated; but also requires the use of acid-resistant and air-tight processing equipment (Yao et al., 2015).

Si extraction – Given the high content of Al and Si in CFA, the separation between Si and Al plays an integral part in the recovery of Al from CFA. Prior extraction of Si from CFA results in an enriched alumina residue which can be recovered in the form of alumina using the acid leaching process discussed above. This ensures that SiO_2 can also be recycled or recovered as Si nano-based products. The separation of Al and Si is possible (Wang et al., 2014b) and can, for instance, be achieved by thermochemically treating the CFA with ammonium bisulphate. Extraction efficiencies of ca. 90 % have been reported.

Extraction methods of Si typically entails the dissolution of CFA using alkaline leaching or alkali hydrothermal reactions using NaOH, Na_2CO_3 or KOH, or a combination thereof (Murayama et al., 2002). The glass phase (SiO_2) is more susceptible to alkaline leaching in comparison to Al-rich phases, thus resulting in the formation of a sodium-silicate rich solution. Alkaline leaching allows for the extraction of SiO_2 at atmospheric pressure resulting in lower costs and lower energy consumption. An alternative method for the extraction of Si was developed by Bai et al., 2010 which consists of two steps, (i) sodium silicate dissolution using NaOH, followed by (ii) two stage carbonation process which facilitates the removal of impurities prior to the precipitation of silicon which can then be recovered as a mesospheric nano-product. This carbonation method appears to be advantageous, with lower cost, and environmental gain from using the CO_2 generated by existing coal-fired power plants.

2.5.1.2 Steel slags

Steel slags is the by-product of metallurgical processing generated by the smelting of ore (Chowdry et al., 2014), which are either disposed of or recycled for different engineering applications. Re-processing of non-ferrous and ferrous slags are a common process and often used within the steel plant as blast furnace feed or for the production of Fe metal. Secondary metal recovery from slags have been studied using aqueous leaching processing (chloride-, sulphate-ammonia-based solvents, H_2SO_4 , HNO_3) and oxidative acid leaching, which have proved successful in secondary metal recovery however many of these processes have not been up-scaled (Piatak et al., 2014).

In recent years, the reprocessing of disposed slags has been studied for CO₂ sequestration via mineral carbonation, which could create an economic gain for the reprocessing of slags. Process routes studied typically include (i) chemical extraction of Ca and Mg from steel slags using solvents (e.g. HNO₃, H₂SO₄, NaOH, etc.), (ii) separation of Ca and Mg from other elements which were leached out and (iii) carbonation of Ca- and/or –Mg-rich solution in order to form CaCO₃ or MgCO₃. The primary disadvantage of these processes is that the use of acid leaching in step 1 results in the formation of an acidic Ca-rich leachate, which requires pH adjustment to levels about ca. 9 in order for Ca to precipitate in the form of Ca(OH)₂ and its subsequent conversion to CaCO₃ (Doucet, 2010). Teir *et al.*, (2007b) has demonstrated that slags dissolve more readily in acetic acid however an additional separation step will be required to separate the co-extracted elements prior to recovery of solvent (Teir *et al.*, 2007b). Overall the efficiency of the process is restricted to the successful extraction and precipitation of Ca-based species. None of the studied processes are currently economically viable.

2.5.1.3 Ores and tailings

Tailings are by-products resulting from the removal of economic metals and minerals from a mined resource (ores) which are typically disposed of in a TSF. The reprocessing and recovery of metals from South African ores and tailings have been studied using acid leaching (H₂SO₄; Zhao *et al.*, (2015); Jiang *et al.*, (2014)), as well as carbothermic reduction and carbochlorination (Zhao *et al.*, 2015). Although these processes were successful in co-extracting Cr, Fe, Mg and Al, the complete reaction of the mineral phases were hindered by secondary coating of particles by a silicon-rich phase. Furthermore, carbothermic and chlorination processes suffer from chemical erosion and the generation of toxic substances which have not been resolved (Zhao *et al.*, 2015).

South African PGM tailings have been previously assessed and studied for application as a potential feedstock for mineral carbonation. Although several mineral sequesters (enstatite, diopside, olivine, serpentine, chlorite and feldspar; Vogeli *et al.*, 2011) have been identified in the complex mineralogy of the tailings, efficient extraction of Mg and Ca have been problematic. Acid leaching of PGE tailings using both strong inorganic (2M HCl at 70°C for 8h) and organic (oxalic acid, EDTA) acids has been shown to be of limited value for cation extraction from PGM tailings, with only up to 3% Mg, 9% Fe and 30% Ca extracted (Meyer *et al.*, 2014). This suggests that the mineral phases present in the tailings are unreactive under direct acid-leaching.

2.5.2 Advantages of thermochemical treatment using ammonium salts

In comparison to the above mentioned processes or methods of recovery, processes making use of thermochemical treatment of ammonium salts as extracting agents present a number of advantages. For instance, ammonium sulphate is widely available, generally at low-cost, and can be regenerated using e.g. crystallization (Highfield *et al.*, 2012). Also, no specialized equipment/ apparatus is required for this type of process. However, some of the practical aspects that must be taken into account are to minimize the amount of water used to dissolve thermochemically-treated solids, since the use of large amount of water would impact negatively on the energy requirement for the downstream recovery of ammonium sulphate through crystallization (Romao *et al.*, 2015). The preferred use of ammonium bisulphate over ammonium sulphate, if found to be necessary for improved elemental efficiency, would challenge the economics of the process since ammonium bisulphate recovery is more challenging and energy-consuming. Investigations on better understanding and improving thermochemical treating using ammonium salts are therefore required to fully comprehend the potential of this type of process.

2.5.3 Mineral activation using ammonium salts

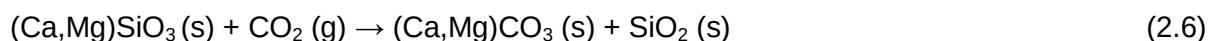
One of the approaches to reprocess mine residues is to convert parent minerals into water-soluble compounds to ensure maximum recovery and reduce reagent and energy requirements. This may be achieved by thermochemical treatment with an ammonium based salt. This process was originally developed for the production of silica, iron oxide and magnesium oxide and is commonly researched for mineral carbon sequestration applications favoured for the potential reagent recovery and selectivity of the leaching process (Bobicki *et al.*, 2012). Extensive fundamental and applied research on ammonium salts and its use in mineral activation has been applied to various materials including kaolinite, silicates and oxide minerals since the early 1980's (Nagaishi *et al.*, 1984; Bayer and Mueller-Vonmoos, 1982). More recently, their reaction with other materials such as low grade nickel ores (Liu *et al.*, 2013; Ma *et al.*, 2013; Tong *et al.*, 2013; Zuniga, 2013; Guo *et al.*, 2012; Medvedev and Sannikova, 2012), low-grade copper ores (Liu *et al.*, 2012; Yu, 2012), polymetallic ores (Jiang *et al.*, 2013), bauxite ores and tailings (Jin *et al.*, 2014), serpentine (Song *et al.*, 2013) and coal combustion by-products (coal fly ash; Guo *et al.*, 2014) for the beneficiation and extraction of metal oxides.

Mineral activation using ammonium salts for mineral carbonation has extensively been studied using serpentine (Nduagu *et al.*, 2013, 2012a, 2012b, 2012c, 2012d; Fagerlund *et al.*, 2012, 2011; Highfield *et al.*, 2012; Romão *et al.*, 2012; Wang and Mercedes-Maroto-Valer 2011a, 2011b; Fagerlund and Zevenhoven, 2011; Teir, 2007a) and nickel mine ore (Romão *et al.*, 2015; 2013). PGE tailing have been assessed for mineral carbonation (Meyer *et al.*, 2013, Mohamed, 2012, Vogeli *et al.*, 2011) and its physicochemical characteristics are suitable for carbonation. However, the overall conversion of Mg into

MgCO₃ is relatively low and may be due to the unreactive nature of orthopyroxene (enstatite) group minerals. Mineral activation using ammonium salts has not been applied to PGE tailings. This provided the rationale for the preliminary study conducted by Mohamed (2012) which focused on the extraction of Ca and Mg from PGE tailings for Carbon Capture and Mineral carbonation CCMC technologies. However due to the low extraction yield of Mg and Ca coupled with slow carbonation reaction kinetics, the focus of the study was reconsidered for metal recovery particularly Fe for its potential application in contaminated water which is investigated in this study.

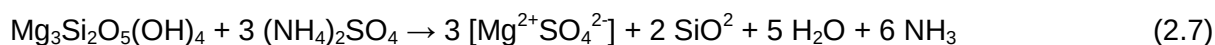
2.5.4 Extraction of Ca and Fe from silicates for the purpose of mineral carbonation

Mineral carbonation was first reported by Seifritz (1990) and has continued to grow interest as a possible mechanism for the removal of excess CO₂ from the atmosphere. Mineral carbonation mimics natural weathering of silicate minerals whereby alkali metals are extracted through water and water-rock interactions and react with ambient atmospheric CO₂ to produce carbonate minerals (equation 2.6; Hitch and Dipple, 2012). Ca and Mg silicates are best suited for mineral carbonation applications. However, the focus has been on Mg-silicate minerals, mostly serpentine, which is available in abundant quantities relative to Ca-bearing minerals such as wollastonite (CaSiO₃), and limited work has been done on PGE tailings (Meyer *et al.*, 2013).



Previous studies have shown that direct aqueous and gas-solid mineral carbonation processes are constrained by rate-limiting steps such as mineral dissolution, slow-limited carbonation reaction kinetics (Highfield *et al.*, 2012). This has shifted the research on mineral carbonation towards indirect aqueous and gas-solid process routes. The most successful attempts of direct aqueous carbonation of silicate minerals (olivine and serpentine) was by Gerdemann *et al.* 2007 and O'Connor *et al.* (2001) at temperatures of 155-185 °C, under supercritical conditions (P_{CO2}=115-190 atm) in a aqueous medium containing sodium bicarbonate and sodium chloride; however the process suffers from drawbacks due to mass transfer limitations. The carbonation reaction kinetics of the process needs to be improved in order to become an economically acceptable commercial process.

Researchers at the Åbo Akademi University (ÅAU) have developed and optimized a process for the purpose of indirect mineral carbonation which focuses on the utilisation of Mg-silicate minerals such as olivine and serpentine. The process entails three steps, *Step 1* - the extraction of magnesium from serpentine or magnesium-rich rocks using ammonium sulphate (AS) which forms magnesium sulphate (MgSO₄) (equation 2.7). AS is non-toxic, relatively inexpensive and a recyclable salt which can be recovered by crystallising the AS from the aqueous solution. *Step 2* - the conversion of MgSO₄ to magnesium hydroxide (Mg(OH)₂) (equation 2.8) is achieved through the addition of NH₄OH in an aqueous medium. *Step 3* - the solid-gas conversion of Mg(OH)₂ into stable magnesium carbonate (MgCO₃) (equation 2.9) using a pressurised fluidised bed (Figure 2.8)



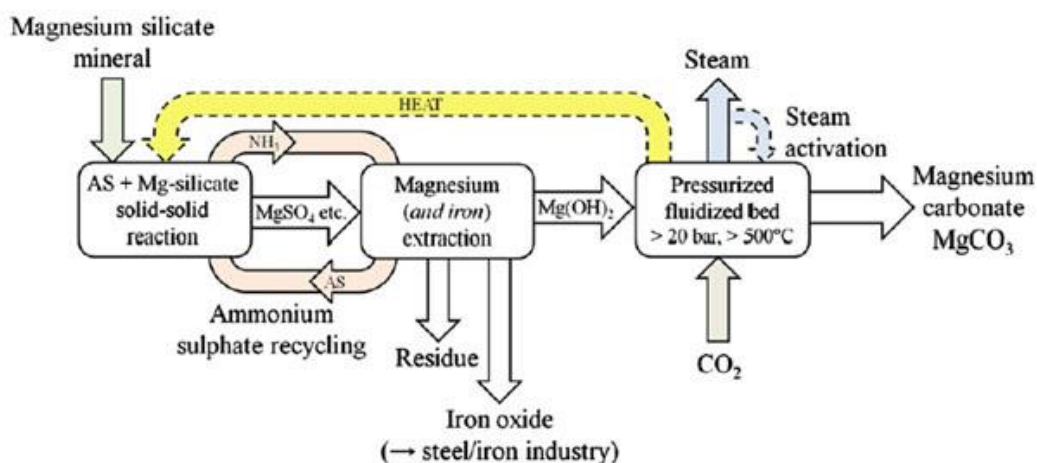
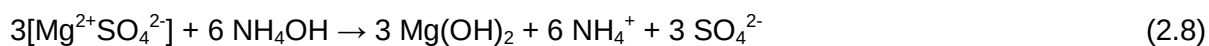


Figure 2.8. Schematic illustration of the CO₂ mineralisation process developed the Åbo Akademi University, Finland (adapted from Fagerlund *et al.*, 2012).

The life cycle analysis conducted by Hitch and Dipple (2012) and Nduagu *et al.*, (2012a) has shown that this technology may be able to sequester a considerable amount of CO₂. However, it can only compete as a viable CO₂ mitigation option if it is applied to flue gases directly avoiding the energy and environmental penalty of CO₂ capture. The integration of this process into metal ore processing for MgO production or residual recovery of PGM's would be economically beneficial (Bodor *et al.*, 2013; Meyer *et al.*, 2013; Zevenhoven *et al.*, 2002).

2.5.5 Implications for Mg and Fe extraction

The extent of Mg and Fe extraction from silicate minerals using AS depends on the process route and reaction conditions which have been modelled by Nduagu *et al.*, 2012c. The dominant solid products formed during the reaction of serpentinite with AS is typically MgSO₄, FeSO₄ and SiO₂ with water and ammonia being the major gas phases (Figure 2.9A). Mg extraction (Figure 2.9B) has been found to be most optimal during the production of SO₃ gas (430°C) produced using higher stoichiometric amounts of AS (4 kmol). The Mg:Fe ratio in serpentinites is an additional factor which affects the extraction of Mg. It has been found that Fe is co-extracted with Mg when leached in an aqueous NH₄OH solution resulting in the formation of an Fe-rich by-product which could be utilized in the iron and steelmaking industry. The Fe in serpentinite is generally present as oxides; however the oxidation state of Fe is generally unknown and can exist as either FeO, Fe₂O₃ and Fe₃O₄, all of which may be

present and could form either intermediate products such as FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ between 200 °C and 650 °C (Figure 2.9C).

The optimal temperatures observed for the formation of MgSO_4 , FeSO_4 and Fe_2SO_4 was investigated in the preliminary study by Mohamed (2012), which focused on the reaction between PGE tailings and AS and it was found that mineral transformation into (ammonium) metal-sulphate species is possible. The positive identification of $\text{Fe}_2(\text{SO}_4)_3$ (Mikasaite), $(\text{NH}_4)_2\text{Mg}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$ (boussingaultite) and $\text{NH}_4\text{Al}(\text{SO}_4)_2$ (ammonium aluminium sulphate) among other various sulphates (Table 2.7) suggested that mineral transformations were most apparent within the 45 - 75 μm size fraction compared to the 150 - 250 μm size fraction in the temperature range of 350 °C - 550 °C. No further attempt was made to quantify these findings however it has provided the groundwork for this study. Furthermore the use of the 45 – 75 μm size fraction in this study was selected based on the finding discussed herein and was attributed to the formation of the thermodynamically stable Fe - sulphate compounds. The recovery of Fe from the sulphate-based compounds (which is investigated in this study) may be an effective, low cost, reactive medium for the synthesis of iron nanoparticles and for their subsequent use in environmental technological applications such as the remediation of contaminated waters (section 2.6).

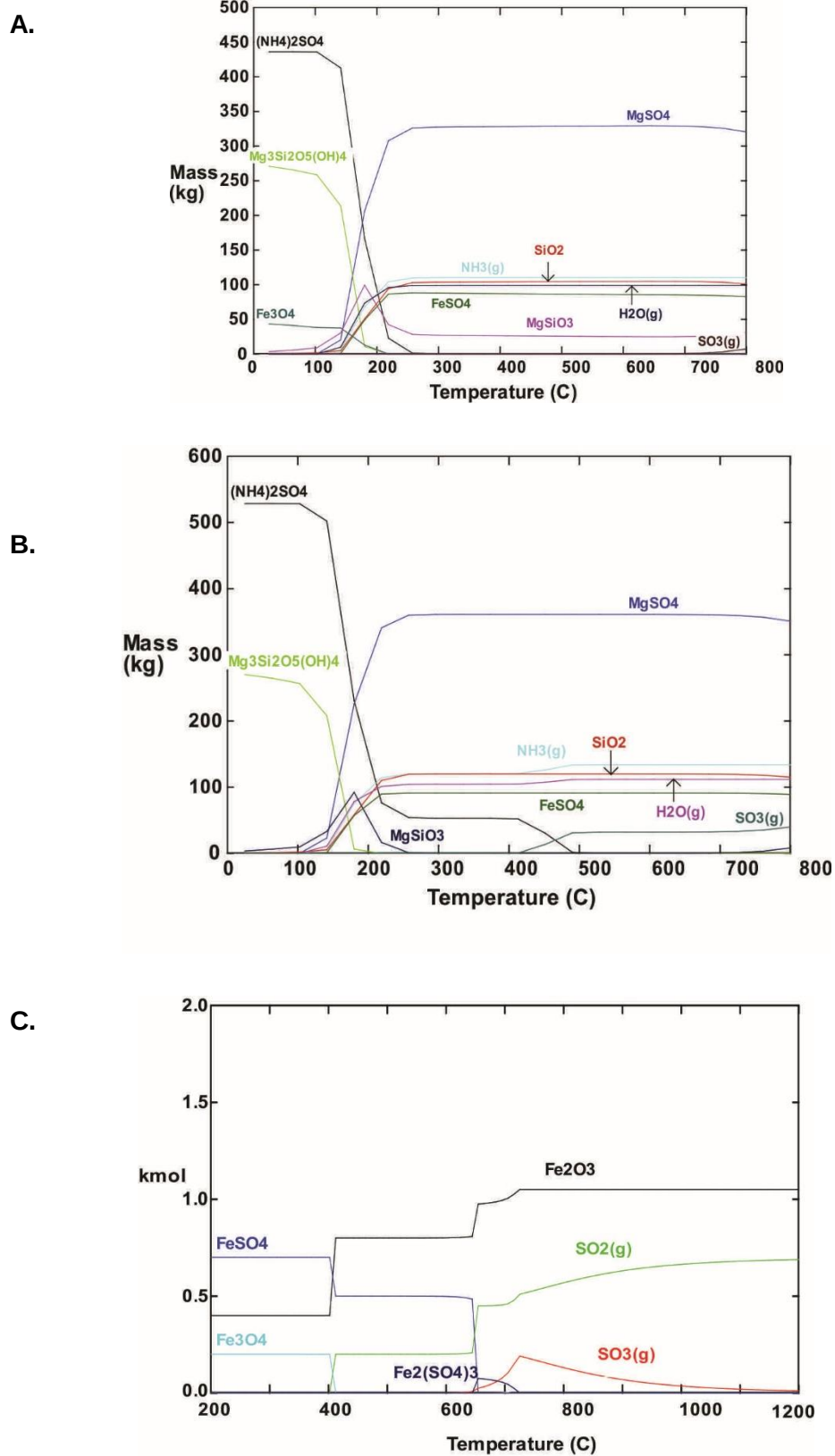


Figure 2.9. Thermodynamic equilibrium compositions for the reaction between serpentinite and ammonium sulphate (AS) for (A.) Mg extraction using 3.3 kmol AS, (B.) Mg extraction using 4 kmol AS and (C.) Fe extraction (adapted from Nduagu *et al.*, 2012c).

Table. 2.7. Intermediate products identified for the reaction between PGE) tailings (45 - 75 µm and 150 - 250 µm and AS of (2:6) between 350 °C and 650 °C. One cross and two crosses were used to provide a qualitative appreciation of the abundance of minerals/compounds present in the thermochemically treated tailings

			45 - 75 (µm)				150 - 250 (µm)			
Mineral	Formula	untreated	treated at (temperature °C)							
			350	450	550	650	350	450	550	650
Calcite	CaCO ₃	2.9		X	X					X
Siderite	FeCO ₃							X		X
Magnetite/ Spinel	Fe ²⁺ Fe ²⁺³ O ₄ / MgAlO ₄	31.13	XX	XX	XX	XX		X	X	X
Clinopyroxene -(Augite)	(Ca,Na)(Mg,Fe,Al,Ti) (Si,Al) ₂ O ₆	3.09			XX					
Orthopyroxene (Enstatite)	Mg ₂ Si ₂ O ₆	29.93	XX	xx	XX		XX		XX	
Plagioclase	(Na,Ca)(Si,Al) ₄ O ₈	20.45		X	XX	XX	X	XX	XX	XX
Chlorite	(Mg ₅ Al)(Si,Al) ₄ O ₁₀ (OH) ₈	4.43				X			X	X
Serpentine (Lizardite)	Mg ₃ Si ₂ O ₅ (OH) ₄	trace			X					
Amphibole (Actinolite/Hornblende)	Ca ₂ [Mg ₄ (Al,Fe ³⁺)] Si ₇ AlO ₂₂ (OH) ₂	6.08	XX	X	X	X			X	X
Amphibole (Anthophyllite/Gedrite)	Mg ₇ Si ₈ O ₂₂ (OH) ₂				X	X			XX	X
Talc	Mg ₃ (OH) ₂ Si ₄ O ₁₀	0.58	XX	XX	X	X	X	X	X	X
Mica (Biotite)	KFeMg ₂ (AlSi ₃ O ₁₀)(OH) ₂	1.09					X	X	X	X
Mikasaite	Fe ₂ (SO ₄) ₃				XX					
Boussingaultite	(NH ₄) ₂ Mg(SO ₄).2H ₂ O								X	X
Ammonium Aluminum Sulfate	NH ₄ Al(SO ₄) ₂		XX	XX			X	X		
Ammonium Sulfate Hydrogen Sulfamate	(NH ₄) ₂ SO ₄ H ₃ NS		XX							
Ammonium Hydrogen Sulfate	(NH4)2SO4 H ₃ NS		XX				XX			
Ammonium Hydrogen Sulfate	NH ₄ HSO ₄		XX				XX			
Ammonium Sulfonate	C ₃ H ₈ F ₃ N ₁ O ₃ S ₁		XX							

2.6 Analytical techniques applicable to this study

Theoretical background of the analytical techniques used in this study is presented.

2.6.1 Analysis of solid samples

2.6.1.1 Chemical composition by X-Ray Fluorescence (XRF)

XRF is an analytical technique which is used to determine the bulk chemical composition (major and trace elements) of powdery samples (e.g. rocks and inorganic substances). XRF is a rapid quantitative technique. This technique allows for a near-zero background and is sensitive to trace element compositions in the ppm range. XRF entails irradiating the sample with polychromatic X-rays which are generated in a high intensity X-ray tube and absorbed according to Beers law (equation 2.11) where I_0 is the incident X-ray intensity, I is the intensity of the X-ray beam not absorbed by the sample, K_d is the proportionality constant and Δd is the thickness of the sample.

$$\log \frac{I_0}{I} = K_d \Delta d \quad (2.11)$$

The X-rays which are absorbed in the sample results in an X-ray emission spectrum which is characteristic for each element present in the sample. During the absorption process, electrons are displaced from the innermost shells and are replaced by an electron from the next outer shell. This results in a new vacancy continuously being created and filled by an electron from the outer shells. The emission phenomenon is called X-ray fluorescence and the characteristic X-rays which are generated are known as secondary X-rays. The wavelengths of the generated spectrum can be related to the chemical elements responsible for their production and is achieved using an X-ray spectrometer which consists of a diffracting crystal with a known spacing between the atomic planes and an X-ray detector. The crystal diffracts the multiple wavelengths according to the Bragg Equation (equation 2.12) where n is an integer, λ is the wavelength of the X-rays, d is the inter-planer spacing of crystal layers and Θ is the angle of incidence. The intensity and position of the spectra is recorded by an X-ray counting device. Quantitative elemental XRF analysis is achieved by comparing the intensity of each X-ray to an elemental standard (of a known composition). The resulting peak and background intensities located near the peak are counted in order to estimate peak heights (Klein and Dutrow, 2008; Beckhoff *et al.*, 2007; Kalnicky and Singhvi, 2001).

$$n\lambda = 2d\sin\Theta \quad (2.12)$$

2.6.1.2 Mineralogical composition analysis by X-Ray Diffraction (XRD)

X-ray diffraction is an analytical technique used for the identification and under some instances semi-quantification of crystalline phases in a powder. Structural information in terms of unit cell dimensions can also be obtained. XRD is based on the constructive interference between monochromatic X-rays and the sample. X-rays are defined as three-

dimensional periodic array of atoms in a crystal that has periodic repeat distances of the same order of magnitude as the wavelength of the X-rays. XRD analysis is typically conducted using an X-ray diffractometer which generally consists of an X-ray tube, sample holder and X-ray detector. The x-ray diffractometer rotates in the path of the collimated x-ray beam at an angle Θ , and the X-ray detector is mounted on an arm to detect diffracted X-rays which rotates an angle of 2Θ . X-rays are generated in a cathode tube by heating the filament to produce electrons which bombard the sample. The electrons with sufficient energy dislodge the inner shell electrons creating characteristic X-ray spectra of specific wavelengths. Constructive interference and a diffracted ray is produced during the interaction of the incident rays with the sample according to Bragg's law (equation 2.12). The diffracted X-rays are detected, processed and counted. Scanning the sample through a range of 2Θ angles enables the detection of all possible diffraction directions of the lattice. The diffraction peaks are converted into d-spacing's to allow identification of minerals whereby each mineral has a unique set of d-spacing's and can be aided with comparisons to standard reference patterns. The most common problem associated with XRD is peak overlap due to phases with distinct but closely related crystallographic characteristics. The Rietveld refinement technique is a whole pattern fitting least squares refinement technique which can be used to overcome the problem of peak overlap and enables the quantification of multiple phase systems. XRD is a non-destructive technique which requires a small sample size and minimum sample preparation (Klein and Dutrow, 2008; Waseda *et al.*, 2001; Murad *et al.*, 1994; Szostak, 1989).

2.6.1.3 Particle size distribution (PSD)

Particle size distribution plays an important role in determining the effectiveness of grinding and to ascertain the degree of liberation of economic elements from gangue rock of various particle size (Wills, 2006). The well-established technique used to measure particle size is laser light diffraction, which measures angular variation in intensity of light scattered as a laser beam passes through the suspension. Larger particles tend to scatter light in smaller angles relative to the laser beam compared to smaller particles which scatter light at larger angles. PSD by laser light diffraction was designed on the basis of the Mie theory of light scattering which assumes a volume equivalent sphere model. The particle size is reported as a volume equivalent sphere diameter. The measuring system comprises of three main elements, (1) an optical bench which facilitates the laser beam to illuminate the particle and the resulting intensity of scattered light is measured by multiple detectors, (2) a sample dispersion unit which introduces the particles into the measurement area in a suitable state of dispersion and in the correct concentration and (3) instrument software to facilitate the measuring process and analysis the scattering data to calculate the PSD. The advantages of using laser light diffraction to measure particle size include small sample size required, fast and accurate analysis. It should be noted that that different particle size measurement techniques (e.g. sieve analysis) using different equivalent sphere models will not produce the same results, i.e. particle diameter (Malvern, 2012).

2.6.1.4 Reflected light microscopy

Reflected light microscopy is a useful technique which aids in the preliminary identification of minerals, observing mineral textures, particle shapes and mineral associations. This is achieved using a typical polarising petrographic microscope. The scope of ore microscopy is relatively extensive; the reader is referred to Klein and Dutrow, (2008) for a full description and overview of the features of an optical microscope. The study of ore minerals is generally aided with the use of reflected light which is directed downwards onto the surface of a polished section. The petrographic microscope allows for the study of powdered mineral fragments which facilitates the study of the optical properties and in some cases the identification of the mineral(s). Reflected light microscopy enables the study of colour, reflectance and bireflectance which are the diagnostic optical properties. Under reflected light, minerals commonly appear in different shades of grey and/or yellow and the subtle differences are used for differentiation. Reflectivity (reflectance and bireflectance) is expressed as the percentage of incident light that is reflected from a minerals surface. Under polarised light, a non-isometric mineral show bireflectance i.e. a change in brightness and colour upon rotation of the stage and varies from one mineral to another. Isotropic minerals (particles remains dark in colour upon rotation of the stage under transmitted light) do not exhibit bireflectance and can therefore be differentiated from anisotropic minerals (light varies depending on direction through the mineral) (Klein and Dutrow, 2008; Murphy, 2001; Spencer, 1982).

2.6.1.5 Scanning Electron Microscopy (SEM)

A SEM utilises a focused electron beam to generate a variety of signals at the surface of a sample which can provide information regarding the morphology and sizes of particles present in the sample. Typical components of a SEM include an electron source, detectors for specific signals and a display. The surface of the sample is bombarded with an electron beam under high vacuum. The electron beam can be programmed to scan the surface of the sample. The electron source is typically made up of a tungsten filament and produces different types of electrons from the interaction of the electron and the sample namely secondary electrons, backscattered electrons and characteristic X-rays. *Secondary electrons* are weakly bound, low energy electrons which are generally recaptured. Secondary electrons can only be detected if they have escaped near the surface of the sample and are generally used to obtain topographic information. Backscattered electrons (BSE) result from elastic collisions due to the interaction of a primary electron and the nucleus of an atom in the sample and can provide compositional information. Characteristic X-rays are produced as the electron beam ejects an inner shell electron from its orbital and provides elemental information from the sample. Sample analysed by SEM must be coated using carbon or gold in order to prevent charging.

The irradiated sample produces BSE, X-rays and other signals. The BSE detector resolves the signal into greyscale images which varies in contrast based on their relative atomic numbers. In general silicates appear dark grey and heavy metals appear in lighter shades of grey. The brightness and contrast can be adjusted to enhance image resolution. Field emission scanning electron microscopy (FE-SEM) follows the same principle as SEM

however FE-SEM allows higher magnification imaging which typically results in higher resolution images and analysis of particles in the nanoscale (Echlin, 2009; Klein and Dutrow, 2008; Goldstein *et al.*, 2003).

2.6.1.5.1 Scanning Electron Microscopy coupled to Energy Dispersive spectroscopy (SEM-EDS)

SEM-EDS is a qualitative technique used to obtain information regarding the chemical composition of a sample. This technique allows for spectral analysis of the X-rays generated from a sample specimen under the influence of an electron beam using an energy dispersive X-ray analyser (EDS). The EDS analyser correlates the signal to the different elements present in the sample and calculates the X-ray counts for each element. The advantage of using this technique compared to FE-SEM and SEM on its own is its ability to simultaneously generate information about the topographic, crystallographic and chemical properties of the sample from the same area. SEM-EDS can be set to perform either quantitative or semi quantitative analysis however quantitative analysis can only be achieved using a flat polished sample, preferably carbon coated, which is stable, homogeneous and free of voids. Qualitative analysis can be conducted on powdered samples which are deposited on a substrate (Echlin, 2009; Klein and Dutrow, 2008).

2.6.1.6 Thermal analysis

Thermal analysis is defined as the measurement of change in the physical properties of a sample as a function of temperature at a constant heating rate or as a function of time and constant temperature (Brown, 2001). Thermal analysis by means of TGA, DSC, TGA-FTIR are complementary techniques which were used to study the solid-solid transitions which take place during the thermochemical treatment of the tailings. A brief description of each technique is given below.

2.6.1.6.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis measures changes in weight relative to temperature or time in a controlled atmosphere. The resulting weight loss curve (thermogram, TG) provides information regarding changes in sample composition, thermal stability and kinetic parameters of physical reactions such as gas adsorption, gas desorption and phase transitions and/or chemical reactions which include decomposition or chemisorption. The differential or derivative weight loss curve (DTG) is used to indicate the point(s) at which a change in weight is most apparent. Thermo-gravimetric or simultaneously differential thermal analysis (SDTA/DTA) combines the measurement of heat flow and weight of a sample and can be used to differentiate between endothermic and exothermic reactions and associated changes in weight which may have occurred. TGA consists of a precision balance, a loaded sample pan and a programmable furnace used to define the heating program. The sample chamber can be purged with an inert gas to prevent oxidation and undesired reactions. TGA

is a useful complementary technique which is easy to use, reproducible and requires minimal sample preparation however it is destructive and cannot identify volatiles unless coupled to a complimentary technique e.g. thermogravimetric analysis coupled to Fourier Transform Infrared spectroscopy (TGA-FTIR) or thermogravimetric analysis coupled to a mass spectrometer (TGA-MS). The complimentary techniques are employed for qualitative analysis of the volatile decomposition products. TGA cannot be used in qualitative analysis of the solid sample or residue.

2.6.1.6.2 Thermogravimetric analysis coupled to Fourier Transform Infrared spectroscopy (TGA-FTIR)

TGA-FTIR is a hyphenated thermal analysis technique used to observe the relative changes in weight loss and associated release of volatile components as a function of temperature. FTIR measures vibrational and rotational transitions within a chemical bond due to changes in the dipole moment. Different bonds and functional groups result in infrared (IR) absorptions at different wavelengths thus creating characteristic spectra. The Fourier Transform Infrared spectroscopic technique (FTIR) utilizes a modern spectrometer which acts as a detector and operates in the infrared and near infrared range. The FTIR spectrometer is comprised of a Michelson interferometer which analyses the frequencies present in the sample. TGA-FTIR uses the total volume of purge gas (N_2 or air) which do not exhibit IR-absorption and gaseous decomposition products produced during the TGA analysis. The produced gases are transferred through a heated transfer line (glass-coated steel) into a heated gas cell in the FTIR spectrometer. The absorption bands of each spectrum are integrated over the entire spectral range over characteristic spectral regions and the intensity is presented as a function of time as a Gram-Schmidt curve or chemigram. Advantages of FTIR are that the radiation emitted by the source is continuously monitored thus resulting in higher sensitivity than a conventional spectrometer and the analysis can be conducted in an inert or oxidative environment (Atkins and Paula, 2010). The resulting IR spectra can be compared to a reference library such as National Institute of Standards and Technology (NIST) Chemistry Web Book for positive identification.

2.6.1.7 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique which can be used to for chemical identification and physical characterization. Raman spectroscopy is based on the light scattering technique which examines the frequencies present in the radiation scattered by molecules representing a change in molecular state. Upon interaction of monochromatic radiation with the sample, incident photons are scattered from a molecule and will either increase or decrease in frequency depending on whether the radiation collects or loses energy to the molecule. The increase or decrease in frequency creates the anti-stokes and stokes lines respectively and scattering without a change of frequency results in the formation of a Rayleigh line. The energy of the photon ($h\nu$) which is either absorbed or emitted is given by Bohr frequency (2.13) where E is attributed to either the emission or absorption. The different frequencies denoted by the scattered and incident radiation determines the molecular vibrations which take place within a molecule making this

technique suitable to study molecular vibrations, rotations and electronic level transitions (Atkins and Paula, 2010; Horiba, 2014).

$$h\nu = |E_1 - E_2| \quad (2.13)$$

Raman spectroscopy is a non-destructive technique which can be used to study solids and aqueous solutions with minimum requirements for sample preparation. This technique has been useful in the study of water-metal interfaces and can detect minute changes in chemical composition due the detection of strong vibration modes (ν) of $\nu(\text{Si-O-Si})$, $\nu(\text{X}_{\text{metal}}\text{-O})$ and $\nu(\text{SO}_4)$ which will be useful for this study. Raman spectroscopy has previously been used to differentiate between different iron oxides (Hosterman, 2011; McCarty and Boehme, 1989; de Faria *et al*, 1997; Wang *et al*, 1998), end members present in a solid-solution in spinel mineral phases (Hosterman, 2011), amphiboles (Apopei and Buzgar, 2010), and metal sulphates (Ling and Wang, 2010) which is not always possible by XRD. The RRUFF project website (Ruff, 2014) which includes an integrated database of Raman spectra, X-ray diffraction and chemistry data for minerals was used to obtain reference spectra to aid data interpretation (Atkins, 2010; Horiba, 2014).

2.6.2 Analysis of liquid samples

2.6.2.1 Chemical composition analysis by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Chemical composition by ICP-OES is a quantitative technique used to determine metal concentrations in liquid samples. Compared to other spectroscopic techniques, ICP-OES is considered to be the best overall multi-element atomic spectroscopic technique which detects elements at a ppb level using > 5 mL of sample. ICP-OES measures the light emitted by the elements in a sample which is present in the ICP source and the emission intensities are compared to standards of known concentration in order to determine the elemental concentrations of the unknown sample. The ICP-OES system is made up of three principal components namely, an ICP source or plasma, a spectrometer and a detector. The ICP source generally consists of an argon plasma excitation source which is maintained by the interaction of radio-frequency (RF) field and ionized argon gas. The ability of the plasma to reach high temperature (~ 9727 °C) allows for the complete atomization of the elements and minimizes the potential for chemical interferences. The spectrometer separates the individual wavelength of light and focuses the desired wavelengths on the detector which is used to convert radiation into an electric current or voltage for the appropriate signal processing and display. Older ICP-OES systems utilize a series of multiplier tubes to determine selected wavelengths; however, this limits the number of elements which can be analysed. Sequential-type analysis systems allow for variable wavelength selection focused on a single detector; however, this has to be done on an element by element basis and results in long analysis time. Modern ICP-OES systems make use of a charge-coupled device (CCD) detector which is a solid state detector system and provides more flexibility and eliminates the need for multiple detectors (Perkin Elmer, 2013).

The literature review established the context for this study. The following chapter (Chapter 3) provides a brief geological overview of the area from which the tailings were sampled, discusses the PGE mine tailings used in this study, the process under development, experimental design and analytical techniques used to achieve the specific objectives of this study.

Chapter Three - Materials and methods

Specific PGE tailings used in this study are presented together with a description of the process under development, experimental design and the equipment used. Analysis methods are also presented.

3.1 Materials used in this study

PGE mine tailings from different South African mines were used for the major element extraction experiments. PGE mine tailings from the Two Rivers mine was used for preliminary testing and for optimisation of the leaching step of the process, whilst other PGE tailings with varying chemical and mineralogical compositions were used to study the effect of Fe:Cr ratio and particle size on elemental extraction efficiency.

3.1.1 Two Rivers PGE mine tailings

Two Rivers platinum operations – The Two Rivers mining operation is a beneficial joint venture between African Rainbow Minerals (ARM, 55%) and Impala Platinum (45%). The mine is situated at 24°57'03" S and 30°06'20" E, alongside the eastern limb of the Bushveld Igneous Complex (BIC) on the 372KT Dwarsrivier farm (Figure 3.1). Mining operations include underground and open pit mining producing PGM's, nickel, copper and cobalt-rich concentrates; they are currently at steady state production with over 15 years of life-of-mine (LoM) remaining. The Merensky and UG2 + internal pyroxenite are the main resources and reserves being explored, with the UG2 remaining the main target at the moment. The feasibility of refining the Merensky was placed on hold pending improvement in market conditions. Efficiency of the operation was also recently improved, with the commissioning of a tertiary milling and PGM enhancement and chrome recovery plant in 2013 (African Rainbow Minerals, 2013).

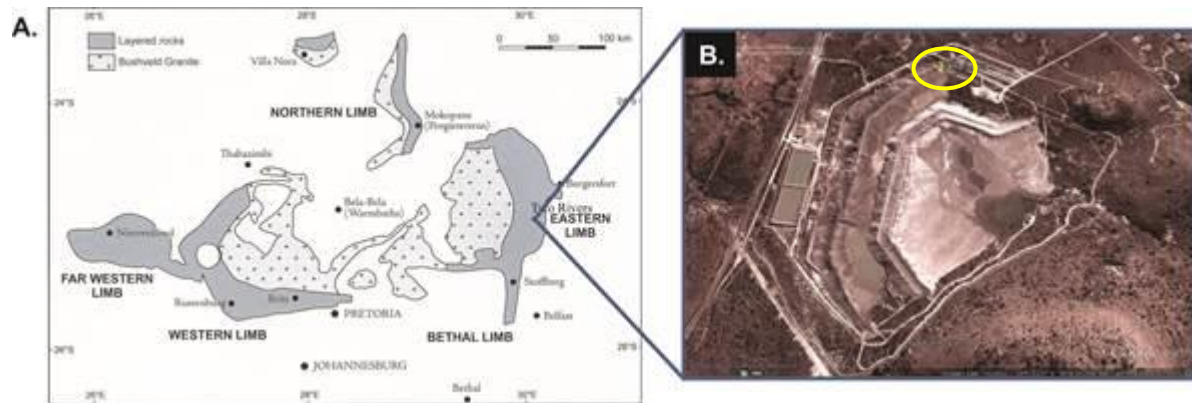


Figure 3.1. Map (A.) illustrating the location of the Two Rivers Mine along the eastern limb of the Bushveld Complex (adapted from Eales, 2014), and aerial photograph (B.; Google Earth, 2014a) showing the tailings storage facility (TSF). The sampling site is indicated by a yellow circle.

Local geology – The Two Rivers Mine is underlain by the Critical Zone, which comprises chromite deposits and platinum-bearing ore-bodies, i.e. UG2 and Merensky Reefs. The main rock types and diagnostic mineral phases are summarised in Table 3.1. The regional strike is north-south with a general dip between 7 - 10° west. The Critical Zone is a 800m thick succession of alternating cyclical rock units of chromitite, pyroxenite, norite and anorthosite, comprising disseminated chromite (Eales, 2014; Cawthorn *et al.*, 2006). The diagnostic mineral phases include orthopyroxene, plagioclase, chromite and olivine. Mining is currently restricted to the chromitite layers within the sequence (Figure 3.2). Dykes and faults are aligned north-northeast and south-southeast are secondary structures which allow for the lateral displacement of groundwater. The differences in stratigraphy observed at Dwarsrivier are due to the Steelpoort lineament which separates the central and southern region of the eastern limb of the BIC (Huisamen, 2013; Hornsey and van der Merwe, 2003).

Table 3.1. Zonal subdivision, diagnostic mineral phases and rock types of the critical zone in layered sequence (adapted from Eales, 2014).

Zone associations	Diagnostic minerals present	Dominant rock type
Upper Critical Zone	Orthopyroxene	Orthopyroxenite, norite, anorthosite, chromitite and harzburgite
	Plagioclase	
	Chromite	
	Olivine	
Lower Critical Zone	Orthopyroxene	Orthopyroxenite, harzburgite and chromitite
	Olivine	
	Chromite	

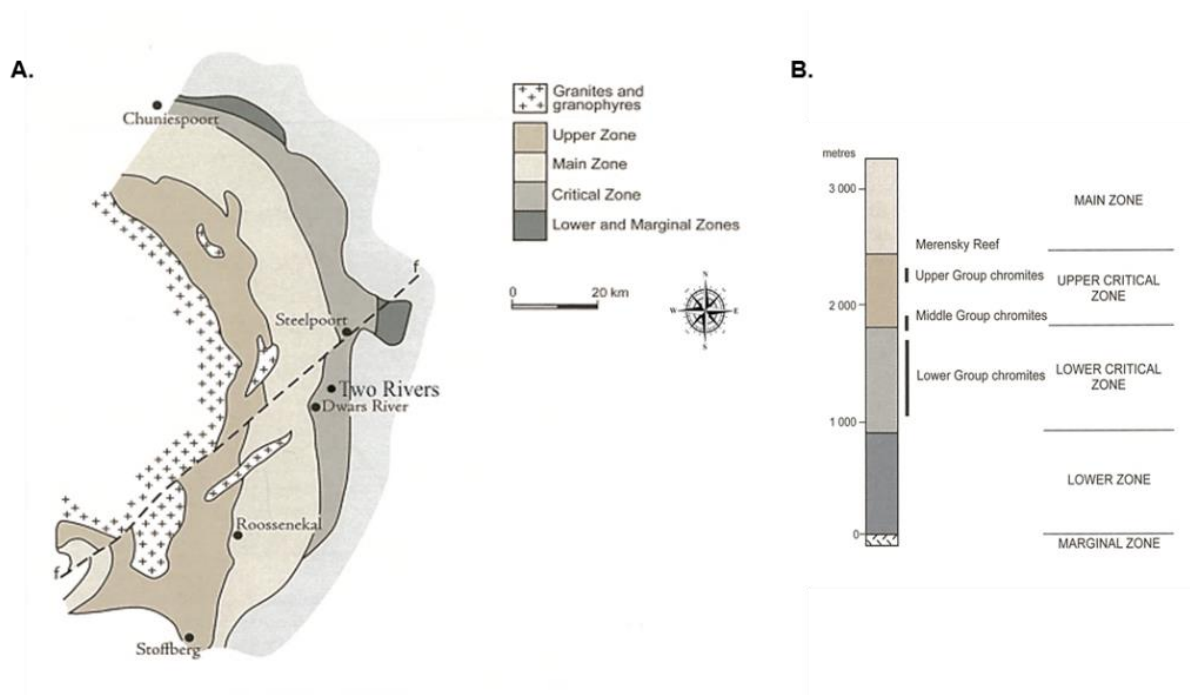


Figure 3.2. Simplified geological map of the Eastern limb of the Bushveld Igneous Complex (A.), illustrating the zonal subdivision of the layered suite, economic deposits present within the cyclical unit (B.) and stratigraphic displacement along the Steelpoort lineament (dashed line and f symbol) (modified from Eales, 2014).

Sample collection, preparation and characterisation – Deposition of the tailings occurs via the jet method, which causes fractionation of the particles whereby coarser particles are deposited on the bank and the finer particles are found within the dam itself (African Rainbow Minerals, 2013; Huisamen, 2013). About 200 kg of PGE mine tailings was collected from the top of the tailings dam using the grab sampling technique. Since the focus of this study is to develop and test an extraction process, no attempt was made to have a representative sample of the tailing dam. Several core samples representing depth profiling would need to be collected and composite samples to be produced to test and optimise the process prior to scale up. Immediately upon arrival at the laboratory, the sample was air-dried up to constant weight. Homogeneous sub-samples were then obtained using a sample splitter for future experiments. A sub-sample was selected and was sieved using Endecotts test sieves with apertures of 250 μm , 150 μm , 75 μm and 45 μm placed on an Endecotts EFL2 mk3 shaker. Preliminary findings (Mohamed, 2012) suggested that the 45 - 75 μm sieved fraction may yield the highest extraction of iron (Fe) from silicate matrices contained in the tailings and its subsequent conversion to sulphate compounds (Table 2.7). For this reason, the 45 – 75 μm fraction (hereafter denoted MT₄₅₋₇₅) was selected and used in all experiments reported in this study, except when otherwise stated. It was first characterised

using a range of complementary techniques, including XRF, XRD, TGA, reflected light microscopy, FE-SEM, Raman spectroscopy and PSD.

3.1.2 Other PGE mine tailings

Background – The Council for Geoscience is currently managing the national strategic mine water management programme (SMWMP-national), which is commissioned by the Department of Mineral Resources (DMR). The overall objective of this project is to investigate the impact of mine pollution on water resources of South Africa (Yibas *et al.*, 2013). To this effect, detailed depth profile sampling was carried out on numerous PGE tailings dumps in South Africa (e.g. Amandelbult mine, Limpopo province; Marico Chrome, North West province; and Rhovan mine, North West province) in 2013 - 2014. Permission was granted to sub-sample PGE tailings collected for this national project, which are characterised by distinct chemical and mineralogical compositions (e.g. different Fe/Cr ratio), for the purpose of the present work.

Amandelbult mining operations – The Amandelbult mining operation owned by Anglo American Platinum is one of the major contributors of PGE minerals. The mine is situated at 24° 48'24.771" S and 27° 21' 9.399" E, alongside the western limb of the Bushveld Complex on the farm Amandelbult 383 KQ (Figure 3.3). The current deposition of the UG2 tailings from the Amandelbult section into the tailings dam is regarded as “sub-optimal use of resources” and the construction of a chrome recovery plant (CRP) is proposed in order to extract chromite which is produced as a by-product of the Pt beneficiation process. The construction of this CRP will lead to a decrease in the tonnes of tailings needed to be stored in the tailings dam, increase the life of the tailings dam and also minimise the environmental risks associated with the tailings dams (Prime Resources, 2013).

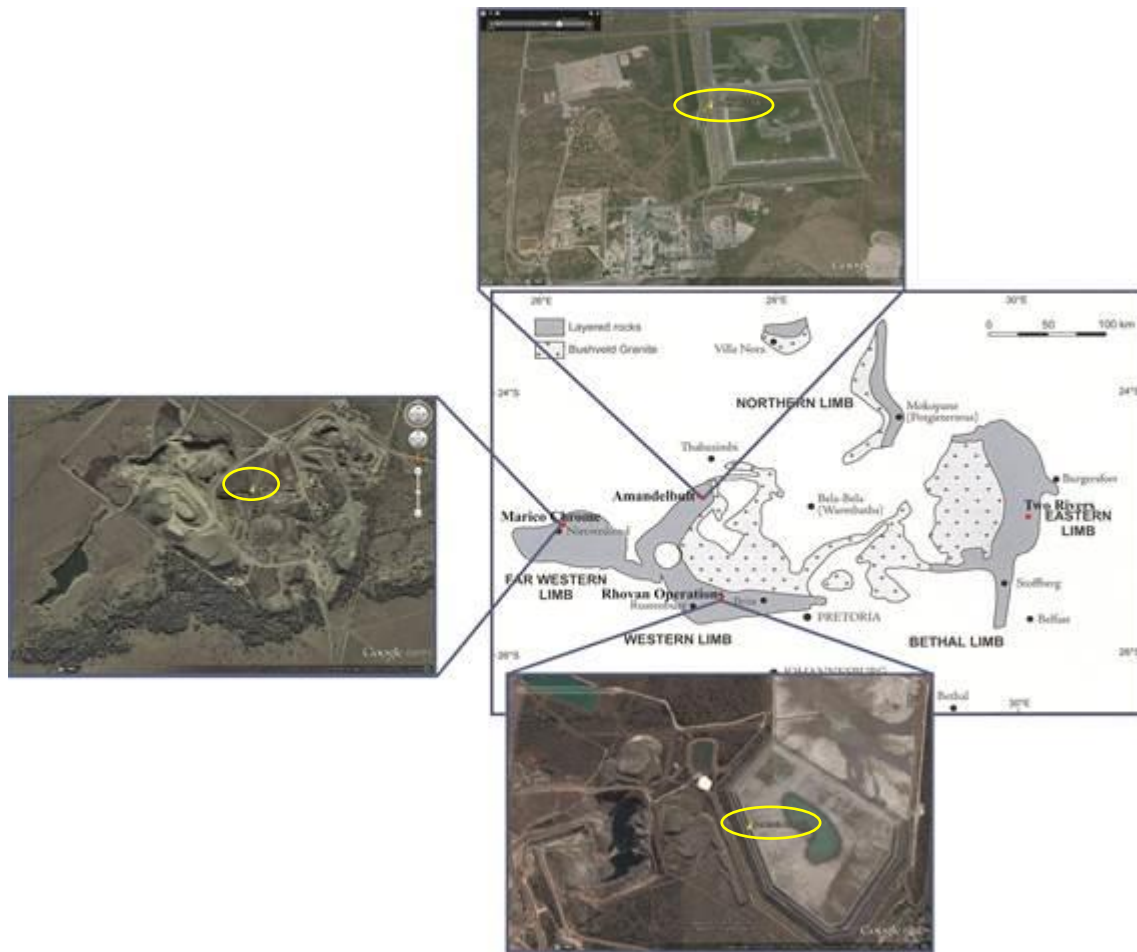


Figure 3.3. Location (modified from Eales, 2014) and aerial photographs (Google Earth, 2014b,2014c,2014d) of the Amandelbult, Marico Chrome and Rhovan Operations and TSF's along the western limb of the Bushveld Igneous Complex.

Marico Chrome mining operations – Marico Chrome Corporation is a chromium-processing plant established as a joint venture between Vereeniging Refractories (Verref) and Samancor Chrome South Africa (McEwan *et al.*, 2011). The Marico Chromite deposit is located at 25°5'56.558" S and 20°15'10.094" E, alongside the western limb on the Bushveld Complex (Figure 3.3). The mine produces metallurgical and refractory-grade chromite for the domestic and export markets, along with secondary mining of PGE's, Fe and SiO₂.

Rhovan mining operations – Rhovan Operations, previously known as Rhovan Vanadium Mine, is a joint venture between Glencore and XStrata Alloys trading as Glencore XStrata. The mine is located at 25°34'4.156" S and 27°34'20.229" E along the western limb of the Bushveld Complex (Figure 3.3). Rhovan Operations is the primary vanadium producer in South Africa and uses open cast mining methods (Glencore Xstrata, 2013).

Local geology – The three mining operations are underlain by the lower - Critical Zone and overlain by the Main Zone of BIC (Table 3.2; Figure 3.4). The main rock types housing the ore minerals include gabbro, norite, anorthosite, orthopyroxenite, chromitite, harzburgite and dunite. The diagnostic mineral phases include pyroxenene, chromite and olivine. The Amandelbult mining operation is restricted to the Upper Critical and lower Main Zones (Scoon and Eales, 2002), exploiting the Merensky and UG2 reefs. The Marico Chrome deposit is a kidney shaped deposit comprising of mafic rocks formed along the north-south central synclinal axis. Extensive exploration and mining has stratigraphically linked the five chromitite layers to the lower zone of the BIC. The chromitite layers vary in composition relative to the other chromitite layers of the BIC and typically have higher Cr: Fe ratios and lower SiO₂ and magnetite content (McEwan *et al.*, 2011). Rhovan Operations is restricted to the vanadiferous, titaniferous magnetite gabbro which lies within the upper zone of the BIC. The V is trapped within the magnetite and Cr is mined as a secondary product.

Table 3.2. Zonal subdivision of layered suite along western limb of the Bushveld Igneous Complex (modified from Eales, 2014).

Zone associations	Diagnostic minerals present	Dominant rock type
Upper Zone	Fe-rich clinopyroxene Fe-rich olivine Plagioclase Alkali feldspar Magnetite Apatite	Various gabbros, anorthosite, magnetite and diorite
Main Zone	Orthopyroxene Clinopyroxene Plagioclase	Gabbronorite, gabbro and anorthosite
Upper Critical Zone	Orthopyroxene Plagioclase Chromite Olivine	Orthopyroxenite, norite, anorthosite, chromitite and harzburgite
Lower Critical Zone	Orthopyroxene Olivine Chromite	Orthopyroxenite, harzburgite and chromitite
Lower Zone	Olivine Orthopyroxene	Dunite, harzburgite, orthopyroxenite

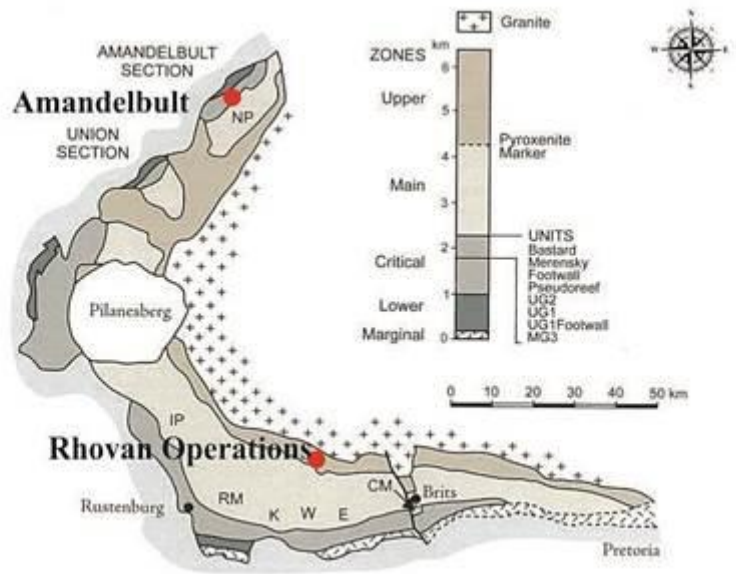


Figure 3.4. Simplified geological map of the Western limb of the Bushveld Igneous Complex (BIC), illustrating the zonal subdivision of the layered suite, economic deposits present within the cyclical unit (modified from Eales, 2014).

Sample collection, preparation and characterisation –The samples from Amandelbult and Rhovan operations were collected by scientists and technicians from the Environmental Geoscience Unit of the Council for Geoscience, using a truck mounted auger drill to a depth of up to 16 m below surface, whilst the tailings and waste rocks acquired from Marico Chrome were obtained from the surface of the waste piles using the grab sampling method. Their chemical (XRF) and mineralogical (XRD) compositions were determined as part of the SMWMP-national programme and were made available for preliminary screening.

3.2 Process description

The process of extraction under development at the Council for Geoscience is composed of four main steps (Figure 3.5), although this study has focused on the investigation of Steps 1) and 2):

- 1) Thermochemical solid-solid treatment (i.e. roasting) of PGE tailings using ammonium-based salts, for major element extraction from silicate and oxide crystal-lattice mineral structures and conversion to soluble reaction products (metal salts)
- 2) Aqueous dissolution of soluble reaction products
- 3) Synthesis of nanoparticles
- 4) Ammonium salt recovery

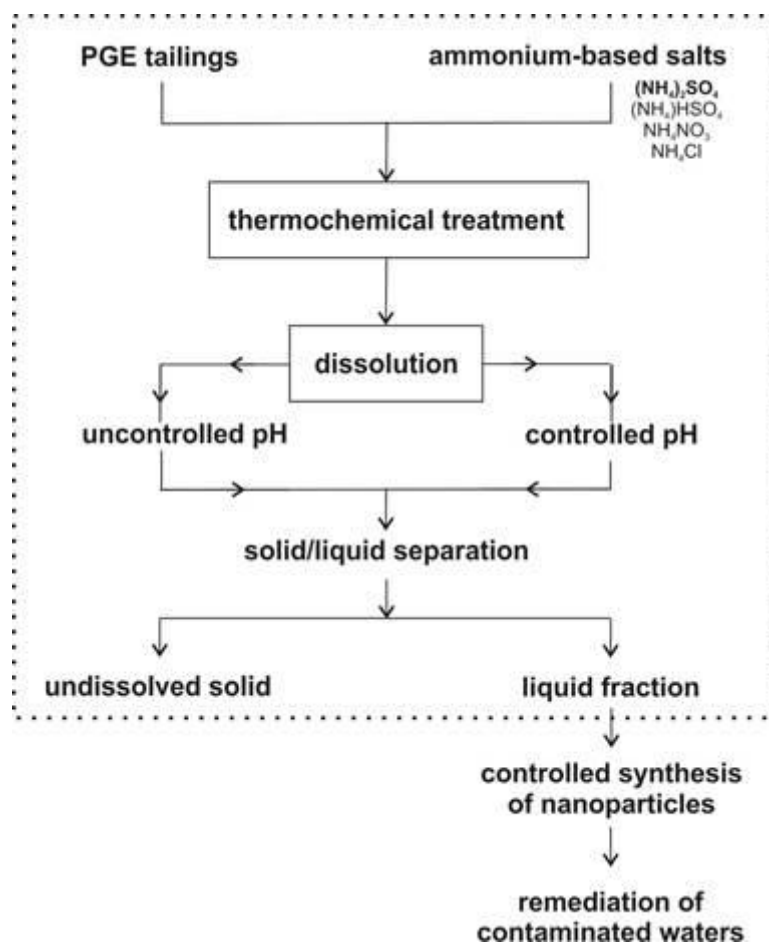


Figure 3.5. Block flow process diagram for the extraction of major elements from PGE mine tailings.

3.3 Case study No 1: Two rivers PGE mine tailings

3.3.1 Thermochemical treatment of tailings using ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$

3.3.1.1 Preliminary static furnace experiments

In a preliminary study, the 45 - 75 μm size fraction (MT_{45-75}) was mixed thoroughly with ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$; Merck, South Africa; hereafter abbreviated AS) at a constant solid-solid mass ratio of 2:6 (m/m) using a stainless steel spatula. It is difficult to mix two solids (MT_{45-75} and AS) with different physical properties (e.g. different particle size), and even more difficult to appreciate the extent to which the solids are evenly mixed. However, the mixing method was the same for all experiments. It could be argued that the

use of a rotary reactor could resolve the issue of uneven solid mixing (Nduagu *et al.*, 2012c), although it is the CGS group's experience that the use of rotary reactors catalyses the thermal degradation of AS, which has a negative effect on the thermochemical treatment.

The resulting mixture was placed in a fused quartz crucible and subsequently heat - treated in a muffle furnace set at varying temperatures (350 - 550°C) for 45 minutes. Thermally-treated mine tailings (hereafter abbreviated as MT_{ro}) was characterised by XRD to identify phase transformations, and by TGA and TGA-FTIR to understand the decomposition mechanisms and evolved gas products produced from the solid-state reaction. Whenever necessary, MT_{ro} obtained in all future experiments was further characterized by SEM, FE-SEM, TGA-FTIR, DSC and/or Raman spectroscopy.

3.3.1.2 Preliminary *in situ* TGA experiments

In parallel to the above study, the interaction between (NH₄)₂SO₄ and MT₄₅₋₇₅ was also monitored *in situ* using TGA in order to understand the thermodynamics, phase transformations and evolved products formed under static temperature conditions. Therefore, in an attempt to mimic the experiments conducted in the muffle furnace, approximately 20 mg of the sample (MT₄₅₋₇₅ and (NH₄)₂SO₄) was thermally treated under static temperature conditions. The sample was inserted at the desired temperature (i.e. 550 °C) and isothermally heated for 45 minutes, thereafter the sample was heated up to 1000 °C at a constant heating rate of 10°C per minute.

Conventional TGA experiments were also performed. In this case, approximately 20 mg of the sample (MT₄₅₋₇₅ and (NH₄)₂SO₄) was mixed using a solid-solid mass ratio of 2:6 (m/m) and subsequently heat-treated in the TGA furnace under dynamic temperature conditions from 25 °C to 1000 °C at a constant heating rate of 10 °C per minute. All TGA experiments were conducted in air with a constant flow rate of 60 mL per min.

In order to be able to evaluate the extent of the mineral transformations (sulphation) undergone by major elements present in MT₄₅₋₇₅ during the thermochemical process, it is necessary to dissolve newly-formed sulphate species using an optimal dissolution process. Based on the results obtained in the preliminary studies (sections 3.3.1.1 and 3.3.1.2), a temperature of 550 °C was adopted to produce a batch of MT_{ro} using the thermochemical treatment described previously. This batch was then used to develop an optimal dissolution process to quantify major element extraction efficiencies from MT₄₅₋₇₅ (see sections 3.3.1.3 and 3.3.1.4).

3.3.1.3 Extraction efficiencies under uncontrolled pH conditions of dissolution

All dissolution experiments were performed in closed high-density polyethylene bottles in duplicate. Untreated MT₄₅₋₇₅ (control) and MT_{ro} (treated) samples (3.00 ± 0.02 g; dry weight) were dispersed in 500 ml of ultra-pure water (electrical conductivity < 1 µS cm⁻¹; hereafter referred to as 'uncontrolled pH condition'). All control and treatment solutions were continuously stirred at a constant speed of 850 rpm using a mechanical overhead stirrer (WiseStir HS30D, Wisd Lab Instruments) with a 50 mm 3 - bladed propeller-type impeller to maintain the particles in suspension throughout the experiments (Figure 3.6). Dissolution

experiments were performed at room temperature and at 80 °C for varying amounts of time ranging from 30 minutes up to 64 hours. Progress of the reaction was monitored by measuring the solution pH and electrical conductivity using a Hanna HI 2829 multi-parameter logger as dissolution progressed.

At the end of the experiments, the leachates were filtered under reduced pressure through 0.4 µm membrane filters (polycarbonate track-etched membrane, Sartorius Stedim Biotech, Germany) in closed polycarbonate filtration vessels (Sterifil, Millipore). The concentrations of dissolved Fe, Cr and other elements in the filtrates were determined by ICP-OES (Waterlab as service provider), which were used to calculate elemental extraction efficiencies. The non-dissolved residues were rinsed thoroughly with ultra-pure water, oven-dried at 40 °C up to constant weight, and characterized by XRD and FE-SEM.

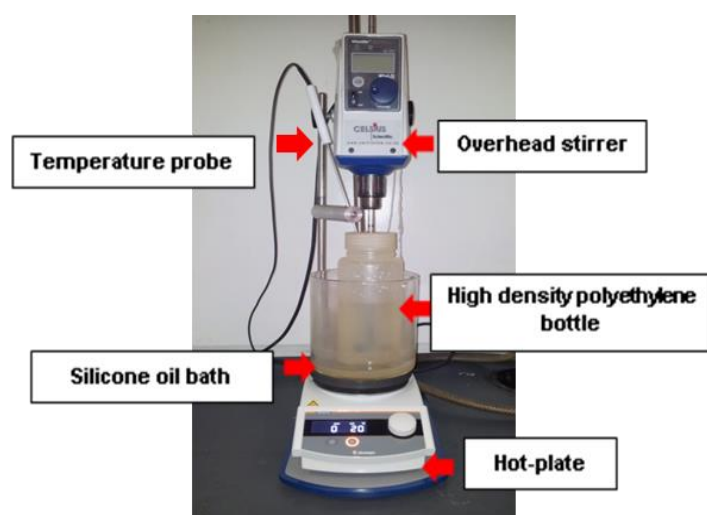


Figure 3.6. Experimental setup used for dissolution experiments.

3.3.1.4 Extraction efficiencies under acidic conditions of dissolution (0.6 M HNO₃)

The formation of secondary precipitates was identified during dissolution in ultra-pure water (i.e. uncontrolled pH conditions; section 3.3.1.3). In order to prevent secondary precipitation of released major elements, acidic dissolution experiments were also performed in 0.63M HNO₃ solutions (hereafter referred to as ‘acidic conditions’) at various temperatures (60, 80, and 95°C) between 4 and up to 17 hours. The presence of HNO₃ caused the solution conductivity to be greater than the maximum permissible measuring range of the logger (i.e. > 200 mS cm⁻¹) used to monitor the reaction under uncontrolled pH conditions (see section 3.3.1.3). Progress of the reactions occurring under acidic conditions could therefore not be monitored over time. As a substitute, the determination of total dissolved solid (TDS) content of the filtrates according to standard 2540 C (Rice *et al.*, 2012; Appendix A) was attempted. The results of the experiments described in sections 3.3.1.3 and 3.3.1.4 were used to identify the optimal dissolution conditions. This optimal dissolution process, which is

summarised in section 3.3.6, was then used to quantify the influence of other parameters on major element extraction from PGE tailings (i.e. other ammonium-based salts; seeding with sodium sulphate; humidity; multi-step thermochemical activation).

3.3.2 Effect of repeated thermochemical treatment on major element extraction efficiencies (hereafter called 'loop experiment')

This experiment was performed in order to ascertain whether an excess of AS can yield improved extraction efficiencies. For this purpose, MT_{45-75} was mixed with AS in a 2:6 (m/m) ratio and subsequently heat-treated at 550°C in a muffle furnace for 45 minutes. The resulting mixture (MT_{r01}) was weighed and then mixed with AS in a 2:6 (m/m) ratio before being subjected to the same thermal treatment (i.e. 550 °C, 45min), which yielded MT_{r02} . This cycle was repeated five times. MT_{r05} obtained at the end of the five cycles was subjected to the optimised dissolution process (see section 3.3.6). MT_{r05} was characterized by XRD and the concentrations of dissolved elements in the leachates following filtration were determined by ICP-OES.

3.3.3 Thermochemical treatment of tailings using other ammonium-based salts

Other sources of ammonium salts (ammonium chloride (NH_4Cl); ammonium nitrate (NH_4NO_3), and ammonium bisulphate (NH_4HSO_4)) were also tested during thermochemical treatment of tailings and their effectiveness in converting major elements into sulphate compounds were compared to that of $(NH_4)_2SO_4$. For this purpose, MT_{45-75} and ammonium salts were mixed in a 2:6 (m/m) ratio and thermochemically treated at varying temperatures (350 °C - 550° C) for 45 minutes. MT_{r0} was subjected to the optimised dissolution conditions (see section 3.3.1) to investigate the effect of the different ammonium salts on the extraction efficiency. MT_{r0} was characterized by XRD. MT_{r0} produced in the muffle furnace were also studied using TGA in order to understand the decomposition mechanisms of the different metal sulphates/phases formed in the solid state reaction. TGA will be used as comparative quantitative technique. The TGA analyses will be accompanied with complimentary qualitative techniques (e.g. XRD, TGA-FTIR) to confirm the identity of the products which have formed and at which temperature range they decompose.

TGA was also used in three separate experiments:

- to study the decomposition mechanisms of the different ammonium salts. About 20 mg of each reagent was weighed and subjected to heat-treatment from 25 °C to 1000 °C at a constant heating rate of 10 °C per minute.
- To study the interactions of these ammonium-based reagents with tailings under static temperature conditions in an attempt to compare the weight loss observed from the TGA experiments to the weight loss observed from the laboratory furnace experiments. Here,

the mixture was inserted at the desired temperature (i.e. 550°C), and isothermally heated for 45 minutes; at the end of this step, the thermochemically treated mixture was heated up to 1000 °C at a constant heating rate of 10 °C per minute.

- to study the interaction between the MT₄₅₋₇₅ and ammonium salts during the thermochemical treatment. The ammonium salt and MT₄₅₋₇₅ mixtures were prepared as described in section 3.3.1.2 and were subsequently heat-treated in the TGA furnace under dynamic temperature conditions from 25 °C to 1000 °C at a constant heating rate of 10 °C per minute.

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3.3.4 Optimal thermochemical treatment and dissolution procedure

The optimal thermochemical treatment and dissolution procedure is summarised below and was applied to study the suitability of other PGE mine tailings for efficient major element extraction (see section 3.4).

- The optimised thermochemical process involves reacting mine tailings (45 - 75µm sieved fraction) with (NH₄)₂SO₄ at a MT₄₅₋₇₅: AS ratio of 2:6 (m/m) for 45 minutes under static (non-mixing) conditions in a furnace to yield roasted MT (MT_{ro}).
- The optimised dissolution process is as follows: An aqueous suspension of 3 g MT_{ro} in 0.63M HNO₃ solution (500 ml) is constantly stirred at 850 rpm using an overhead stirrer at a temperature of 95 °C for 6 hours.

3.4 Case study No 2: Other PGE mine tailings

Since the work on Two Rivers PGE tailings reported in this study made use of the 45 - 75µm fraction, homogeneous sub-samples of Amandelbult, Marico Chrome and Rhovan PGE tailings were obtained using a sample splitter, and were subsequently sieved using 200 mm diameter Endecotts test sieves and an Endecotts EFL2 mk3 shaker. As mentioned earlier, the sieved fractions with a particle size between 45 - 75µm were used in all experiments reported here, except when otherwise stated. The chemical composition and mineralogy of the sieved fractions were characterised by XRD and XRF.

3.4.1 Characterisation data and pre-screening

The screening procedure for the selected samples relied primarily on the qualitative and quantitative mineral and elemental data provided by XRD and XRF on unsieved samples, which were kindly released by the Environmental Geoscience Unit of the Council for Geoscience. Since some tailings are reprocessed for chromium recovery by the mining operations, and chromium may show a similar chemical affinity than iron for sulphate compounds such as (NH₄)₂SO₄ used in this study, this screening criterion was used to

identify subsamples with different mineralogical composition and varying Fe:Cr ratios along the depth profiles studied. Chemical and mineralogical characterization using XRF and XRD respectively was then performed on sieved samples to better understand differences in elemental distribution between size fractions.

3.4.2 Effect of Fe/Cr ratio in PGE tailings on major element extraction efficiencies

The effect of the Fe:Cr ratio in tailings on major element extraction efficiencies was studied by applying the optimised thermochemical treatment and dissolution process (see section 3.3.6) to the selected tailings from the Amandelbult, Marico Chrome and Rhovan Operations (25 samples). All filtrates were analysed by ICP-OES. The mine tailings sampled from Rhovan Operations contained very little, if any, Cr as the operation is currently recovering Cr as a secondary commodity and this has altered the gangue mineralogy of the tailings. The absence of Cr may be favourable to the sulphation roasting of iron during the thermochemical step, which may increase the extraction of Fe in the subsequent dissolution step. A sample selected from the Rhovan Operations TSF underwent a detailed characterisation using XRF, XRD, FE-SEM, reflected light microscopy and Raman spectroscopy.

3.5 Analytical methods, sample preparation and procedures

3.5.1 Analysis of solid samples

3.5.1.1 Chemical composition analysis by XRF

The chemical compositions of bulk and sieved tailings pre- and post-treatment (i.e. sulphate roasting and/or dissolution) were obtained using a PANalytical Axios X-ray fluorescence spectrometer equipped with a 4 kW Rh tube. Tailings were milled down to a particle size < 75 µm for increased accuracy prior to XRF analysis. The sample was roasted at 1000 °C for approximately 3 hours to oxidise Fe²⁺ and S and to determine the loss of ignition (L.O.I.). 1 g of the roasted sample and 9 g of flux consisting of 34 % lithium meta-borate (LiBO₂) and 66 % lithium tetra-borate (Li₂B₄O₇) were fused at 950 °C to form stable glass disks. For trace element analysis, 12 g of milled sample and 3 g Lico wax were mixed and pressed into a powder briquette by hydraulic press with an applied pressure of 25 ton. Certified IGGE (China) standard references 12/76 (secondary amphibolite) and GSS-1 (soil reference) were analysed to evaluate and confirm accuracy and precision.

3.5.1.2 Mineralogical composition analysis by XRD

XRD was used to identify, and wherever possible quantify, the crystalline phases present in treated and untreated tailings using a Bruker D8 Advance X-ray diffractometer. Untreated tailings were micronized to a particle size $< 30\ \mu\text{m}$ for increased accuracy prior to XRD analysis and treated tailings were carefully crushed with an agate mortar and pestle to reduce their particle size. A homogenous sub-sample was pressed into a shallow Poly methyl methacrylate (PMMA) sample holder against a rough filter paper in order to ensure random orientation. Where possible, phase concentrations were determined by Rietveld quantitative analysis with DIFFRAC.TOPAS software with accuracy in the region of $\pm 1\%$.

3.5.1.3 Particle size distribution analysis (PSD)

PSD for the various sieved tailings fractions were obtained by laser diffraction (Malvern Mastersizer 2000 fitted with a Hydro 2000G dispersion unit, Malvern Instrument Ltd., Worcester, UK) in duplicate. The samples were dispersed in water at ambient temperature and the analysis was conducted under the following set of variables: obscuration between 10 and 20%, stirring speed = 650 rpm, pump speed = 1650 rpm, ultrasonic = 20%. The results were recorded as particle per volume percent and averaged to produce the particle size distribution. The particle sizing analyses were done in order to confirm the effectiveness of the sieving procedure.

3.5.1.4 Reflected light microscopy

Reflected light microscopy was conducted on selected untreated and treated (post-roasting and post-dissolution) samples in order to identify oxide minerals and their distribution. The analyses were conducted on polished stubs using an Olympus petrographic microscope connected to an external light source. Magnification oculars included a 4 x, 10 x, 20 x and 40 x magnification. The powder samples were embedded in a cylindrical block of resin and one of the circular faces were polished in order to study the sample under the microscope.

3.5.1.5 Field-emission SEM

Field emission SEM was used to visualize the morphology of untreated and treated samples. Analyses was conducted on a Gemini® Ultra plus Field Emission Microscope (Carl Zeiss, Germany) operating under dry high - vacuum conditions with an accelerating voltage of 1 kV. SmartSEM® software was used to facilitate data collection. The samples were mounted on a metal substrate by means of adhesive double-sided carbon tape and subsequently sputter-coated using with carbon using an Emitech K550X coater (Ashford, England) in order to prevent and minimize charging. The edges of the sample were painted with carbon paint to improve the conductivity of the sample.

3.5.1.6 SEM-EDS

Elemental mapping was conducted on an Ultra Field Scanning Emission Microscope operating at 3 kV coupled to an Oxford energy dispersive X-ray detector system (Carl Zeiss, Germany) in order to determine the distribution of elements in selected treated samples. The unconsolidated sample was impregnated and embedded in a polished resin stub prior to analyses. The sample was sputter-coated with carbon to minimize charging during the analysis.

Spot analysis was conducted using a JEOL 5800 LV scanning electron microscope fitted with a Nanotrace detector (JEOL, USA). The analysis was carried out using an accelerating voltage of 20 kV which covers a working distance of approximately 8 – 12 mm. The sample preparation required was the same as for the FE-SEM analysis, therefore the same samples were used for the spot analysis.

3.5.1.7 TGA

Thermogravimetric analyses were carried out using a Mettler Toledo TGA/SDTA851 with a TS0801RO sample robot TS0800GC1 gas control unit. Approximately 20mg of the sample (tailings and AS mixed in a solid-solid mass ratio of 2:6 (m/m)) was weighed in a 150 µl alumina pan and heated in the TGA furnace under dynamic conditions from 25°C to 1000°C at a constant heating rate of 10°C per minute. Experiments were also performed under static temperature conditions, where the samples were inserted at the desired temperature (i.e. 550°C) and isothermally heated for 45 minutes; thereafter the samples were immediately heated from 550°C up to 1000°C at a constant heating rate of 10°C per minute. All TGA experiments were conducted in air with a constant flow rate of 60 mL per min.

3.5.1.8 TGA-FTIR

TGA-FTIR was used to detect and identify the gases which are liberated during the thermal decomposition of tailings, ammonium salts and mixtures thereof. Analyses were performed using a Perkin Elmer TGA 4000 interfaced with Perkin Elmer Spectrum 100S FTIR via Perkin Elmer Redshift TG-IR. Analyses were conducted under dynamic temperature changes at a constant heating rate of 200°C per min from 35 – 550°C using air as the purging gas at a flow rate at 20 mL per min.

3.5.1.9 Raman spectroscopy

Raman spectroscopy has been conducted on selected untreated and treated samples to identify and differentiate chemical species and mineral phase transformations which took place following thermochemical treatment and subsequent leaching of tailings. Reagent-grade sulphate compounds, corresponding to products which may have been

formed during thermochemical treatment were also analysed (aluminium sulphate hydrate ($\text{Al}_2(\text{SO}_4)_3$), ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$), chromium (III) sulphate hydrate ($\text{Cr}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$), iron (III) sulphate hydrate ($\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$), magnesium sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), and manganese sulphate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) (Sigma Aldrich, South Africa). Analyses was conducted using a T64000 Advanced Research Raman System from HORIBA Scientific, Jobin Yvon Technology (Villeneuve d'Ascq, France) accompanied by LabSpec Spectroscopy Suite for data analyses (Horiba Scientific). The excitation source used consisted of a mixed gas Krypton-Argon set at 514.6 nm. An standard acquisition time of 2 x 60 seconds and spectral resolution of 1 cm^{-1} was used. Raman spectra was obtained with the aid of an Olympus microscope, which consists of 3 objectives (10 x, 50 x and 100 x magnifications), a three stage monochromator fitted with a triple grating spectrometer at 1800 lines/mm and a 1024 symphony CCD detector. The powder samples were placed and levelled on a glass substrate for analyses.

3.5.2 Analysis of liquid samples

3.5.2.1 Chemical composition analysis by ICP-OES

Aliquots of the leachates were quantitatively analysed by ICP-OES to identify major, minor and trace elements in the leachates. Analyses were performed by Waterlab (PTY) Ltd, Pretoria, South Africa. They were done using a Perkin Elmer® Optima 2100 DV ICP-OES (Perkin Elmer, USA). Calibration was performed using a 1 ppm multi-element stock solution for all elements and 100-500 ppm standards for Al, Ca, Fe, Mg, K and Na. A mass balance was calculated in order to determine the elemental extraction efficiency of the process.

This chapter provided a detailed methodology of the experiments which were conducted and analytical techniques used in this study. The following chapter will discuss the characterisation of the PGE tailings and the results of the experiments will be discussed in Chapter 5.

Chapter Four – Characterisation of PGE tailings

This chapter provides a detailed characterisation of PGE tailings which were used as starting materials for the thermochemical and dissolution experiments.

4.1 PGE mine tailings from Two Rivers Platinum

As formulated in Chapter 3, the 45 - 75 μ m fraction (hereafter denoted MT₄₅₋₇₅) of the Two Rivers Platinum tailings sample was selected and used in all experiments reported in this study, except when otherwise stated. MT₄₅₋₇₅ was characterised using a range of complementary techniques, including PSD, XRF, XRD, reflected light microscopy, FE-SEM, and Raman spectroscopy.

4.1.1. Physicochemical characterisation

4.1.1.1 Particle size distribution

PGE's commonly exist as inclusions within the base metal sulphides and gangue mineral phases associated with the Merensky and UG2 chromite ores. The process of recovering PGE's from the ore entails fine particle processing, which consists of liberation through crushing, semi-autogenous and autogenous grinding, ball and rod milling followed by separation most commonly by froth flotation. Several developments have been made to improve the recovery and liberation of PGE's from the ore, with the most recent being the implementation of tower and IsaMill™ mills within the ultra-fine grinding circuits which has not only enhanced the liberation and recovery of PGE's but has led to the production of finer grained tailings (Vogeli *et al.*, 2011). The particle size distribution (PSD) of bulk and sieved tailings was determined by laser diffraction. It was therefore expressed in terms of volume percent, which is different from dry-sieving techniques where mass percentages are generally the reported units (Rodriguez and Uriarte, 2009). PSD was reported as both, the frequency curve (i.e. volume percent) and the undersize (i.e. cumulative volume percent), as illustrated in Figure 4.1. The frequency curve did not exhibit a Gaussian shape; it was mostly unimodal and was characterised by a tail towards smaller particle sizes. It also showed the fine grained nature of the tailings sample. Particles from the new Two Rivers sample were coarser ($D(v,90) = 328.7 \mu\text{m}$; Table 4.1) than those contained in the previous batch ($D(v,90) = 236 \mu\text{m}$; Mohamed 2012), which had been similarly fine-grained to the particles from Northam Platinum mine ($D(v,90) = 238 \mu\text{m}$; Vogeli *et al.*, 2011) and Lonmin ($D(v,90) = 293 \mu\text{m}$; Meyer *et al.*, 2013) but was coarser than the BRPM tailings sample ($D(v,90) = 138 \mu\text{m}$; Vogeli *et al.*, 2011) these same authors studied. The variation between the Two Rivers tailings sampled indicated that the (tailings storage facility) TSF is heterogeneous. In comparison to the findings of Amponsah-Dacosta and Reid, (2014; $D(v,90)$ not reported), the particles of the Two Rivers MT are similar in size to the tailings from Waterval, Oókiep and Amandelbult, finer than the particles of the tailings from Union and Impala, and coarser than the particles of the Mogalakwena and Nkomati mines. This indicated the variability in particle size of tailings from different TSF's, which may be due to different comminution techniques used and the mineralogical properties of the ore from which they were derived. The specific surface area of the Two Rivers sample was not determined because PGE tailings are

generally characterised by low values (e.g. $< 1.5 \text{ m}^2/\text{g}$ for BRPM, Northam and Lonmin tailings; Meyer *et al.*, 2013; Vogeli *et al.*, 2011).

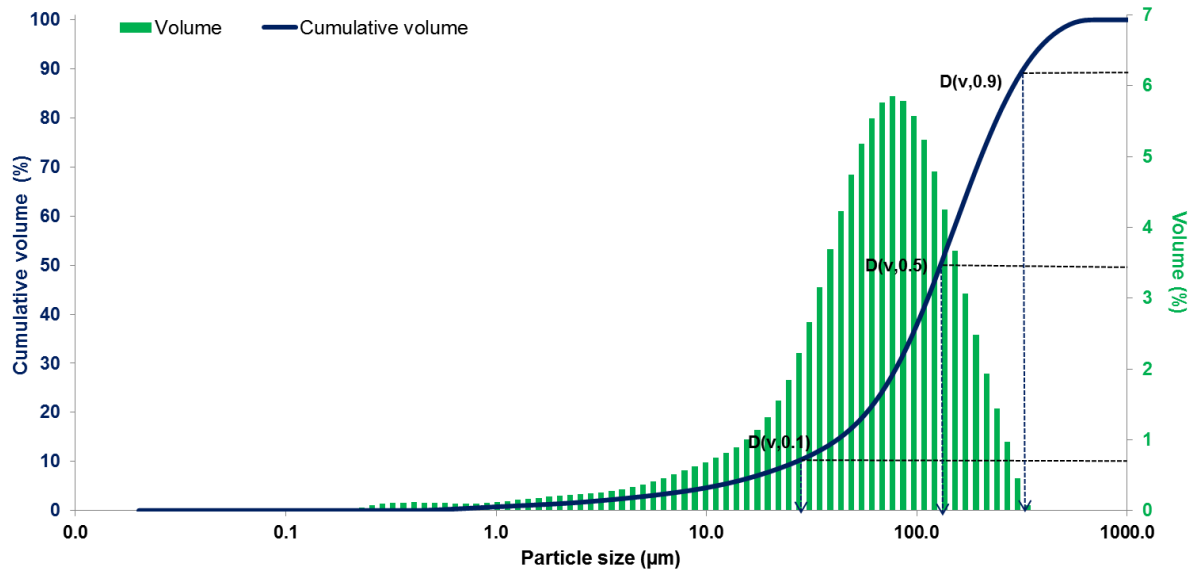


Figure 4.1. Particle size distribution of the bulk Two Rivers mine tailings sample, expressed as volume percent (green) and cumulative percent (blue). The D-values are indicated where the cumulative volume intersects at 10, 50 and 90% (dashed blue lines).

The results of the sieve analysis were used to estimate the PSD using the percentage weight retained within the different sieves (Table 4.1). The results indicated that the highest proportion of particles in terms of weight percent (wt. %) are within the $150 < x < 250 \text{ } \mu\text{m}$ (20.6 wt. %), $75 < x < 150 \text{ } \mu\text{m}$ (40.0 wt. %) and $45 < x < 75 \text{ } \mu\text{m}$ (26.0 wt. %) fractions. The largest fraction lies in the size range between $75 < x < 150 \text{ } \mu\text{m}$. The coarser particles ($x > 250 \text{ } \mu\text{m}$) and finest particles ($x < 45 \text{ } \mu\text{m}$) only constitute 6.8 wt. % and 6.6 wt. % respectively. From the frequency curves of the different size fractions, the coarser mine tailings ($x > 250 \text{ } \mu\text{m}$ and $150 < x < 250 \text{ } \mu\text{m}$) conformed to a Gaussian curve with a unimodal distribution, whereas the finer tailings ($75 < x < 150 \text{ } \mu\text{m}$, $45 < x < 75 \text{ } \mu\text{m}$ and $x < 45 \text{ } \mu\text{m}$) exhibited a bimodal distribution with a tail towards smaller particle sizes (Figure 4.2).

Table 4.1. Particle size distribution of the Two Rivers mine tailings sample, expressed as volume percent (%) (The calculated diameters $D(v,0.1)$, $D(v,0.5)$ and $D(v,0.9)$ are the given size of particles for which 10 %, 50 % or 90 % of the sample is below the specified size).

Particle Size (μm)	Mass (%)	Calculated diameters (μm)		
		$D(v,0.1)$	$D(v,0.5)$	$D(v,0.9)$
Bulk	-	26.4	131.4	328.7
$x > 250$	6.8	288.6	463.2	792.6
$150 < x < 250$	20.6	148.1	229.9	353.9
$75 < x < 150$	40.0	76.5	125.5	198.3
$45 < x < 75$	26.0	7.7	50.8	100.9
$x < 45$	6.6	3.9	26.1	56.7

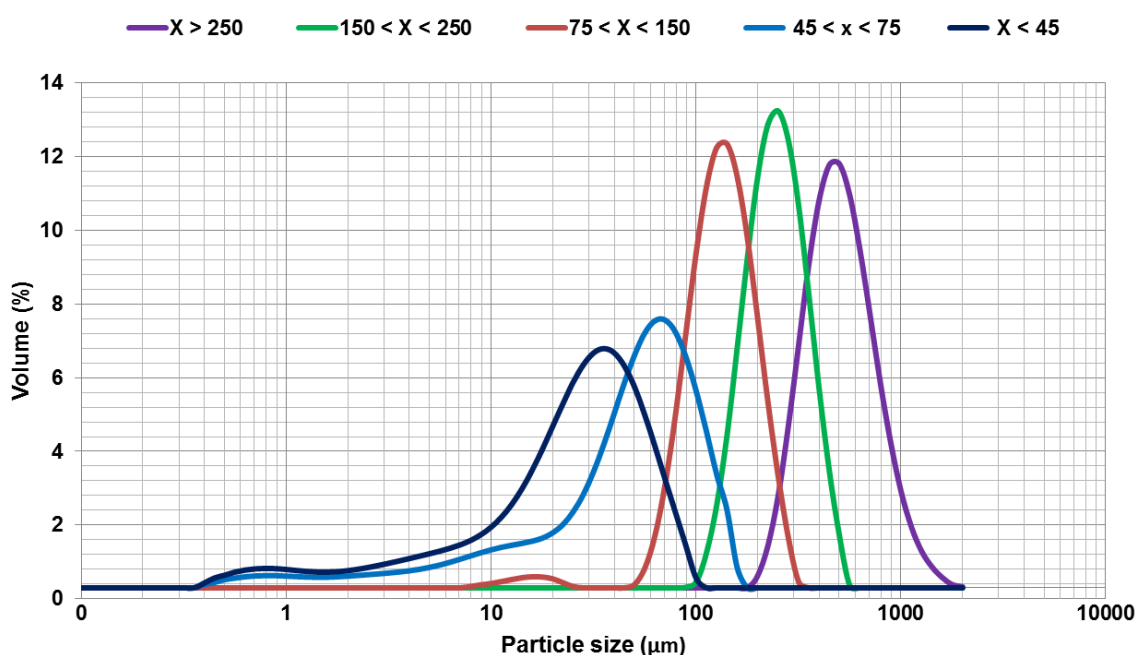


Figure 4.2. Particle size distribution for the different sieved fractions of Two Rivers mine tailings sample, expressed as volume percent (%).

4.1.1.2 Mineralogy and chemical composition

Quantitative XRD was used to determine the relative proportions of the crystalline phases present in the 45–75 μm size fraction (MT_{45-75}) of the Two Rivers tailings sample following micronization (Table 4.2). The dominant mineral phases included chromite/magnetite spinel (29.5 %), enstatite (the Mg end-member in the orthopyroxene group; 27.8 %), and plagioclase (25.2 %). The mineralogy of MT_{45-75} was similar to that of the previous batch (Mohamed, 2012). On the other hand, it was characterised by a different mineralogy than that of the tailings from Northam, BRPM and Lonmin (Meyer *et al.*, 2013; Vogeli *et al.*, 2011). In particular, the Two Rivers MT was enriched in spinel, enstatite and plagioclase, compared to Northam and BRPM which are more enriched in enstatite and plagioclase respectively. A

variation in the modal abundance of alteration minerals (serpentine, talc, chlorite, and calcite) was also observed (Table 4.2). The Two Rivers MT displayed a higher modal abundance of chlorite compared to Northam, BRPM and Lonmin, which are more enriched in serpentine and talc. The trace amounts of serpentine (the alteration product of olivine), in the Two Rivers MT further confirmed the low modal abundance of olivine mineral phases. Smaller variations were observed for the remaining mineral phases. The mineralogy reported correlates to the critical zone of the BIC and illustrates that the Two Rivers tailings are produced from UG2 whereas Northam, BRPM and Lonmin are produced from Merensky reef. Tailings produced from the UG2 are generally enriched in the chromite compared to the Merensky Reef which is more enriched in plagioclase and orthopyroxene minerals (Dzvinamurungu *et al.*, 2013).

Table 4.2. Mineralogy of the 45 - 75µm fraction of the Two Rivers tailings sample, as determined by quantitative XRD.

Mineral	Chemical Formula	Mineralogical composition (%)
Chromite/Magnetite /Spinel	$\text{Fe}^{2+}\text{Cr}_2\text{O}_4 / \text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4 / \text{MgAl}_2\text{O}_4$	29.5
Orthopyroxene - Enstatite	$\text{Mg}_2\text{Si}_2\text{O}_6$	27.8
Plagioclase	$(\text{Na,Ca})(\text{Si,Al})_4\text{O}_8$	25.2
Amphibole - Hornblende	$\text{Ca}_2[\text{Mg}_4(\text{Al,Fe}^{3+})]\text{Si}_7\text{AlO}_{22}(\text{OH})_2$	7.9
Chlorite	$(\text{Mg}_5\text{Al})(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8$	3.1
Calcite	$\text{Ca}(\text{CO}_3)$	2.4
Clinopyroxene - Augite	$(\text{Ca,Na})(\text{Mg,Fe,Al,Ti})(\text{Si,Al})_2\text{O}_6$	1.7
Mica – Biotite	$\text{KFeMg}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	1.6
Talc	$\text{Mg}_3(\text{OH})_2\text{Si}_4\text{O}_{10}$	1.0
Serpentine - Lizardite	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	trace

The chemical composition of the Two Rivers mine tailings sample is presented in Tables 4.3 (major elements). The bulk and the sieved size fractions were analysed in order to determine the elemental enrichment in the different size fractions. The concentrations of major elements are controlled by the modal proportions of the mineral phases present (Kearey, 2001). The bulk MT sample was dominated by Cr_2O_3 (34.0 wt. %), Fe_2O_3 (22.5 wt. %) and SiO_2 (18.3 wt. %), with lesser amounts of Al_2O_3 (10.8 wt. %) and MgO (12.4 wt. %). Na_2O_3 and K_2O were present in very small proportions (< 0.3 wt. %). The 45 - 75 µm size fraction followed the same trend and was more enriched in Cr_2O_3 (31.9 wt. %) compared to Fe_2O_3 (23.3 wt. %), SiO_2 (17.4 wt. %), Al_2O_3 (12.2 wt. %) and MgO (13.6 wt. %). A variation in elemental concentrations across the particle size range was observed for SiO_2 (16.5 - 30.5 wt. %) and Cr_2O_3 (16.6 -33.1 wt. %) compared to Fe_2O_3 , Al_2O_3 , MgO . No distinctive trend or preferential partitioning was observed for the other elements. The variability in the chemical composition of the tailings used in this study was similar to the other PGE tailings (section 2.5.2.2).

Table 4.3. Major element composition of the Two Rivers mine tailings expressed as weight percent (wt. %).

	Particle size (μm)					
	Bulk	$x > 250$	$150 < x < 250$	$75 < x < 150$	$45 < x < 75$	$x < 45$
SiO₂	18.3	21.9	30.5	16.5	17.4	25.9
Al₂O₃	10.8	10.9	8.4	11.5	12.2	12.7
Fe₂O₃ (total)	22.5	24.3	20.9	25.6	23.3	21.7
Cr₂O₃	34.0	24.9	16.6	33.1	31.9	22.2
MnO	0.3	0.3	0.3	0.3	0.3	0.3
MgO	12.4	15.5	19.7	13.1	13.6	14.5
CaO	1.8	2.2	3.4	1.7	2.5	3.1
Na₂O	0.3	0.2	0.3	0.2	0.3	0.3
K₂O	0.1	0.1	0.1	0.0	0.1	0.1
TiO₂	0.6	0.7	0.5	0.7	0.7	0.7
LOI*	-1.4	-0.8	-1.4	-1.7	-1.3	-1.1
Total	99.8	100.0	99.4	100.9	100.9	100.5

* LOI : Loss on Ignition.

Loss on Ignition (LOI) is used to estimate the total proportion of water, carbon dioxide and volatile content in a sample. LOI is commonly determined by simply heating the sample at elevated temperatures (1000 °C and above) for approximately 1 hour and recording the change in sample mass. In the case of Fe-rich minerals, the LOI may be an important indicator of oxidation processes which result in a weight gain which is equivalent to a negative LOI. This suggested that the negative LOI observed for the tailings (Table 4.3) may be attributed to a weight increase arising from the oxidation of ferrous iron (Fe^{2+}) contained in e.g. spinel group minerals to ferric ion (Fe^{3+}), which would have been higher than the weight loss caused by removing volatiles from the mineral structures. Similar observations were already made (i) for iron-rich coal ashes, in which case negative LOI was also best explained by the oxidation of Fe^{2+} to Fe^{3+} (FeO to Fe_2O_3) and its associated weight increase (Vandenberghe *et al.*, 2010), and (ii) for calcium sulphide (CaS)-rich samples which exhibited a negative LOI due to the oxidation of CaS to CaSO_4 (de Beer *et al.*, 2014).

4.1.1.3 Raman spectroscopy

Raman spectroscopy was used to identify and differentiate between spinel species present in the tailings. The Raman spectrum of the bulk sample is presented in Figure 4.3 and the observed Raman modes are summarised in Table 4.4 Raman active photons for spinel mineral phases, which correspond to the A_{1g} symmetry point group (symmetric breathing mode of the metal-oxygen unit (AO_4)), is more pronounced compared to E_g (symmetric bending mode of the oxygen anion within the AO_4 unit) and F_{2g} (translation of the AO_4 unit) symmetries due to the complexity of the mineral phases (Hosterman, 2011). The Raman spectrum indicated sharp peaks at 236 cm^{-1} , 342 cm^{-1} , a set of overlapping peaks at

661 cm^{-1} and 680 cm^{-1} , and 1008 cm^{-1} . The observed peaks correlated well with the literature and were attributed to the presence of spinel and/or orthopyroxene mineral phases (Table 4.4).

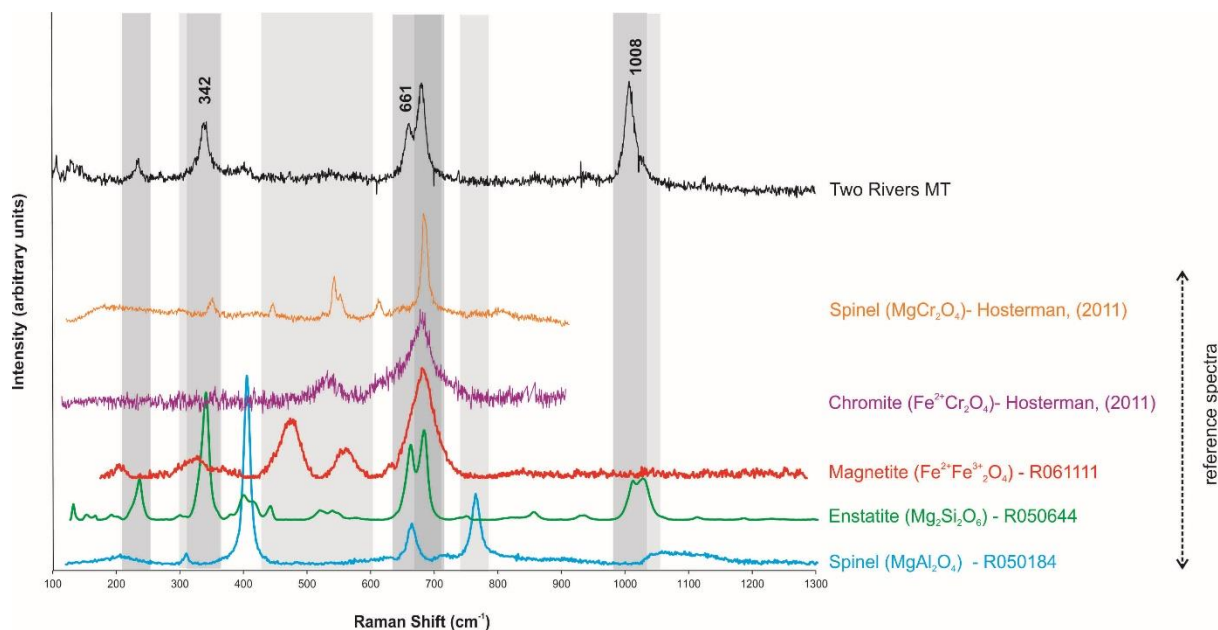


Figure 4.3. Raman spectra of the Two Rivers mine tailings compared to mineral reference spectra of magnetite (R061111), enstatite (R050644) and spinel (R050184) from RRUFF project database of Raman spectra, X-ray diffraction and chemistry data for minerals (RRUFF, 2014).

Natural spinels which have cation distributions between normal and inverse structure types are affected by the substitution of different cations in the tetrahedral and octahedral sites (Klein and Dutrow, 2008). The presence of overlapping peaks in the region between 630 cm^{-1} and 690 cm^{-1} indicated the presence of a solid solution series between the Fe, Mg and Cr end members of the spinel mineral phase. The Raman spectral range for natural chromites is between 667 cm^{-1} and 730 cm^{-1} ; however, Lenaz and Lughi (2013), have observed the shift of the A_{1g} mode to lower values due to the increase in Fe and/or Cr content. The overlapping peaks observed at 661 cm^{-1} and 668 cm^{-1} correspond to the symmetric stretch of oxygen atoms along the M-O bonds of the spinels, i.e. chromite and magnetite respectively.

Minerals of the pyroxene group form an extensive solid solution series between the Mg, Fe and Ca end-members. From the results of the Rietveld quantification discussed in section 4.2.3.1, enstatite had a higher modal abundance (27.8 wt.%) than that of augite (1.7 wt. %). The Raman spectra of orthopyroxene and clinopyroxene are distinctive and therefore a clear differentiation can be made between them (Huang *et al.*, 2000). The moderate and intense peaks observed at 235 cm^{-1} , 342 cm^{-1} and 1008 cm^{-1} may be attributed to the SiO_4 rotation, to the symmetric bends of oxygen with respect to Fe (M-O transformations), and to the Si-O stretching vibrations which are related to the non-bridging Si-O_{nbr} modes of enstatite and spinel (Huang *et al.*, 2000, Shebanova and Lazor, 2003). The shift of these peaks to lower wavelengths indicates the increase in Fe content ascribed by the substitution of Fe^{2+} which has a larger atomic radius compared to Mg^{2+} (Buzatu and Buzgar, 2010).

Table 4.4. Raman vibrational modes for the predominant mineral phases reported by XRD and identified in the Raman spectra of the Two Rivers mine tailings.

				assignment; wavelength (cm ⁻¹)		
Mineral Phase				M-O stretch	Si-O _{br} stretch	Si-O _{nbr} stretch
Single-chain silicates	Enstatite	Mg ₂ Si ₂ O ₆	Observed	342		1008
			Haskin <i>et al.</i> (1997)	337	681	1007
			Huang <i>et al.</i> (2000)	344	685	1013
	Clinopyroxene	(Ca,Mg,Fe) ₂ Si ₂ O ₆	Observed		662	1010
			Buzatu and Buzgar (2010)		667,663	1006
			Huang <i>et al.</i> (2000)		662	1007
Spinel	Iron	Fe ₂ O ₃	Observed		667	
			Hosterman (2011)	531	667	
			McCarty and Boehme (1989)	542	671	
			de Faria <i>et al.</i> , (1997)	533.6	662.7	
			Shebanova and Lazor (2003)	538	668	
			Wang <i>et al.</i> (1998)		667	
	Chromium	FeCr ₂ O ₄	Observed		661	
			Wang <i>et al.</i> (1998)	550	680	
	Aluminium	MgAl ₂ O ₄	Wang <i>et al.</i> (1998)	408	770	

4.1.1.4 Optical microscopy

Reflected light microscopy was applied to the tailings in order to identify the presence of the reported mineral phases and determine grain morphology. The micrographs were obtained from both powder samples and polished stubs and the resulting micrographs are presented in Figure 4.4. Figure 4.4A illustrates the powdered sample viewed under reflected light at 10x magnification and Figure 4.4B illustrates the petrographic characteristics of the polished stub.

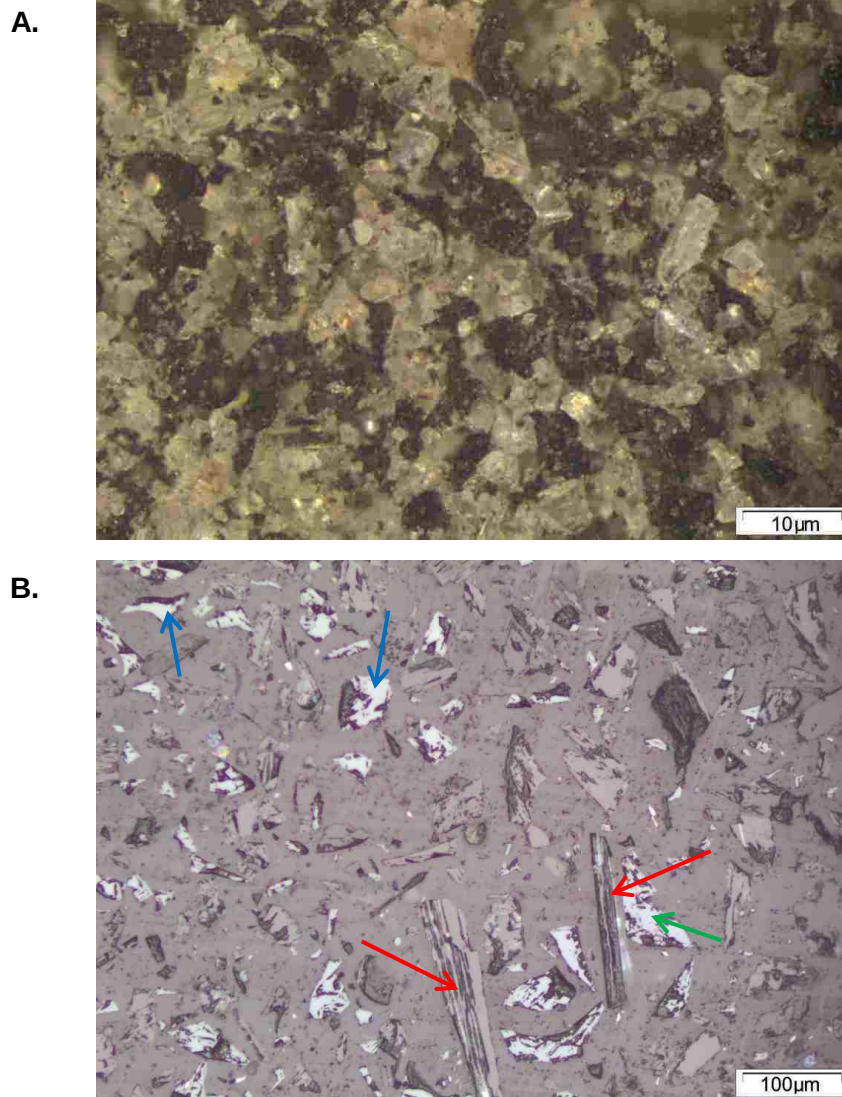


Figure 4.4. Optical micrographs of the mine tailings sampled from the Two Rivers tailings storage facility (TSF). (A.) visible light at 10x magnification and (B.) reflected light at 20x magnification. Blue arrow points to composite particles which contain one or more mineral phases, green arrow indicates spinel mineral phases and the red arrow points the plagioclase mineral grains.

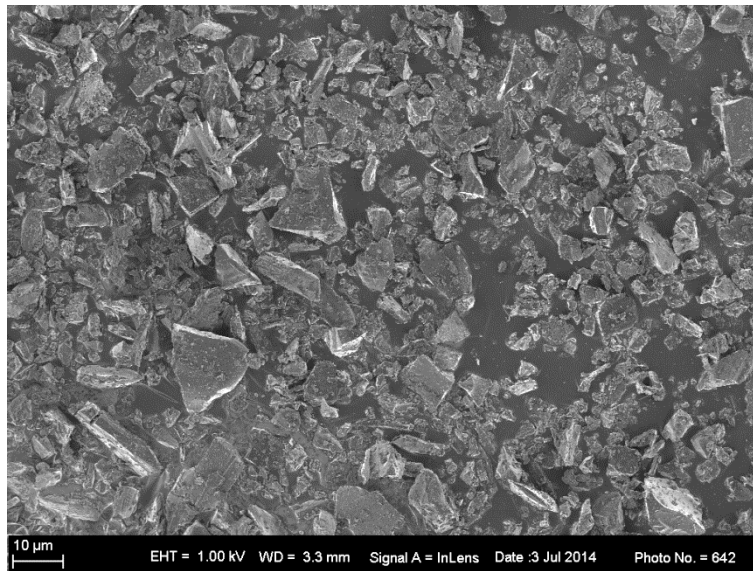
As discussed in sections 4.2.3.2 and 4.2.3.3, the predominant mineral phases present in the sample are spinel, enstatite and plagioclase with lesser amounts of amphibole, chlorite and clay minerals. Optical microscope examination of MT₄₅₋₇₅ revealed that the sample consists primarily of silicate and aluminosilicate gangue mineral grains, i.e. with spinel, feldspar

(plagioclase), mica (biotite), hornblende, pyroxene which are consistent with the XRD results. Figure 4.4A illustrates the presence of spinel and other dark coloured minerals such as amphibole and pyroxene in a matrix of translucent crystals, most likely silicate minerals. Under reflected light, most silicate minerals appear in shades of grey. As illustrated in Figure 4.4B, the sample was dominated by silicate mineral phases which appear as contrasting shades of grey. The silicates and aluminosilicates appeared to be composite particles which contain one or more mineral phases (blue arrow). Individual grains appeared to be angular. The isotropic nature of the spinel mineral phases (i.e. particles remains dark in colour upon rotation of the stage under transmitted light) is indicated by the light grey-white anhedral crystals (green arrow). Plagioclase-rich particles can be identified by their well-formed (euhedral) and easily recognised tabular morphology (red arrow).

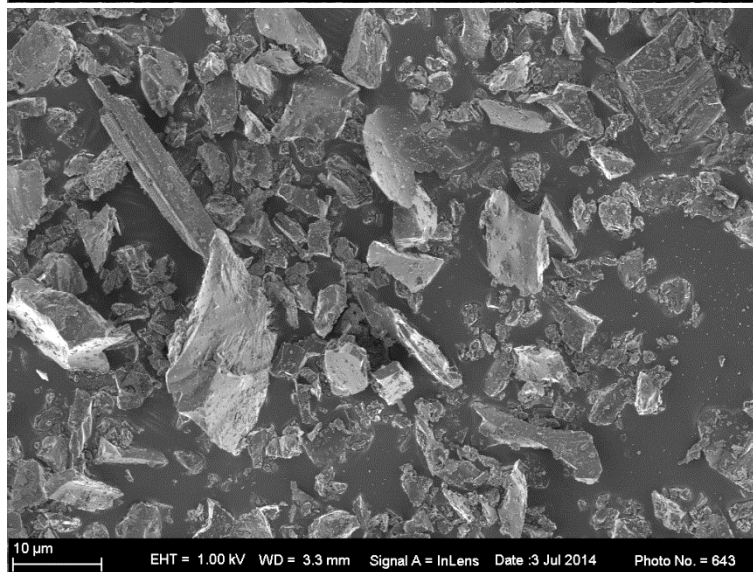
4.1.1.5 FE-SEM

A field emission scanning electron microscope was used to obtain information on the morphology and surface features of the tailings sample (Figure 4.5). The particles displayed a poor crystal form (anhedral), were angular and irregularly shaped with a non-uniform grain size indicated by the presence of larger particles surrounded by smaller fragmented particles. The particles which displayed a tabular morphology are characteristic of the crystal habit of plagioclase minerals. These findings depicted the grinding and fine milling of the ore required to liberate the PGE's and were consistent with the findings of crushed South African Chromite (Zhao et al., 2014) (Figure 4.6).

A.



B.



C.

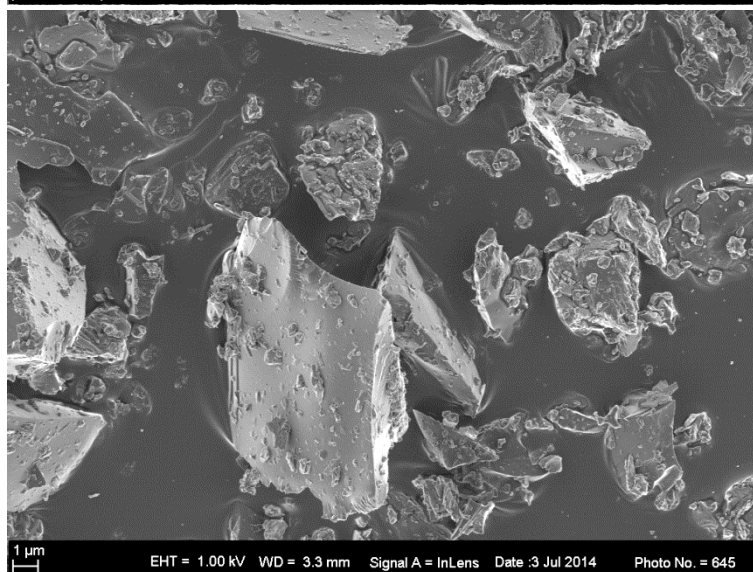


Figure 4.5. FE-SEM micrographs of the PGE mine tailings sampled from the Two Rivers tailings storage facility (TSF). The micrographs were taken at (A.) 2000x, (B.) 3500x and (C.) 10000x magnification.

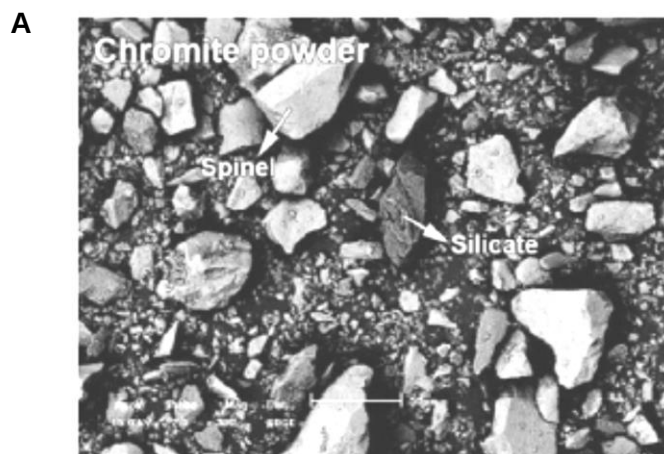


Figure 4.6. SEM micrographs of a crushed chromite studied by Zhao *et al.* (2014).

4.2 PGE mine tailings from Amandelbult, Marico Chrome and Rhovan Operations as feedstock material

The results from the preliminary study (Mohamed, 2012) and subsequent dissolution experiments on the Two Rivers tailings sample (Section 5.1) have suggested that the variability in the cation arrangement within the spinel structure may have an effect on the extraction efficiency of Fe. For this reason, the chemical composition of bulk tailings from other TSF's was determined using XRF and their Fe/Cr ratio was calculated (section 4.4.1.1). 25 sub-samples were selected from the Amandelbult, Marico Chrome and Rhovan operations TSF's, on the basis of their differences in Fe:Cr ratio (Fe and Cr range between 0-20 % and 0-30 % respectively) (Figure 4.7). As examples, samples from Rhovan Operations were depleted in Cr whilst their Fe content varied in the range 1-19 wt. %, depending on the depth of sampling. On the other hand Fe and Cr content of Amandelbult samples varied greatly between boreholes. For instance, samples from borehole 1 had Fe and Cr varying between 13 and 18 wt. %, and 8 and 28 wt. % respectively while Fe and Cr content in samples from borehole 2 varied in the range 8 – 15 wt. % and 1 – 13 wt. % respectively.

The selected samples were sieved and the particle size distribution was determined. Subsequently, the 45 – 75 μm fraction was selected and used in all experiments reported in this study, except when otherwise stated. MT_{45-75} was characterised using a range of complementary techniques, including PSD, XRF, XRD, reflected light microscopy, FE-SEM, and Raman spectroscopy.

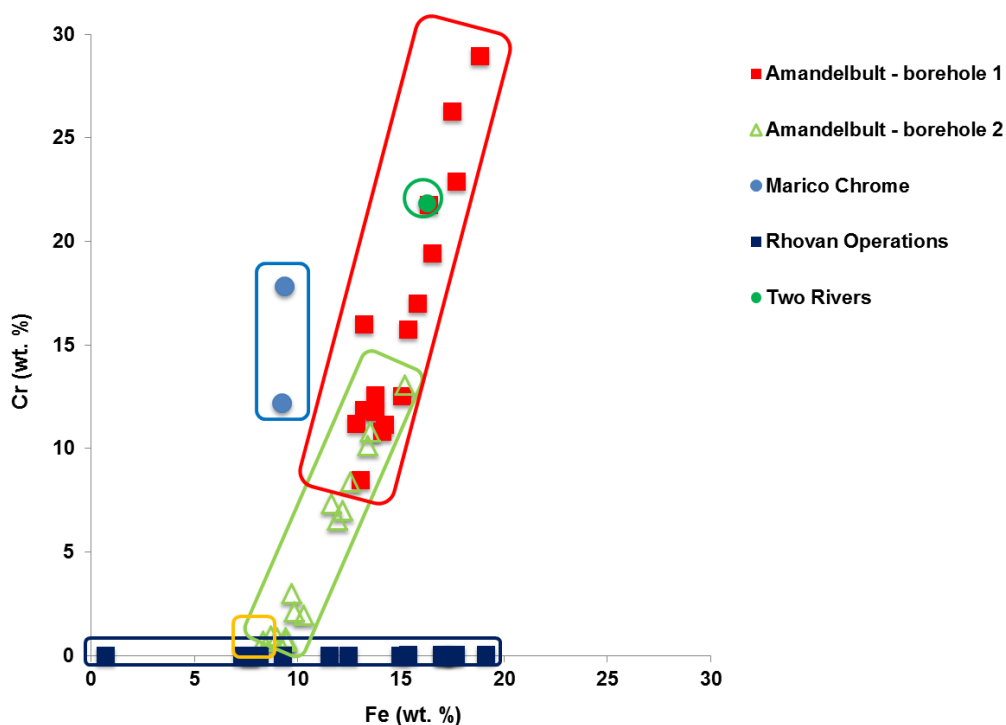


Figure 4.7. Bulk elemental percentage of Fe and Cr of PGE mine tailings sampled from Amandelbult, Marico Chrome, Rhovan Operations and Two Rivers tailings storage facilities.

4.2.1 Physicochemical characterisation

4.2.1.1 Bulk Chemistry

The elemental composition of MT was determined and the results of the major elements are summarised in Table 4.5. The composition of the various MT rocks was dominated by SiO_2 (9.9 - 51.7 wt. %), Cr_2O_3 (0.04. – 32.1 wt. %), Fe_2O_3 (11.3 - 27.1 wt. %), MgO (3.2 - 25.3 wt. %) and Al_2O_3 (3.5 - 18.4 wt. %). The elemental concentrations of Na_2O , TiO_2 and K_2O are low and vary from < 0.21 wt. %, < 2.32 wt. % and < 5.63 wt. % respectively. The chemical composition reported for the different MT correlate to the findings of Amponsah-Dacosta and Reid, 2014; Vogeli *et al.*, 2011) and confirmed the variability in the mineralogy of PGE tailings from different sites.

SiO_2 was the most abundant oxide in MT and can be used to illustrate chemical variation between MT from different sources. Harker diagrams (plots of oxides against silica) were used to illustrate the chemical variation between the MT's. The chemical composition of the bulk MT obtained using XRF was used to plot Harker diagrams of the major elements against SiO_2 (Figure 4.8). The elemental proportions of CaO , K_2O , Na_2O and MgO showed a positive correlation with SiO_2 , whilst Fe_2O_3 , Cr_2O_3 , and TiO_2 were negatively correlated with SiO_2 . Only a minor variation in Al_2O_3 with an increase in SiO_2 was observed. The MT sampled from Rhovan Operations and Marico has been reprocessed to recover Cr, which may explain why these samples appear as outliers not fitting within the general trend of the other samples with respect to SiO_2 . The variation in concentration of the major oxides can be attributed to the origin of the MT which furthermore confirmed the variation in the mineralogy between the different MT.

Table 4.5. Major element composition of the mine tailings sampled from Amandelbult, Marico Chrome and Rhovan Operations tailings storage facilities (TSF's) expressed as weight percent (wt. %).

		Chemical Composition (wt. %)												
Tailings storage facility (TSF)	Depth (m)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Cr ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	LOI	Total	
Amandelbult	borehole 1	1	24.57	13.22	21.28	22.47	0.19	14.46	2.71	0.63	0.07	0.65	-0.79	99.89
		2	26.22	12.23	20.26	23.17	0.19	13.99	3.00	0.63	0.07	0.66	-0.68	100.10
		3	28.16	10.63	19.09	22.88	0.14	13.94	3.65	0.69	0.08	0.50	-0.51	99.70
		4	26.93	10.00	18.91	27.21	0.12	13.18	3.31	0.62	0.08	0.51	-0.54	100.81
		5	26.03	9.92	19.30	27.36	0.12	13.25	3.18	0.62	0.07	0.48	-0.56	100.23
		6	31.96	11.36	18.18	17.02	0.15	15.15	4.10	0.73	0.09	0.46	-0.25	99.43
		7	30.03	10.65	18.22	19.64	0.15	15.12	4.02	0.72	0.09	0.45	-0.24	99.26
		8	28.94	10.45	18.43	22.46	0.13	14.62	3.59	0.67	0.09	0.43	-0.25	99.94
		9	28.62	10.34	17.70	23.99	0.11	14.06	3.82	0.71	0.09	0.42	-0.16	100.09
		10	25.81	9.92	19.25	27.41	0.11	13.20	3.33	0.67	0.08	0.50	-0.29	100.43
		11	30.75	11.04	18.29	19.79	0.14	14.71	3.84	0.67	0.08	0.45	-0.18	100.04
		12	31.85	10.63	17.89	18.76	0.14	15.02	3.98	0.68	0.09	0.43	-0.08	99.83
		13	32.17	10.51	18.33	17.74	0.15	15.24	4.01	0.70	0.09	0.44	-0.11	99.71
		14	34.51	10.55	17.60	14.54	0.15	15.69	4.45	0.76	0.10	0.44	0.09	99.53
		15	34.00	10.39	17.74	15.68	0.15	15.53	4.49	0.73	0.10	0.45	0.08	99.67
	borehole 2	16	33.21	10.54	17.17	17.63	0.14	14.91	4.47	0.80	0.10	0.43	0.15	99.94
1		38.86	11.39	16.18	8.11	0.232	18.62	4.83	0.57	0.10	0.43	-0.35	99.00	
4		41.74	11.50	14.19	6.13	0.213	18.32	5.69	0.72	0.16	0.38	0.33	99.42	
13		47.26	10.41	12.30	1.47	0.188	19.95	6.12	0.73	0.16	0.30	0.80	99.73	
Marico Chrome	grab sample	51.70	3.79	11.34	1.06	0.20	25.04	2.21	0.79	0.09	0.39	1.87	98.71	
	grab sample	51.35	3.45	11.60	0.79	0.21	25.30	2.02	0.57	0.07	0.46	2.55	98.64	
Rhovan Operations	12	39.29	16.28	23.97	0.04	0.16	3.28	8.71	2.32	0.20	4.87	0.42	99.56	
	14	36.78	15.41	27.13	0.04	0.18	3.22	8.08	2.20	0.21	5.63	0.38	99.28	
Two Rivers	grab sample	17.44	12.24	23.27	31.90	0.25	13.63	2.47	0.26	0.06	0.70	-1.34	100.89	

◆ Amandelbult - borehole 1 △ Amandelbult - borehole 2 ■ Rhovan Operations ● Marico Chrome ● Two Rivers

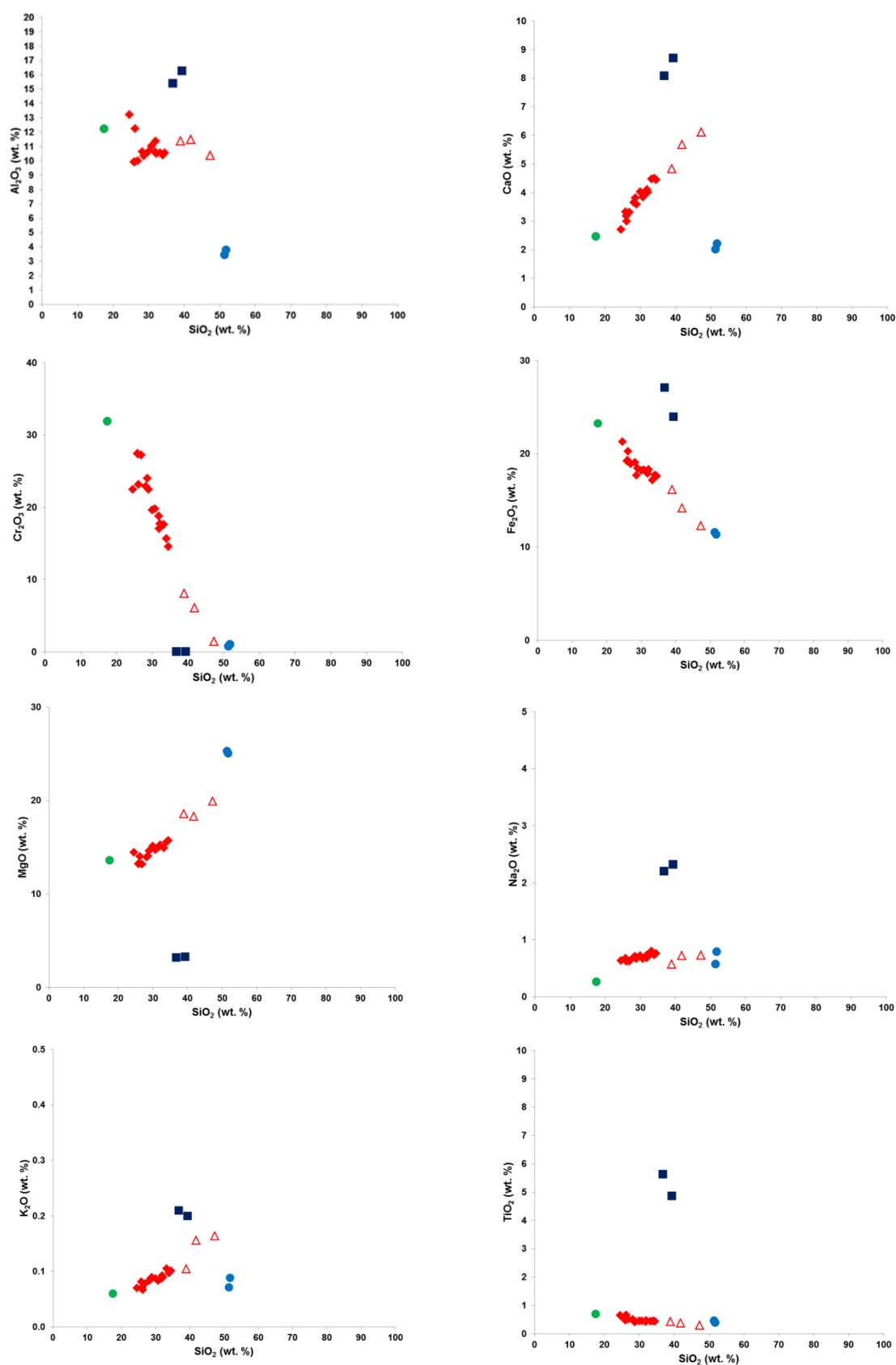


Figure 4.8. Harker diagrams of the major oxides present in the PGE mine tailings sampled from Amandelbult, Marico Chrome, Rhovan Operations and Two Rivers tailings storage facilities (TSF's).

Silicate minerals which form simultaneously often compete for major elements like Fe_2O_3 , MgO , Cr_2O_3 and Al_2O_3 . Using scatter plots, the elemental competition between the major elements present in the MT can be determined. Scatterplots of Al, Cr and Mg plotted against Fe are presented in Figure 4.9. Overall there was a higher elemental concentration of Cr (0.0 - 21.94 wt. %), Fe (7.9 – 19.0 wt.%) and Mg (1.9 - 15.3 wt.%) compared to Al (1.8 - 9.9 wt.%). The MT sampled from Rhovan operations contained no Cr and little Mg (2.0 ± 0.0 %) and appeared as outliers relative to the other MT. A positive trend was observed for Al and Cr as Fe increased and a negative trend was observed between Mg and Fe which may be ascribed to preferential substitution of Fe for Mg. These results suggested that Fe, Cr, Al and Mg coexisted possibly in the form of a solid solution series.

◆ Amandelbult - borehole 1 ▲ Amandelbult - borehole 2 ■ Rhovan Operations ● Marico Chrome ● Two Rivers

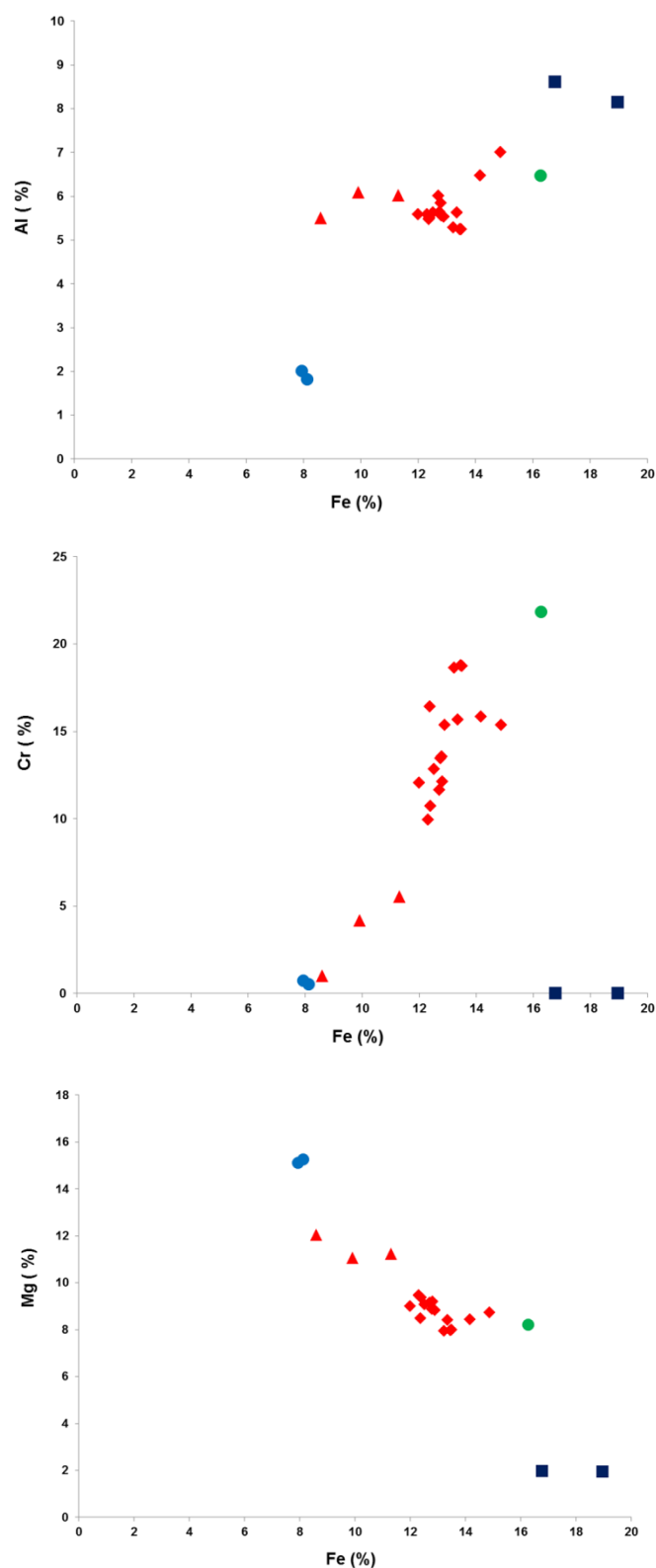


Figure 4.9. Scatter plots of Fe against Al, Cr and Mg in the PGE mine tailings sampled from Amandelbult, Marico Chrome, Rhovan Operations and Two Rivers tailings storage facility (TSF's)

4.2.1.2 Mineralogy

The identification and quantification of the mineral phases present in the bulk MT was determined. The major mineral phases identified by XRD are presented in Table 4.6 and indicated lateral variation between the mine tailings. Mineral phases which were present included spinel (11.0 – 79.0 wt. %), plagioclase (2.0 - 65.0 wt %), chlorite (2.0 – 18.0 wt %) and dolomite (2.0 - 42.0 wt. %), with smaller and trace amounts of talc/pyrophyllite (1.0 - 23 wt. %), amphibole (1.0 - 4.0 wt. %) and smectite (2.0 - 26.0 wt. %). The minor modal abundance of alteration minerals indicated the presence of secondary weathering products which gives an indication of the reactivity of the MT and possibly the preferential pathway in which trace elements, acidity or alkalinity is introduced into the environment (Piatak *et al.*, 2015). The mineralogy of the tailings from Amandelbult (boreholes 1 and 2) was similar to Two Rivers and had a relatively high modal abundance of spinel and plagioclase. However, higher amounts of carbonate, chlorite and talc were present. The Marico Chrome MT had a higher modal abundance of spinel, talc and smectite. Tailings from Rhovan Operations displayed a distinct variation in the relative abundance of spinel and plagioclase between the two samples. The variation in mineralogy of the tailings may be attributed to the different mineralogical properties of the ores from which they were produced and/or changes in the recovery process of PGE's.

Table 4.6. Mineralogical composition in weight percent (wt. %) of the mine tailings sampled from Amandelbult, Marico Chrome and Rhovan Operations tailings storage facilities (TSF's).

Mineral phases (wt. %)											
Tailings storage facility (TSF)	Depth (m)	Chromite/ Magnetite/ Spinel	Plagioclase	Orthopyroxene	Calcite/ Dolomite	Chlorite	Mica	Talc/ Pyrophyllite	Amphibole	Smectite	
Amandelbult	borehole 1	1	79.0	4.0	-	2.0	2.0	3.0	3.0	2.0	tc*
		2	77.0	9.0	-	6.0	6.0	tc*	2.0	-	tc*
		3	64.0	12.0	-	9.0	2.0	3.0	3.0	3.0	2.0
		4	59.0	12.0	-	12.0	12.0	tc*	2.0	tc*	-
		5	65.0	9.0	-	12.0	12.0	tc*	-	-	tc*
		6	50.0	23.0	-	11.0	11.0	3.0	2.0	tc*	-
		7	57.0	11.0	-	21.0	2.0	tc*	3.0	2.0	tc*
		8	66.0	13.0	-	8.0	8.0	1.0	1.0	tc*	tc*
		9	49.0	15.0	-	16.0	16.0	2.0	2.0	tc*	-
		10	63.0	11.0	-	9.0	9.0	2.0	2.0	2.0	-
		11	53.0	14.0	-	14.0	14.0	tc*	2.0	2.0	tc*
		12	53.0	4.0	-	18.0	18.0	tc*	2.0	1.0	-
		13	-	-	-	-	-	-	-	-	-
		14	61.0	10.0	-	12.0	12.0	tc*	3.0	2.0	-
		15	51.0	9.0	-	14.0	14.0	2.0	3.0	4.0	tc*
		16	63.0	6.0	-	22.0	2.0	tc*	2.0	2.0	-
	borehole 2	1	-	-	-	-	-	-	-	-	-
		4	53.0	13.0	-	20.0	2.0	2.0	4.0	3.0	-
		13	14.0	40.0	-	25.0	2.0	2.0	4.0	4.0	-
Marico Chrome	grab sample	11.0	2.0	-	37.0	tc*	2.0	23.0	2.0	19.0	
	grab sample	13.0	2.0	-	42.0	tc*	2.0	15.0	2.0	20.0	
	grab sample	40.0	5.0	-	3.0	3.0	2.0	13.0	4.0	26.0	
	grab sample	75.0	4.0	-	2.0	2.0	tc*	5.0	tc*	7.0	
Rhovan Operations	12	11.0	65.0	-	3.0	3.0	3.0	3.0	4.0	7.0	
	14	59.0	24.0	-	2.0	2.0	3.0	3.0	3.0	tc*	
Two Rivers	grab sample	29.5	25.2	27.8	2.4	3.1	1.6	1.0	7.9	-	

*tc : trace

4.2.1.3 Raman spectroscopy

Raman spectroscopy was used to identify and differentiate between the different mineral species present in the Cr depleted MT (Rhovan Operations) as described in section 3.4.1.9 and to confirm the mineralogy reported by XRD. The Raman spectrum of the Cr depleted MT is presented in Figure 4.10 and the corresponding bands are summarised in Table 4.7.

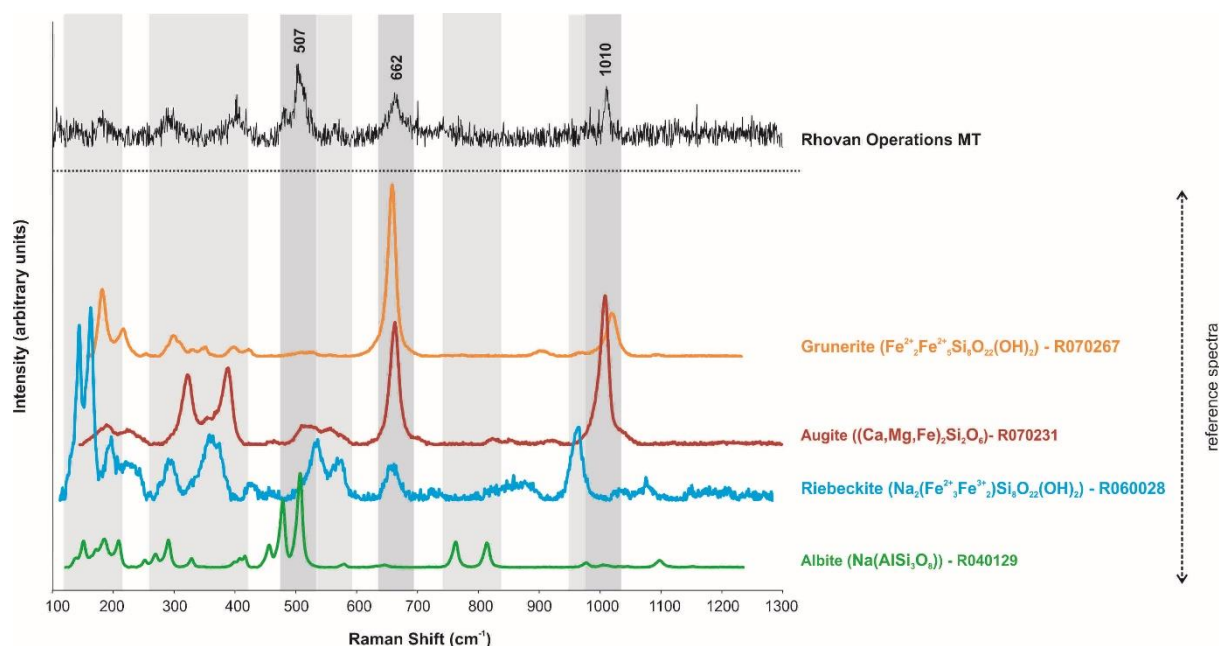


Figure 4.10. Raman spectra of the Cr depleted mine tailings obtained from Rhovan Operations compared to mineral reference spectra grunerite ($\text{Fe}^{2+}_2\text{Fe}^{2+}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$; R0070267), augite ($(\text{Ca,Mg,Fe})_2\text{Si}_2\text{O}_6$; R070231), riebeckite ($\text{Na}_2(\text{Fe}^{2+}_3\text{Fe}^{3+}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$; R060028) and albite ($\text{Na}(\text{AlSi}_3\text{O}_8)$; R040129) from RRUFF project, which is comprised of an integrated database of Raman spectra, X-ray diffraction and chemistry data for minerals (RRUFF, 2014).

The Raman spectrum of the MT had a high signal-noise ratio relative to the reference spectra, which may be due to a lower count rate or may be obscured by the background due to fluorescence and/or contamination and often influences the interpretation of peaks (Zhang *et al.*, 2010). Despite the high signal-to-noise ratio, the Raman spectrum revealed distinctive sharp peaks at 507 cm^{-1} , 662 cm^{-1} and 1010 cm^{-1} . The broad peak at 507 cm^{-1} is in the Raman peak range of feldspars and corresponds to the ring breathing modes of the four-membered tetrahedral rings. The peak position for the albite end-member of plagioclase is at 507.6 cm^{-1} suggesting that albite is the major silicate mineral phase present. The 662 cm^{-1} peak is the most distinct peak of the amphibole and pyroxene group minerals and corresponds to ν_1 (A_{1g}) asymmetric stretching (ν_s) of the $\text{Si-O}_b\text{-Si}$ bridge of grunerite, riebeckite and/or augite. Grunerite and riebeckite are the Fe end-members of the cummingtonite-grunerite and glaucophane and riebeckite series respectively (Apopei and Buzgar, 2010). The identification of Fe-rich mineral phases in the MT corresponds to the visual analyses of small black inclusions found in the white-translucent silicate particles (Figure 4.11). The 1010 cm^{-1} peak corresponds to the stretching vibrations of the

non-bridging Si-O (Si-O_{nbr}) mode of augite. The low to moderate peaks present at 290 cm^{-1} and 400 cm^{-1} may be ascribed to the rotation- translation (lattice) modes of albite and Fe^{2+} -O vibrational modes of the amphibole minerals respectively (Apopei and Buzgar, 2010, Freeman *et al.*, 2008). These Raman peaks are consistent with the mineralogical results determined by XRD, however the absence of the spinel peaks suggests that the focus of the laser was on the silicate minerals only.

Table 4.7. Raman vibrational modes for the predominant minerals phases reported by XRD and identified in the Raman spectra of the Rhovan Operations mine tailings.

				assignment; wavelength (cm ⁻¹)			
	Mineral Phase			T-O-T bond angles	M-O stretch	Si-O _{br} stretch	Si-O _{nbr} stretch
Tectosilicates	Feldspar		Observed	507			
	Maximum Microcline			513			
	Orthoclase	K(AlSi ₃ O ₈)		513			
	Sanidine		Freeman <i>et al.</i> (2008)	514			
	Low Albite			507			
	High Albite	Na(AlSi ₃ O ₈)		507			
	Plagioclase	(Ca,Na)(AlSi ₃ O ₈)		510			
Double-chain silicates	Amphibole		Observed		400	662	
	Grunerite	Fe ²⁺ ₂ Fe ²⁺ ₅ Si ₈ O ₂₂ (OH) ₂	Apopei and Buzgar (2010)		415	665	
			Downs (2006)		410	663	
			Rinaudo <i>et al.</i> (2004)		400,423	659	
	Amphibole		Observed			662	
	Riebeckite	Na ₂ (Mg ₃ Fe ³⁺ ₂)Si ₈ O ₂₂ (OH) ₂	Apopei and Buzgar (2010)			665	
			Downs (2006)			663	
Single-chain silicates	Orthopyroxene		Observed				1007
	Enstatite	Mg ₂ Si ₂ O ₆	Haskin <i>et al.</i> (1997)			681	1007
			Huang <i>et al.</i> (2000)		344	685	1013
	Clinopyroxene		Observed			662	1010
	Augite	(Ca,Mg,Fe) ₂ Si ₂ O ₆	Buzatu and Buzgar (2010)			667,663	1006
			Huang <i>et al.</i> (2000)			662	1007

4.2.1.4 Optical Microscopy

Optical microscopy was used to determine the presence of oxide minerals and their distribution within the Cr deficient tailings from Rhovan Operations. The microphotographs were obtained from powder and polished stubs which were prepared as described in section 3.4.1.4. The micrographs are presented in Figure 4.11. Figure 4.11A illustrates the powdered sample viewed under reflected light at 10x magnification and Figure 4.11B illustrates the petrographic characteristics of the polished stub. As discussed in section 4.4.1.2, the predominant mineral phases present in the MT are spinel and plagioclase, with trace amounts of chlorite, dolomite and clay minerals. Figure 4.11A illustrates the presence of spinel and other dark coloured minerals such as amphibole and pyroxene in a matrix of translucent and yellow crystals. The translucent and yellow crystals indicate the high abundance of silicate minerals. Under reflected light, the silicate mineral phases appear in different shades of grey. From Figure 4.11B, it is evident that the MT is dominated by silicate and spinel mineral phases. The isotropic nature of spinel mineral phase is evident as light grey anhedral crystals (blue arrows).

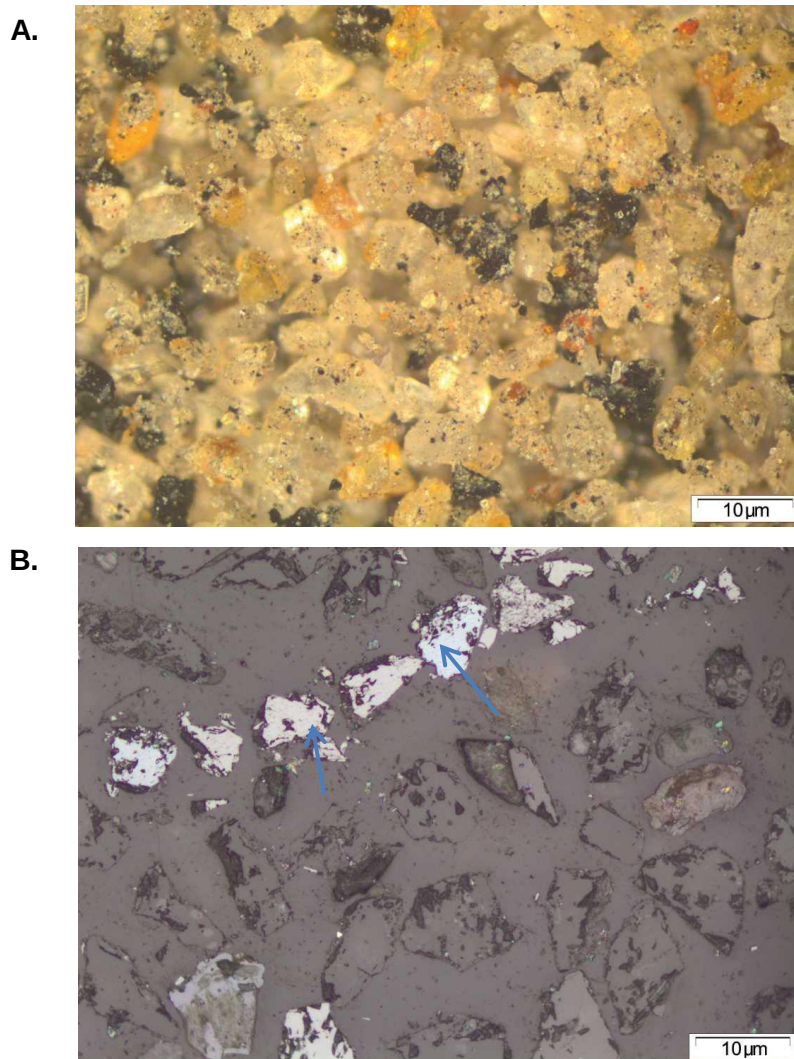


Figure 4.11. Optical micrographs of the mine tailings sampled from Rhovan Operations tailings storage facility (TSF). (A.) visible light at 10x magnification and (B.) reflected light at 20x magnification. Blue arrows indicate to particles comprised of spinel mineral phases.

4.2.1.5 FE-SEM

FE-SEM was used to obtain information on the morphology and surface features of the Cr depleted tailings sampled from Rhovan Operations. The MT (Cr depleted) displays similar characteristic features observed for MT from Two Rivers. The MT (Cr depleted) comprises of large anhedral to massive particles surrounded by smaller particles which indicate a non-uniform grain size (Figures 4.12A, 4.12B, 4.12C, and 4.12D). Figures 4.12E and 4.12F indicate that the very fine particles appear as agglomerates on the surface of the larger particles. The angular morphology is consistent with the MT from Two Rivers and the crushed chromite studied by (Zhao et al., (2014).

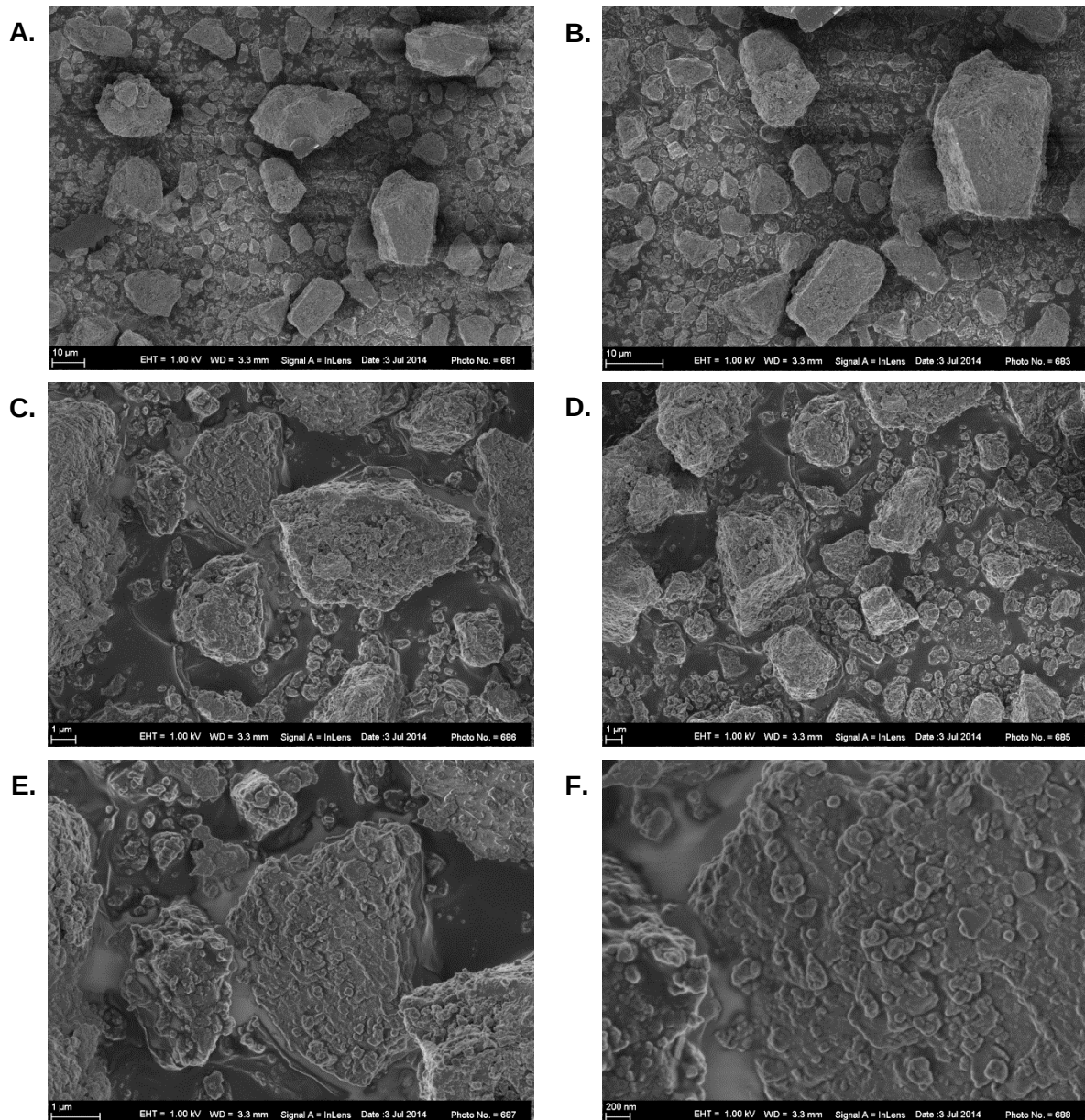


Figure 4.12. FE-SEM micrographs of the MT sampled from Rhovan Operations tailings storage facility (TSF). The micrographs were taken at (A.) 2 000x, (B.) 3 500x, (C) 15 000x, (D.) 10 000x, (E.) 30 000x and (F.) 75 000x magnifications.

4.3 Implications of tailings mineralogy on major element extraction

The qualitative and quantitative mineralogy information gathered on the various tailings indicated mineralogical variations between samples. The variation may be due to the Run-of-mine (RoM) lithology and the distribution of major elements within the different mineral phases which has implications for their recovery in processing. The RoM lithology is generally characterised by one rock type with a varying mineralogical composition, generally determined by abundance and average grade. Localized mineralogical variation in lithology of the BIC determines the mineralogical proportions of mineral phases present in the resulting tailings. Conventional rock names and associated minerals are summarized in Table 2.4.

4.3.2.1. Local variation in lithology

In summary, tailings from Two Rivers and Amandelbult were derived from the mining of the UG2 and/or the Merensky Reef which lies within the Upper Critical Zone comprised of cyclic units of harzburgite – pyroxenite - norite rocks types and consistent with orthopyroxene, plagioclase, chromite and olivine. The major lithological variations along the Merensky Reef in the western limb of the BIC represent a change from a harzburgitic rock-type in the north to a pyroxenetic rock-type further south and, finally a noritic rock-type further southeast (Vogeli *et al.*, 2011). The UG2 chromitite is generally characterized by two or three layers containing intervening silicate rock lenses which are relatively consistent throughout the BIC. The upper layer (termed the UG3 chromitite) is distinctly defined by a significant thickness of silicate rocks from the UG2 in the northeastern region. The variation in thickness of the chromitite layer and the absence of a pyroxenite-norite-anorthosite cyclical unit is however restricted to the northeastern region of the BIC (Cawthorn, 2011). The variation in the tailings mineralogy reported for Amandelbult and Two Rivers is consistent with the mining of both, Merensky and UG2 which is denoted by a high modal abundance of plagioclase (4.0 – 40.0 wt.%), pyroxenes (27.8 wt.%; Two Rivers) and spinel (14.0 – 79.0 wt.%) mineral phases (Table 4.6) typically associated with orthopyroxenite and noritic-leuconorite lithology. The tailings from Marico Chrome were derived from the chromite layers within the Lower Zone which also originate from a harzburgite-noritic rock type with olivine and orthopyroxene present as the predominant mineral phases. In general Marico Chromite's are characterized by high Cr₂O₃ content, High Cr:Fe ratios and low modal abundance of magnetite (McEwan *et al.*, 2011). These mineralogical and chemical characteristics are evident in the tailings sampled. The tailings are generally depleted in Cr (0.8 – 1.1 wt. % Cr) due to the additional recovery of Cr at the operation. The high modal abundance of spinel (11.0 – 75 wt. %) and talc (5.0 - 23.0 wt. %; Table 4.6) is consistent with the harzburgite lithology. Tailings from Rhovan Operation which were processed for Cr recovery, originate from the Upper Zone which is characteristic of Fe-rich gabbroic rocks with a high S content. The main mineral phases include Fe-rich clinopyroxene, Fe-rich olivine, plagioclase, alkali feldspar, magnetite and apatite. The high modal abundance of Fe₂O₃ (24.0 - 27.1 wt.%) in the Rhovan Operations tailings are consistent with an Fe-rich ore predominantly composed of spinel (11.0 – 59 wt.%), plagioclase (24.0 - 65 wt. %) and minor amounts pyroxene (Table 4.7) mineral phases.

4.3.2.2. Variation in the RoM tailings mineralogy

The Two Rivers tailings are predominantly comprised of chromite/magnetite/spinel, orthopyroxene and plagioclase, compared to those from Amandelbult, Marico Chrome and Rhovan Operations which contain a higher modal abundance of chromite/magnetite/spinel and plagioclase and lesser amounts of orthopyroxene. The lower modal abundance of amphibole, mica and alteration minerals talc, chlorite and carbonate is observed for all tailings (Table 4.6). The observed mineralogy for the tailings is consistent with the mineral phases present in the various lithologies described previously; however, the absence of olivine mineral phases indicated that the RoM lithologies may be confined to the orthopyroxenites, chromitite, norite and gabbroite rock sequences for Two Rivers, Amandelbult, Rhovan and Marico Chrome mining operations.

4.3.2.3. Factors of importance for successful elemental extraction

The intrinsic properties of minerals contained in the tailings, which may influence their reactivity in the thermochemical treatment under development, include the presence of cumulus mineral phases (minerals which formed first are generally larger with well-formed crystal shapes) throughout the rock sequence and the varying degree of solid-solution and coexisting nature the major elements which is summarized in Table 4.8. The general decreasing trend in the modal abundance of Cr_2O_3 and Al_2O_3 with stratigraphic height produces variation in the Cr:Fe ratio (McEwan *et al.*, 2011). This in combination with the Mg number (mg#, expressed as a percentage), calculated based on the atomic ratio $\text{Mg}/(\text{Mg}+\text{Fe})$ (Figure 2.4) indicates the variability in the extent of solid solution between Cr, Al, Fe, Mg within the mineral phases. The high modal abundance of Fe in the Rhovan Operations tailings (24.0 - 27.1 wt. %) confirms the presence of Fe-rich mineral phases further confirmed by a low mg# of 30-60 compared to Two Rivers (23.3 wt. % Fe), Amandelbult (12.3 – 21.3 wt. % Fe) and Marico Chrome (11.3 -19.9 wt. % Fe) which have a higher mg# numbers, 75-89 (Figure 2.4).

These properties confirm the variation observed in the bulk chemistry and mineralogy between the different tailings and demonstrate that the major elements are spread amongst different mineral species. The reactivity of the mineral phases present in the tailings is a controlling-factor for the extraction of the major elements and should ideally follow the activity series of metals, i.e. $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Al}^{3+} > \text{Cr}^{2+} > \text{Fe}^{2+}$, however that would assume a natural system which is not applicable in this case where Fe is the preferred element for extraction. The coexisting nature and strong chemical affinity of Ca^{2+} , Mg^{2+} , Al^{3+} , Cr^{2+} and Fe^{2+} for ammonium sulphate (AS) (Bayer *et al.*, 1982; Nagaishi *et al.*, 1984) may hinder preferential elemental extraction of e.g. Fe. The presence of carbonates may also have a negative effect on the extraction efficiency of e.g. Fe, due to the low decomposition temperature of carbonate (CO_3) and the expected strong chemical affinity of Ca for AS during thermochemical treatment. The extent of the mineralogical analysis did not consider the determination of the mineral associations of the Fe at this stage. It is envisaged that the Fe is trapped within various silicate and oxide mineral phases however a more detailed characterization will need to be done to confirm this. This may include a bulk mineralogical analysis (BMA) and particle map analysis (PMA) using QEMSCAN. A detailed description of the required mineralogical characterization will be discussed in Chapter 6.

Table. 4.8. Summary of mineral phases present in the Bushveld Igneous Complex and identified by XRD for tailings sampled from Two Rivers, Amandelbult, Rhovan Operations and Marico Chrome (compiled using data from Tables 4.6 – 4.7 and Eales, 2014). One cross and two crosses were used to provide a qualitative appreciation of the abundance of minerals present in the tailings (the greater the number of crosses reported, the most abundant the minerals).

Mineral group	End-member	Formula	Two Rivers	Amandelbult	Rhovan Operations	Marico Chrome
olivine	fayalite	$\text{Fe}^{2+}_2(\text{SiO}_4)$				
	forsterite	$\text{Mg}_2(\text{SiO}_4)$				
pyroxene	orthopyroxene	$(\text{Mg,Fe})\text{SiO}_3$	XX		X	
	clinopyroxene	$\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$				
feldspars	anorthite	$\text{CaAlSi}_2\text{O}_8$				
	albite	$\text{NaAlSi}_3\text{O}_8$	XX	XX	XX	XX
	orthoclase/microcline	KAlSi_3O_8				
amphiboles	hornblende	$\text{Ca}_2((\text{Fe}^{2+}, \text{Mg}^{2+})_4\text{Al})(\text{Si}_7\text{Al})\text{O}_{22}(\text{OH})_2$	X	X	X	X
micas		$\text{KMg}_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$	X	X	X	X
	muscovite	$\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$				
spinel	magnetite	$\text{Fe}^{2+}\text{OFe}^{3+}_2\text{O}_3$	XX	XX	XX	XX
	chromite	$(\text{Mg, Fe})\text{O}(\text{Cr, Al, Fe})_2\text{O}_3$				
quartz		SiO_2				
apatite		$\text{PCaO}_3(\text{P}_2\text{O}_5)\text{CaF}_2$				
sulphides	pyrite	FeS_2				
	chalcopyrite	CuFeS_2				
	pentlandite	$(\text{Fe, Ni})_9\text{S}_8$				
	pyrrhotite	Fe_7S_8				
calcite/ dolomite		$(\text{Ca, Mg})(\text{CO}_3)_2$	X	XX	X	X
chlorite		$(\text{Mg}_5\text{Al})(\text{Si, Al})_4\text{O}_{10}(\text{OH})_8$	X	X	X	X
talc/ pyrophyllite		$\text{Mg}_3(\text{OH})_2\text{Si}_4\text{O}_{10}$	X	X	X	XX
smectite	montmorillonite	$(\text{Na, Ca})_{0.3}(\text{Al, Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$		X		XX

In summary, the characterisation of PGE tailings has shown that the physicochemical properties of the PGE's tailings utilised in this study are consistent with the other PGE tailings from the Bushveld Igneous Complex. The PGE mine tailings comprise of silicates and aluminosilicates with various compositions. The primary gangue and host rock minerals are generally unaltered and the most abundant mineral phases include spinel, plagioclase, enstatite and amphiboles. The chemical composition of the various tailings is similar, with relatively high concentrations of Fe, Mg, Al, and or Cr, consistent with the presence of a solid-solution series between the elements in more than one mineral phase. Particle size analysis confirmed the fine grained nature of the tailings and the angular grain morphology in the tailings is consistent with the size reduction achieved by multiple comminution processes required for the liberation of PGE's. The variability of the bulk elemental compositions and mineralogy of the MT are expected to have a direct effect on the elemental extraction efficiency investigated in the process under development in this study. The results of the thermochemical treatment and various dissolution experiments will be discussed in the following chapter.

Chapter Five - Results and Discussion

Characterisation of thermochemically-treated MT_{45-75} (i.e. MT_{r0}) and findings resulting from the aqueous dissolution of MT_{r0} are presented, with a focus on the extraction efficiency of iron and other major elements. The extent of extraction, limiting factors and implications for the preferential extraction of iron are discussed.

5.1 Case Study No 1: Two Rivers mine tailings

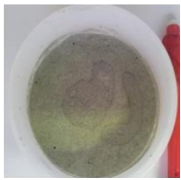
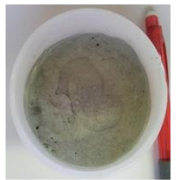
5.1.1 Thermochemical treatment of tailings using ammonium sulphate, $(NH_4)_2SO_4$

5.1.1.1 Preliminary static furnace experiments

In a preliminary set of experiments, the thermochemical treatment of MT_{45-75} using AS was investigated under varying temperature conditions to get a first glimpse at the mineralogical changes taking place and at which temperature they occur. The purpose of this qualitative assessment was to select a treatment temperature, which was then used to develop and optimise the subsequent dissolution step. This approach was essential since an optimal dissolution process is required to assess the efficiency of the thermochemical treatment of MT_{45-75} . Temperatures ranging between 350 °C - 550 °C were used, based on the experimental findings of Bayer *et al.*, (1982) and thermodynamic stability modelling reported by Nduagu *et al.*, (2012), who focused on the reaction between AS and kaolinite, (Mg-) silicates and metal oxides from ambient temperature up to 800 °C. Changes in colour between MT_{45-75} and MT_{r0} , and mass losses observed following thermochemical treatment of MT_{45-75} are presented in Table 5.1.

Table 5.1. Photographs depicting changes in colour and percentage (%) mass loss of MT₄₅₋₇₅ - AS reaction mixture following thermochemical treatment ((B); MT₄₅₋₇₅: AS of 2:6; 45 minutes) between 350 °C and 550 °C. (*n*=4; Photographs of untreated MT₄₅₋₇₅ and MT₄₅₋₇₅ mixed with AS are also reported (A)).

A.	Untreated tailings	
	MT ₄₅₋₇₅	MT ₄₅₋₇₅ :AS of 2:6
		

B.	Temperature of thermochemical treatment (°C)				
	350	400	450	500	550
					
	Observed weight loss (%)				
	14.3 ± 1.3	28.9 ± 0.7	59.9 ± 0.3	62.2 ± 0.5	66.3 ± 0.2

Untreated MT₄₅₋₇₅ was dark grey in colour and was a free-flowing powder. Upon mixing MT₄₅₋₇₅ with AS, MT₄₅₋₇₅ remained partially segregated from AS due to the difference in particle size and density between the two materials. However, great care was taken to follow an identical, thorough mixing procedure for all experiments. As soon as the mixture was carefully homogenised, it appeared light grey in colour because of the white colour of AS. MT_{ro} which was formed at ≤ 400 °C exhibited a molten, viscous-like green appearance when hot, immediately upon removal from the furnace. Upon cooling the reaction product hardened to resemble solid glassy blocks, which had ‘fused’ to the walls of the crucible; this made the recovery process of the product challenging. At these temperatures, the products did not consist of free-flowing powders. At higher temperatures (≥ 450 °C), MT_{ro} were light grey in colour, while also exhibiting a green hue, and they consisted of free-flowing powders. The mass loss following treatment increased with increasing temperature. The mineralogical transformations of part of the structure of MT₄₅₋₇₅ into soluble metal-sulphates during the thermochemical treatment was temperature-dependent, as is the case when serpentinite rocks are subjected to a similar treatment (Nduagu *et al.*, 2012), but this increase in mass loss with increasing temperature was also most probably related to the thermal decomposition of AS.

XRD was used to identify the occurrence of newly-formed mineral phases following thermochemical treatment (Table 5.2). This exercise was purely qualitative, and no attempt to quantify the minerals present was made at this stage.

The mineralogical composition of MT_{ro} produced at temperatures below 550 °C was dominated by ammonium-metal sulphate-based compounds (NH₄⁺-M-SO₄²⁻) as newly-

formed minerals; this was the first indication of a reaction between AS and some of the primary mineral phases present in the mine tailings. In contrast, much less $\text{NH}_4^+ \text{-M-SO}_4^{2-}$ phases were identified in the samples generated at 550 °C and they did not represent the bulk of their composition. At this temperature, the samples were dominated by iron sulphate ($\text{Fe}_2(\text{SO}_4)_3$; identified as mikasaite by the XRD database), which represent the species one can generate with the most iron in its structure. $\text{Fe}_2(\text{SO}_4)_3$ was also identified in the sample generated at 500 °C, but it represented a much smaller proportion of the sample than at 550 °C; it was not identified in the samples generated at lower temperatures. These findings suggested that a temperature of 550°C had facilitated the extraction of Fe to a greater extent, when compared to the lower temperatures. The co-existence of chromium sulphate, $\text{Cr}_2(\text{SO}_4)_3$, with $\text{Fe}_2(\text{SO}_4)_3$ in the samples generated at 550 °C indicated the possible occurrence of competitive reactions between iron and chromium for AS during thermochemical treatment.

At 350 °C and 400 °C, ammonium bisulphate (NH_4HSO_4) was identified. This indicated the partial thermal decomposition of AS, and the incomplete reaction of AS and/or its decomposition products with MT_{45-75} over the duration of the experiment. It also explained the observed hardness of the samples generated at these lower temperatures upon cooling. This species was not identified at higher temperatures.

Table 5.2. Mineralogical composition of MT₄₅₋₇₅ and MT_{r0} (MT₄₅₋₇₅: AS of 2:6; 45 minutes) produced at 350 °C to 550 °C. Main newly-formed phases identified are in bold. No further attempt was made to quantify the primary mineral phases present in MT_{r0}. One cross and two crosses were used to provide a qualitative appreciation of the abundance of newly-formed minerals present in the samples (the greater the number of crosses reported, the most abundant the minerals).

MT ₄₅₋₇₅			MT _{ro}				
untreated			350°C	400°C	450°C	500°C	550°C
Calcite	CaCO ₃	2.4					
Magnetite/Chromite/ Spinel	Fe ²⁺ Fe ³⁺ ₂ O ₄ /Fe ²⁺ Cr ₂ O ₄ /MgAl ₂ O ₄	29.5					
Clinopyroxene – Augite	(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al) ₂ O ₆	1.7					
Orthopyroxene – Enstatite	Mg ₂ Si ₂ O ₆	27.8					
Plagioclase	(Na,Ca)(Si,Al) ₄ O ₈	25.2					
Chlorite	(Mg ₅ Al)(Si,Al) ₄ O ₁₀ (OH) ₈	3.1					
Serpentine – Lizardite	Mg ₃ Si ₂ O ₅ (OH) ₄	trace					
Amphibole – Hornblende	Ca ₂ [Mg ₄ (Al,Fe ³⁺)]Si ₇ AlO ₂₂ (OH) ₂	7.9					
Talc	Mg ₃ (OH) ₂ Si ₄ O ₁₀	1.0					
Mica – Biotite	KFeMg ₂ (AlSi ₃ O ₁₀)(OH) ₂	1.6					
Iron sulphate (Mikasaite)	Fe₂(SO₄)₃					X	XX
Chromium sulphate	Cr₂(SO₄)₃					X	X
Iron sulphate hydrate (Roemerite)	FeFe ₂ (SO ₄) ₄ (H ₂ O) ₁₄				X	X	X
Ammonium aluminium sulphate	NH ₄ Al(SO ₄) ₂			XX	XX	XX	X
Ammonium magnesium sulphate hydrate (Boussingaultite)	(NH ₄) ₂ Mg(SO ₄) ₂ ·6 H ₂ O			X			
Ammonium chromium sulphate	(NH ₄) ₂ (Cr(H ₂ O) ₆)(SO ₄) ₂						trace
Ammonium chromium sulphate hydrate	(NH ₄) ₂ (Cr(H ₂ O) ₆)(SO ₄) ₂		X				
Ammonium iron sulphate hydrate (Mohrite)	(NH ₄) ₂ Fe ⁺² (SO ₄) ₂ ·6H ₂ O		XX	X			
Unidentified species			X	X	X	X	X
Ammonium hydrogen sulphate	NH ₄ HSO ₄		XX	XX			

Results from the XRD structural refinement for MT_{r0} produced between 450 °C to 550 °C have reported that MT_{r0} matches the mikasaite crystal structure. Mikasaite is a rare Fe-rich sulphate analogous to millosevichite (Al₂(SO₄)₃). The natural form of the mikasaite mineral has an ideal formula of Fe₂(SO₄)₃; however it has been found that Fe can be replaced by Al, Mn (Miura *et al.*, 1994) and Cr. Mikasaite is formed from a hexagonal unit cell structure which comprises of pinwheels linked in three-dimensions whereby the octahedron shares its corners with the SO₄ tetrahedron forming layers (Hawthorne, 2000).

Results from the preliminary static furnace experiments have suggested that AS may be a promising chemical agent to transform metal oxides/silicate minerals contained in PGE mine tailings into ammonium-metal-sulphate based compounds. The reaction between MT and AS is strongly temperature-dependent and results in the formation of stable ammonium-metal sulphates (350-500 °C) and metal sulphates (550 °C). The stable metal sulphate species formed at 550 °C might depict isomorphic substitution within a hexagonal crystal system. Isomorphic substitution of Al, Ca, Cr and Mg for Fe during the thermochemical treatment may potentially be a limiting factor for the preferential extraction of Fe. This was studied in greater detail.

5.1.2 Preliminary *in situ* TGA experiments

5.1.2.1 Preliminary *in situ* TGA and TGA-FTIR experiments under dynamic temperature conditions

5.1.2.1.1 TGA

TGA was conducted on MT₄₅₋₇₅, AS and a 2:6 MT₄₅₋₇₅ – AS mixture in order to better understand the effect of thermal treatment on these samples. TGA and DTA curves of MT₄₅₋₇₅ and AS are illustrated in Figures 5.1 and 5.2 respectively.

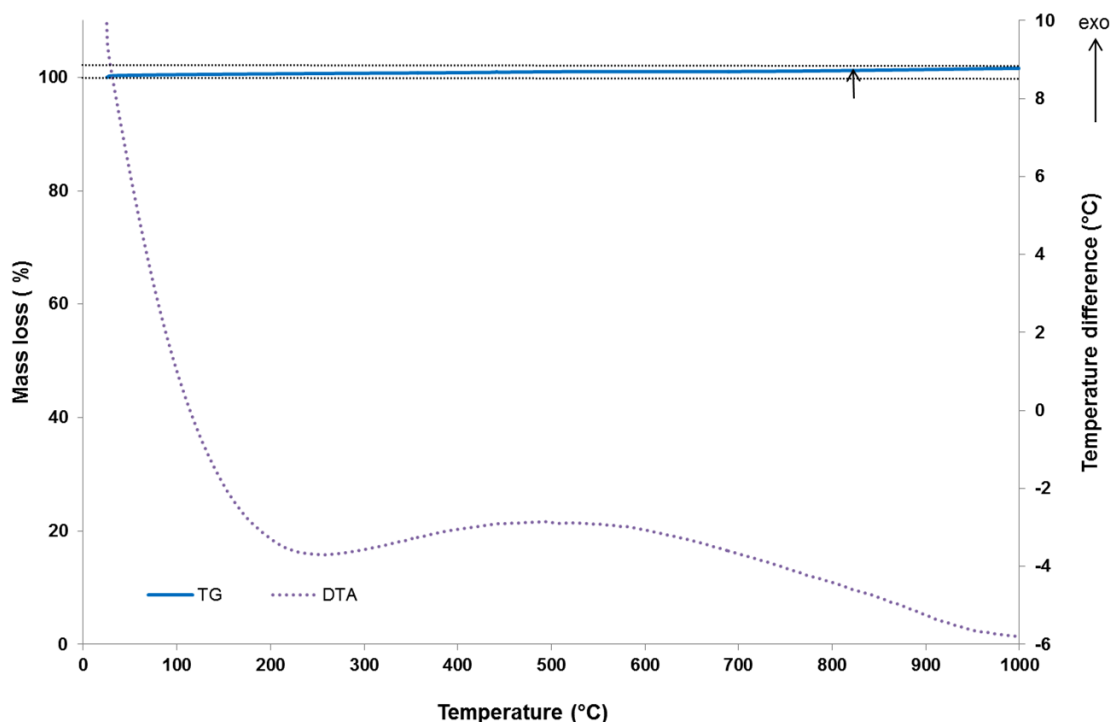


Figure 5.1. TGA (blue line) and DTA (purple dotted line) curves of MT₄₅₋₇₅ heated under dynamic temperature conditions (heating rate of 10 °C per minute in air; $n=2$).

The thermal decomposition of MT₄₅₋₇₅ and AS produced significantly different TGA profiles (Figures 5.1 and 5.2). The thermogram of MT₄₅₋₇₅ was essentially constant with no distinctive events identified over the duration of the heating program. This indicated that the mineral phases present in MT₄₅₋₇₅ are thermally stable up to 1000 °C. No information regarding solid phase transitions or release of volatiles could be obtained. However, a mass gain of 1.6 % was observed (indicated by arrow) and may be attributed to the oxidation of Fe. As discussed in section 4.1.1.2, negative LOI values are common for Fe-rich minerals and this confirms the negative LOI result which was reported by XRF.

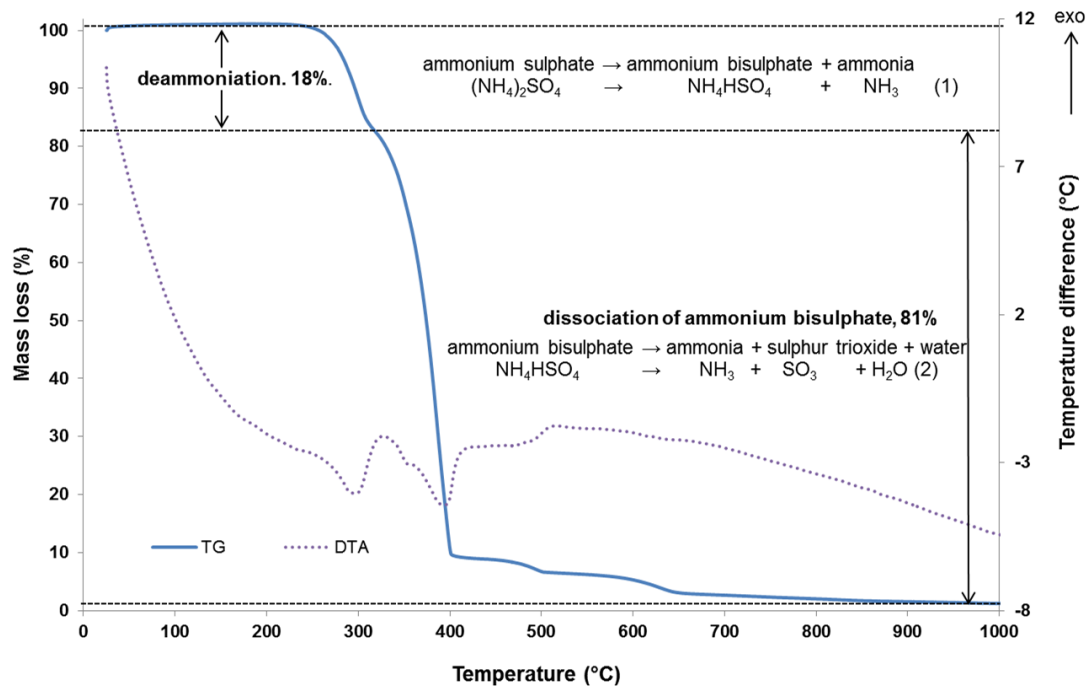
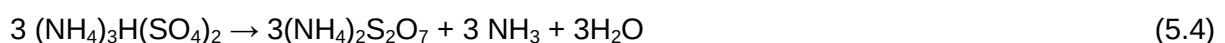


Figure 5.2. TGA (blue line) and DTA (purple dotted line) curves of AS heated under dynamic temperature conditions (heating rate of 10 °C per minute in air; $n=2$).

The thermal decomposition mechanisms of AS are well known (Bayer *et al.*, (1982); Erdey *et al.*, (1964); Halstead, (1970); Highfield *et al.*, (2012); Kiyoura *et al.*, (1970); Nakamura *et al.*, (1980); Pelovski *et al.*, (2003); Song *et al.*, (2013)) and comprises of three stages of decomposition. The first stage of decomposition is the process of deammoniation from 200 °C, which corresponds to the loss of ammonia and the formation of ammonium bisulphate and/or triammonium bisulphate (equations 5.1 - 5.3), followed by the decomposition of ammonium bisulphate into ammonium pyrosulphate which starts from approximately 350 °C (equation 5.4), and decomposition of ammonium pyrosulphate and the remaining AS into gaseous decomposition products (equations 5.5 and 5.6).





The thermogram for AS is presented in Figure 5.2 and only indicates two mass loss transitions in the region 200 °C – 500 °C. The DTA curve indicated the occurrence of four different transitions in the same temperature range. The theoretical mass loss for the deammoniation step is 12.9 % and 77.1 % for the dissociation of NH_4HSO_4 . The observed mass loss is 18 % and 81 % for the two steps respectively.

The solid-solid reaction between AS and MT_{45-75} was studied *in situ* under dynamic thermal conditions as described in section 3.3.1.2. The corresponding TGA and DTA curves (green curve) are presented in Figure 5.3. The TGA and DTA results for AS and MT_{45-75} are also included for reference. The TGA curve for the reaction mixture conforms to the shape of AS decomposition, however an increase in the temperature range observed for the AS decomposition (shown by results from both TGA and DTA) indicate changes in the thermodynamics of this reaction. This result can possibly be ascribed to the stabilization of AS due to formation of sulphate species through the solid-state reaction with the tailings. A broad asymmetric exothermic peak was observed in the DTA curve (dotted green curve) of the mixture between 450 °C and 510 °C, which may indicate the solid phase transition into (ammonium)-metal sulphate based compounds.

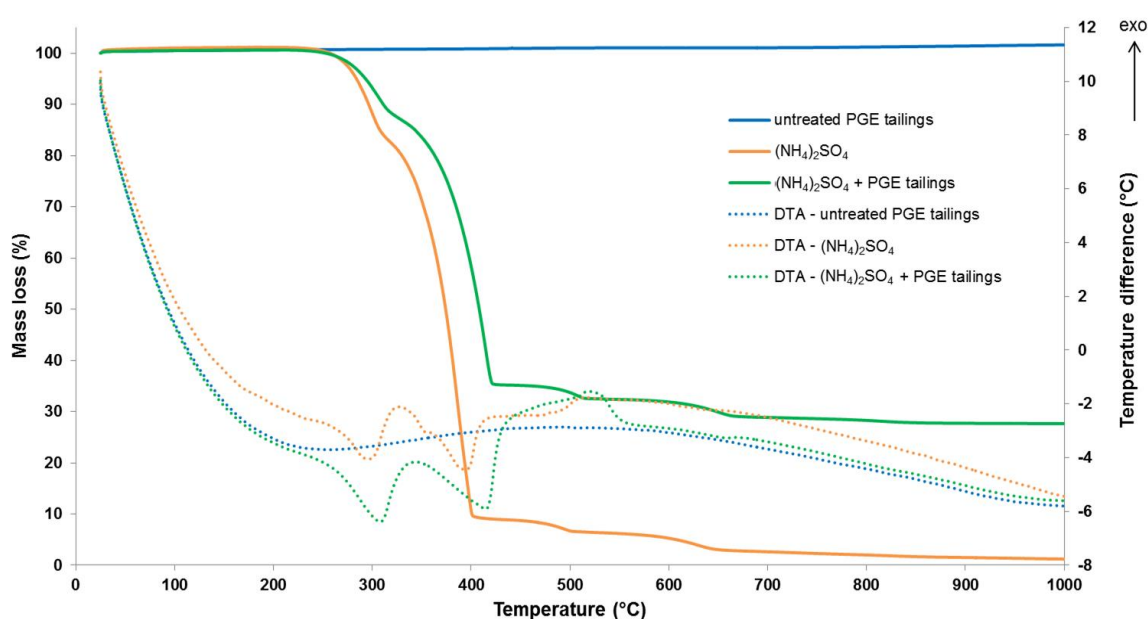


Figure 5.3. Comparative TGA and DTA (dotted line) curves of MT_{45-75} (blue), AS (orange) and a 2:6 mixture of MT_{45-75} and AS (green) under dynamic temperature conditions (heating rate of 10 °C per minute in air; $n=2$).

5.1.2.1.2 TGA-FTIR

TGA-FTIR analysis was conducted during thermochemical treatment of MT₄₅₋₇₅ and AS in an attempt to complement the XRD data and to gain a better understanding of the chemical composition of the newly-formed phases. Due to the incapability of the instrument to insert the sample at temperatures above ambient temperature, the evolved gas products formed under static temperature conditions could not be studied. However, under dynamic temperature change, chemical changes can be observed by following the sequence of the thermal reactions and may provide qualitative data of the products formed during thermochemical treatment. The IR spectra were recorded continuously, therefore making it possible to evaluate the characteristic absorption band over temperature as a function of time. The TGA-FTIR analyses were conducted as described in section 3.5.1.8 and the IR spectra of the reaction between MT₄₅₋₇₅ and AS are presented in Figure 5.4. Collected IR spectra were compared to reference spectra (ammonia (NIST, 2014a); water (H₂O;NIST, 2014b); carbon dioxide (CO₂; NIST, 2014c); sulphur dioxide (SO₂;NIST, 2014d); sulphur trioxide (SO₃;NIST, 2014e); nitric oxide (NO;NIST,2015a) and nitrogen dioxide (NO₂;NIST,2015b)) obtained from the National Institute of Standards and Technology (NIST) Chemistry Web Book and AS aerosol obtained from Cziczo *et al.*, (1997).

The FTIR data confirmed the XRD results (Table 5.2) and graphically illustrated the phase transformations which occurred during thermochemical treatment. According to the decomposition reaction of AS and the results obtained from TGA (Figure 5.2), NH₃ should be released as the first decomposition product during the solid-solid reaction and this result is confirmed by “*spectrum a*” whereby the sharp peaks between 900 – 1000 cm⁻¹ (green asterisks) correspond to the reference spectrum of NH₃. “*Spectrum b*” indicated the simultaneous release of NH₃ (green asterisks) and CO₂ centered around 2400 cm⁻¹ (pink asterisks). The peaks observed between 2800 – 3300 cm⁻¹ and additional peaks between 1420 – 1450 cm⁻¹ and around 620 cm⁻¹ (blue asterisks) suggested the presence of AS based aerosol (Badger *et al.*, 2006; Cziczo *et al.*, 1997) which may have formed due to the rapid heating rate of the experiment. Further studies will be required to confirm this observation. “*Spectrum c*” indicated the continued release of NH₃ (green asterisks), CO₂ (pink asterisks) and AS (blue asterisks) in the form of an aerosol. The additional “split-peak” centered between 1230 – 1010 cm⁻¹ correlate to the release of SO₂ (purple asterisks) and SO₃ at approximately 1390 cm⁻¹ (orange asterisks; Rawlins *et al.*, 2005) respectively. “*Spectrum d*” indicated that AS is no longer present however NH₃, CO₂ and SO₂ and SO₃ are still released as residual products. This result confirms that no water or NO_x is released during the reaction however, further investigation will be required to confirm the sequence of evolved gas products by decreasing the heating rate sufficiently to allow for gas stabilisation and separation prior to detection.

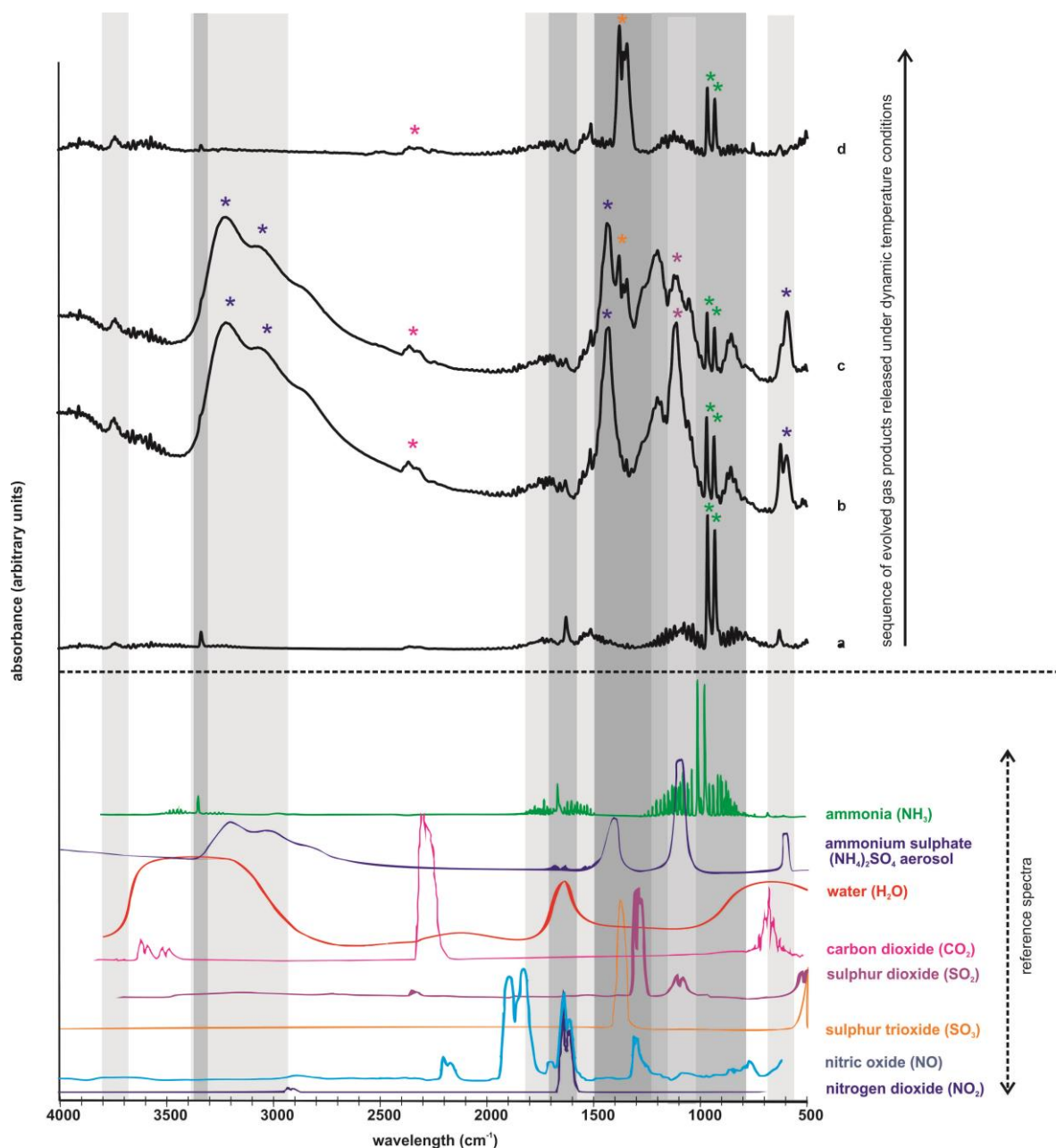


Figure 5.4. Evolved gas products released during the thermochemical treatment of MT₄₅₋₇₅ with AS under dynamic temperature conditions (heating rate of 200 °C per minute in air; $n=2$). Spectra sequence collected after (a) 2.6 minutes (520 °C), (b) 3.0 minutes (600 °C) (c) 3.1 minutes (620 °C) and (d) 3.7 minutes (740 °C).

5.1.2.2 Preliminary *in situ* TGA experiments under static temperature change

TGA was conducted on the reaction mixture between MT₄₅₋₇₅ and AS as described in section 3.3.1.2 in an attempt to understand the thermodynamics, phase transformations and evolved gas products formed under static temperature conditions. The TG and DTA curves are presented in Figure 5.5. The TGA curves for the isothermal reaction between MT₄₅₋₇₅ and AS indicate that the reaction mechanisms are different at varying temperatures. The mass loss observed is not in agreement with the static furnace experiments conducted in the

laboratory furnace and may be due to the different physical properties of the MT_{45-75} and AS and the small sample size required for the analysis. The mass loss observed after the 45 minute isothermal reactions at 350 °C (ca. 53 %), 400 °C (ca. 20 %), 450 °C (ca. 2 %), 500 °C (ca. 1 %) and 550 °C (ca. 4 %) is different compared to the static furnace experiments (Table 5.1) which increased from approximately 14 % - 66 % from 350 °C to 550 °C. The sudden mass loss observed at the beginning of the isothermal reactions at 350 °C and 400 °C may be ascribed to the rapid decomposition of AS with an increase in temperature. The sudden mass loss which is not observed for the isothermal reactions between 400 °C and 550 °C indicated that the decomposition of AS has begun prior to the sample pan reaching the balance arm. The sharp endothermic peaks in the DTA curves observed at the end of the isothermal heating programs (45 minutes) indicate a change to the dynamic heating program at a faster heating rate. These results indicate that AS decomposes more rapidly under the set conditions therefore impeding the reaction with the MT_{45-75} during the isothermal heating segment.

The DTA curve for the reaction at 550 °C indicates the presence of an exothermic peak after the static heating program which was also observed during the dynamic heating program (Figure 5.3) and may indicate the solid phase transition into ammonium metal sulphates. The onset of the dynamic heating program (after 45 minutes) is characterized by constant mass followed by smaller step transitions (TGA curves) which may be ascribed to the decomposition of the remaining reagent and/or products formed during the isothermal heating stage. The TGA curves indicate an additional mass loss step above 800 °C which may be attributed to the decomposition of remaining sulphates. The DTA curves indicate the presence of endothermic peaks which coincide with the onset of the mass loss.

Results from the TGA and TGA-FTIR experiments indicate that the thermal instability of $(NH_4)_2SO_4$ controls reaction mechanism between MT_{45-75} and $(NH_4)_2SO_4$. The decomposition reactions for $(NH_4)_2SO_4$ and the interaction with the MT_{45-75} is temperature dependent and results in the formation of ammonium bisulphate below 350 °C and ammonium metal sulphates and metal sulphates above 400 °C.

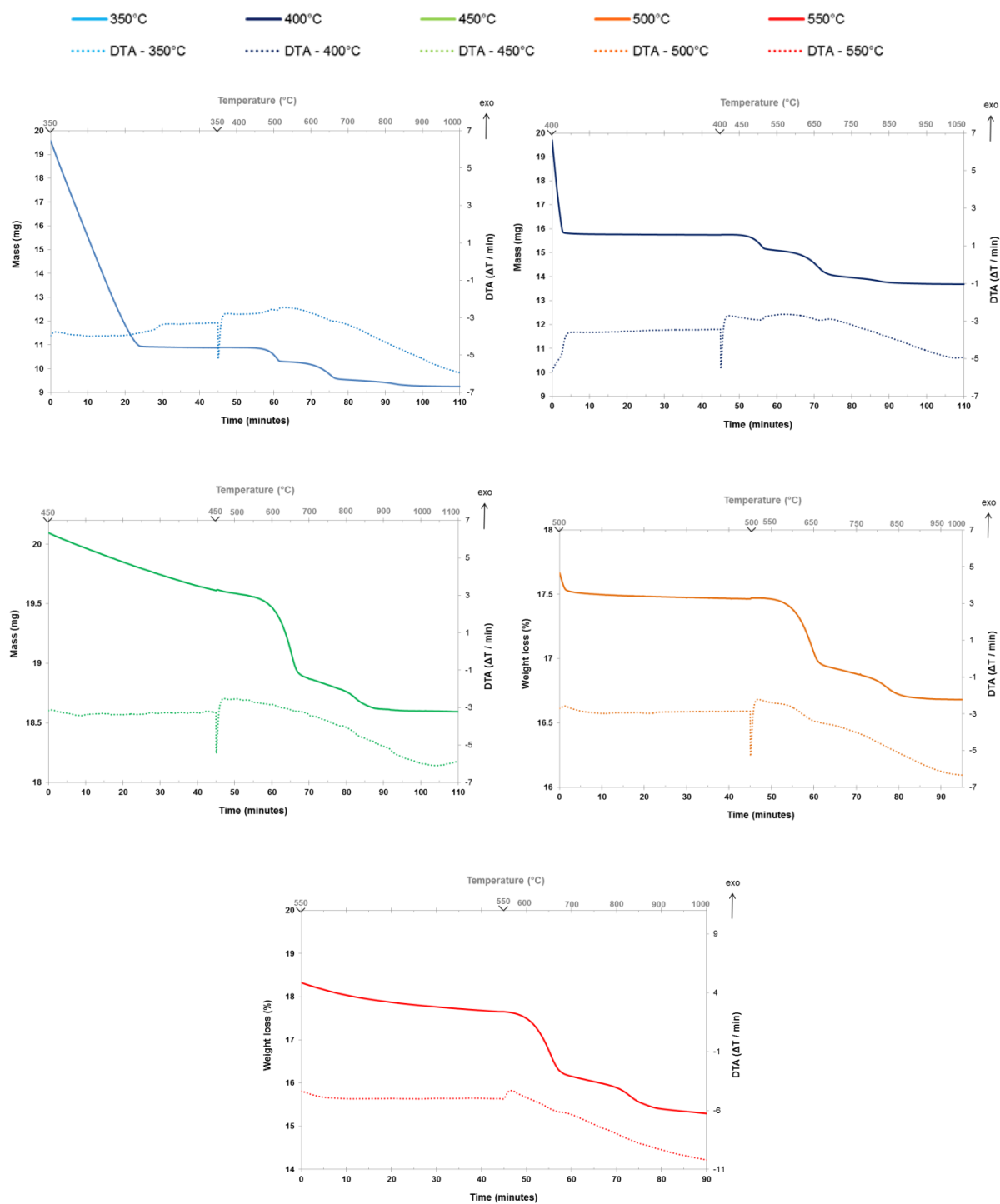


Figure 5.5. TGA (solid lines) and DTA (dashed lines) curves of the isothermal reactions between MT₄₅₋₇₅ and AS (2:6; 45 minutes) between 350 °C – 550 °C followed by a dynamic heating program up to 1000 °C (heating rate of 10 °C per minute in air, $n=2$).

5.1.3 Characterisation of thermochemically-treated mine tailings (MT_{ro})

5.1.3.1 Thermal characteristics of thermochemically-treated mine tailings (MT_{ro})

TGA was used to determine the phase transformations of MT_{ro} to complement the XRD data reported in section 5.1.1.1. The TGA and DTA curves of MT_{ro} produced in the laboratory furnace are presented in Figure 5.6. The TGA curves indicate a different mass loss for each temperature condition and the DTA curves indicates differences in the decomposition mechanisms of the different metal sulphates. Mass losses observed in the temperature range 25 °C – 100 °C were due to dehydration of the samples. MT_{ro} produced at 350 °C and 400 °C in the furnace exhibited a higher degree of hydration than MT_{ro} produced at higher temperatures (450 °C and 550 °C). The formation of ammonium metal sulphates and the presence of ammonium bisulphate at low temperatures (blue curves) was indicated by the loss of NH₃ between 350 °C – 400 °C (confirmed by the endothermic peaks of the DTA curve), followed by dissociation of metal-sulphate phases between 450 °C – 700 °C.

Products formed at 450 °C and above contained very little, if any, NH₃, which was confirmed by the absence of weight loss transitions and endothermic peaks between 350 °C – 400 °C; only the dissociation of metal-sulphate phases was observed between 450 °C – 700 °C. These findings validated the results reported by XRD (Table 5.2) which identified ammonium bisulphate, ammonium metal sulphates and/or metal sulphates as the primary mineral phases present in the MT_{ro} produced at 350 °C – 550 °C.

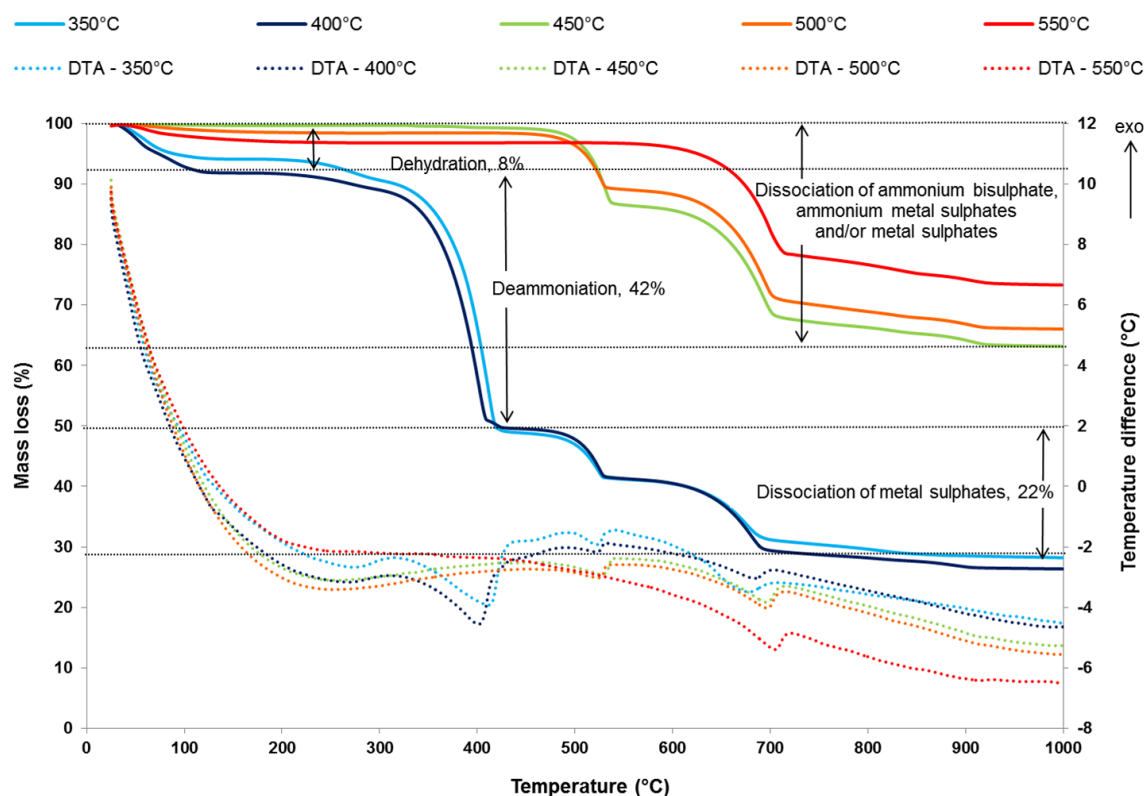


Figure 5.6. TGA (solid lines) and DTA (dashed lines) curves of MT_{ro} formed between 350 °C to 550 °C via thermochemical treatment under static temperature conditions ($n=2$).

The TGA results confirmed that the thermal stability of the reaction products generated following thermochemical treatment of MT_{45-75} at temperatures ranging between 350 °C and 550 °C was different. The newly formed ammonium-metal-sulphate and metal sulphate phases identified by XRD were confirmed from the different decomposition mechanisms of the reaction products.

5.1.3.2 Mineralogical and morphological characteristics of thermochemically-treated mine tailings (MT_{r0})

The optimal preparation of thermochemically-activated tailings containing iron sulphate and/or iron-metal sulphates, without any residual ammonium bisulphate products, was achieved using a 2:6 (m/m) MT_{45-75} :AS ratio, at 550 °C for 45 minutes. Only MT_{r0} prepared under these optimal conditions underwent a detailed characterisation using a range of complementary techniques, which included XRD, SEM, FE-SEM and Raman spectroscopy.

5.1.3.2.1 XRD

XRD analysis was conducted on a new batch of MT_{r0} produced using the optimal thermochemical treatment described above to confirm the presence of the metal-sulphate phases. The XRD diffractograms of untreated MT_{45-75} and generated MT_{r0} are presented in Figure 5.7. Although the primary peaks of enstatite, spinel and amphibole were still present in MT_{r0} , new XRD peaks, indicated by blue asterisks, indicated the occurrence of the so-called mikasaite phase. This indicated the transformation of some mineral phases present in untreated MT_{45-75} into iron-rich sulphates. It also confirmed the XRD results obtained during the preliminary experiment, and this demonstrated the reproducibility of the thermochemical treatment.

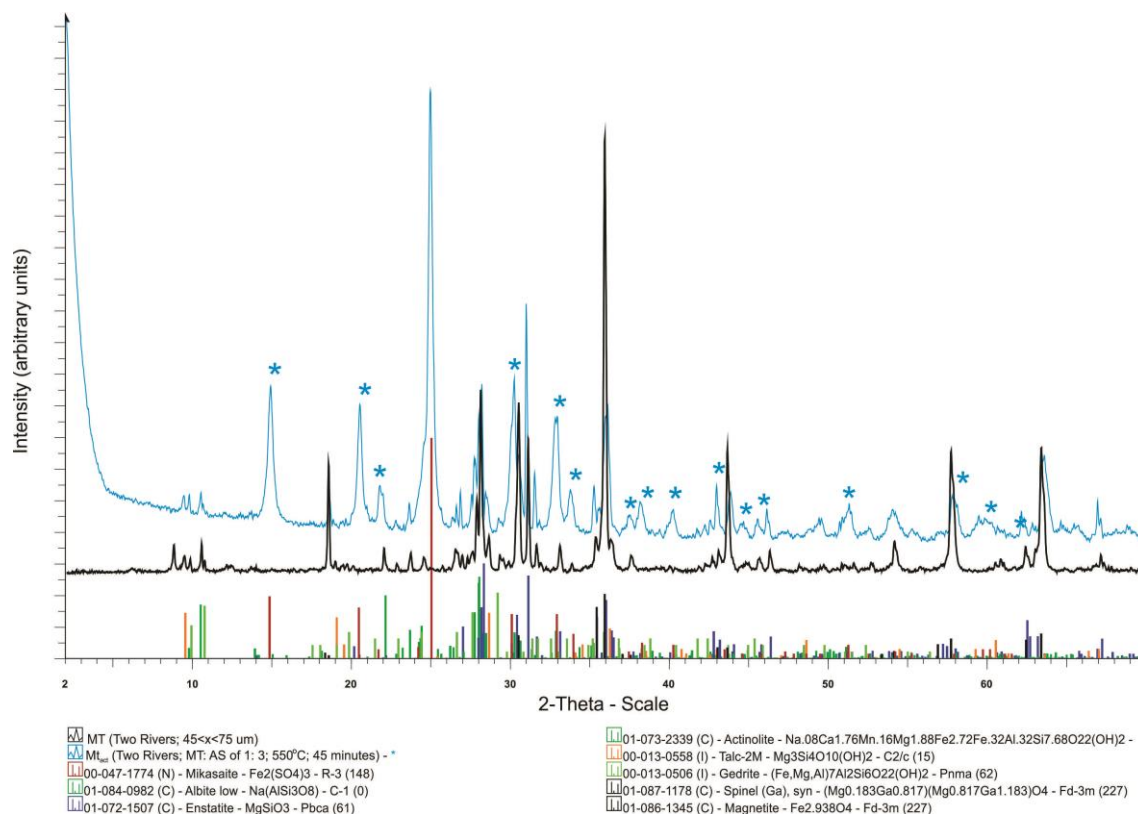


Figure 5.7. XRD diffractograms of untreated MT₄₅₋₇₅ (black) and MT_{ro} (blue) prepared under optimal thermochemical treatment conditions (MT₄₅₋₇₅:AS of 2:6; 550 °C; 45 minutes). Asterisks (*) indicate the diffraction peaks of the Fe₂(SO₄)₃ (mikasaite) mineral phase.

5.1.3.2.2 Raman Spectroscopy

In an additional attempt to identify the newly-formed metal sulphate phases, MT_{ro} was analysed by Raman spectroscopy and its Raman spectrum was compared to those collected for reagent-grade sulphate compounds ((Al₂(SO₄)₃), AS, Cr₂(SO₄)₃·H₂O, Fe₂(SO₄)₃·H₂O, MgSO₄·7H₂O, and MnSO₄·H₂O) which may have been formed during thermochemical treatment. The Raman spectra are presented in Figure 5.8. The Raman spectra of untreated MT₄₅₋₇₅ and AS are included for reference purpose. The Raman spectrum of MT_{ro} contained peaks which corresponded to the active Raman modes of several sulphate compounds. Weak and intense peaks are observed for MT_{ro} in the spectral regions between 150-340 cm⁻¹, 440 - 510 cm⁻¹ and 1059 – 1142 cm⁻¹, which correlate with the active Raman modes for different sulphates, although the peaks characteristic of iron (III) sulphate hydrate were predominant in the spectrum of MT_{ro}. This may indicate that the optimal thermochemical treatment has resulted in the formation of mostly iron sulphate which is probably not pure, but which may rather constitute a solid-solution between Fe (main elements) possibly co-existing with Cr, Al, and Mg in varying proportions, or of several co-existing metal sulphate compounds.

Based on the results obtained by XRD (section 5.1.1.1) the main reported mineral phase should be mikasaite; this was investigated further. A study on ferric sulphates by Ling and Wang (2010) has reported that iron sulphate compounds with varying degrees of hydration have different active Raman modes and can therefore be distinguished from one another.

Majzlan (2010) has reported that Fe^{2+} sulphate mineral phases vary both chemically and structurally and an increase in hydration state will result in the depolymerisation from an anhydrous framework structure to hydrated isolated polyhedra. The increase in hydration varies the O-S-O angle in the SO_4 tetrahedra, creating distortions within the crystal structure. The Raman spectrum of MT_{r0} was compared to the published spectra (Ling and Wang, 2010) of eight different sulphates with varying degrees of hydration (Figure 5.9). The intense peak formed in the spectral region between $1059 - 1142 \text{ cm}^{-1}$ is distinctive of mikasaite (also reported as belonging to the $\text{R}\bar{3}$ space group), where the main peaks correlate with the (ν_1) symmetric stretching mode of the SO_4 tetrahedra. Furthermore, the split of the ν_1 peak into two distinct peaks indicates small distortions of the SO_4 tetrahedra and may be attributed to changes of the angle and/or bond length caused by the isomorphic substitution of elements during the thermochemical treatment.

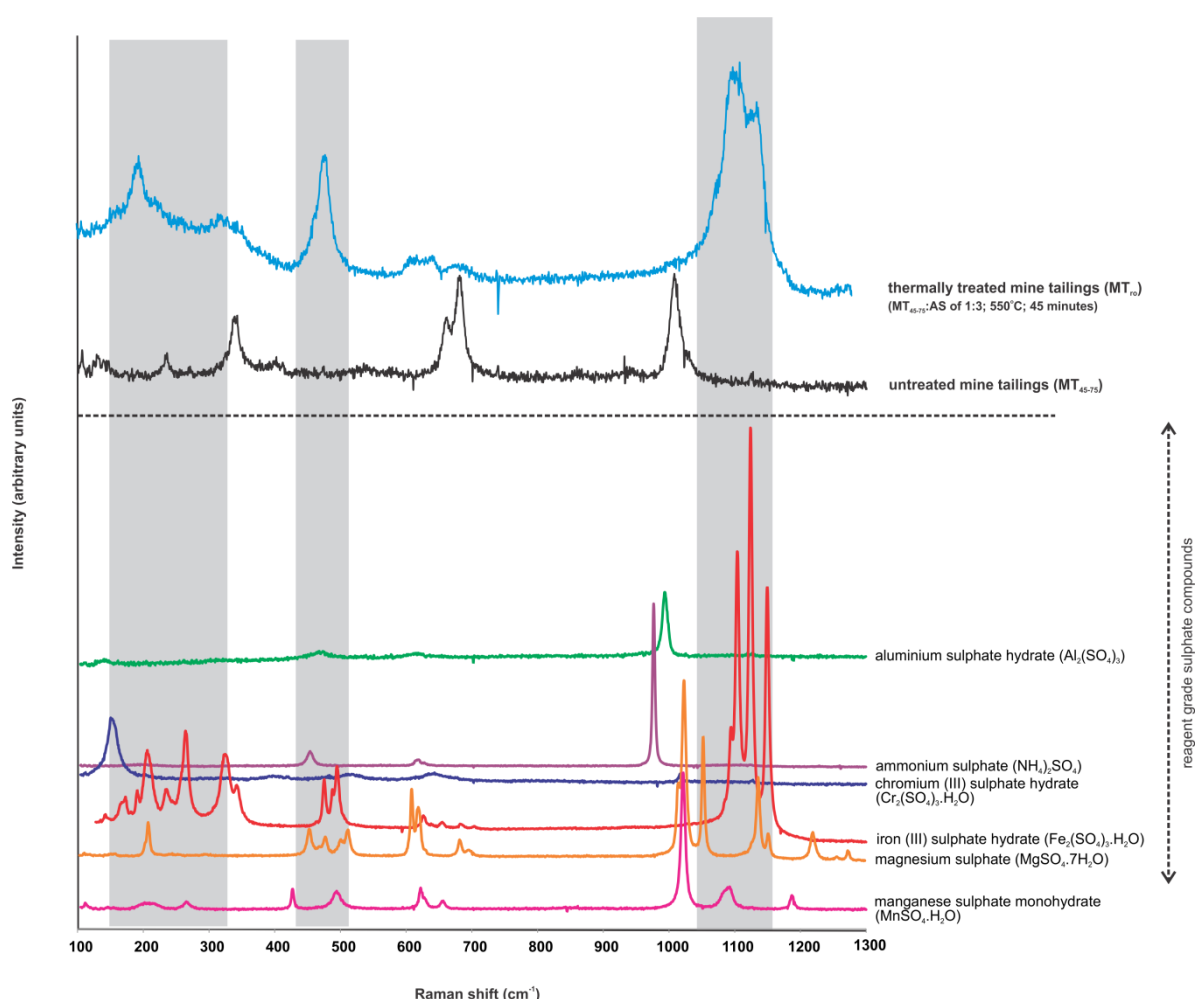


Figure 5.8. Raman spectral analyses of MT_{r0} (MT_{45-75} :AS of 2:6; 550°C ; 45 minutes) compared to Raman spectra obtained for reagent grade sulphate compounds.

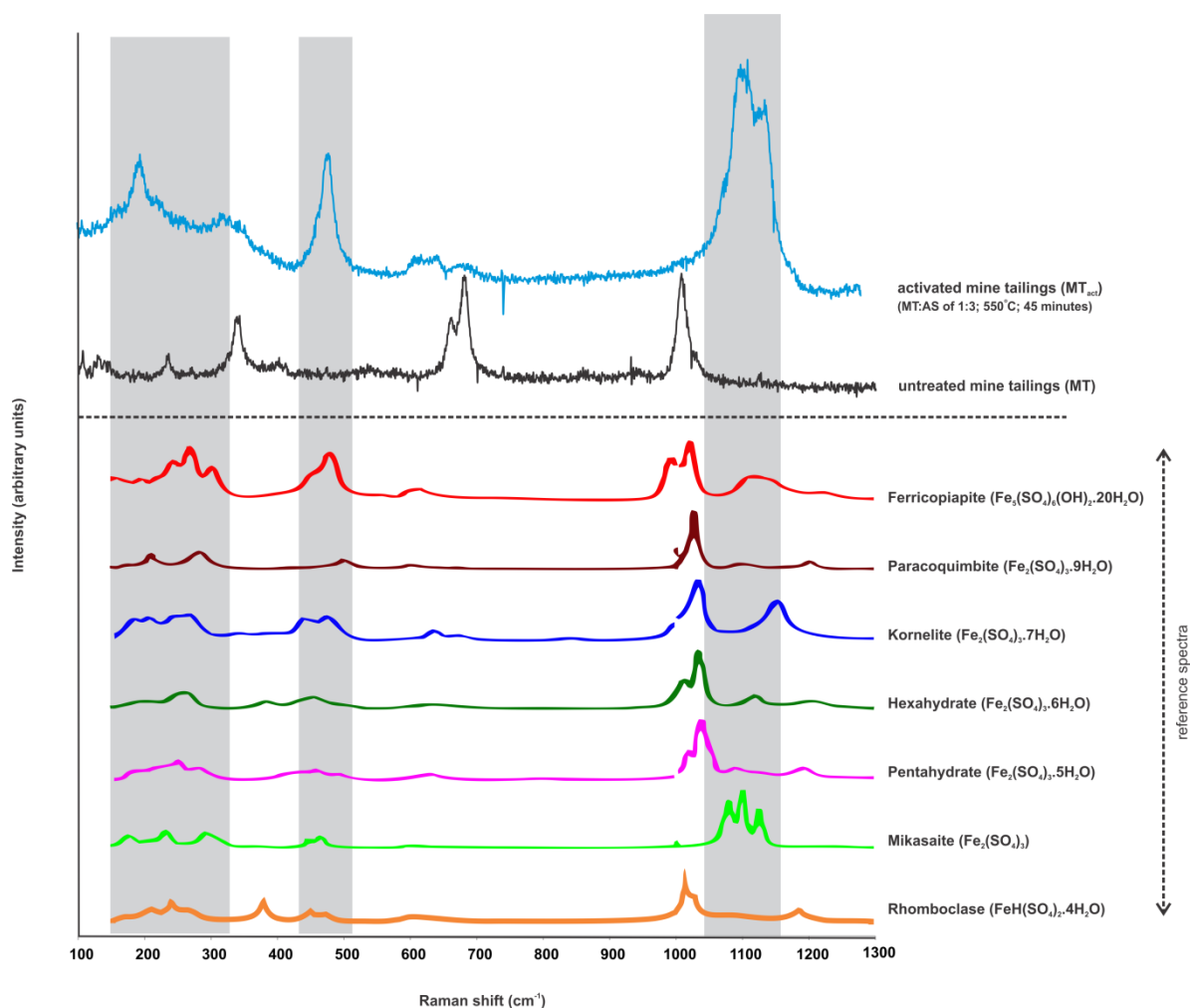
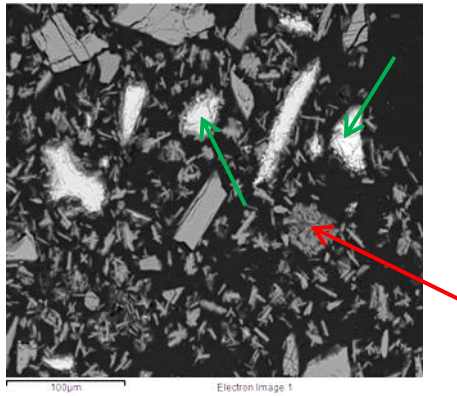


Figure 5.9. Raman spectral analyses of MT_{ro} (MT₄₅₋₇₅: AS of 2:6; 550 °C; 45 minutes) compared to published spectra (Ling and Wang, 2010) of iron sulphate with varying degrees of hydration.

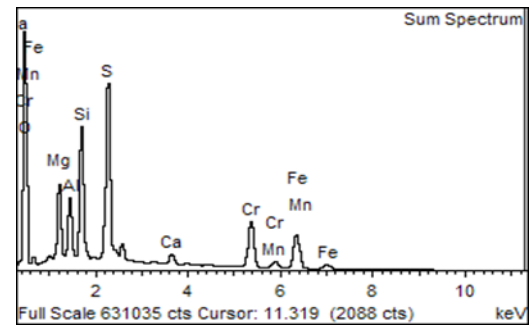
5.1.3.2.3 Elemental mapping and spot analysis

The SEM-EDS technique was used to qualitatively assess the elemental composition of selected particles contained in MT_{ro}. The micrograph, corresponding SEM-EDS spectrum and elemental maps of Al, Ca, Cr, Fe, Mg, Mn, O, S and Si are presented in Figure 5.10. The elemental spectrum indicates that the most abundant elements present in MT_{ro} are Fe, Cr, Mn, O, Si, Ca, Mg and S. There appears to be an inhomogeneity in elemental distributions within different particles. The particles denoted by the green arrows are enriched predominantly in Cr, Fe, Al with lesser amounts of O and no Si. S appears to be concentrated at the surface of the particles only. A spot analysis was conducted on the cluster of smaller particles (red arrow) which appear to be aggregating within the mineral matrix (Figure 5.11B). The elemental spectrum and elemental maps (Figure 5.11C) indicate that the most abundant elements present in the cluster are Cr, Fe, O and S. The high intensity of Cr and Fe detected on the same particle suggests preferential substitution within the transformed sulphate matrix and furthermore confirms the co-existence of Fe and Cr in metal sulphate reaction products.

A.



B.



C.



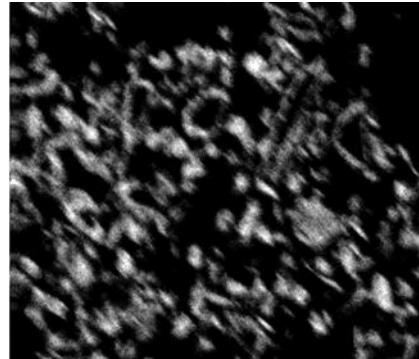
Fe Ka1



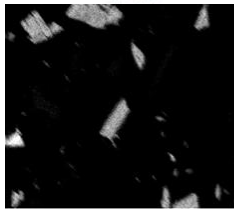
Al Ka1



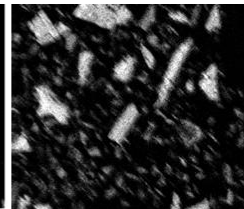
Cr Ka1



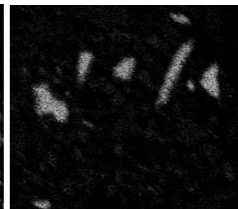
S Ka1



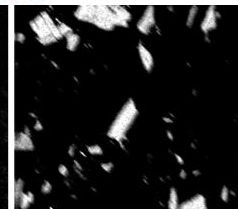
Mg Ka1_2



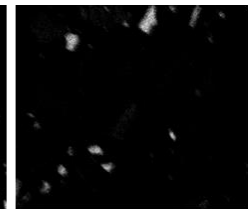
O Ka1



Mn Ka1



Si Ka1



Ca Ka1

Figure 5.10. SEM-EDS micrographs of (A) MT_{ro} (B) the corresponding elemental spectrum and (C.) corresponding elemental maps.

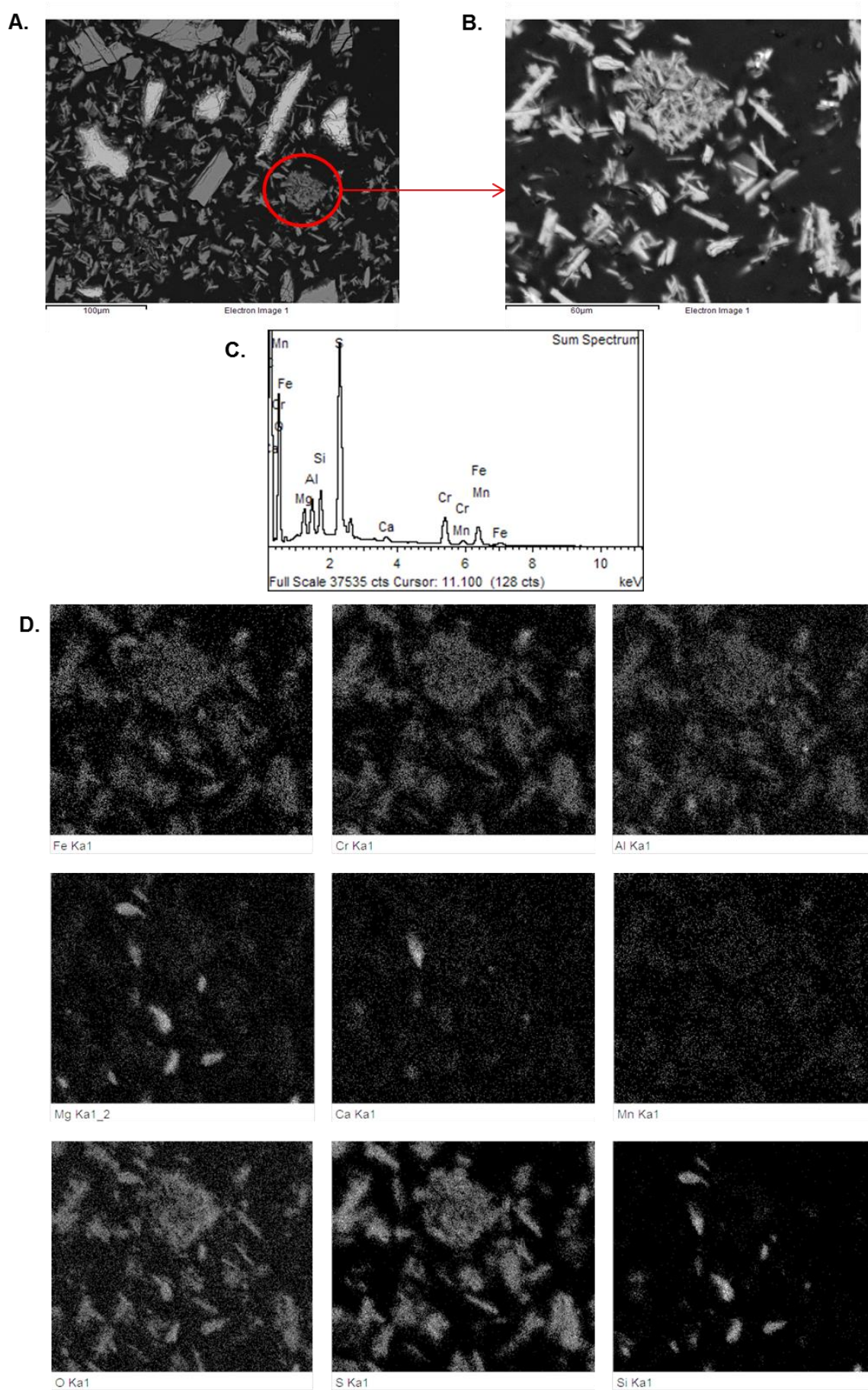


Figure 5.11. SEM-EDS micrographs of (A.) MT_{r0} and (B) area of smaller particles analysed and (C) corresponding elemental spectrum and (D) corresponding elemental maps.

MT_{ro} produced via the optimal thermochemical treatment was selected for characterisation using FE-SEM. Micrographs of MT₄₅₋₇₅ and MT_{ro} are presented in Figures 5.12 and 5.13 respectively. FE-SEM analysis has shown that untreated MT is comprised of anhedral particles which are angular, irregularly shaped with a non-uniform grain size (section 4.1.1.5). Further analysis revealed a distinct change in the mineralogical features after the thermochemical treatment. MT_{ro} contains micrometer plates with a hexagonal symmetry which was attributed to the formation of the $R\bar{3}$ space group (Figure 5.13). The formation of the $R\bar{3}$ space group with hexagonal lattice parameters have also been reported for the natural mineral in the literature (Miura *et al.*, 1994); Not all particles have reacted during the thermochemical treatment (Figure 5.13C), which supports the presence of original minerals from the tailings reported by XRD.

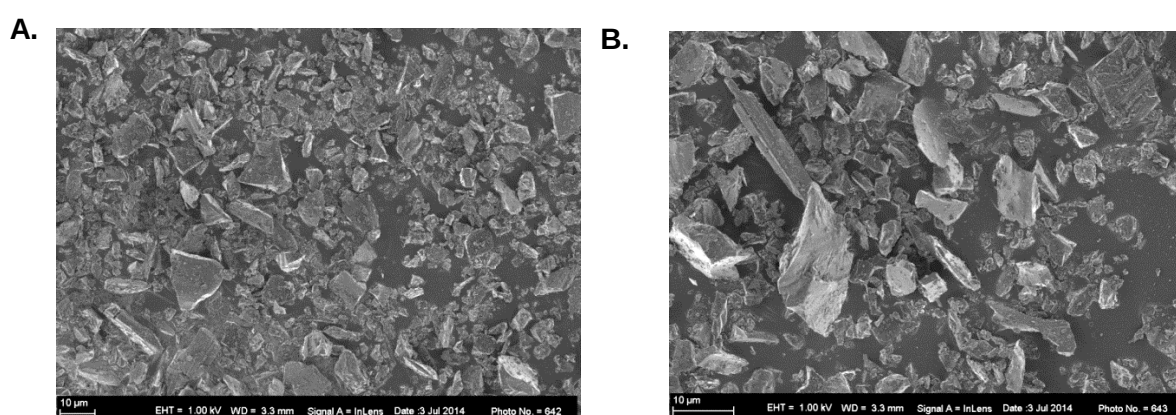


Figure 5.12. FE-SEM micrographs of untreated MT₄₅₋₇₅. The micrographs were taken at (A.) 2000x and (B.) 3500x magnifications.

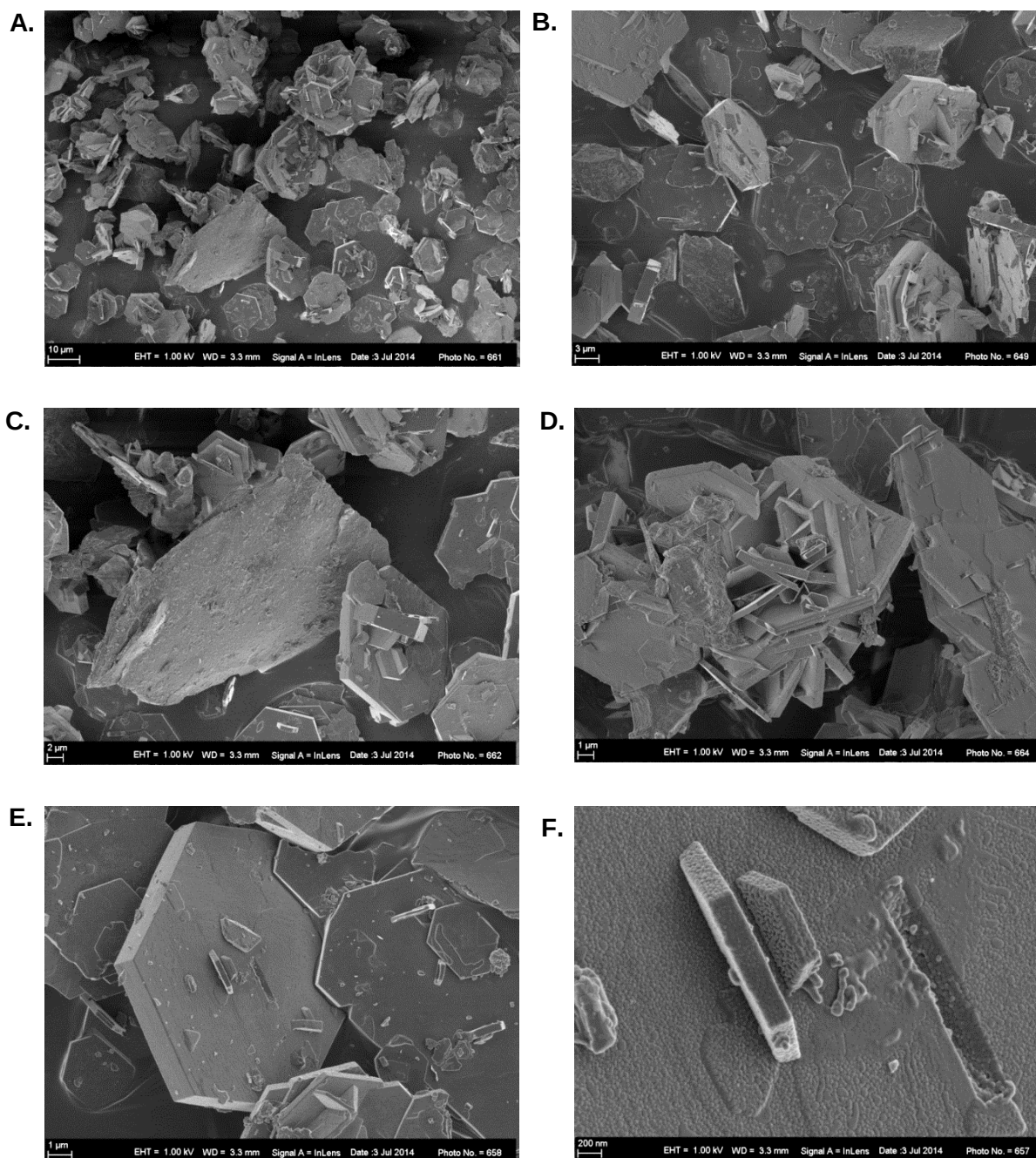


Figure 5.13. FE-SEM micrographs of MT_{ro} ($MT_{45-75}:AS$ of 2:6; 550 °C;45 minutes) taken at (A.) 2000x, (B.) 3500x, (C.) 5000x, (D.) 10 000x, (E.) 15 000x and (F.) 75 000x magnifications.

Qualitative elemental distributions in the hexagonal microstructures were obtained by spot analysis using SEM-EDS. Quantitative elemental composition of MT_{ro} cannot be directly inferred from these results as the analysis was performed on a powder substrate, and not on a polished surface. Low magnification maps were initially conducted in order to obtain an overview of the sample and higher magnification maps were then used to collect elemental composition data over an area and/or at a given point (between 1-2 μm region). Additional semi-quantitative analyses for each spot analysis can be found in Appendix B.

Figure 5.14 depicts a hexagonal crystal which was selected for elemental map analysis. The corresponding elemental spectrum (Figure 5.14C) illustrates a combination of Fe, Al, Mg, Cr, S and O, and the absence of Si. This result was later confirmed using spot analysis along the grain boundaries of the hexagonal crystal (Figure 5.15A). The corresponding elemental spectra for points analysis 1 – 6 (Figure 5.15B) also identified the presence of Fe, Al, Mg, Cr, S and O. Results from the FE-SEM revealed the presence of tabular crystals (Figure 16A). Spot analyses were conducted on several tabular particles (Figure 5.16B). The corresponding elemental spectra for the point analysis at 3 different locations (Figure 5.16C) also identified the presence of Fe, Al, Mg, Cr, S and O. The absence of nitrogen in all the elemental spectra confirmed the complete volatilisation of NH_3 during treatment at 550 °C.

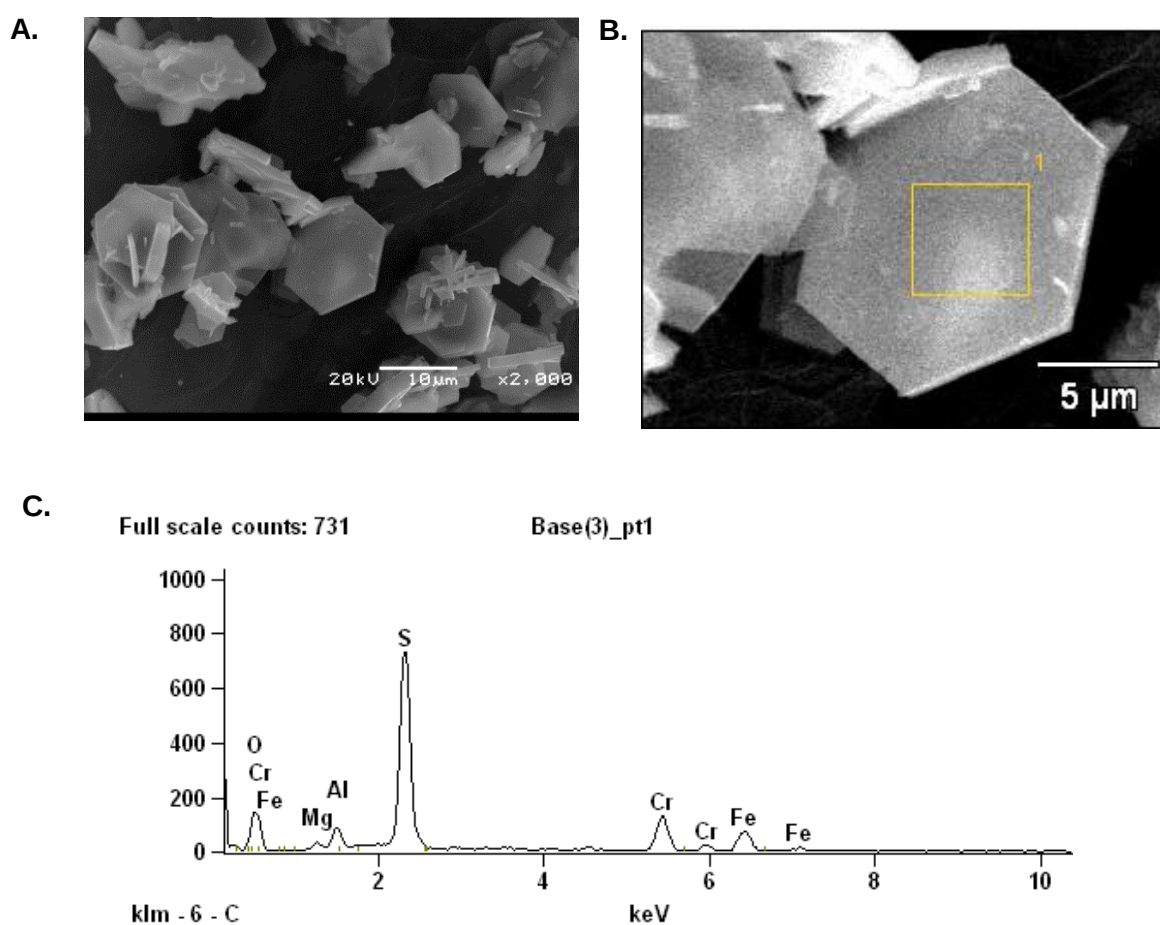


Figure 5.14. (A.) SEM-EDS micrographs of MT_{10} depicting hexagonal crystals taken at 2000x magnification, (B.) area selected for analysis, and (C.) elemental spectrum for selected area.

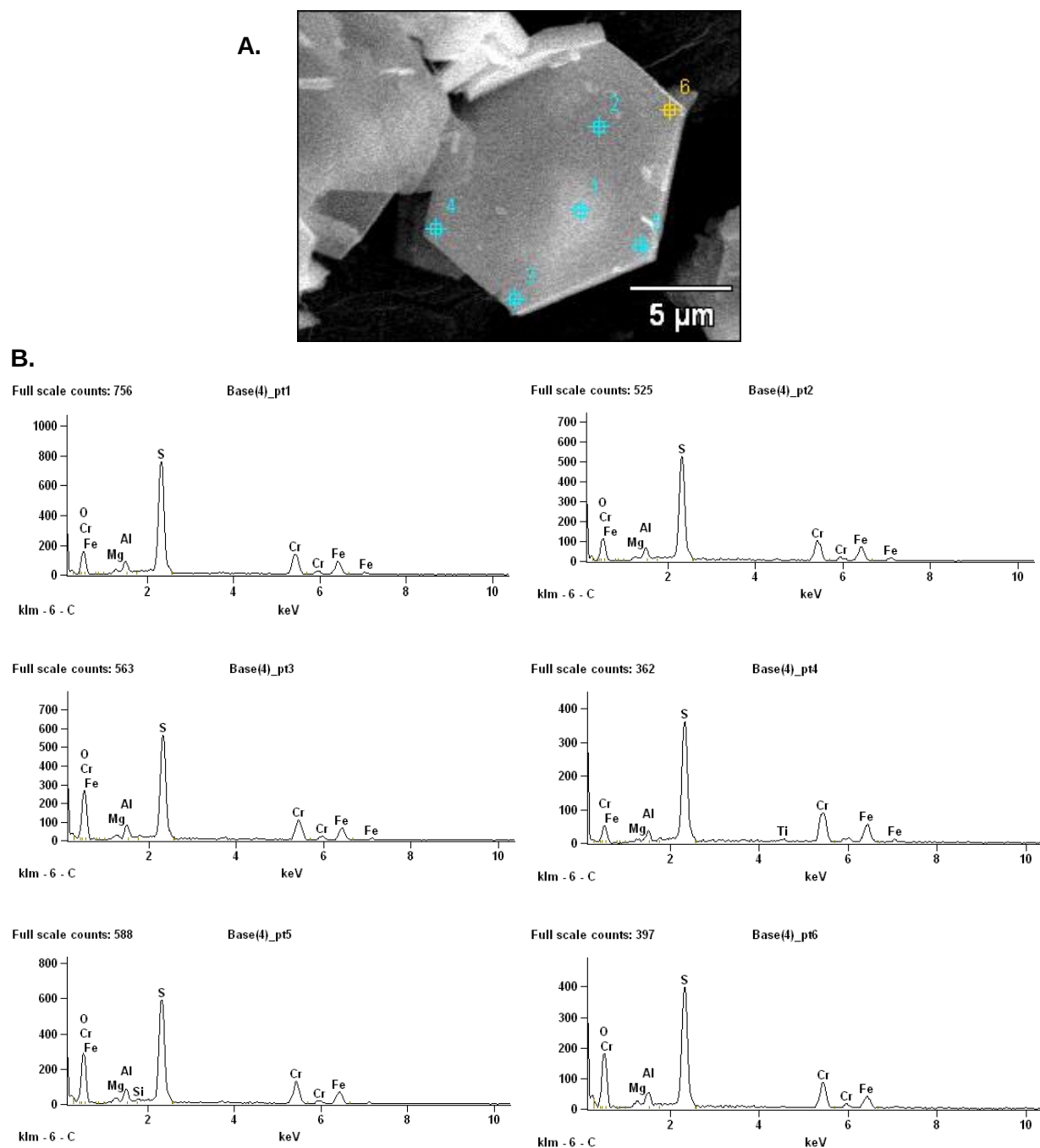
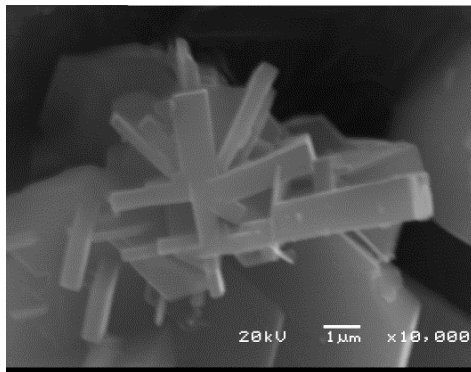
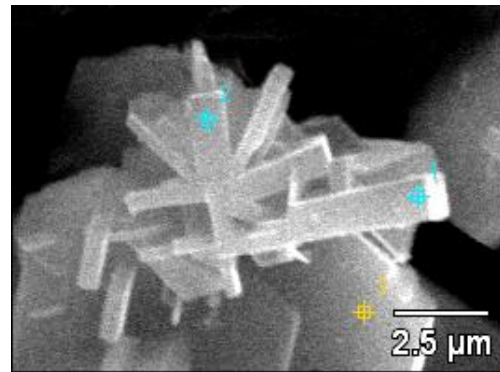


Figure 5.15. SEM-EDS micrographs of a hexagonal crystal present in MT_{ro} illustrating (A.) the relative location selected for the spot analysis along the grain boundaries and (B.) corresponding elemental spectrum for points 1- 6 respectively.

A.



B.



C.

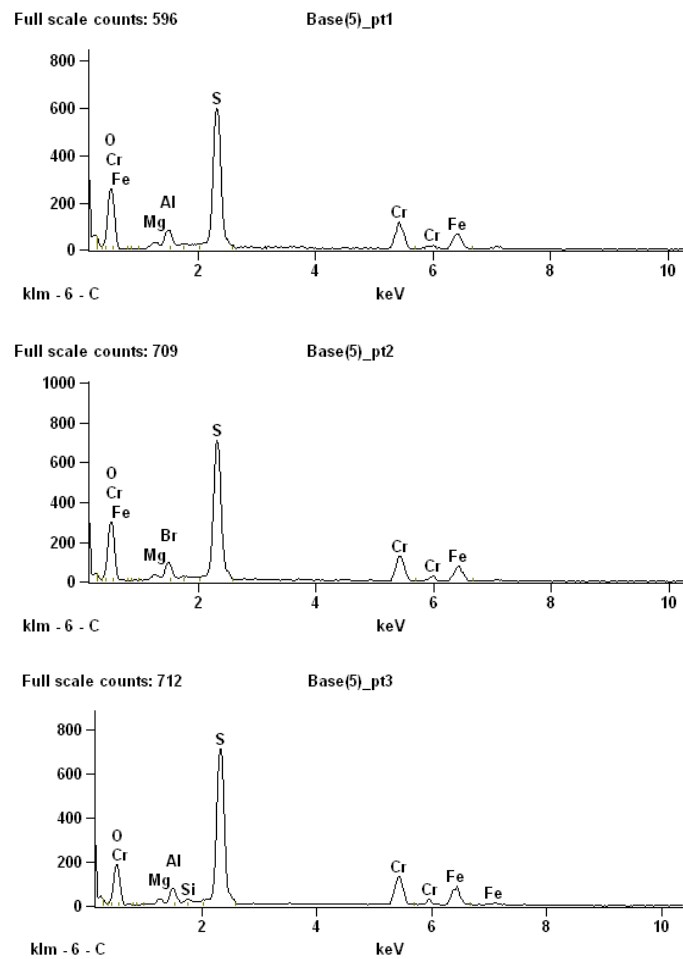


Figure 5.16. SEM-EDS micrographs of tabular crystals present in MT_{10} taken at (A.) 10 000x magnification (B.) the relative location selected for the spot analysis and (C.) corresponding elemental spectrum for points 1 - 3 respectively.

XRD, Raman spectroscopy, SEM-EDS and FE-SEM have shown that the reaction product generated during thermochemical treatment was reproducible. Raman spectroscopy complemented the XRD results, and confirmed the formation of an anhydrous mikasaite-like phase. The morphological transformation of some mineral features of MT₄₅₋₇₅ into hexagonal metal-containing sulphate particles indicated that the reaction of extraction of metals from the silicate matrix of MT₄₅₋₇₅ using AS as activator was thermodynamically favourable and the results from the spot analyses confirmed the isomorphic substitution and suggested that solid-solution series may exist between Al, Ca, Cr and Fe. Due to the favourable transformation and thermodynamic stability of the mikasaite mineral phase, 550 °C was selected as the optimised temperature of the thermochemical treatment and was used for all further static furnace experiments unless otherwise stated.

5.1.4 Extraction efficiencies under uncontrolled pH conditions

The rate of mineral dissolution is the primary factor which governs the extraction of metals from a mineral phase(s) in a particular compound. The thermochemical treatment in this study was applied to convert metal oxides and metal silicates present in MT into water-soluble metal-sulphates and thereby make the metals more readily available for extraction. In an attempt to optimise the dissolution parameters required to fully extract Fe and other elements from MT_{ro}, which will ultimately help to quantify the efficiency of the thermochemical activation step, a series of dissolution experiments were conducted to quantitatively determine the total amount of extractable elements which can potentially be converted into value-added products.

Theoretically, the dispersion of MT_{ro} in water should yield a sulphate-rich solution containing Mg²⁺, Fe²⁺ or Fe³⁺, Cr²⁺ - Cr⁶⁺ and/or Al³⁺ in varying proportions, assuming that sufficient dissolution time is allowed to overcome the rate of diffusion and chemical reactions on the surface of particles (Wang and Mercedes Maroto-Valer, 2011).

The extraction efficiency of the major elements was determined using the results obtained from the chemical composition of the starting solid material and ICP-OES analysis of the leachates. The percentage extraction for any given element (X) was calculated using equation 5.3, where C₁ is the concentration of the element in the leachate, and C₂ is the theoretical concentration of the element in solution if total dissolution of MT_{ro} is assumed (both expressed in mg/l).

$$X_{\text{extraction}} (\%) = \frac{C_1}{C_2} \times 100 \quad (5.3)$$

Naturally occurring Fe-oxides are generally insoluble in water and their solubility may increase with a decrease in pH. A study by Schwertmann (1991) indicates that the primary factors governing the dissolution of Fe-oxides include solution variables such as Eh, pH, reactant concentration, and solid phase properties such as the type of oxide, surface area, crystallinity and crystal chemistry. Although MT_{ro} is comprised of M-SO₄²⁻ (where M = Fe, Cr, Al, Mg, Ca) rather than naturally occurring Fe-oxides, understanding these factors will provide insight on the factors which limit the rate of dissolution within the M-SO₄²⁻ system. In this study, the influence of several variables was assessed, including solution temperature and pH during dissolution, moisture content of MT_{ro} used in the dissolution experiments, and

seeding of the mixture of MT₄₅₋₇₅ and AS with sodium silicate during thermochemical treatment.

5.1.4.1 Baseline dissolution experiments

Baseline dissolution experiments were initially conducted in an attempt to assess and compare the dissolution behaviour of untreated MT₄₅₋₇₅ vs thermally treated MT₄₅₋₇₅ (MT_{ht}) vs thermochemically treated MT₄₅₋₇₅ (MT_{ro}). The dissolution experiments were conducted in ultrapure water at ambient temperature for a duration of 6 hours. The percentage mass loss, which was calculated from the mass of undissolved solids after dissolution, was used as the first indicator of the effect of the thermochemical treatment on MT (Table 5.3). The observed changes in solution pH and EC are also presented in Table 5.3 and the extraction efficiency for several major elements is presented in Table 5.4.

Table 5.3. Differences in solution pH and EC, and in percentage (%) mass loss between MT₄₅₋₇₅, MT_{ht} and MT_{ro} (MT₄₅₋₇₅ : AS of 2:6; 550 °C; 45 minutes) after dissolution in ultra-pure water under uncontrolled pH conditions (3 g/500 ml; ambient temperature, 850 rpm; mean ± sd; *n*=2) for 6 hours.

	pH	EC (μS/cm)	mass loss (%)
untreated (MT ₄₅₋₇₅)	6.8 ± 0.0	27.5 ± 0.7	2.9 ± 0.0
treated <u>without</u> AS (MT _{ht})	6.8 ± 0.1	29.0 ± 1.4	2.9 ± 0.0
treated with AS (MT _{ro})	3.4 ± 0.1	594.5 ± 75.7	23.3 ± 13.7

Table 5.4. Concentrations of several elements in solution after dissolution of MT₄₅₋₇₅, MT_{ht} (550 °C; 45 minutes; *n*=2) and MT_{ro} (MT₄₅₋₇₅ : AS of 2:6; 550 °C; 45 minutes; *n*=2) under uncontrolled pH conditions (3g/500 ml; ambient temperature ; mean ± sd; *n*=2), and corresponding elemental extraction efficiency (%).

		Al	Ca	Cr	Fe	Mg
untreated (MT ₄₅₋₇₅)	mg/l	0.1 ± 0.0	2.8 ± 1.3	0.0 ± 0.0	0.1 ± 0.1	2.1 ± 0.0
	%	0.0 ± 0.0	4.0 ± 1.9	0.0 ± 0.0	0.0 ± 0.0	0.6 ± 0.0
treated <u>without</u> AS	mg/l	0.1 ± 0.0	3.5 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	2.1 ± 0.0
	%	0.0 ± 0.0	4.9 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.6 ± 0.0
Treated <u>with</u> AS (MT _{ro})	mg/l	7.9 ± 1.7	5.8 ± 4.0	6.2 ± 0.9	2.7 ± 0.4	47.3 ± 8.2
	%	1.7 ± 0.4	4.0 ± 0.5	0.9 ± 0.2	0.4 ± 0.1	8.2 ± 1.0

The dissolution of untreated MT₄₅₋₇₅ and thermally treated MT_{ht} under the experimental conditions tested caused little elemental extraction. The solution pH was about circumneutral (6.8 ± 0.1), the EC was low ($\leq 29.0 \pm 1.4 \mu\text{S cm}^{-1}$) and a mass loss of 2.9 ± 0. % was observed for the MT₄₅₋₇₅ and MT_{ht}. The undissolved residue was grey with no noticeable changes in colour when compared to the untreated sample before dissolution (Figure 5.17A). As expected, the extraction of major elements from MT₄₅₋₇₅ and MT_{ht} was low and

represented less than 0.6 % of the total elemental content in the tailings (for Al, Cr, Fe and Mg) extraction efficiency. The most extractable element was Ca, with 3.5 - 4.9 % extraction efficiency achieved for MT₄₅₋₇₅ and MT_{ht} (Table 5.4).

Dissolution of MT_{ro} under the same experimental conditions yielded a much lower pH (3.4 ± 0.1) and a significantly higher conductivity ($594.5 \pm 75.7 \mu\text{S}/\text{cm}^{-1}$). The increase in EC was supported by the higher mass loss obtained (23.3 ± 1.9 %); this indicated that the newly-formed metal sulphate species were water-soluble. The undissolved residue appeared murky grey – green in colour (Figure 5.17B) and looked significantly different from the grey residue generated after leaching of untreated tailings (Figure 5.17A).

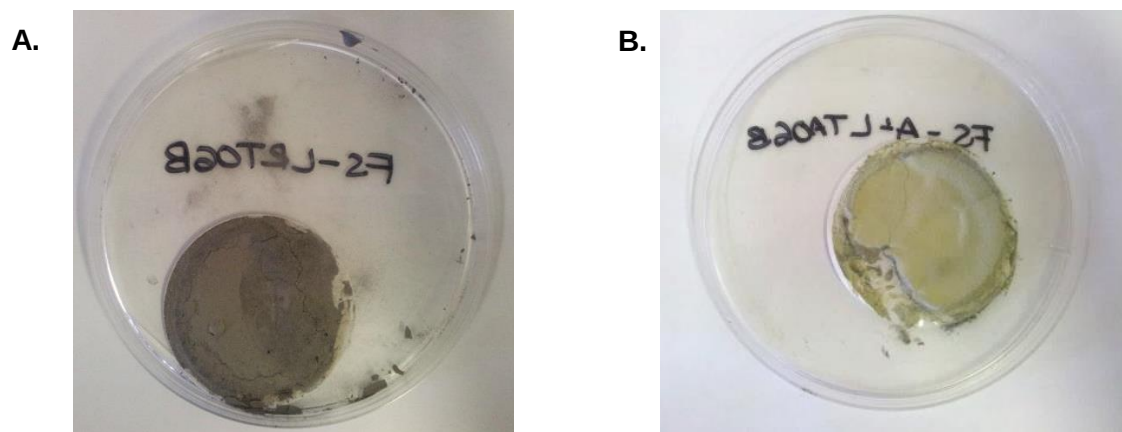


Figure 5.17. Photographs showing undissolved residues following dissolution of (A.) untreated MT₄₅₋₇₅ and (B.) MT_{ro} (MT: AS of 2:6; 550 °C; 45 minutes) under uncontrolled pH conditions (3g/500ml; ultrapure water; 850 rpm) and ambient temperature.

Elemental extraction was greater for thermochemically-activated MT. For instance, Al (7.9 ± 1.7 mg/l), Ca (5.8 ± 4.0 mg/l), Cr (6.2 ± 0.9 mg/l), Mg (47.3 ± 8.2 mg/l) and Fe (2.7 ± 0.4 mg/l) were reported and represented 0.4 % to 8.2 % of the total extraction efficiency, depending on the elements. The thermochemical treatment did not affect the extraction of all elements in the same way. For instance, Ca extraction increased marginally (from 3.5 % for untreated MT to 4.0 % for MT_{ro}) whereas Mg extraction increased from 0.1 % to 8.2 %. Fe extraction only increased from 0 % to 0.4 %.

Contrasting results were found by Nduagu *et al.*, (2012) who have reported 60 % - 94 % extraction of Mg and 0 % – 35 % for Fe from a Finnish serpentinite after pre-treatment with AS under the same dissolution conditions (i.e. uncontrolled pH conditions and ambient temperature). This suggests that the reactivity of MT is much lower than that of serpentine and the dissolution parameters may need to be altered in order to improve the efficiency of the process.

5.1.4.2 Time-series experiments at ambient temperature and at 80°C

In order to complement the above baseline dissolution experiment, a time-series dissolution experiment was conducted using MT_{ro} suspended in ultrapure water under uncontrolled pH

condition over a period of 18 hours. The experiment was conducted at two temperature conditions (ambient and 80 °C). Temporal changes in solution pH and EC are presented in Figure 5.18A. Upon immersing MT_{ro} in ultrapure water at ambient temperature, the solution pH decreased rapidly to 3.5 within 1 min and stabilised at about 2.9 after 17 hours. On the other hand, EC increased rapidly from <1 $\mu\text{S cm}^{-1}$ to 400 $\mu\text{S cm}^{-1}$ within 1 min and continued to increase over time before stabilising at 755 $\mu\text{S cm}^{-1}$ after 17 hours.

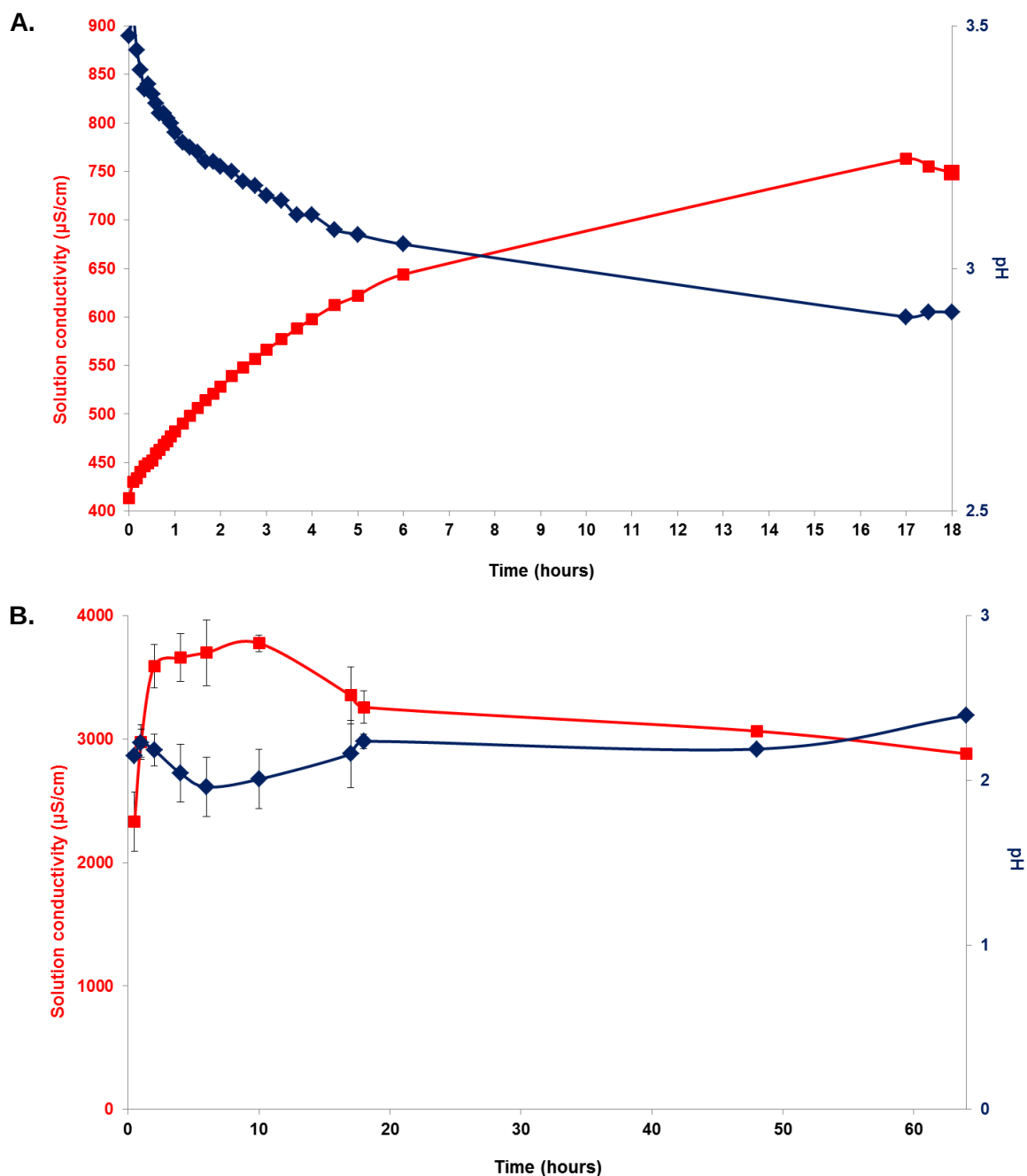


Figure 5.18. Changes in solution conductivity (red) and pH (blue) during dissolution of MT_{ro} (MT₄₅₋₇₅: AS of 2:6; 550 °C; 45 minutes) at (A.) ambient temperature ($n=1$) and (B.) at 80 °C ($n=3$) under uncontrolled pH conditions over time (3 g/500 ml; ultrapure water; 850 rpm). Note: experiment performed in (A.) is a single experiment where data was collected at time intervals (5 minutes up to 18 hours) whereas experiment performed in (B.) reports data points collected at completion of different experiments at different durations (30 minutes up to 64 hours).

Increasing the dissolution temperature from ambient condition to 80 °C resulted in an increase in the rate and extent of dissolution (Figure 18B). Upon immersing MT_{ro} in water, the solution pH decreased to 2.0 immediately before stabilising between 2.0 - 2.4. The decrease in pH was accompanied by an increase in EC from 2330.3 $\mu\text{S cm}^{-1}$ at 30 minutes to 3777.7 $\mu\text{S cm}^{-1}$ after 10 hours before decreasing to $2882.7 \pm 131 \mu\text{S cm}^{-1}$ at the end of the experiment. The percentage mass loss (calculated from the measured mass of the undissolved solids) also increased rapidly to ca. 20.3 % within 30 minutes and plateaued at about 41% after 17 hours of leaching (Figure 5.19A.). No decrease in the percentage mass loss was identified, which suggested that this parameter was less sensitive than EC when changes in reaction dynamics took place

Prior to filtration, a change in the colour of the suspension from murky green to brown was observed from the first hour of dissolution and progressed to a darker hue of brown as the reaction progressed further. A colour bar was created from the colour of the undissolved residues following dissolution for ease of presentation (Figure 5.19B). A photograph for the undissolved residues generated at different times can be found in the Appendix C. The observed colour changes coincided with the plateauing and drop in solution EC from 3778 $\mu\text{S cm}^{-1}$ to 3354 $\mu\text{S cm}^{-1}$ between 10 and 17 hours. The decrease in EC and gradual colour change suggested that secondary precipitation of one or more of the dissolved elements or coating of the undissolved particles may have taken place at this temperature (80 °C). This phenomenon was not observed at ambient temperature. A similar phenomenon was observed in the study by Nduagu *et al.*, (2012) which focused on Mg extraction from serpentinite to produce Mg(OH)₂. During the precipitation stage of FeOOH, the precipitate formed after the addition of ammonia to MgSO₄-rich filtrate turned brown after being exposed to air and drying at 100 °C and was attributed to the transformation of water-soluble iron compounds (iron sulphates) to less soluble iron oxides (possibly hematite). The change in colour observed in the present study may also be attributed to the secondary precipitation of iron, although this had to be investigated further.

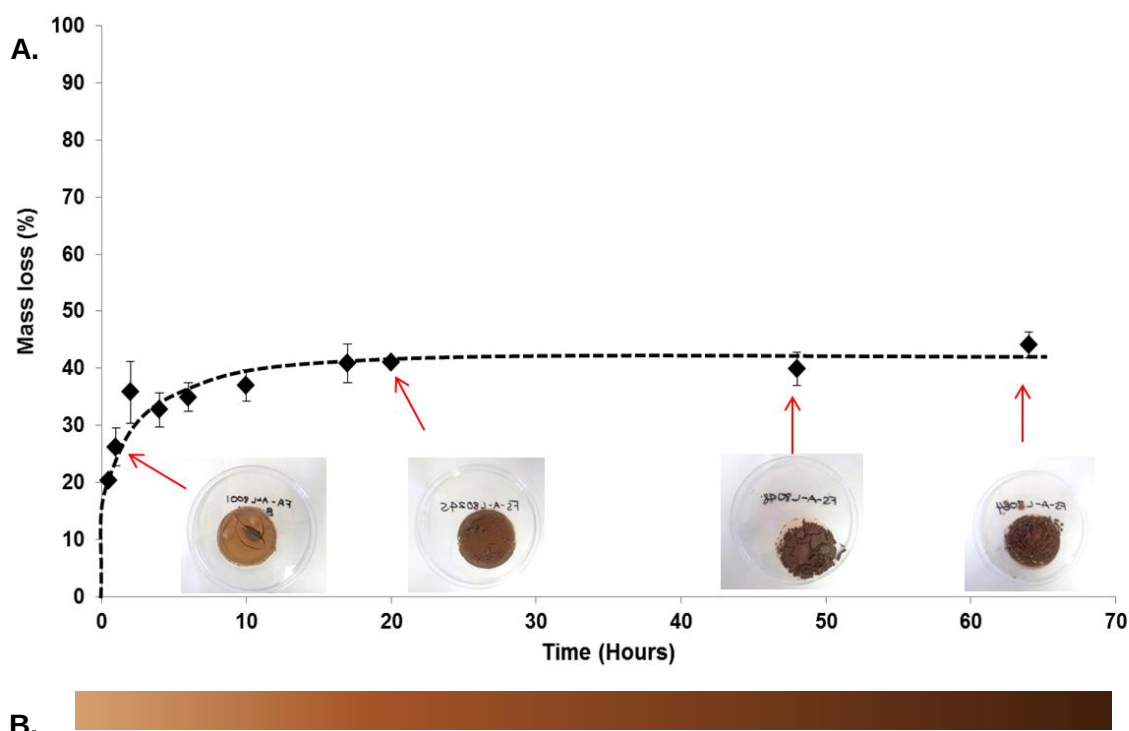


Figure 5.19. Temporal changes observed for (A) percentage (%) mass loss and (B.) colour changes of the undissolved residue following dissolution of MT_{r0} (MT_{45-75} : AS of 2:6; 550 °C; 45 minutes) under uncontrolled pH conditions (3 g/500 ml; ultrapure water; 80 °C; 850 rpm, $n=3$).

The elemental extraction efficiency obtained following the dissolution of MT_{r0} at 80 °C is presented in Figure 5.20 and is significantly higher than that obtained at ambient temperature (Table 5.4) for all elements. From Figure 5.20A, it can be said that the extraction efficiency of Fe follows a similar decreasing trend as the EC in comparison to the other elements and to Cr, which rapidly increases during the first 10 hours, and remains relatively stable until the end of the experiment. The elemental concentration of Fe began to decrease prior to the EC and coincides with to the plateauing of the EC which is followed by a further decrease. The temporal changes in EC may be attributed to the extraction of elements which increase the EC followed by secondary precipitation of one or more elements which will decrease the EC. This indicated the formation of a secondary precipitate which is probably Fe-rich owing to the relatively low pH (< 3); which made it impossible to quantify the effective Fe extraction efficiency. The decrease in EC may be a result of several reaction dynamics that might be occurring i.e. Fe re-precipitates but it is unclear whether the $Fe_2(SO_4)_3$ phase is still dissolving, some of the major elements continue being extracted (Al), while elements such as Mg and Ca seems to have reached a plateau. It is unclear whether Cr has re-precipitated.

This indicated that the extent of elemental extraction was not the same for all elements. The elemental concentration in solution increased in the order $Ca < Mg < Al$ and Cr however the elemental concentration of Fe was much lower due to the secondary precipitation (discussed above). Upon converting these values to percentage elemental efficiency, the elemental extraction efficiency followed a different order and increased in the order $Cr < Mg < Al$ and Ca. This indicated that Ca was the most extractable element (53.9 %) under the experimental conditions tested, followed by Al which (46.5%), Mg (24.2%) and Cr (17.8%) which were significantly lower.

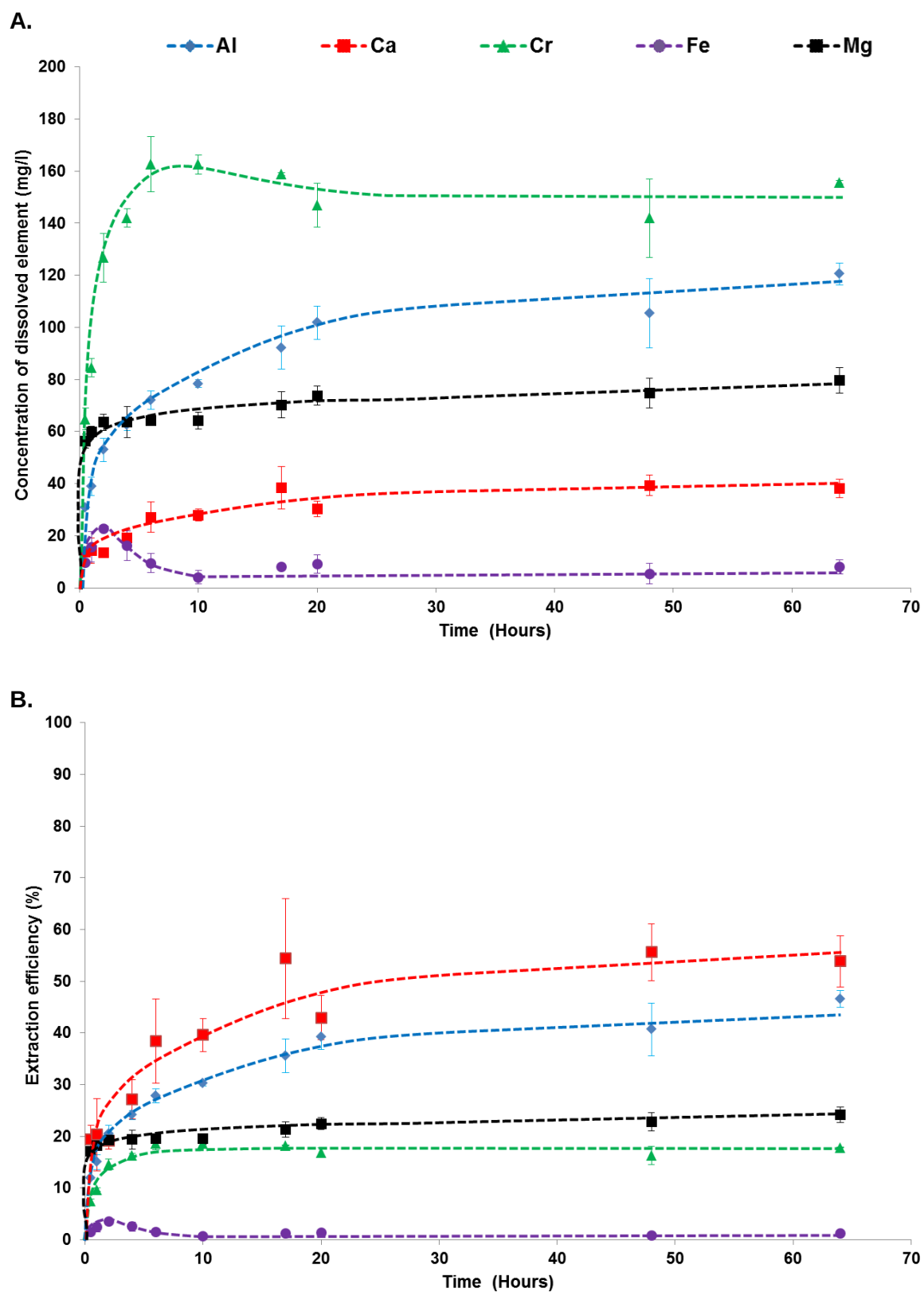


Figure 5.20. Temporal changes on elemental extraction efficiency in (A.) mg/l and (B.) percentage (%) after dissolution of MT_{r0} (MT: AS of 2:6; 550 °C; 45 minutes) under uncontrolled pH conditions (3g/500ml; ultrapure water; 80°C; 850 rpm; $n=2$).

The undissolved residue generated at 80 °C contained grey and brown particles. It was assumed that the grey particles consisted mostly of unreacted mine tailings whereas the brown particles were likely to represent secondary Fe precipitates. An attempt to recover most of the brown particles contained in the undissolved residue was made during the filtration step. The sample was subsequently dried for further analyses (XRD, FE-SEM and SEM-EDS) in order to elucidate its chemical and mineralogical composition. The dried brown residue (Figure 5.21B) had the appearance of a compacted powder with a smooth surface, which was significantly different from the appearance of undissolved residues obtained under uncontrolled pH conditions at ambient temperature (Figure 5.21A).

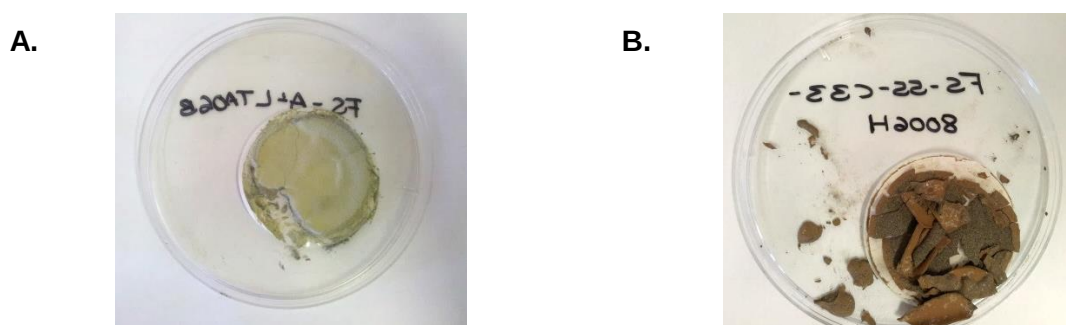


Figure 5.21. Photographs depicting (A.) undissolved residues (for ambient condition dissolution experiment) and (B.) brown secondary precipitate (for dissolution experiment at 80 °C) recovered following dissolution of MT_{ro} (MT: AS of 2:6; 550 °C; 45 minutes) under uncontrolled pH conditions (3g/500ml; ultrapure water; 850 rpm; $n=2$).

The XRD diffractogram of the brown portion of undissolved residue generated following dissolution of the MT_{ro} (MT: AS of 2:6; 550 °C; 45 minutes) under uncontrolled pH condition at 80 °C is presented in Figure 5.22. The XRD diffraction spectrum (brown) confirmed the absence of the mikasaite phase (blue asterisks) and indicated presence of the primary mineral phases, enstatite, spinel, albite, and talc which are present in the MT (black), suggesting that no new mineral phases have formed during dissolution. The peak intensities of the undissolved residue are relatively lower compared to the MT and may be due to the varying nature of the sample (Figure 5.21) and changes in crystallographic orientation of the mineral grains. XRD failed to recognise crystalline phases corresponding to the brown precipitate and may be attributed to the presence of precipitated Fe oxides which are generally amorphous within the detection of X-rays and tend to obscure XRD measurements resulting in ill-defined asymmetrical peaks with an uncertain peak position (Landa and Gast, 1973).

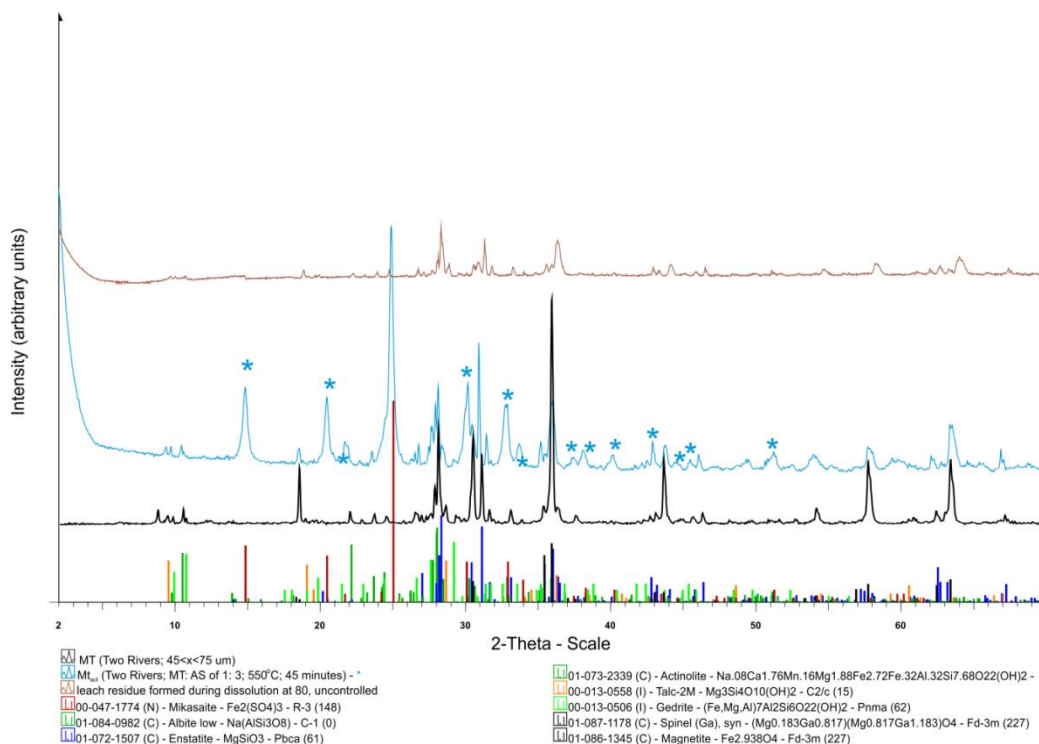


Figure 5.22. XRD diffractograms of untreated MT₄₅₋₇₅ (black), MT_{ro} (blue) and brown portion of undissolved residue (brown) generated following the dissolution of MT_{ro} (MT: AS of 2:6; 550 °C; 45 minutes) under uncontrolled pH condition (3g/500ml; ultrapure water, 850 rpm, $n=2$) at 80 °C. Asterisks (*) indicate the diffraction peaks of the Fe₂(SO₄)₃ (mikaite) mineral phase.

The morphology of the secondary precipitate was assessed by FE-SEM. The precipitate comprised of micron-sized particles which exhibit an irregular shape (Figure 5.23). Several hexagonal structures had rounded edges (green arrows) which suggested the partial or incomplete dissolution of the metal-sulphate hexagonal structures. This indicated that the dissolution process was not optimised and therefore the efficiency of the thermochemical activation process could not be quantified.

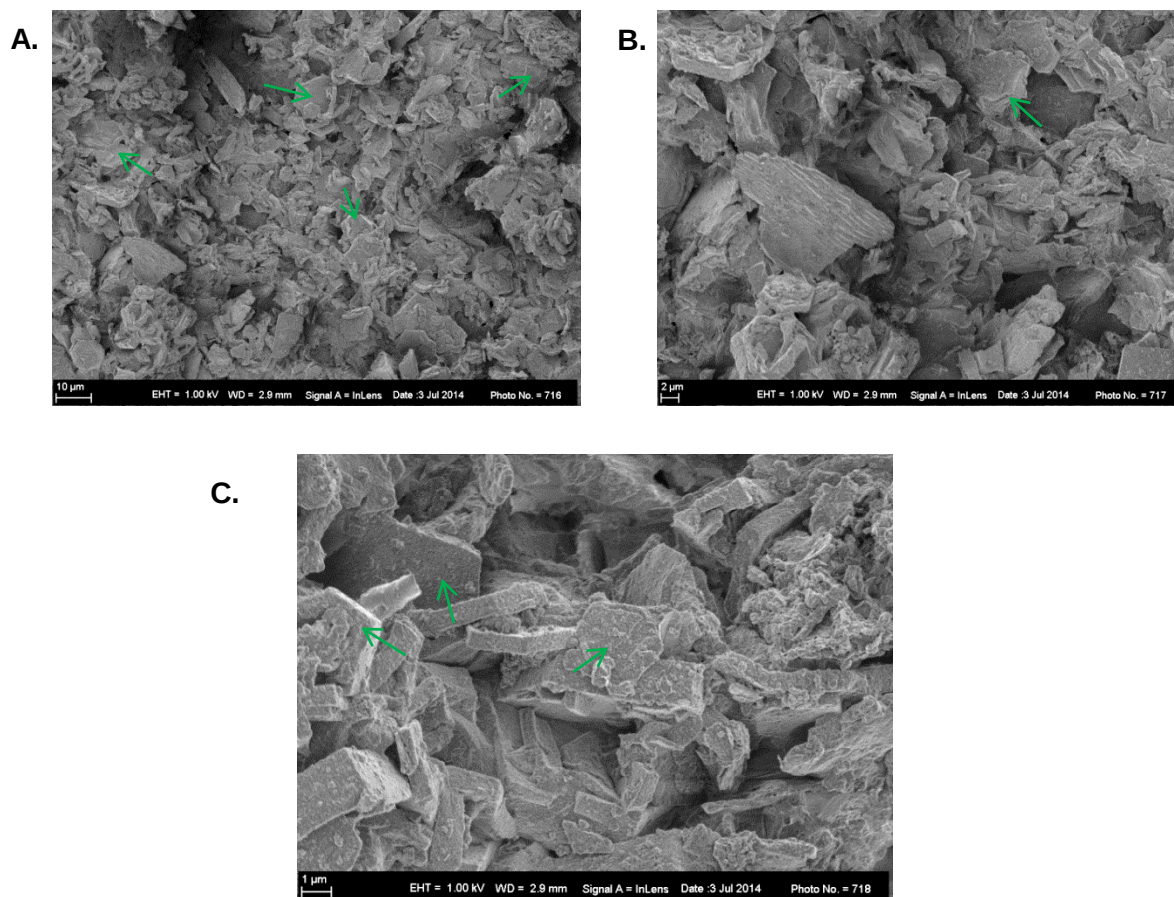


Figure 5.23. FE-SEM micrographs of the brown portion of undissolved residue generated following the dissolution of the MT₁₀ (MT: AS of 2:6; 550 °C; 45 minutes) under uncontrolled pH conditions (3g/500ml; ultrapure water, 80 °C; 850 rpm, $n=2$). Micrographs taken at (A.) 2000 X, (B.) 5000 X and (C.) 15000x magnification. Green arrows point to hexagonal structures with rounded edges.

It was mentioned earlier that the suspensions before filtration exhibited a continuum in the change in colour intensity from light brown to dark brown as the dissolution reaction unfolded over the 64 hour period. A similar observation was made for the filtrates, except that those solutions displayed a blue hue (Figure 5.24). The blue hue may be attributed to the formation of soluble transition metal complexes and was further investigated using ultraviolet-visible (UV-Vis) spectroscopy. The absorption spectra collected for the leachates collected at different times had a high noise to signal ratio, which presented difficulties in its interpretation. “Noise” in UV-Vis spectroscopy is defined as variation of the signal around the true value which may be caused by inhomogeneity of the sample and fluctuations of the light source and/or spectrophotometer (Antonov and Nedeltcheva, 2000). The collected spectra are reported in Appendix D. Although the presence of Cu(II) in a solution is commonly known to produce a blue colour, however a study by Hakimi *et al.*, (2008) has indicated that Fe³⁺ transition metal compounds are more stable than those of Cr³⁺ and Cu²⁺. ICP-OES analysis of the leachates confirmed that the concentration of Cu is low (≤ 0.298 mg/l) compared to Fe (8 - 23 mg/l) and Cr (65 – 156 mg/l). This suggests that the observed blue colour may be ascribed to either Fe³⁺ and/or Cr³⁺-based soluble complexes. Further investigation of the composition of these solutions was outside the scope of the project.

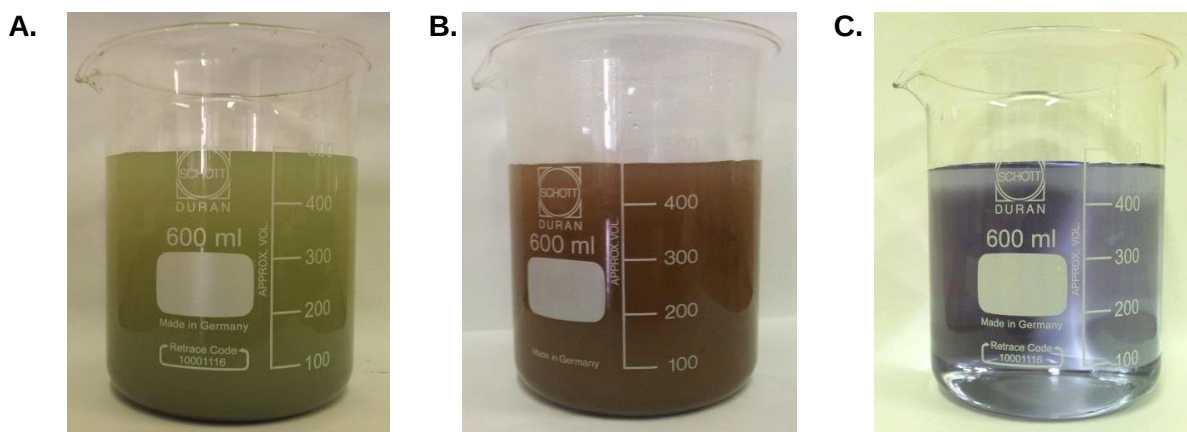


Figure 5.24. Observed colour during and following dissolution of MT_{ro} (MT: AS of 2:6; 550 °C; 45 minutes) under uncontrolled pH conditions (3g/500ml; ultrapure water, 80 °C, 850 rpm, $n=2$). (A.) During the first hour of dissolution, (B.) after 64 hours of dissolution and (C.) after filtration.

It was mentioned earlier that the dissolution process under uncontrolled pH condition was not optimal. Increasing the temperature of dissolution to 80°C was found to improve elemental extraction efficiency considerably. However, it also caused the secondary precipitation of the main element of interest, iron. As a result, the efficiency of the thermochemical activation process could not be quantified.

The next step of the project was to investigate whether performing the dissolution process under acidic conditions (0.6 M HNO_3) increases the dissolution of hexagonal metal sulphate particles, thereby improving elemental extraction efficiency while preventing secondary precipitation of Fe.

5.1.5 Extraction efficiencies under acidic conditions (0.6 M HNO_3)

5.1.5.1 Baseline dissolution experiments

The use of HNO_3 as a solvent was further examined in order to optimise the elemental extraction from MT_{ro} and prevent the re-precipitation of Fe which is crucial. A baseline test was conducted to investigate the effect of pH on the elemental extraction efficiency. The effect of pH was initially investigated by leaching MT and MT_{ro} in 0.6M HNO_3 at ambient temperature for 6 hours. The colour of the suspension changed from colourless to grey for MT and murky green for MT_{ro} . The non-occurrence of a brown suspension suggested that no secondary precipitation of Fe had occurred under these conditions. After filtration, the solution was not blue as observed previously, but was colourless. The undissolved residues of the MT and MT_{ro} was grey and murky green with no noticeable changes in colour compared to the leachate following dissolution. The percentage mass loss for MT and MT_{ro} were 13.9 % and 10.7 % respectively. This provided an indirect indication that the extraction efficiency of MT and MT_{ro} was low when dissolution had been performed at ambient temperature.

The elemental extraction efficiency obtained under acidic conditions at ambient temperature is presented in Table 5.5. Compared to the initial baseline experiments conducted in section 5.1.4.1 (uncontrolled pH and ambient temperature), the elemental extraction efficiencies remained quite low. Results from the ICP-OES analysis for the untreated MT₄₅₋₇₅ reports low concentrations of Al (11.0 mg/l), Ca (8.0 mg/l), Cr (11.0 mg/l), Fe (18 mg/l) and Mg (0.6 mg/l). The elemental extraction efficiency for MT_{ro} was nevertheless significantly higher than for MT and MT_{ro} under uncontrolled pH conditions for Al (24.2 mg/l), Cr (30.2 mg/l), Mg (67 mg/l) and Fe (31.6 mg/l) but not for Ca (8.1 mg/l). The highest percentage elemental extraction achieved was for Mg (20.4 %), Ca (11.4 %) and Al (9.3 %). The elemental extraction efficiencies for Fe and Cr were 4.9 and 3.5 % respectively. These results suggested that dissolution under acidic conditions (0.6 M HNO₃) does not yield higher iron extraction efficiencies at ambient temperature. Higher dissolution temperatures may be required in order to improve the extraction efficiency. This was tested.

Table 5.5. Elemental extraction efficiency in mg/l and percentage (%) of MT₄₅₋₇₅ and MT_{ro} (MT₄₅₋₇₅ : AS of 2:6; 550 °C; 45 minutes; n=1) after dissolution under acidic conditions (3g/500mL; 0.6M HNO₃; ambient temperature; 850 rpm; n=1).

		Al	Ca	Cr	Fe	Mg
untreated (MT ₄₅₋₇₅)	mg/l	11.0	8.0	11.0	18.0	62.0
	%	2.8	7.6	0.8	1.8	12.6
treated (MT _{ro})	mg/l	24.2	8.1	30.2	31.6	67.0
	%	9.3	11.4	3.5	4.9	20.4

5.1.5.2 Elemental extraction efficiency under acidic conditions (0.6 M HNO₃) at 80°C

Following the results of the above baseline dissolution experiment, dissolution of MT_{ro} produced using the optimal thermochemical treatment was performed in 0.6M HNO₃ at 80 °C for 17 hours. Prior to filtration the suspension turned blue – grey in colour and this was the first indication that Fe was no longer precipitating. After filtration, the solution remained blue in colour which indicates the presence of soluble metal complexes. As discussed in section 3.3.1.4, the EC could not be monitored for the dissolution reaction, instead the total dissolved solids (TDS) were calculated. The TDS compared to the mass of the undissolved residue is presented in Figure 5.25.

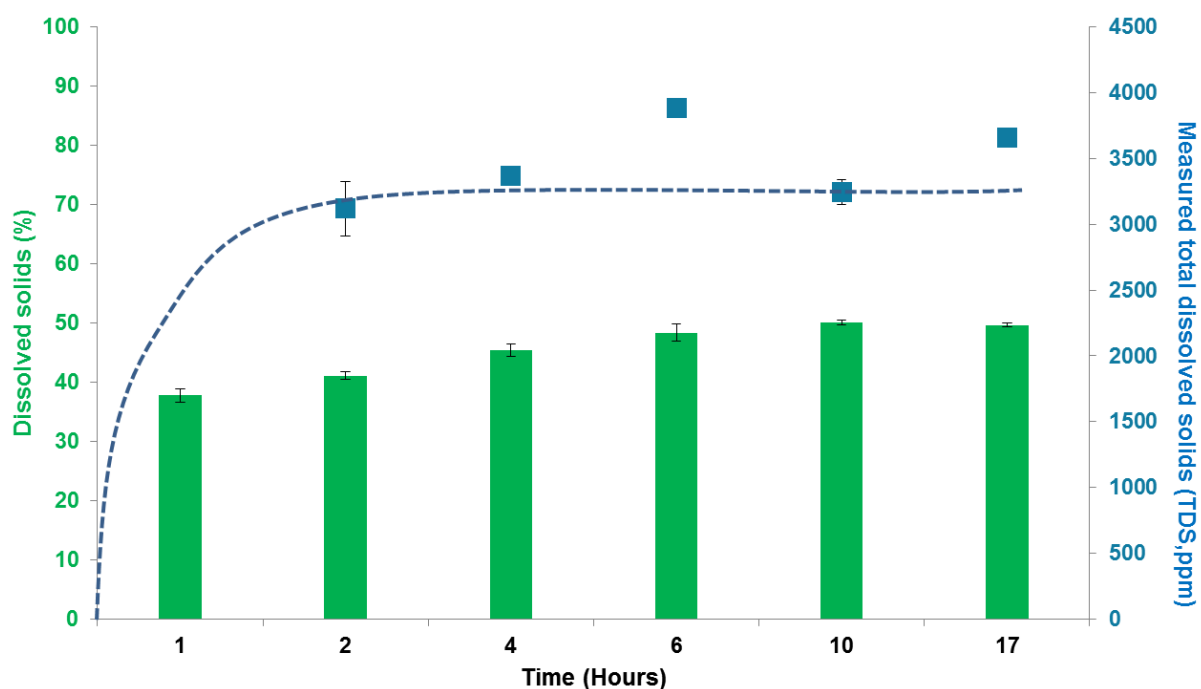


Figure 5.25. Effect of leaching duration on the measured total dissolved solids (TDS; ppm) in the leachate (closed blue square) and percentage (%) mass loss (closed green bars) after dissolution of MT_{ro} (MT:AS of 2:6; 550 °C; 45 minutes) under acidic conditions (3g/500mL; 0.6M HNO₃; 80 °C; 850 rpm; *n*=2).

From Figure 5.25, it is evident that TDS increases with an increase in dissolution time. The TDS gradually increases up to 3118.9 ± 206.6 ppm during the first 2 hours of dissolution before reaching a plateau within 4 to 6 hours, stabilising at 3496.4 ± 337.3 ppm. The same trend is observed for the percentage mass loss which increases from 37.8 ± 1.0 % after 1 hour to 45.4 ± 1.0 % before reaching a plateau at 46.9 ± 1.0 % within 4 to 6 hours. These results indicated that the optimal dissolution lies within the 4 to 6 hour region after which further dissolution may be negligible. The percentage mass loss increased from ≤ 41 % under uncontrolled pH conditions to ≤ 49 % under acidic conditions.

The corresponding elemental extraction efficiency data is presented in Figure 5.26 and is significantly higher for all elements in comparison to the uncontrolled pH conditions (Figure 5.20). The elemental extraction efficiency followed the same trend as the TDS where the extraction efficiency of all elements rapidly increased during the first 4 to 6 hours and then plateaued until the end of the experiment.

The most concentrated elements in the filtrates (Figure 5.26A) at completion of the dissolution experiments were Fe (188.8 ± 35.5 mg/l) and Cr (187.7 ± 34.9 mg/l). This was followed by Al (148.8 ± 10.1 mg/l), Si (109.8 ± 8.2 mg/l), Mg (94.4 ± 6.3 mg/l) and Ca (60.49 ± 4.4 mg/l). The extraction of all elements had stabilised after 6h of leaching and this reaction time was therefore adopted for all future experiments. Mg extraction appeared to be more rapid and have completed within 4h dissolution. Although the highest extraction efficiencies were obtained at different times during the reaction, the relative concentration at which Fe and Cr is leached is noteworthy. Fe and Cr is leached at a similar and almost equal

rate throughout the dissolution experiment. These findings suggest that Fe and Cr compete for the sulphate component of AS to form soluble Fe and Cr sulphate compounds during the thermochemical treatment. Altering the initial Fe:Cr ratio or using a Cr - deficient tailing may enhance the elemental extraction of Fe. The effect of Fe:Cr was investigated further in section 5.2.1.

The highest overall extraction in terms of percentage presented in Figure 5.26B is for Ca (85.7 ± 6.3 %) followed by Al (57.4 ± 3.9 %) and Si (33.7 ± 2.5 %). Elemental extraction is much lower for Fe (29.0 ± 6.1 %), Mg (28.7 ± 4.5 %) and Cr (21.2 ± 1.7 %). The co-extraction of the five elements Fe, Cr, Al, Mg and Ca demonstrates the competitive affinity of these elements for the activator, AS, during the thermochemical activation process. This also means that the thermochemical treatment is not element-specific. This co-extraction is also responsible for the limited extraction of Fe obtained.

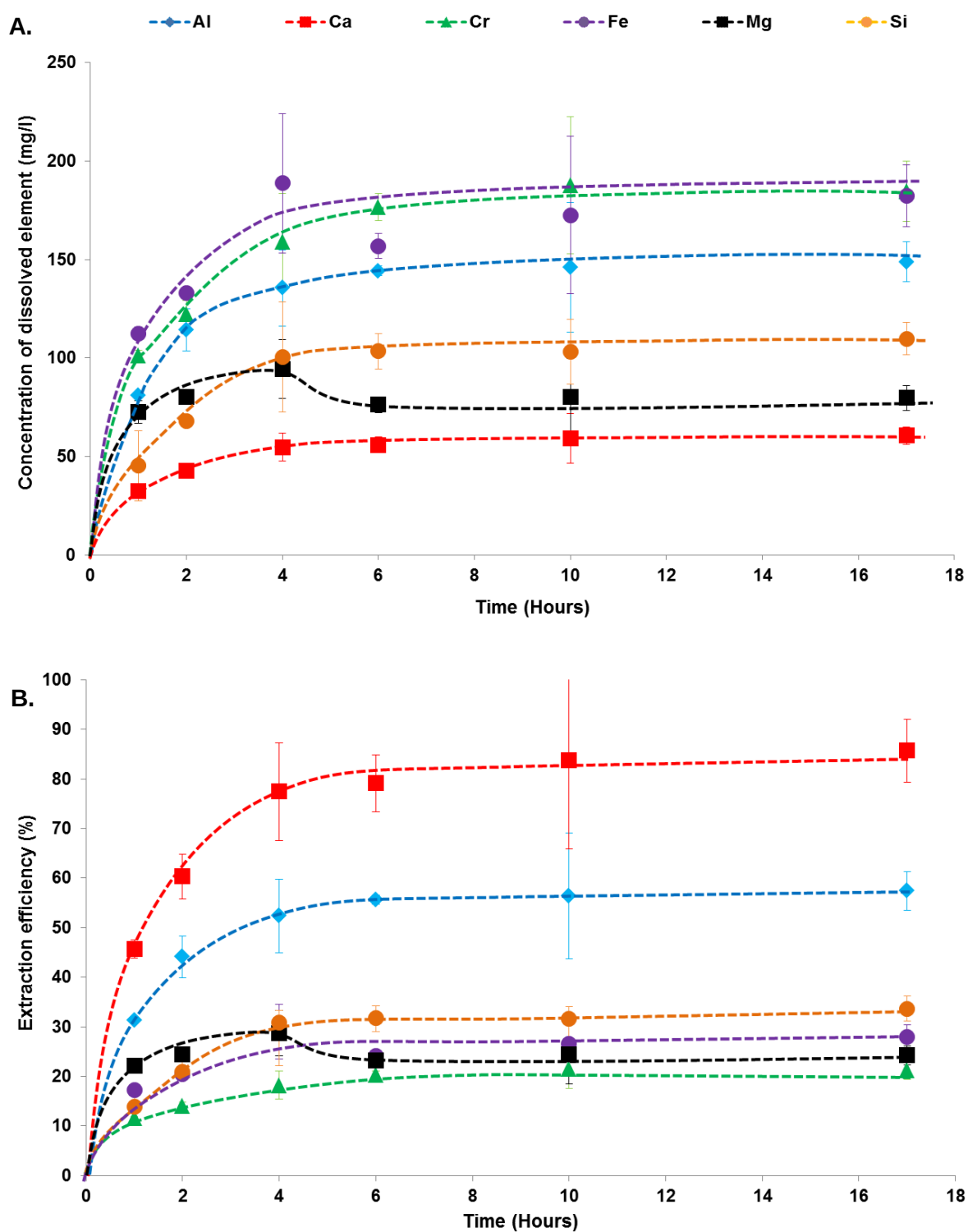


Figure 5.26. Temporal changes in the concentration of dissolved elements (A.) and corresponding elemental extraction efficiency (B.) after dissolution of MT_{ro} (MT: AS of 2:6; 550 °C; 45 minutes) under acidic conditions (3g/500ml; 0.6M HNO_3 ; 80°C; 850 rpm; $n=2$).

5.1.5.3 The effect of dissolution temperature on elemental extraction efficiency

The effect of dissolution temperature on elemental extraction efficiency was further investigated in an attempt to optimise the elemental extraction efficiency of the major elements. MT_{10} formed using the optimal thermochemical treatment was subjected to the dissolution procedure as described in section 3.3.4 at 60 °C and 95°C for 6 hours. The effect of dissolution temperature on the TDS and percentage mass of undissolved residues is presented in Table 5.6. The effect of temperature on elemental extraction efficiency is presented in Figure 5.27.

Table 5.6. Effect of dissolution temperature on the total dissolved solids (TDS;ppm) and percentage (%) mass loss for MT_{10} (MT_{45-75} : AS of 2:6; 550 °C; 45 minutes) after dissolution under acidic conditions (3 g/500 ml; 0.6M HNO_3 ; 850 rpm; mean $\pm$ sd; $n=2$).

	dissolution temperature (°C)		
	60	80	95
TDS (ppm)	2243.1 $\pm$ 34.7	3035.1 $\pm$ 186.1	3470.3 $\pm$ 318.4
Mass loss (%)	30.8 $\pm$ 0.7	48.4 $\pm$ 1.4	49.4 $\pm$ 0.2

During the 6 hour dissolution period, no differences in the colour of the suspensions were observed for the different temperatures. The leachates appeared greyish – blue and the colour of the undissolved residues remained grey. After filtration, the leachate produced at 60 °C displayed a light blue hue whereas the leachate produced at 95 °C exhibited a more intense blue colour. This suggested differences in the concentrations of transition metal complexes in the leachates produced at different temperatures.

Table 5.6 indicates that the TDS increased from 2243.1 $\pm$ 34.7 ppm to 3470.3 $\pm$ 318.4 ppm with an increase in dissolution temperature from 60 to 95 °C. The use of an intermediate temperature of 80 °C yielded an intermediate TDS value of 3035.1 $\pm$ 186.1 ppm which was slightly lower than that obtained at 95 °C. The same trend was observed for the mass loss following dissolution, which increased from 30.8 $\pm$ 0.7 % at 60 °C to 48.4 $\pm$ 1.4 % at 80 °C and slightly more to 49.4 $\pm$ 0.2 % at 95 °C. It was therefore anticipated that the elemental extraction efficiency would increase with increasing dissolution temperature, although the increase between 80 °C and 95 °C was much lower than the increase between 60 °C and 80 °C.

The elemental extraction efficiency as a function of temperature is presented in Figure 5.27. As expected, the rate of dissolution was temperature-dependent. Dissolution at 60° C yielded much lower elemental extraction efficiencies than at 80 °C and 95 °C. Fe and Cr are still leached out at a similar rate despite the change in dissolution temperature.

Overall, the elemental extraction achieved after dissolution at 60 °C is $\leq$ 6.2 % lower for all elements compared to dissolution at 80 °C, however after dissolution at 95 °C, an increase of $\leq$ 24.3 % for all elements was achieved. The highest elemental concentrations in solution after dissolution at 95 °C was obtained for Fe (225.8 $\pm$ 7.6 mg/l), Cr (234.8 $\pm$ 11.4 mg/l) and Al (153.2 $\pm$ 1.3 mg/l) which is equivalent to 34.7 $\pm$ 1.2 %, 26.9 $\pm$ 1.3 % and 59.1 $\pm$ 0.5 % respectively. Ca (56.5 $\pm$ 2.5 mg/l), Mg (82.9 $\pm$ 3.2 mg/l) and Si (99.5 $\pm$ 3.8 mg/l) is present in much lower concentrations, reaching a maximum of 80.0 $\pm$ 3.6 %, 25.2 $\pm$ 1.0 % and

30.5 ± 1.2 % respectively. This suggests that dissolution at 95 °C favours the extraction of Fe, Cr and Al. In contrast to these results Meyer *et al.*, (2014) have only obtained 31.2 % for Ca, 5.0 % for Mg and 9.1 % for Fe using untreated Merensky tailings in 2 M HCl at 70 °C after 8 hours. This suggests that the thermochemical treatment increases the reactivity of the MT therefore improving its extraction efficiency for all elements.

The relatively low elemental extraction from the MT is consistent for all variables investigated. The rate and extent of dissolution of the MT appears to be much higher after the thermochemical treatment. Teir *et al.*, (2007a) obtained higher elemental extractions for Mg (100 %) and Fe (38 – 67 %) from serpentinite obtained from the Hitura nickel mine stockpile following dissolution at 70 °C in acidic conditions. The extent of elemental extraction observed in this study is lower and this may be attributed to the combination of chemical and physical properties, reactivity of the mineral phases present in the MT and other factors such as the Fe:Cr ratio.

The optimised dissolution process so far was therefore as follows: An aqueous suspension of 3 g MT_{ro} in 0.6 M HNO₃ solution (500 ml) is constantly stirred at 850 rpm using an overhead stirrer at a temperature of 95 °C for 6 hours. In order to better understand the reaction, the undissolved solid residue generated under these conditions was characterised.

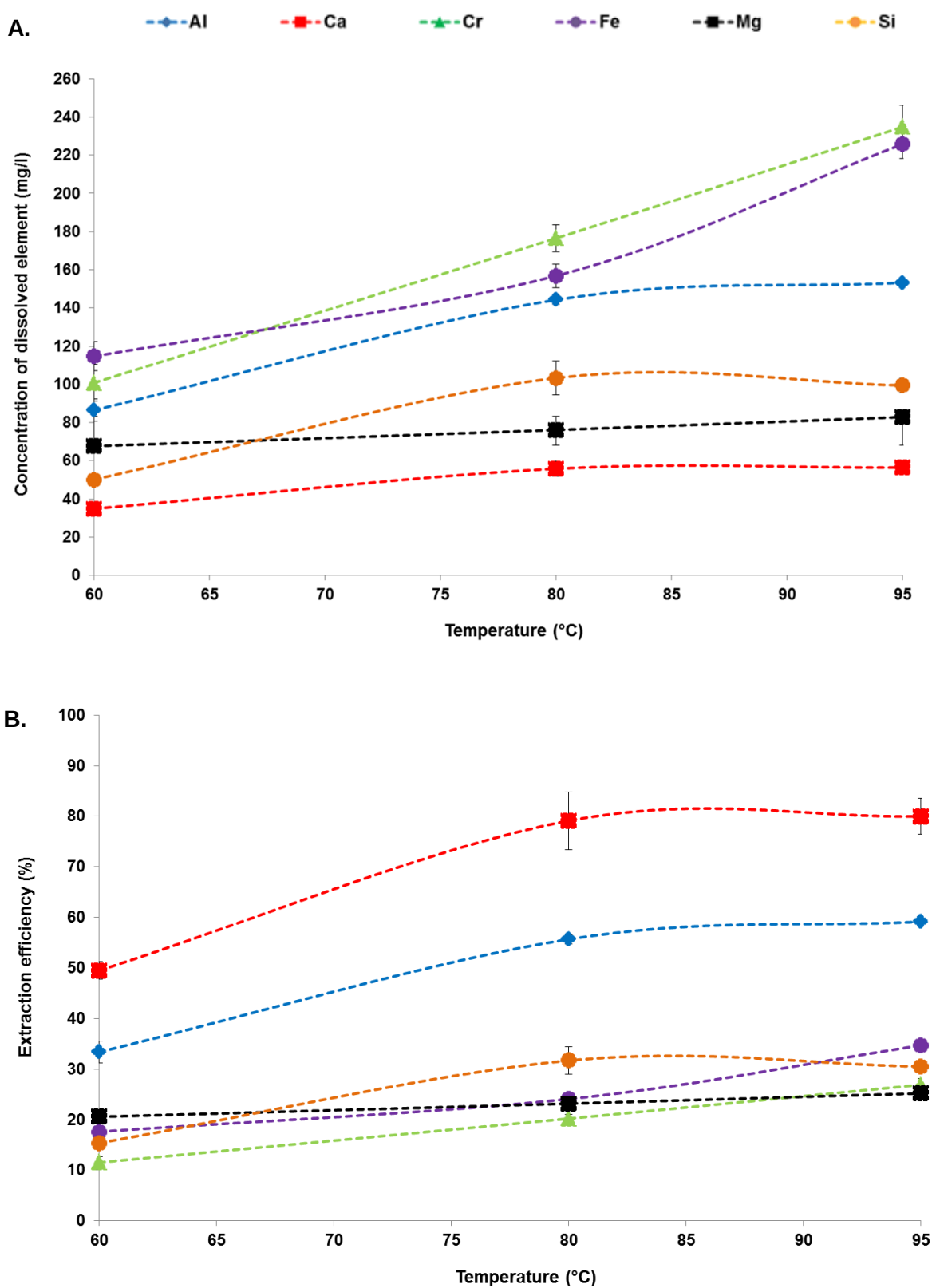


Figure 5.27. Effect of dissolution temperature on elemental extraction efficiency in (A.) mg/l and (B.) percentage (%) following dissolution of MT_{ro} (MT: AS of 2:6; 550 °C; 45 minutes) under acidic conditions (3g/500ml; 0.6M HNO_3 ; 6 hours, 850 rpm; $n=2$).

5.1.5.4 Characterisation of undissolved residue (MT_{res})

The characterisation of MT_{res} collected after the optimised dissolution procedure summarised above was completed using a combination of complementary techniques. These included XRD, Raman spectroscopy, FE-SEM and reflected light microscopy in order to examine the physical and chemical changes of MT_{ro} after the dissolution time has lapsed. By identifying the unreacted mineral phases present in MT_{res}, the rate limiting factors present in the thermochemical treatment and dissolution procedure could potentially be identified.

The XRD diffractogram of the undissolved residue generated following dissolution of the MT_{ro} (MT: AS of 2:6; 550 °C; 45 minutes) under acidic conditions at 95 °C is presented in Figure 5.28. The XRD spectrum of the MT_{res} (purple) demonstrated that the mikasaite phase (asterisks) formed during the thermochemical treatment is no longer present and was soluble under the optimal conditions of dissolution. The primary peaks of enstatite, spinel and amphibole are still present in MT_{res} however at a lower intensity possibly due to changes in crystallographic orientation of the mineral grains. This confirmed that these mineral phases had not fully reacted during the optimal thermochemical treatment owing to their high stability.

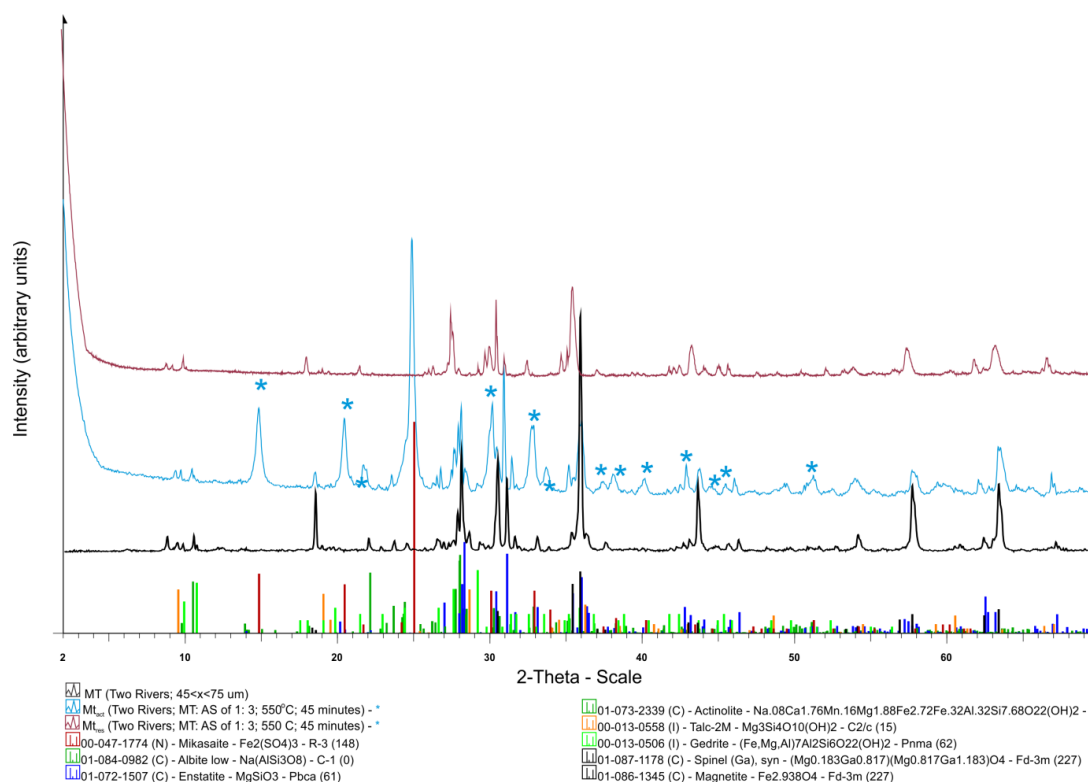


Figure 5.28. Comparative XRD diffractogram of the MT₄₅₋₇₅ (black), MT_{ro} (blue) and MT_{res} (purple) formed during dissolution of the MT_{ro} (MT: AS of 2:6; 550 °C; 45 minutes) under acidic conditions (3g/500ml; 0.6M HNO₃; 6 hours, 95 °C; 850 rpm). Asterisks (*) indicate the diffraction peaks of the Fe₂(SO₄)₃ (mikasaite) mineral phase.

Raman spectroscopy was conducted on MT_{res} to confirm the phases of the unreacted mineral phases. The comparative Raman spectra for MT_{45-75} (black), MT_{ro} (blue) and MT_{res} (orange) are presented in Figure 5.29. The results confirmed that the mikasaite phase was not present in MT_{res} and that the Raman spectrum for MT_{res} conformed to that of MT_{45-75} . The relatively intense peaks at 507 cm^{-1} , 662 cm^{-1} and 1010 cm^{-1} indicated the presence of feldspar, amphibole and pyroxene group minerals. This result confirmed that MT_{res} contained the primary mineral phases present in MT_{45-75} . Multipoint analysis will be required in order to obtain a representative spectrum of the MT_{res} .

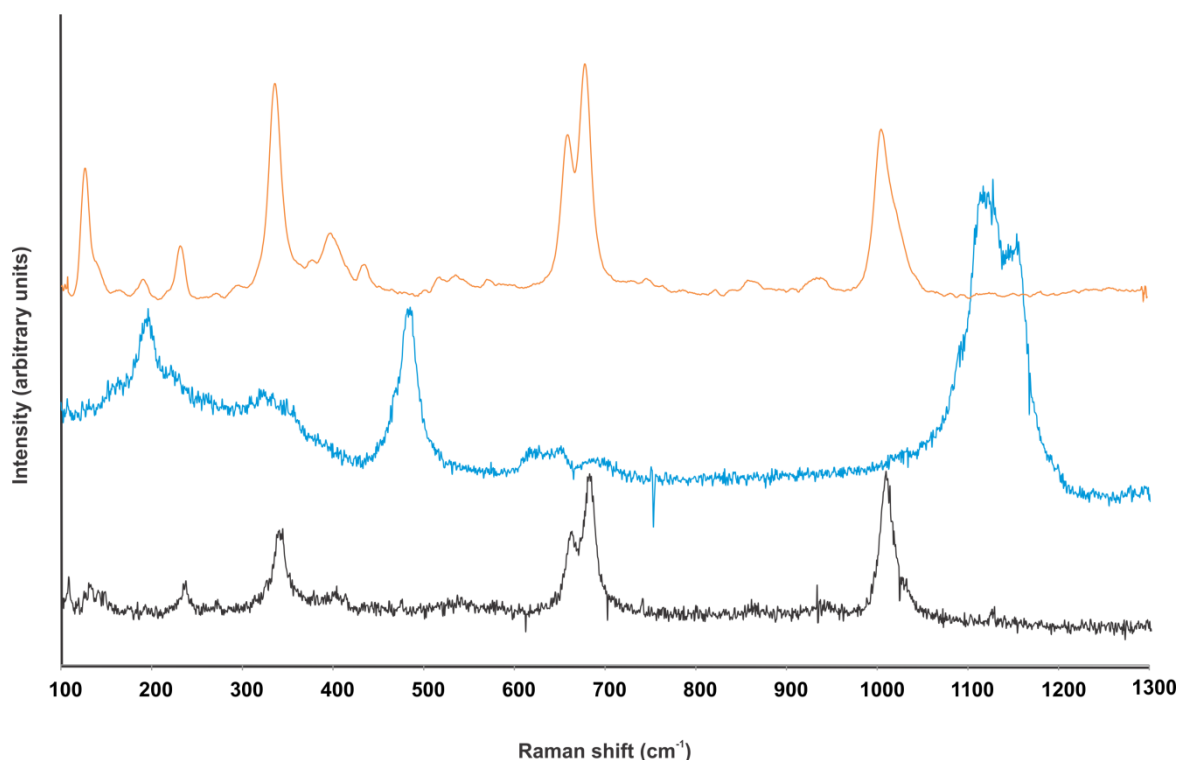


Figure 5.29. Comparative Raman spectra of MT_{45-75} (black), MT_{ro} (blue) and MT_{res} (orange) formed during dissolution of MT_{ro} (MT: AS of 2:6; $550\text{ }^{\circ}\text{C}$; 45 minutes) under acidic conditions (3g/500ml; 0.6M HNO_3 ; 6 hours, $95\text{ }^{\circ}\text{C}$; 850 rpm).

In order to examine the morphological changes of the MT_{ro} after dissolution, FE-SEM was conducted on the MT_{res} (Figure 5.30). The particles present in the MT_{res} are represented by a wide distribution in particle size ranging between 1 and $100\text{ }\mu\text{m}$ (Figure 5.30A). Some larger particles remained unreacted (Figure 5.30B) while others appeared fractured and showed signs of etching which has been caused by the thermochemical treatment and subsequent dissolution (Figure 5.30C). Figure 5.30D, Figure 5.30E and Figure 5.30F are taken on a fractured particle (Figure 5.30C, on the right) at higher magnification and clearly illustrates the deposition of smaller particles on the surface. The sub-micron particles are anhedral and indicate the destruction of the hexagonal crystal morphology. Furthermore the absence of hexagonal particles confirms they were soluble under acidic conditions of dissolution, in contrast to the MT_{res} under uncontrolled pH conditions (Figure 5.23) where the hexagonal structures with rounded edges were identified.

Optical microscopy was used to visually observe changes created during the optimal thermochemical treatment and dissolution procedure (section 3.3.4). The micrographs were obtained from both powders and polished stubs. The optical micrographs of the untreated tailings and undissolved residues are presented in Figure 5.31. As discussed in section 4.1.1.4 the MT is predominantly made up of silicates which appear as translucent - yellow crystals, surrounded by darker crystals of spinel, amphibole and pyroxene under visible light (Figure 5.31A) and in different shades of grey under reflected light (Figure 5.31B). From Figure 5.31C and Figure 5.31D, it is evident that the MT_{res} contain a large amount of unreacted particles.

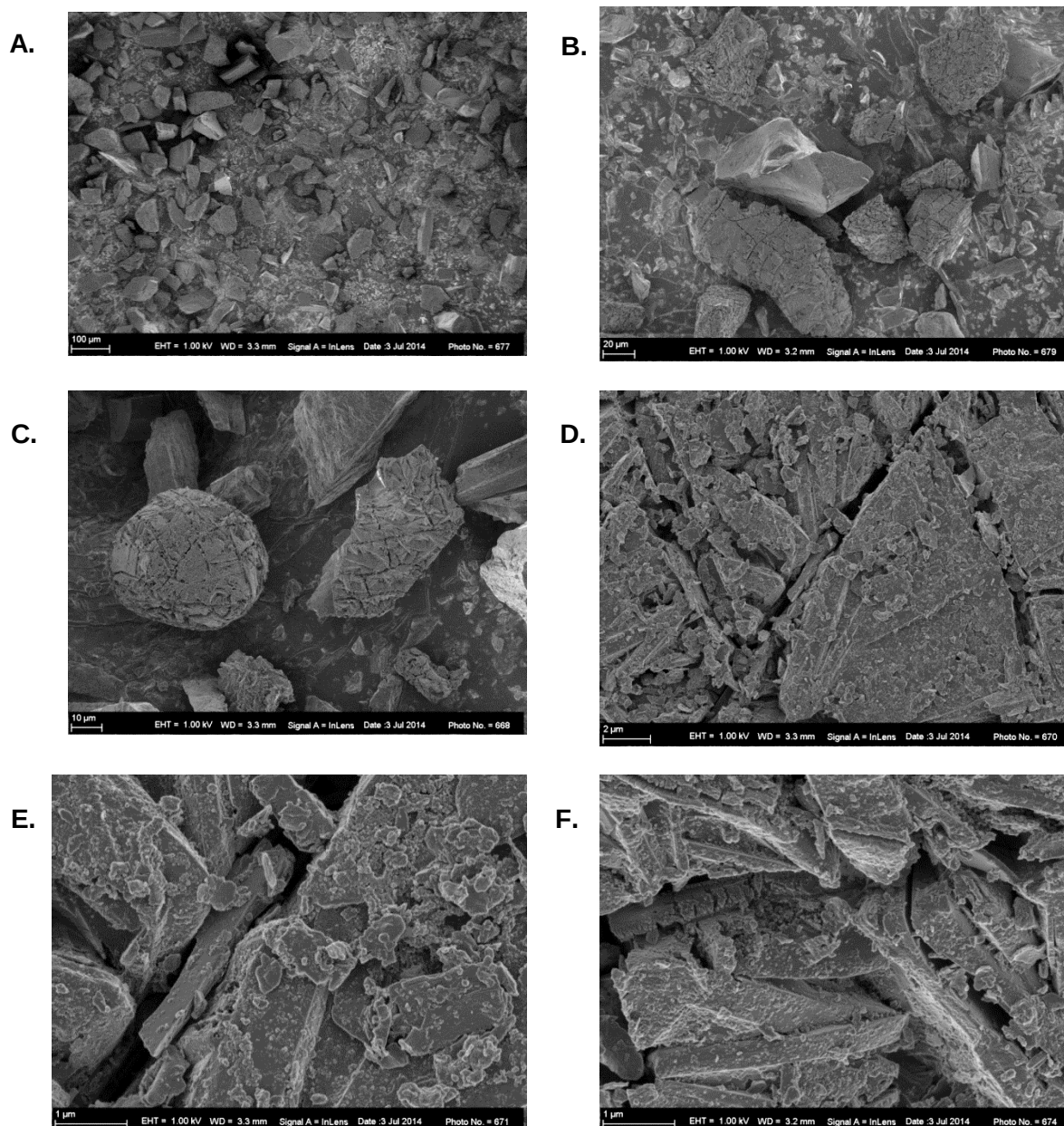


Figure 5.30. FE-SEM micrographs of the MT_{res} formed during dissolution of the MT_{ro} (MT: AS of 2:6; 550 °C; 45 minutes) under acidic conditions (3g/500ml; 0.6M HNO_3 ; 95 °C; 850 rpm; $n=2$). The micrographs were taken at (A.) 250x, (B.) 1000x, (C.) 2000x, (D.) 15000x, (E.) 45000X and (F.) 45000x magnifications.

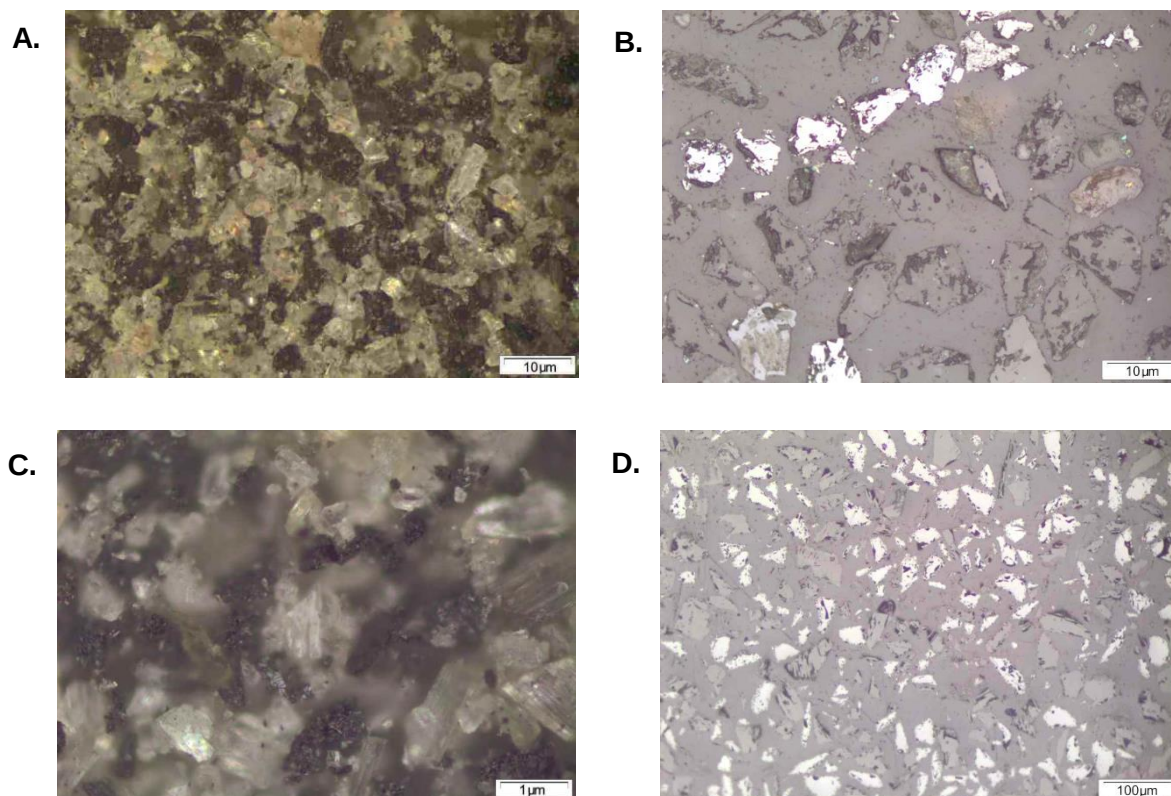


Figure 5.31. Optical micrographs of the MT_{45-75} (A.) under visible light, (B.) reflected light and MT_{res} remaining after the optimal thermochemical treatment (MT: AS of 2:6; 550 °C; 45 minutes) and dissolution procedure (3g/500ml; 0.6M HNO_3 ; 95 °C; 850 rpm) (C.) under visible light and (D.) reflected light.

Results from XRD and Raman spectroscopy indicate that the MT_{res} is composed predominantly of the primary mineral phases present in the MT_{45-75} . This suggests that the rate and extraction efficiency of the optimal thermochemical treatment is limited by the bulk chemistry and mineralogy of the MT_{45-75} . The thermochemical treatment and subsequent dissolution have resulted in a reduction in particle size which was confirmed by FE-SEM and optical microscopy. Further optimisation is required to improve the extraction efficiencies of the thermochemical treatment and dissolution procedure.

5.1.6 Effect of repeated thermochemical treatment on major element extraction efficiencies ('loop experiment')

The effect of repeating the thermochemical treatment was investigated to determine whether AS is the limiting reagent during the thermochemical step. The loop experiment alters the stoichiometric ratio of the MT_{45-75} and AS, which allows for the AS to be in excess. The thermochemical treatment was conducted as described in section 3.3.2 either once (1 cycle) or five consecutive times (5 cycles). The samples were then subjected to the optimal dissolution procedure.

The percentage mass loss following dissolution for the five cycles experiment ($56.4 \pm 0.8 \%$) was about 7 % higher than that obtained for the 1 cycle experiment ($49.4 \pm 0.2 \%$). This was a first indication that the elemental extraction efficiencies should be higher after 5 cycles than after 1 cycle of thermochemical treatment. The concentrations of dissolved metals and their corresponding elemental extraction efficiencies are presented in Figure 5.32. The looped experiment improved the extraction efficiencies of Al, Cr, Fe and Mg but decreased that of Si; the extraction of Ca remained unchanged. Cr ($349.3 \pm 25.6 \text{ mg/l}$) and Fe ($313.6 \pm 28.9 \text{ mg/l}$) were present in the highest concentrations in solution and the percentage extraction efficiencies increased by 13.1 % and 13.5 % respectively. Al ($189.9 \pm 6.1 \text{ mg/l}$) and Mg ($103.3 \pm 10.1 \text{ mg/l}$) were present at much lower concentrations, although they increased by 14.1 % and 6.2 % respectively. Dissolved Si ($65.7 \pm 2.7 \text{ mg/l}$) was present at a lower concentration and showed a decrease in extraction efficiency by 10.4 %. Results from this experiment indicated that the looped experiment improves the overall elemental extraction efficiency for Al, Cr, Fe and Mg. However the multiple steps of thermochemical treatment cause substantially higher energy requirements for a limited gain in elemental extraction efficiency. It could be conceived that two or three cycles may be sufficient to achieve similar improvements in extraction efficiencies, although this was not tested in this study.

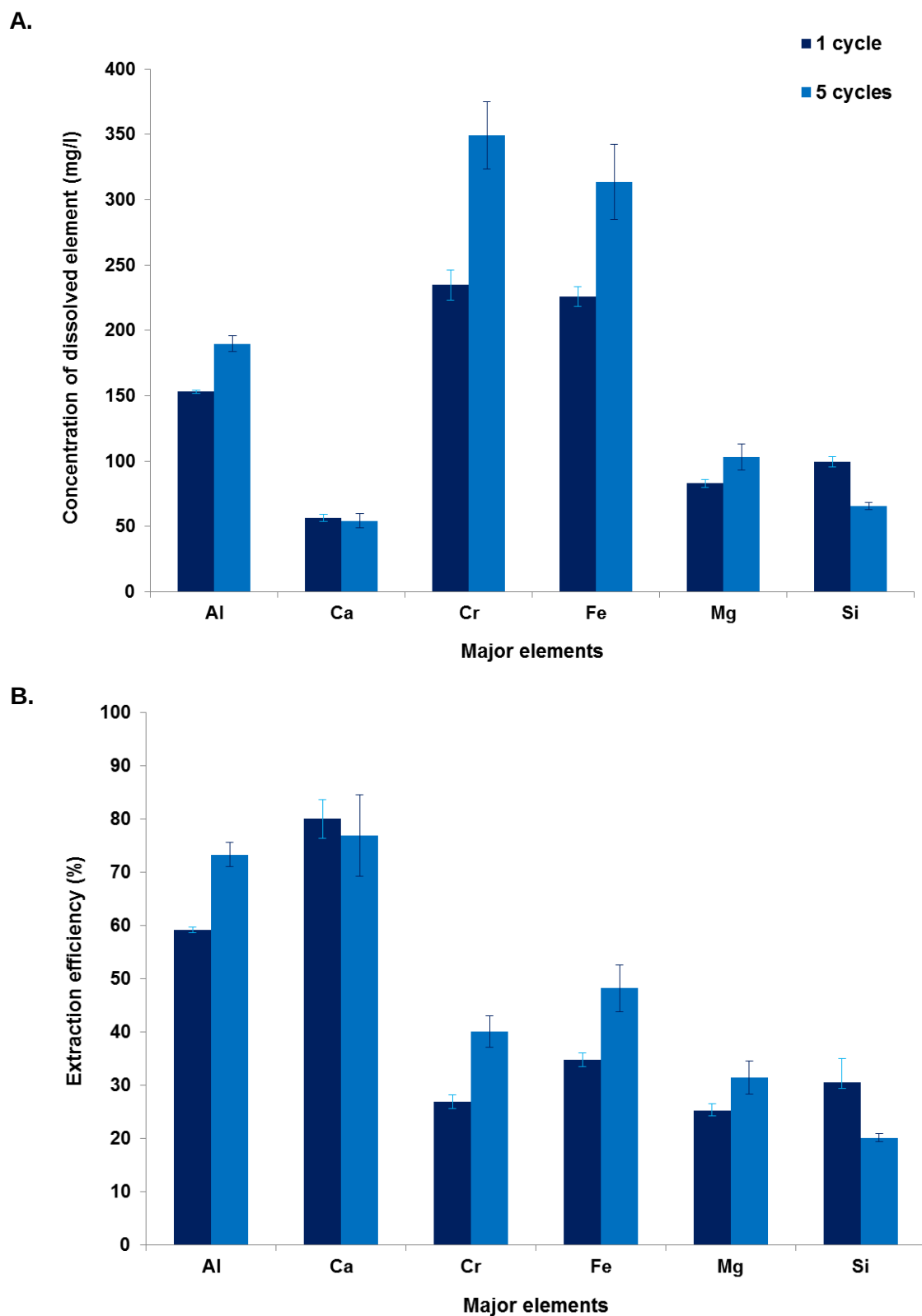


Figure 5.32. Effect of single cycle (dark blue) versus 5 cycles (light blue) of thermochemical treatment (MT₄₅₋₇₅: AS of 2:6; 550°C; 45 minutes) on major element extraction efficiencies in mg/l (A.) and elemental percentage (%) (B.) under optimal dissolution conditions (3g/500mL; 0.6M HNO₃; 95°C; 850 rpm; *n*=2).

5.1.7 Thermochemical treatment of tailings using other ammonium-based salts

5.1.7.1 *In-situ* TGA experiments

5.1.7.1.1 *In-situ* TGA experiments under dynamic temperature conditions

The thermochemical treatment of MT₄₅₋₇₅ using other ammonium-based salts (NH₄Cl, NH₄NO₃ and NH₄HSO₄) was studied and the results were compared to those obtained for (NH₄)₂SO₄ to compare their reactivity with PGE tailings during the thermochemical treatment. TGA analysis was first conducted to better understand the decomposition mechanisms of the ammonium salts and the interaction between MT₄₅₋₇₅ and ammonium salts during the thermochemical treatment.

The decomposition mechanisms of the ammonium salts were studied *in-situ* as described in section 3.3.3. Comparative TGA and DTA curves of NH₄Cl, NH₄NO₃, NH₄HSO₄ and (NH₄)₂SO₄ are presented in Figure 5.33. The thermal decomposition for the different ammonium salts are different. NH₄Cl and NH₄NO₃ have lower decomposition temperatures, i.e. approximately 200 °C compared to (NH₄)₂SO₄ and NH₄HSO₄ which begin to decompose at 300 °C.

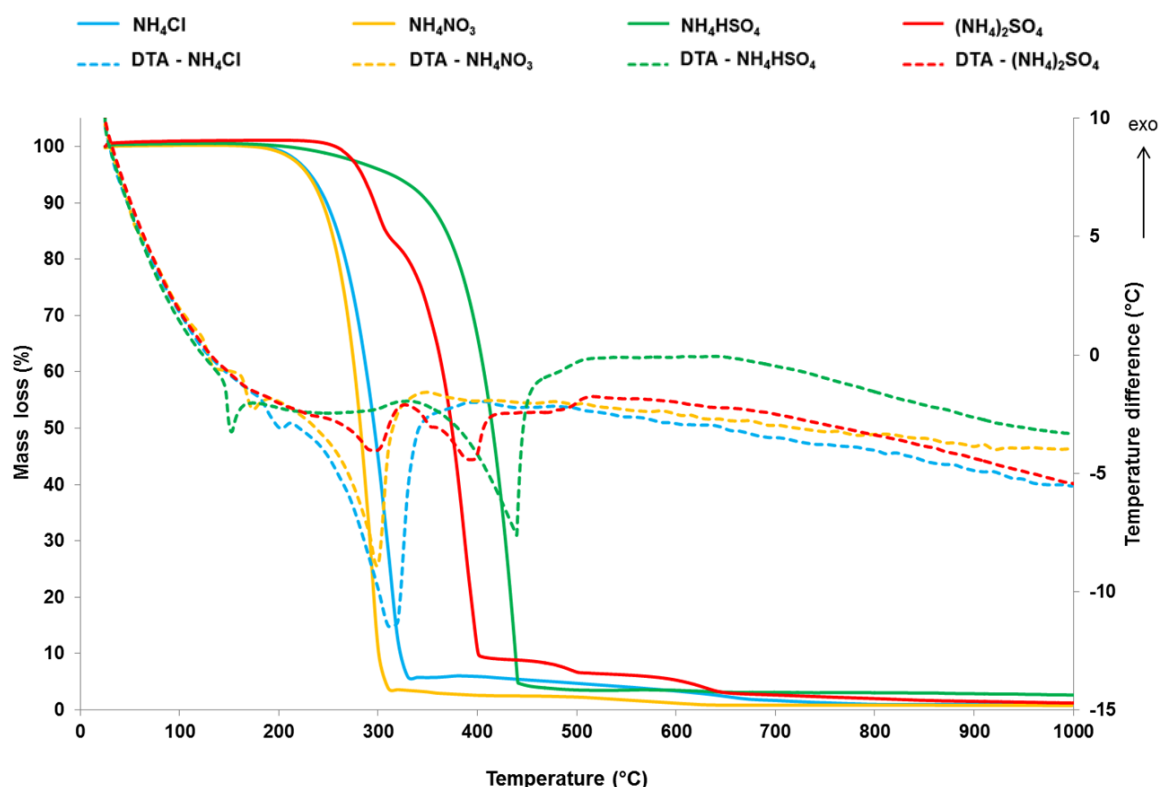


Figure 5.33. Comparative TGA (solid lines) and DTA (dashed lines) curves of NH₄Cl (blue), NH₄NO₃ (orange), NH₄HSO₄ (green) and (NH₄)₂SO₄ (red) under dynamic temperature conditions (heating rate of 10 °C per minute in air; $n=2$).

As indicated by the TGA curves, NH_4NO_3 (orange) had the lowest decomposition temperature compared to the other ammonium salts. The decomposition of NH_4NO_3 was completed by the dissociation of NH_4NO_3 into H_2O and N_2O (Erdey *et al.*, 1964). It can be seen that the mass of NH_4NO_3 remained relatively constant up until 200 °C before losing 96 % of its mass between 200 °C and 310 °C. The DTA curves indicated the presence of two endothermic peaks at 165 °C and 300 °C, which were indicative of melting followed by the thermal dissociation of NH_4NO_3 according to equation 5.5.



Above 300 °C the decomposition of NH_4NO_3 releases more heat and becomes explosive due to the increase in NO and NO_2 (Erdey *et al.*, 1964). The experimental mass loss agreed with the theoretical mass loss calculated for the full decomposition of NH_4Cl which is 100 %.

The decomposition of NH_4Cl is reversible and completed through an initial structural change which begins at approximately 188 °C followed by sublimation and dissociation of NH_4Cl into NH_3 and HCl (equation 5.4) above 200 °C. The HCl released during the decomposition is very reactive and can react with various metal oxides above 300 °C forming chlorides (Erdey *et al.*, 1964 and Olszak-Humienik, 2001).



The TGA curve of ammonium chloride (blue) indicates that the mass loss of NH_4Cl remains relatively constant up to 200 °C before decreasing to approximately 95 % at 330 °C. The DTA curve indicates the presence of two endothermic processes at 202 °C and 310 °C respectively. The endothermic peaks are indicative of a change in crystal structure and dissociation of NH_4Cl respectively. The experimental mass loss agrees with the theoretical mass loss calculated for the full decomposition of NH_4Cl which is 100 % (Erdey *et al.*, 1964).

The decomposition of NH_4HSO_4 is completed by the dissociation of NH_4HSO_4 into NH_3 and H_2SO_4 followed by the release of H_2O and SO_3 in the gas phases (equation 5.6 and 5.7 respectively). The H_2SO_4 formed during the decomposition is capable of fusing with various oxides which may result in the formation of metal sulphate compounds (Erdey *et al.*, 1964).



As indicated by the TGA curve, the mass loss of NH_4HSO_4 (green) remains relatively stable up until 210 °C before decreasing to 95 % at 440 °C. The DTA curves indicate the presence of two endothermic reactions at 153 °C and 440 °C which indicates the point at which the NH_4HSO_4 begins to melt followed by the decomposition of NH_4HSO_4 (Kiyoura and Urano, 1970). The experimental mass loss agrees with the theoretical mass loss calculated for the full decomposition of NH_4Cl which is 100 %.

5.1.7.1.2 *In-situ* TGA experiments under static temperature change

In parallel to this study, the thermal decomposition of the reaction between the different ammonium salts and MT was analysed *in-situ* using TGA as described in section 3.3.3. The results from these experiments may complement the findings of the thermochemical treatment which was conducted in a laboratory furnace. The TGA and DTA curves for the reaction between the MT and different ammonium salts under static temperature conditions are presented in Figure 5.34.

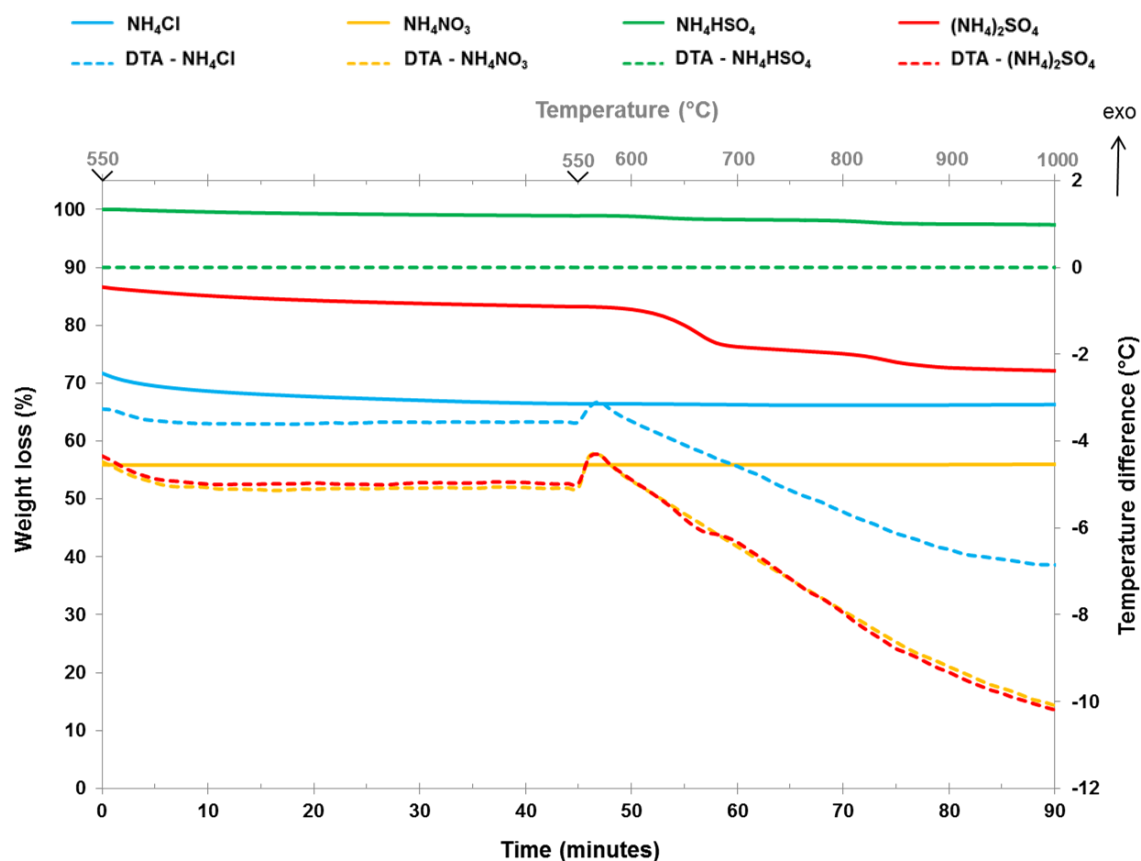


Figure 5.34. Comparative TGA (solid) and DTA (dashed lines) curves for the reaction between the MT and NH_4Cl (blue), NH_4NO_3 (orange), NH_4HSO_4 (green) and $(\text{NH}_4)_2\text{SO}_4$ (red) under static temperature conditions (isothermal heating at 550 °C for 45 minutes followed by dynamic temperature change at a heating rate of 10 °C per minute in air; $n=1$).

It is evident that the reaction mechanism between the different salts and MT is different. The TGA curves for the reaction between NH_4Cl (blue), NH_4NO_3 (yellow) and NH_4HSO_4 (green) remains relatively constant through the isothermal heating range and during the heating ramp. This suggests that the mineral phases present in the MT underwent little, if any, phase transformation during the thermal treatment using NH_4Cl , NH_4NO_3 and NH_4HSO_4 and therefore resulted in little formation, if any, of soluble chloride, nitrate and sulphate metal compounds respectively. This may be due to the small sample size, the in-homogeneity of the mixing prior to the reaction and/or the lower decomposition temperatures of the salts which may have fully decomposed by the time the sample pan was placed in the furnace of the TGA. The exothermic peaks present at the end of the 45 minute isothermal heating

program was also observed when $(\text{NH}_4)_2\text{SO}_4$ was used as an activator (section 5.1.2.2) and may indicate the solid phase transition into ammonium metal sulphate or a change in heat flow observed after the isothermal segment of the experiment. The TGA and DTA results confirm that the reaction between the MT and $(\text{NH}_4)_2\text{SO}_4$ is different to the other ammonium salts. This suggests that $(\text{NH}_4)_2\text{SO}_4$ may be the most suitable reagent capable of forming sulphate-based compounds from the MT.

5.1.7.2 Static furnace experiments

The interaction between the different ammonium-based reagents with MT_{45-75} was studied as described in section 3.3.3 in order to evaluate their effectiveness in converting the major elements into soluble metal compounds. The thermochemical treatment was applied using the standard reaction mixture of MT: ammonium salt (NH_4Cl , NH_4NO_3 , NH_4HSO_4 or $(\text{NH}_4)_2\text{SO}_4$) of 2:6 at 350 °C - 550 °C for 45 minutes. Changes in colour of the MT_{r0} observed during the thermochemical treatment at 550 °C are presented in Figure 5.35.

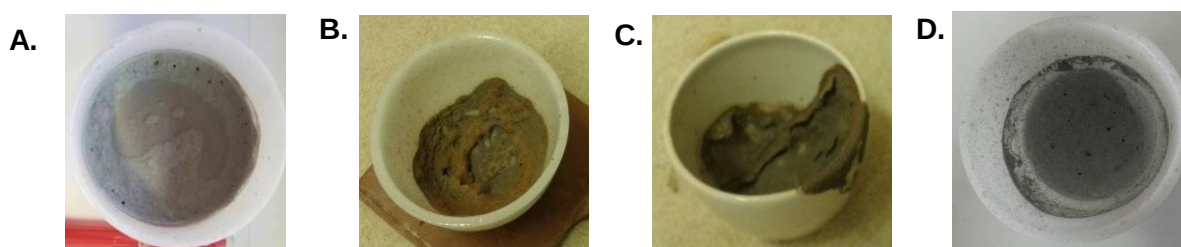


Figure 5.35. Changes in colour after the thermochemical treatment (MT_{45-75} : ammonium salt of 2:6; 45 minutes; 550 °C) of the MT and different ammonium salts, (A.) $(\text{NH}_4)_2\text{SO}_4$, (B.) NH_4Cl , (C.) NH_4NO_3 and (D.) NH_4HSO_4 .

From Figure 5.35, it is evident that the MT_{r0} formed using NH_4Cl and NH_4NO_3 , is different from the MT_{r0} formed with $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 . The MT_{r0} formed using NH_4Cl formed a dark grey mixture with a brown layer at the top whereas the MT_{r0} formed using NH_4NO_3 was dark grey. The sample containing NH_4NO_3 reacted strongly as soon as it was exposed to the experimental temperature, which resulted in the mixture being displaced from the crucible (Figure 5.35C). This observation was expected due to the thermal instability of NH_4NO_3 . The MT_{r0} formed using NH_4HSO_4 was similar to the MT_{r0} formed using $(\text{NH}_4)_2\text{SO}_4$ which appears green-light grey in colour. No noticeable colour changes were observed for the different temperatures however the MT_{r0} produced at 350 °C to 450 °C formed along the walls of the crucibles and hardened upon cooling, making it very difficult to remove. The MT_{r0} produced at 500 °C and 550 °C were in the form of free flowing powders therefore much easier to remove.

The mass loss observed during the thermochemical treatment of the different salts from 350 °C to 550 °C is presented in Figure 5.36. The mass losses obtained were different for the different salts studied, and they were also found to be temperature-dependent. The observed mass loss for the reaction between MT_{45-75} and ammonium salts (NH_4Cl , NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$) increases with an increase in treatment temperature, except for NH_4NO_3 which remains relatively constant. As expected the reactions using NH_4Cl and NH_4NO_3

resulted in a lower mass loss compared to NH_4HSO_4 up to 450 °C and $(\text{NH}_4)_2\text{SO}_4$ for all temperatures tested.

The highest mass loss (ca. 75 %) was observed for the reaction between NH_4NO_3 and MT_{45-75} and may be due to the low decomposition temperature of the salt. The mass loss observed for NH_4Cl increased from ca. 57 % at 350 °C and stabilised at ca. 75 % between 400 °C and 550 °C. This suggests that no further reaction occurs between the MT and NH_4Cl at 400 °C and above. The mass loss observed for NH_4HSO_4 is much lower at 350 °C (ca. 7 %) and 400 °C (ca. 17 %) compared to $(\text{NH}_4)_2\text{SO}_4$ and increases rapidly at 450 °C to 59% and stabilises at 70 % at 550 °C. The mass loss observed for $(\text{NH}_4)_2\text{SO}_4$ gradually increased from 14 % at 350 °C to 66 % at 550 °C. The lower weight loss observed for the reaction between MT and NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ indicates that the decomposition mechanisms of the salts may be slower allowing for more interaction with the MT resulting in a higher reactivity and possibly the formation of metal sulphates.

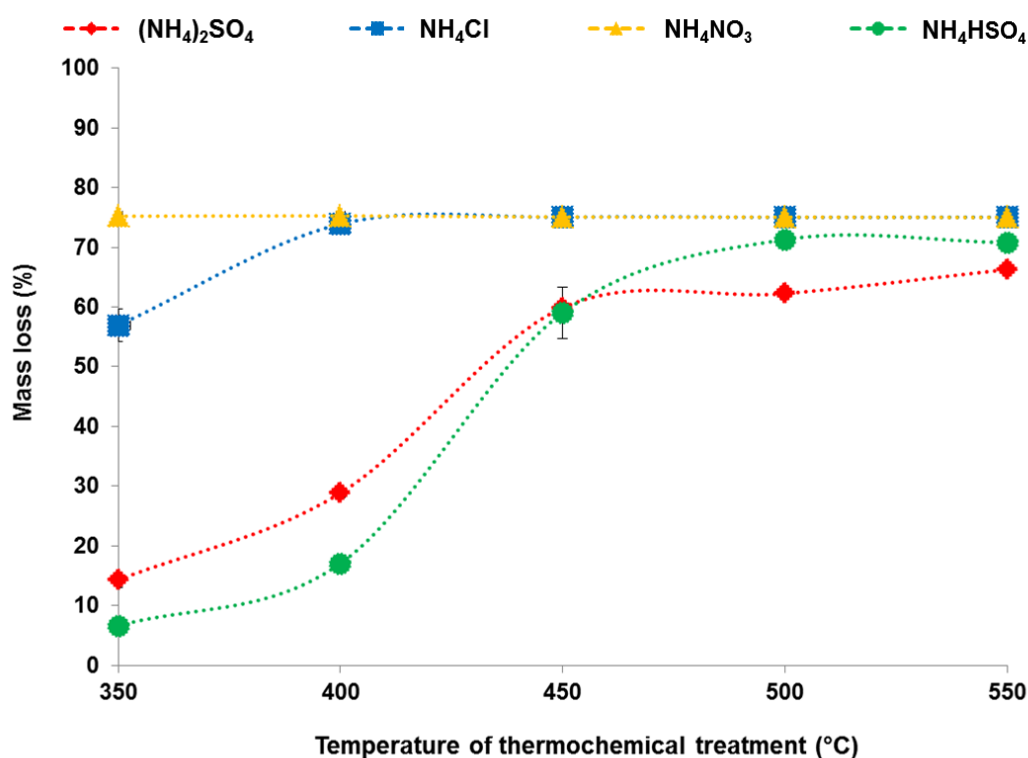


Figure 5.36. Mass loss observed during thermochemical treatment of the MT at different temperatures using different ammonium salts, $(\text{NH}_4)_2\text{SO}_4$ (red), NH_4Cl (blue), NH_4NO_3 (yellow) and NH_4HSO_4 (green; $n=4$).

5.1.7.2.1 Thermal characteristics of the treated mine tailings (MT_{ro})

TGA was used to determine the phase transformations of the MT_{ro} . The TGA and DTA curves of the MT_{ro} produced in the laboratory furnace as described in section 3.3.1.1 using different ammonium salts are presented in Figure 5.37. The TGA curves indicate differences in mass loss for the different products obtained from the thermochemical treatment with the ammonium salts, and the DTA curves indicate differences in the decomposition mechanisms

of the resulting MT_{ro} . The TGA curves for the MT_{ro} obtained using NH_4Cl (blue) and NH_4NO_3 (orange) remain relatively stable throughout the heating programme, with no mass loss observed. The DTA curves for the MT_{ro} obtained using NH_4Cl (blue) and NH_4NO_3 (orange) are baseline curves which indicated that the MT_{ro} did not undergo any phase transformation during the thermochemical treatment and that the NH_4Cl and NH_4NO_3 decomposed without reacting with the MT.

The TGA curve for the reaction between the MT_{45-75} and NH_4HSO_4 (green) follows a similar trend to the TGA curve for the reaction between the MT_{45-75} and $(NH_4)_2SO_4$ however a smaller mass loss (18 %) is observed. This suggests that the reaction between the MT_{45-75} and NH_4HSO_4 was successful in forming sulphate based compounds however the extent of the reaction may have been less than with $(NH_4)_2SO_4$ as indicated by the lower weight loss observed above 700 °C. The DTA curve for the MT_{ro} formed using NH_4HSO_4 indicates the presence of a small endothermic peak at 676 °C and is possibly due to the decomposition of the solid sulphate-based products (Nagaishi *et al.*, 1984).

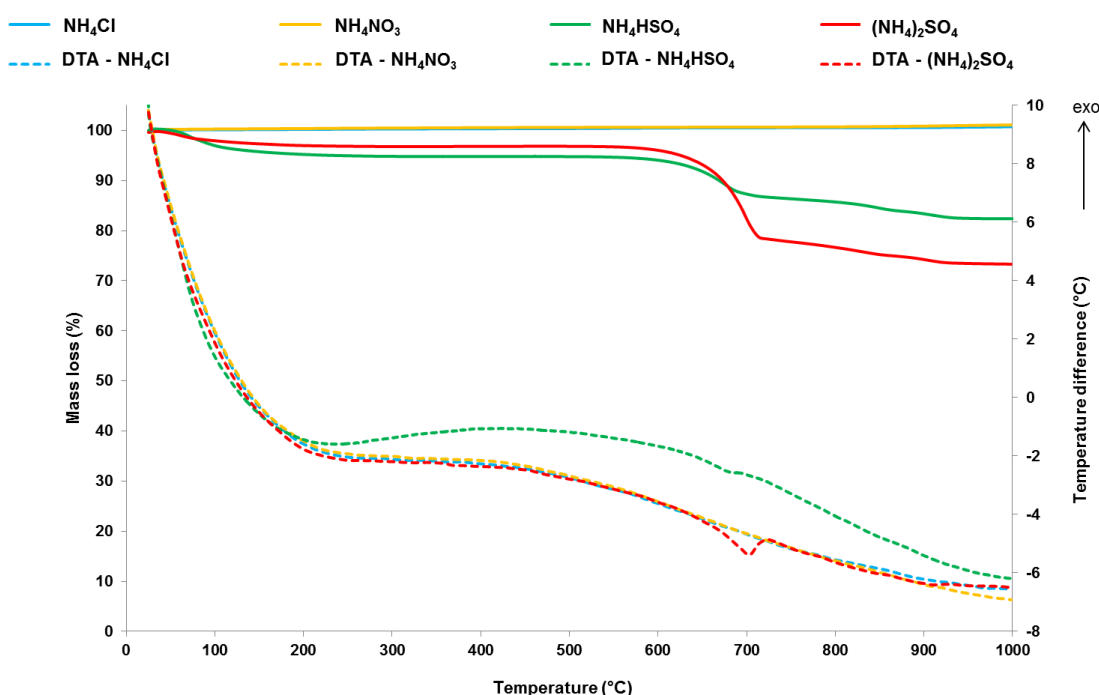


Figure 5.37. Comparative TGA and DTA curves for the MT_{ro} formed from the reaction between the MT and NH_4Cl (blue), NH_4NO_3 (orange), NH_4HSO_4 (green) and $(NH_4)_2SO_4$ (red) under dynamic temperature change (heating rate of 10 °C per minute in air; $n=1$).

5.1.7.3 Extraction efficiencies under acidic conditions (0.6 M HNO_3)

The extraction efficiencies from MT_{ro} formed using NH_4Cl , NH_4NO_3 , NH_4HSO_4 and $(NH_4)_2SO_4$ at 350 °C to 550 °C were examined using the optimal dissolution procedure. During dissolution of the resulting MT_{ro} noticeable colour differences were observed. For NH_4Cl and

NH_4NO_3 the colour of the solution changed from colourless to brown during the dissolution period and colourless after filtration, whereas for NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ the colour of the solution changed from colourless to dark grey during the dissolution period and light blue after filtration. These colour changes were observed for the MT_{ro} produced at different temperatures. From the results obtained in the TGA experiments and mass loss recorded during the thermochemical treatment, it is expected that NH_4Cl and NH_4NO_3 should result in a lower extraction efficiency compared to NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$. This was further examined by measuring the calculated percentage mass loss following dissolution which is presented in Figure 5.38.

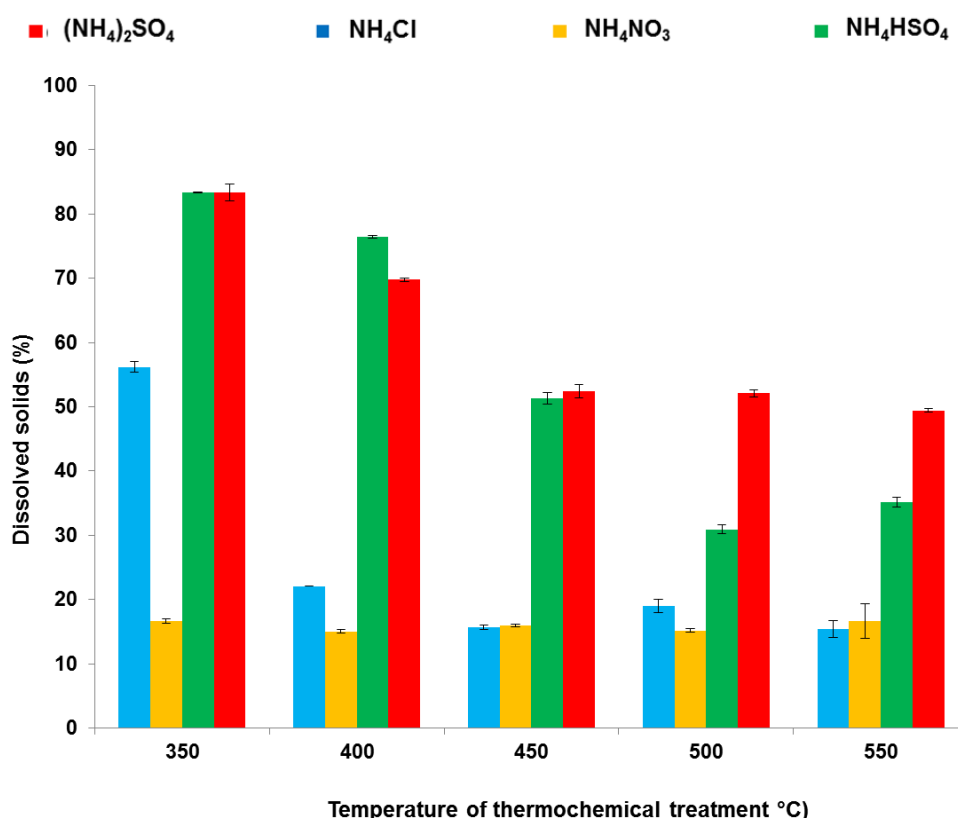


Figure 5.38. Effect of ammonium salt ($(\text{NH}_4)_2\text{SO}_4$ (red), NH_4Cl (blue), NH_4NO_3 (yellow) and NH_4HSO_4 (green)) and temperature on percentage (%) mass loss following dissolution of MT_{ro} (MT: ammonium salt of 2:6; 45 minutes) under optimal dissolution c (3g/500mL; 0.6M HNO_3 ; 80 °C; 850 rpm; $n=2$).

The percentage mass loss following dissolution (Figure 5.38) followed a similar trend when NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ were used. In this case the mass loss obtained after dissolution of the MT_{ro} was greater than when NH_4Cl and NH_4NO_3 were used. The percentage mass loss for NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ decreased with an increase in temperature; however the percentage mass loss for $(\text{NH}_4)_2\text{SO}_4$ increased relative to NH_4HSO_4 at 500 and 550 °C. At 350 °C, the percentage mass loss for NH_4HSO_4 (83.4 ± 0.1 %) and $(\text{NH}_4)_2\text{SO}_4$ (83.3 ± 1.3 %) were similar and may be due to a considerable amount of unreacted starting reagent and/or intermediate products in MT_{ro} which are water-soluble. At 400 °C, the percentage mass loss

was higher for NH_4HSO_4 (76.4 ± 0.2 %) compared to $(\text{NH}_4)_2\text{SO}_4$ (69.8 ± 0.3 %) and may be due to the higher temperature at which NH_4HSO_4 (approximately 200 °C) decomposes in comparison to $(\text{NH}_4)_2\text{SO}_4$ (approximately 300 °C; Figure 5.33). At 450 °C, the percentage mass loss for NH_4HSO_4 (51.3 ± 0.8 %) and $(\text{NH}_4)_2\text{SO}_4$ (52.4 ± 1.0 %) continued to decrease owing to the presence of less water-soluble unreacted reagent or decomposition products. At 500 °C and above, the percentage mass loss for $(\text{NH}_4)_2\text{SO}_4$ (49.4 ± 0.2 %) exceeded that for NH_4HSO_4 (35.2 ± 0.8 %).

The percentage mass loss obtained when using NH_4NO_3 and NH_4Cl was low and remained fairly constant over the temperature range. At 350 °C, the percentage mass loss for NH_4NO_3 (16.6 ± 0.3 %) was much lower in comparison to NH_4Cl (56.2 ± 0.8 %) which is relatively higher. This may be due to the lower decomposition temperatures of NH_4NO_3 (approximately 200 °C) and NH_4Cl (340 °C; Figure 5.33). These data suggest that the reaction between NH_4NO_3 or NH_4Cl with MT_{45-75} was limited, which will most likely result in low elemental extraction efficiencies. These results strongly confirmed that NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ had been more reactive during the thermochemical treatment, probably in the order $(\text{NH}_4)_2\text{SO}_4 > \text{NH}_4\text{HSO}_4 > \text{NH}_4\text{NO}_3 \approx \text{NH}_4\text{Cl}$. ICP analysis of the filtrates was used to complement the above data and showed that the above analysis did not hold for all elements.

The concentrations of dissolved major elements and their corresponding calculated extraction efficiencies are presented in Figures 5.39 and 5.40 respectively. The elemental extraction yield using NH_4Cl and NH_4NO_3 was much lower compared to NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ for all elements, except for Ca, which supported the results from TGA and percentage mass loss. It should be noted that the trend profile of Ca in terms of mg/l and percentage (Figures 5.39 and 5.40) is identical however the trend in mg/l (Figure 5.40) is obscured by the scale of the y-axis.

The elemental extraction efficiency for NH_4Cl and NH_4NO_3 displayed similar reactivity with MT_{45-75} resulting in similar extraction efficiencies for all major elements however at different temperatures. The highest elemental concentrations and efficiencies obtained using NH_4Cl was for Si (131.0 ± 9.1 mg/l; 40.2 ± 2.8 %), Mg (30.9 ± 3.3 mg/l; 9.4 ± 1.0 %) and Fe (42.0 ± 2.7 ; 6.5 ± 0.4 %) at 350 °C and for Ca (55.7 ± 0.4 mg/l; 78.9 ± 0.6 %) and Al (79.6 ± 4.5 mg/l; 30.7 ± 1.7 %) at 450 °C.

In comparison, the highest elemental concentrations and efficiencies using NH_4NO_3 was achieved by Al (78.8 ± 1.7 mg/l; 30.4 ± 0.7 %) and Mg (29.5 ± 0.1 mg/l; 9.0 ± 0.0 %) at 350 °C, Si (118.3 ± 5.0 mg/l; 36.3 ± 1.5 %) at 400 °C, Ca (55.4 ± 0.8 mg/l; 78.4 ± 1.0 %) and Fe (30.5 ± 0.4 mg/l; 4.7 ± 0.1 %) at 450 °C. The elemental concentration and extraction efficiency for Cr was relatively lower for NH_4NO_3 (1.3 ± 0.1 mg/l; 0.1 ± 0.0 %) between 350 °C and 400 °C compared to NH_4Cl (10.6 ± 13.1 mg/l; 1.2 ± 1.5 %) at 400 °C.

For major elements, it could therefore be said that these two ammonium salts are fairly selective for Ca extraction. Most of the Ca would probably come from plagioclase (25.2 wt. %), amphibole (7.9 wt. %), calcite (2.4 wt. %), and/or clinopyroxene (1.7 wt. %) mineral phases which are present in the MT_{45-75} . Ca from the calcite mineral phase may have contributed to the extraction efficiency up until 500 °C, above this temperature the CaCO_3 would have completely decomposed during the thermochemical treatment. Characterisation of the undissolved residues will be required to confirm the absence or decrease in modal abundance of the Ca-rich silicates minerals in order to ascertain the reactivity of the various mineral phases.

The elemental extraction efficiencies for $(\text{NH}_4)_2\text{SO}_4$ was higher than for NH_4HSO_4 and the other ammonium salts for all elements at all temperatures, except for Ca which had similar, if not identical Ca extraction efficiencies for all the ammonium salts tested. As much as about 60 % Al had been extracted when $(\text{NH}_4)_2\text{SO}_4$ was used during thermochemical treatment at 500 and 550 °C. The highest elemental dissolved concentrations reported were for Cr and Fe which were found in similar amounts in solution. $(\text{NH}_4)_2\text{SO}_4$ extracted twice more Fe and three times more Cr than NH_4HSO_4 , although the measured concentrations represented less than 35 % of the total Cr and Fe contained in the tailings. The extraction of Fe using $(\text{NH}_4)_2\text{SO}_4$ increased with an increase in temperature from 204.5 mg/l at 350 °C to 225.8 mg/l at 550 °C which only represented a 3.3 % increase from 31.4 % to 34.7 % respectively. However, the extraction was very similar in the temperature range 350-500 °C. The extraction efficiency for Mg remained low. It was slightly higher when using $(\text{NH}_4)_2\text{SO}_4$ (76.8 mg/l) in comparison to NH_4HSO_4 (45.8 mg/l) across the temperature range studied and represented 23.5 % and 13.9 % Mg respectively.

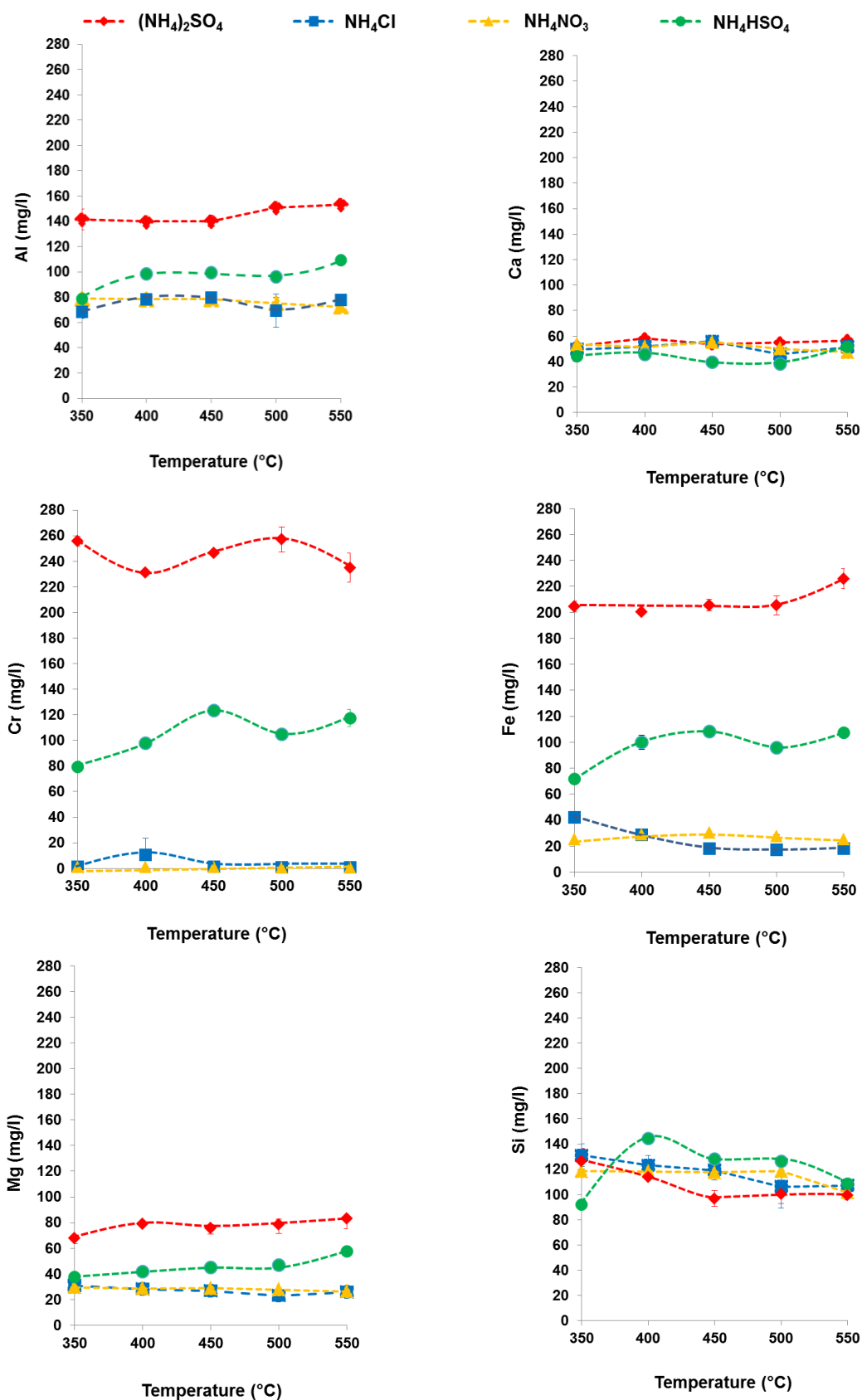


Figure 5.39. Effect of ammonium salt ($(\text{NH}_4)_2\text{SO}_4$ (red), NH_4Cl (blue), NH_4NO_3 (yellow) and NH_4HSO_4 (green)) on the concentration of dissolved elements (mg/l) after dissolution of MT_{ro} (MT: ammonium salt of 2:6; 45 minutes) under acidic conditions (3g/500ml; 0.6M HNO_3 ; 6 hours, 850 rpm; $n=2$).

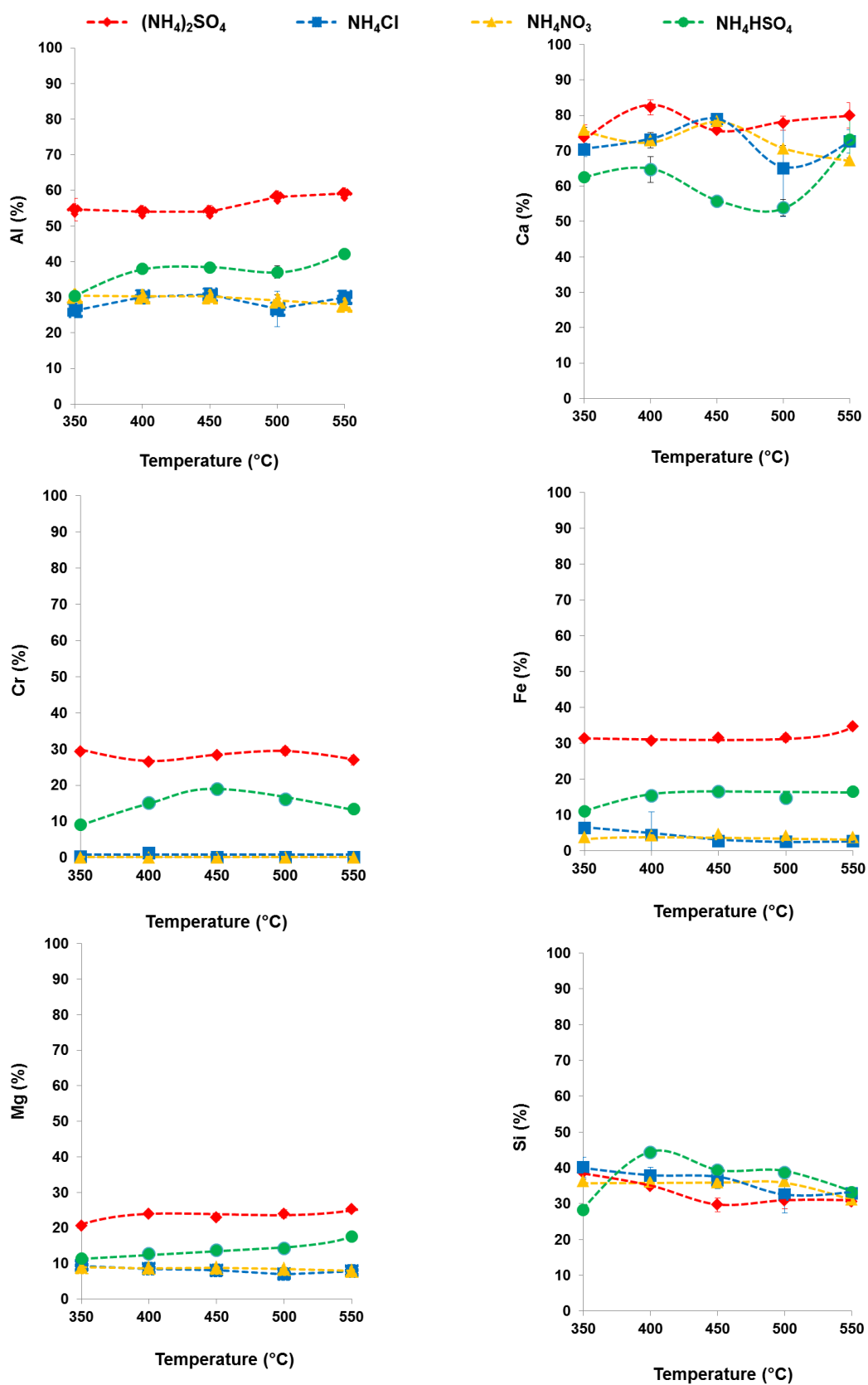


Figure 5.40. Effect of ammonium salt ($(\text{NH}_4)_2\text{SO}_4$ (red), NH_4Cl (blue), NH_4NO_3 (yellow) and NH_4HSO_4 (green)) on elemental extraction efficiency (%) after dissolution of MT_{ro} (MT: ammonium salt of 2:6; 45 minutes) under acidic conditions (3g/500ml; 0.6M HNO_3 ; 6 hours, 850 rpm; $n=2$).

Results from the dissolution experiments indicated that elemental extraction efficiency was strongly dependent on the type of ammonium salt used during the thermochemical treatment. The most suitable ammonium salts which yielded the highest elemental extraction was $(\text{NH}_4)_2\text{SO}_4$ generally between 500 °C and 550 °C for the duration of the thermochemical treatment investigated. Results from the ICP-OES analysis indicated that the extraction of Fe was limited, and suggested that the preferential extraction of Fe may be hindered by Cr and Al during the thermochemical treatment. NH_4Cl and NH_4NO_3 were suitable for the selective extraction of Ca and yielded similar results to NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$. The content of Ca in the tailings is probably too small to consider for a valorisation product. Mg extraction remained poor, which suggested that the element is locked in unreactive mineral phases.

5.2 Case Study No 2: Other PGE mine tailings

The reactivity of MT is influenced by its mineralogy, as well as other factors such as particle size and specific surface area. The study on the Two Rivers tailings suggested that the Fe:Cr ratio in tailings may also be one of the possible factors limiting the extraction of Fe and Al during thermochemical treatment. These elements are most likely to compete in the reaction with the ammonium-based reagent during thermochemical treatment. By controlling the Fe:Cr ratio in the starting material, the elemental extraction efficiency for these elements may be improved and the preferential extraction of Fe may be accomplished. This section investigated the effect of Fe:Cr ratio in the starting tailings on the extraction efficiency of these major elements using the optimal thermochemical treatment with AS combined to the optimal dissolution procedure described in section 3.3.4.

5.2.1 Elemental extraction efficiencies for mine tailings with different Fe:Cr ratio

This section presents and discusses the effect of Fe:Cr ratio in tailings on the extraction efficiencies of major elements. As discussed in section 3.4.1, MT with different Fe:Cr ratios were selected and were subjected to the thermochemical treatment at 350 °C and 550 °C followed by the optimal dissolution procedure described in section 3.3.4. The observed colour changes and mass loss are presented in Table 5.7.

Table 5.7. Changes in colour and percentage (%) mass loss of the MT₄₅₋₇₅ – AS reaction mixtures from Two Rivers (1 sample), Amandelbult (18 samples collected at different depths), Marico Chrome (2 surface samples collected from different locations on the tailings) and Rhovan Operations (2 samples collected at different depths) after thermochemical treatment (MT₄₅₋₇₅: AS of 2:6; 45 minutes) between 350 °C (*n*=2) and 550 °C (*n*=4).

Tailing Storage Facility (TSF)				
	Two Rivers	Amandelbult	Marico Chrome	Rhovan Vanadium
350 °C				
Average mass loss (%)				
	14.3 ± 1.3	22.3 ± 6.1	13.8 ± 0.4	17.8 ± 3.3
550 °C				
Average mass loss (%)				
	66.3 ± 0.2	68.7 ± 0.9	68.2 ± 0.0	70.2 ± 0.0

From Table 5.7, it is evident that the thermochemical treatment at 350 °C and 550 °C produces MT_{ro} of varying texture and colour. The treated MT produced at 350 °C formed viscous-like mixtures which hardened upon cooling. All reaction mixtures exhibited shades of grey. The thermochemical treatment at 550 °C produced reaction mixtures which were in the form of free flowing powder which varied in colour from light grey (Two Rivers and Amandelbult) to light grey – green (Marico Chrome tailings) respectively. However the MT_{ro} from Rhovan Operations formed a light brown reaction mixture and the surface turned a darker brown upon exposure to the atmosphere and may be attributed to oxidation of Fe.

The mass loss observed during thermochemical treatment varied between the different MT. A higher mass loss was observed after thermochemical treatment at 550 °C compared to 350 °C. The mass loss observed varied between 13.8 % and 22.3 % after thermochemical treatment at 350 °C and between 66.3 % and 74.1 % after thermochemical treatment at 550 °C. The colour changes observed prior to filtration after 6 hours of dissolution were the same for MT_{ro} from Amandelbult, Marico Chrome and Two Rivers produced at 350 °C and 550 °C. Initially the solution appeared murky – grey in colour and after filtration the solutions displayed a blue hue. This was observed for all MT (Amandelbult boreholes 1 and 2, Marico Chrome and Two Rivers) except for the Cr-depleted MT from Rhovan Operations which changed from light brown to colourless. The blue colour of the filtrates may therefore be due to soluble Cr complexes. No direct evidence that the blue colour is caused by soluble Cr complexes is provided. Given that the filtrates originating from leaching of treated Cr containing tailings exhibited a blue colour, whereas those generated by Cr-depleted tailings were colourless, provided a strong suggestion that the blue colour may have been due to soluble Cr-complexes.

The percentage mass loss for all MT remaining after the optimal dissolution procedure is presented in Figure 5.41. The mass loss was higher at 350 °C than at 550 °C and this was mainly due to the presence of unreacted AS and/or its thermal decomposition products in the reaction mixture generated at 350 °C, which are water-soluble.

The percentage mass loss for the MT after the thermochemical treatment at 350 °C was of the same order of magnitude as for Two Rivers MT (ca. 83 %). The percentage mass loss for the Amandelbult MT was ca. 83 %, Rhovan Vanadium ca. 86 % and Marico Chrome ca. 78 %. The percentage mass loss after the thermochemical treatment at 550 °C ranged between 41 and 49%, with Two Rivers being ca. 49 %, Rhovan Vanadium ca. 47 %, Amandelbult ca. 49 % and Marico Chrome ca. 41 %. The differences in the percentage mass loss were more likely due to differences in the mineralogy and chemical composition of the starting materials.

■ Amandelbult - borehole 1 □ Amandelbult - borehole 2 ■ Rhovan Operations ■ Marico Chrome ■ Two Rivers

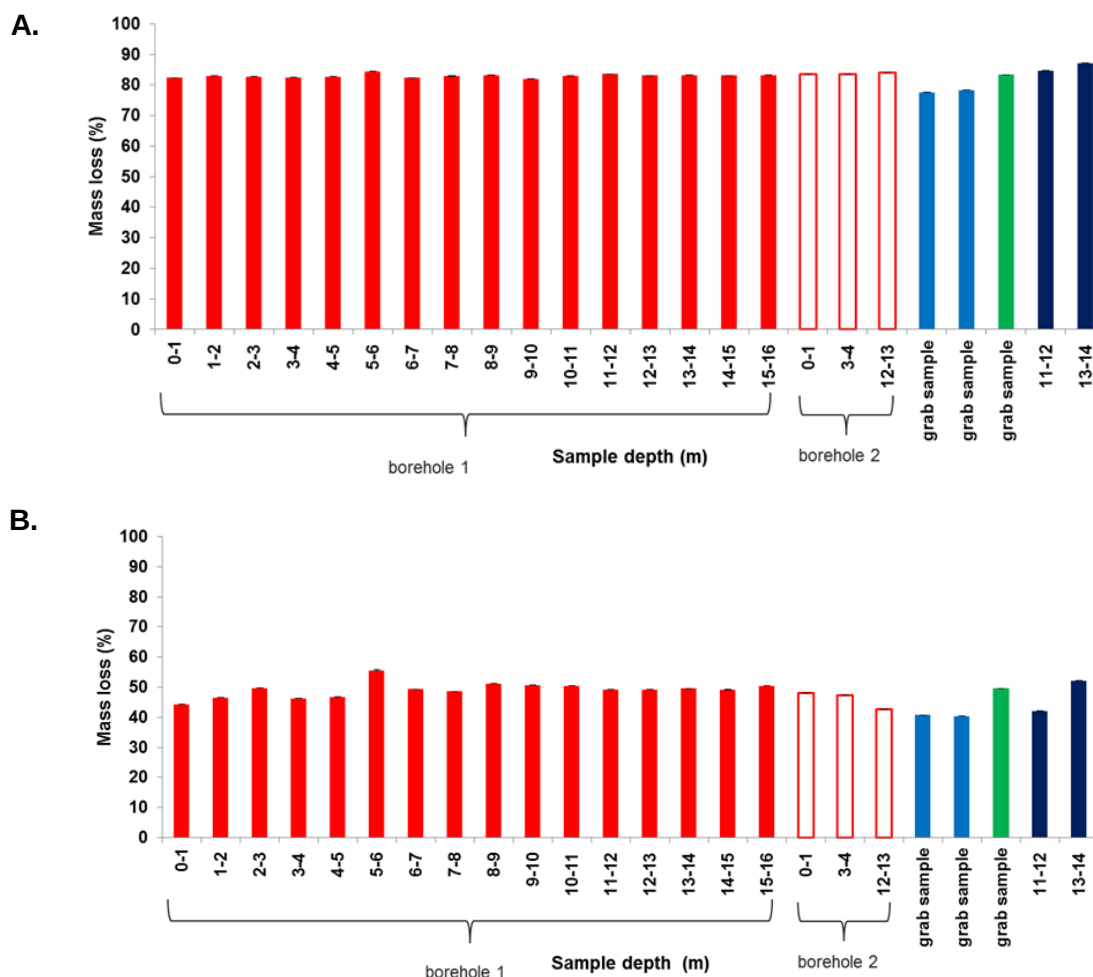


Figure 5.41. Percentage (%) mass loss after dissolution of MT_{ro} (MT: AS of 2:6; 45 minutes) at (A.) 350 °C and (B.) 550 °C under optimal dissolution conditions (3g/500ml; 0.6M HNO₃; 95 °C; 850 rpm; n=2).

The extraction efficiencies for MT with varying Fe:Cr ratio following thermochemical treatment at 350 °C and 550 °C and the optimal dissolution procedure are presented in Figures 5.42 to 5.47. The results for the corresponding concentrations of dissolved elements can be found in Appendix E.

As a general trend, the most efficient extraction (herewith defined as $\geq 50\%$) was achieved for Al and Ca, and the least efficient extraction (herewith defined as $\leq 40\%$) was achieved for Cr, Fe (except for Rhovan samples which was greater than 50%), Mg and Si. No attempt was made to link the results to the mineralogy due to the complexity of the mineralogy of the different tailings, which in some cases represent a mixture of tailings generated during mining of different reefs (e.g. Merensky and UG2). This will be part of a future project which will characterise the tailings in great detail and assess whether a link between the mineralogy and the elemental extraction efficiencies can be drawn.

Al extraction –

Al extraction efficiency obtained for the different temperatures is presented in Figure 5.42. The tailings samples are fairly enriched in Al (9-16 wt. %, except for Marico Chrome, ca. ≤ 4 wt. %; Table 4.6).

- The Marico Chrome tailings contain ca. ≤ 4 wt. % (Table 4.6) of Al and showed a low extraction at the two temperatures studied ($< 15\%$). This suggested that the mineral phases in which Al was trapped had been little reactive in the process and a more detailed characterisation study will be required to provide a proper identification of the non-reactive Al-phases.
- The tailings samples from Rhovan Operations were taken at different depths (11-12m and 13-14 m) and have a similar chemical composition (15-16%; Table 4.6). The ICP data shows no improvement in Al extraction when increasing the temperature of the thermochemical treatment from 350 °C to 550 °C. Al from the two samples were extracted to different extents, at ca. 46 % at 11-12 m and ca. 87 % at 13-14 m, which indicated significant differences in the reactivity of the two samples, although they were collected from the same core at a similar depth. One of the reasons for the difference in reactivity may have been variation in the mineralogy between the two samples, with XRD having shown that a different ratio between the spinel species and plagioclase characterise the two samples (Table 4.8).
- For the Two Rivers tailings sample, no improvement in Al extraction was observed between the two temperatures (ca. 59 %).
- Amandelbult samples were collected at different depths from the surface down to 16 m. A high variability in Al extraction between samples treated at 350 °C (55 - 100 %) was observed. Variation between samples narrowed down significantly for samples collected between 3 and 16 m (77 – 98 %). Samples collected near the surface ≤ 2 m had similar extraction efficiency at the two temperatures, which was less than 60%.

◆ Amandelbult - borehole 1 ▲ Amandelbult - borehole 2 ■ Rhovan Operations ● Marico Chrome ● Two Rivers

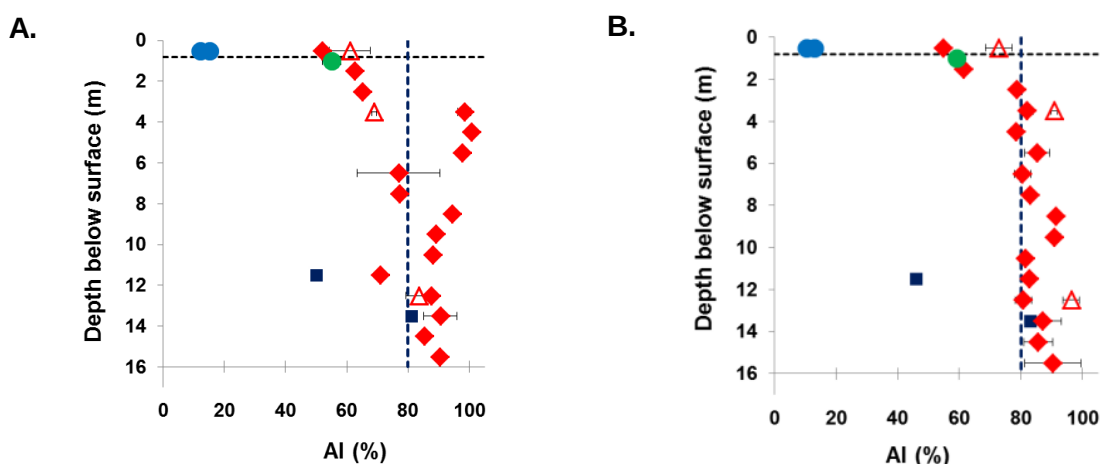


Figure 5.42. Differences in Al elemental extraction efficiency (%) following dissolution of MT_{ro} (MT: AS of 2:6; 45 minutes) at (A.) $350\text{ }^{\circ}\text{C}$ and (B.) $550\text{ }^{\circ}\text{C}$ under optimal dissolution conditions (3g/500ml; 0.6M HNO_3 ; $95\text{ }^{\circ}\text{C}$; 850 rpm, $n=2$) generated from tailings with varying Fe:Cr ratios.

Ca extraction –

Ca extraction efficiency for the different temperatures is presented in Figure 5.43. The Ca content in all tailings regardless of origin from the BIC was fairly low (< 6 wt. %, except for Rhovan Operations which was ca. 8 wt. %; Table 4.6).

- For Rhovan, Marico Chrome and Two Rivers there is no difference in Ca extraction efficiency between the two temperatures. The lowest extraction was obtained for one of the Rhovan Operations sample, ca. 30 % at 11 – 12 m. 50 - 60 % extraction was obtained for the Rhovan sample at 13 – 14 m and one of the Marico Chrome samples. Ca from the other Marico Chrome sample was much more reactive with an extraction efficiency $\geq 60\text{ }%$, which indicated the mineralogical heterogeneity of the tailings at the surface of the TSF. This was also indicated by XRD (Table 4.8).
- In contrast, temperature had a significant effect on Ca extraction for the Amandelbult tailings for all depths sampled (Figure 5.43), with an elevated temperature ($550\text{ }^{\circ}\text{C}$) facilitating more extraction ($\geq 80\text{ }%$) than a lower temperature ($350\text{ }^{\circ}\text{C}$; $< 80\text{ }%$).

◆ Amandelbult - borehole 1 △ Amandelbult - borehole 2 ■ Rhovan Operations ● Marico Chrome ● Two Rivers

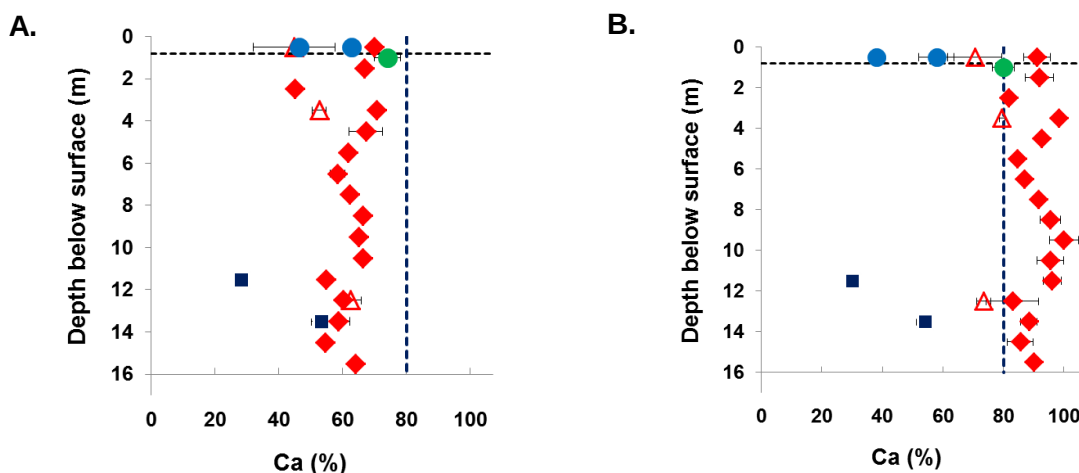


Figure 5.43. Differences in Ca elemental extraction efficiency (%) following dissolution of the MT_{10} (MT: AS of 2:6; 45 minutes) at (A.) $350\text{ }^{\circ}\text{C}$ and (B.) $550\text{ }^{\circ}\text{C}$ under optimal dissolution conditions (3g/500ml; 0.6M HNO_3 ; $95\text{ }^{\circ}\text{C}$; 850 rpm, $n=2$) generated from tailings with varying Fe:Cr ratios.

Cr extraction –

Cr extraction efficiency for the different temperatures is presented in Figure 5.44. The Rhovan and Marico Chrome tailings were deficient in Cr (<1 wt. %; Table 4.6). The Two Rivers tailings sample was the most enriched sample in Cr (ca. 32 wt. %) and the amount of Cr in the Amandelbult decreased from ca. 22 - 27 wt. % down to 15 wt. % or lower with depth.

- Approximately 30 % of Cr was extracted from the Two Rivers tailings sample and this result was not improved when the temperature of the thermochemical treatment was increased from $350\text{ }^{\circ}\text{C}$ to $550\text{ }^{\circ}\text{C}$.
- For the Amandelbult tailings samples, a similar observation regarding the variation in extraction between samples collected at different depths was made for Cr as the one for Al. In short, a higher variation between samples was observed at $350\text{ }^{\circ}\text{C}$ (28 – 68 %) than at $550\text{ }^{\circ}\text{C}$ (20 – 43 %). For about half of the samples, Cr extraction had been reduced at $550\text{ }^{\circ}\text{C}$ compared to $350\text{ }^{\circ}\text{C}$.

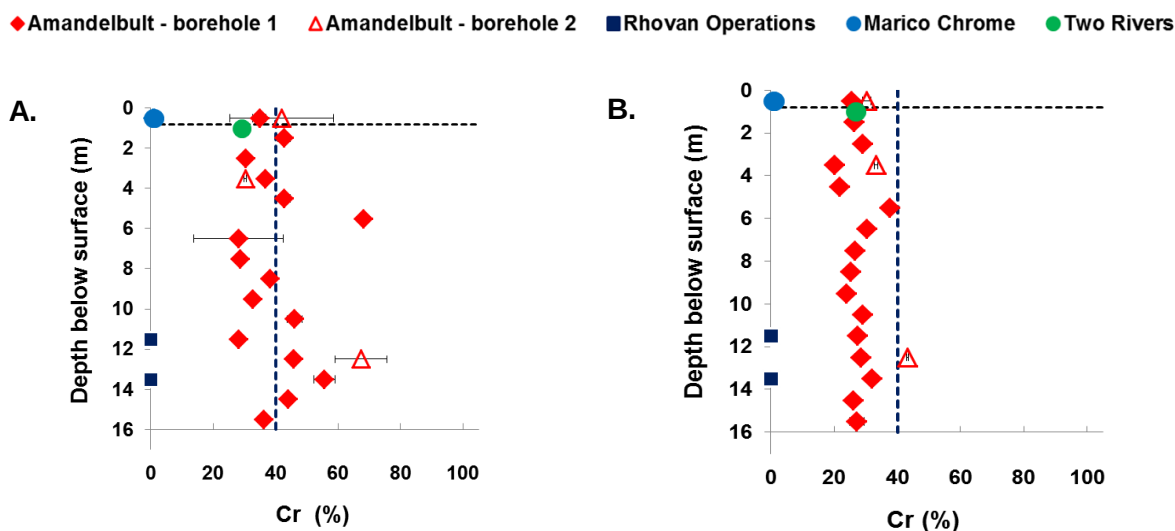


Figure 5.44. Differences in Cr elemental extraction efficiency (%) following dissolution of MT_{ro} (MT: AS of 2:6; 45 minutes) at (A.) $350\text{ }^{\circ}\text{C}$ and (B.) $550\text{ }^{\circ}\text{C}$ under optimal dissolution conditions (3g/500ml; 0.6M HNO_3 ; $95\text{ }^{\circ}\text{C}$; 850 rpm, $n=2$) generated from tailings with varying Fe:Cr ratios.

Fe extraction –

Fe extraction efficiency for the different temperatures is presented in Figure 5.45. All PGE tailings were fairly concentrated in Fe, with concentrations ranging between ca. 15 – 27 wt. % (Table 4.6).

- The most significant improvement in Fe extraction with increasing temperature was achieved for the Cr-depleted Rhovan Operations tailings sample, 40 – 52 % at $350\text{ }^{\circ}\text{C}$ to 63 – 72 % at $550\text{ }^{\circ}\text{C}$. In contrast, a decrease in Cr extraction with an increase in thermochemical treatment was observed for the other Cr-depleted tailings from Marico Chrome from ca. 16 % to 10 %.
- Variation in elemental extraction for the Amandelbult tailings was slightly narrowed down between samples at higher temperatures (28 - 41 %) compared to lower temperatures (23 – 42 %). No significant improvement was made by increasing the temperature of the thermochemical treatment from $350\text{ }^{\circ}\text{C}$ to $550\text{ }^{\circ}\text{C}$.
- The best Fe extraction was achieved for the Rhovan Operations tailings sample. The extent of extraction was different for the samples collected at the two different depths, with ca. 72 % extraction for the sample collected at 11 – 12 m and ca. 63 % extraction for the one collected at 13 – 14 m.

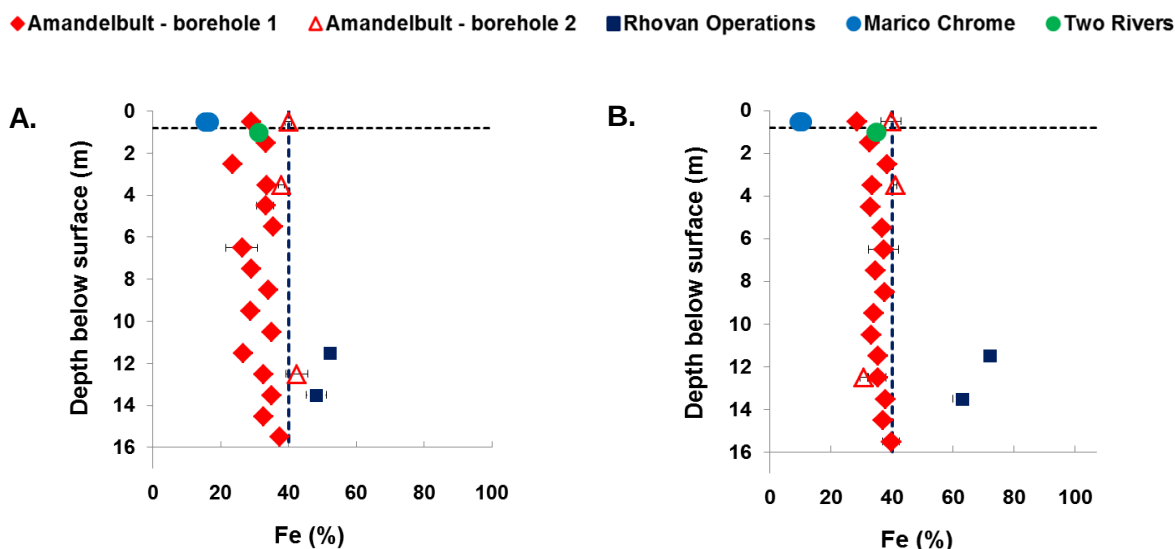


Figure 5.45. Differences in Fe elemental extraction efficiency (%) following dissolution of MT_{ro} (MT:AS of 2:6; 45 minutes) at (A.) 350 °C and (B.) 550 °C under optimal dissolution conditions (3g/500ml; 0.6M HNO_3 ; 95 °C; 850 rpm, $n=2$) generated from tailings with varying Fe:Cr ratios.

Mg and Si extraction –

Mg and Si extraction efficiencies for the different temperatures are presented in Figures 5.46 and 5.47 respectively. Most tailings are fairly concentrated in Mg (≥ 13 wt. %; except for Rhovan Operations which contained ca. 3 wt. %). Si varied between ca. 17 – 51 wt. % between samples (Table 4.6). Mg and Si might not follow the same mechanism of extraction; however, similar trends in the extent of extraction of the two elements for the different tailings were observed and is summarised below.

- Overall there is no improvement in Mg and Si extraction when increasing the temperature from 350 °C to 550 °C.
- Variation in Mg and Si extraction for the Amandelbult samples were narrowed down with an increase in temperature from 350 °C to 550 °C.
- For the Rhovan Operation samples, the extent of Si extraction was doubled when increasing the thermochemical treatment temperature from 350 °C to 550 °C.

◆ Amandelbult - borehole 1 ▲ Amandelbult - borehole 2 ■ Rhovan Operations ● Marico Chrome ● Two Rivers

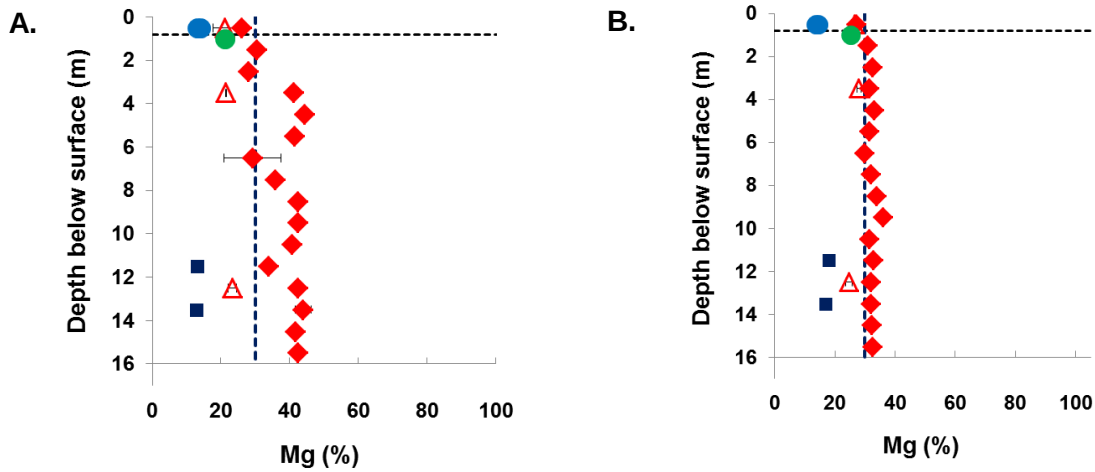


Figure 5.46. Differences in Mg elemental extraction efficiency (%) following dissolution of MT_{ro} (MT:AS of 2:6; 45 minutes) at (A.) $350\text{ }^{\circ}\text{C}$ and (B.) $550\text{ }^{\circ}\text{C}$ under optimal dissolution conditions (3g/500ml; 0.6M HNO_3 ; $95\text{ }^{\circ}\text{C}$; 850 rpm, $n=2$) generated from tailings with varying Fe:Cr ratios.

◆ Amandelbult - borehole 1 ▲ Amandelbult - borehole 2 ■ Rhovan Operations ● Marico Chrome ● Two Rivers

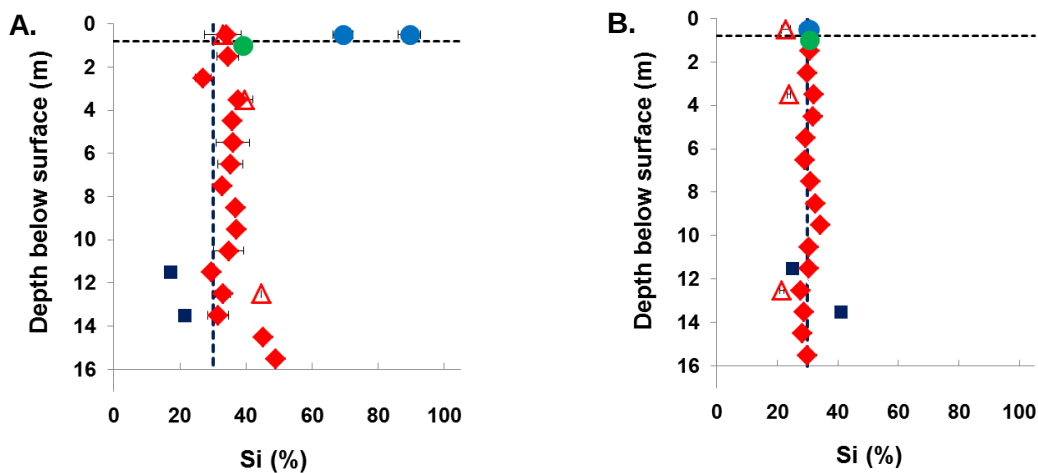


Figure 5.47. Differences in Si elemental extraction efficiency (%) following dissolution of MT_{ro} (MT:AS of 2:6; 45 minutes) at (A.) $350\text{ }^{\circ}\text{C}$ and (B.) $550\text{ }^{\circ}\text{C}$ under optimal dissolution conditions (3g/500ml; 0.6M HNO_3 ; $95\text{ }^{\circ}\text{C}$; 850 rpm, $n=2$) generated from tailings with varying Fe:Cr ratios.

- The correlation between the elemental Fe:Cr ratio in the starting materials (i.e. MT_{45-75}) and the elemental Fe:Cr ratio in solution following thermochemical treatment and optimal dissolution is presented in Figure 5.48. It was found that the higher the Fe:Cr ratio in the starting material, the higher the Fe:Cr ratio in solution. The correlation followed a linear relationship ($R^2 \approx 1$; Figure 5.48) with slopes of about 1.5 and 2 for $350\text{ }^{\circ}\text{C}$ and $550\text{ }^{\circ}\text{C}$ respectively. Although $R^2 = 1$ (Figure 5.48), the data points do not appear on the straight line because of the log scale used. The correlation continued to follow a linear relationship

($R^2 \approx 1$; Appendix E) after the data points of the Cr-depleted MT was removed from the dataset, with slopes of about 0.9 and 1.0 for 350 °C and 550 °C respectively. This linear correlation was unexpected; given the complex mineralogical composition of the samples originating from different tailings generated from varying mineral deposits, and could not be explained at this stage. The result would suggest that Fe and Cr were co-extracted from similar mineral phases. However, Fe and Cr are contained in different types of minerals for the different tailings. A detailed investigation is required in order to better understand the extraction of these two elements from tailings. It can however be speculated that following thermochemical treatment, Fe and Cr are present in a number of similar sulphate-based Fe-Cr solid solutions (which may also contain additional substituting (compatible) elements such as Mg and Al), which are then dissolved during the dissolution process.

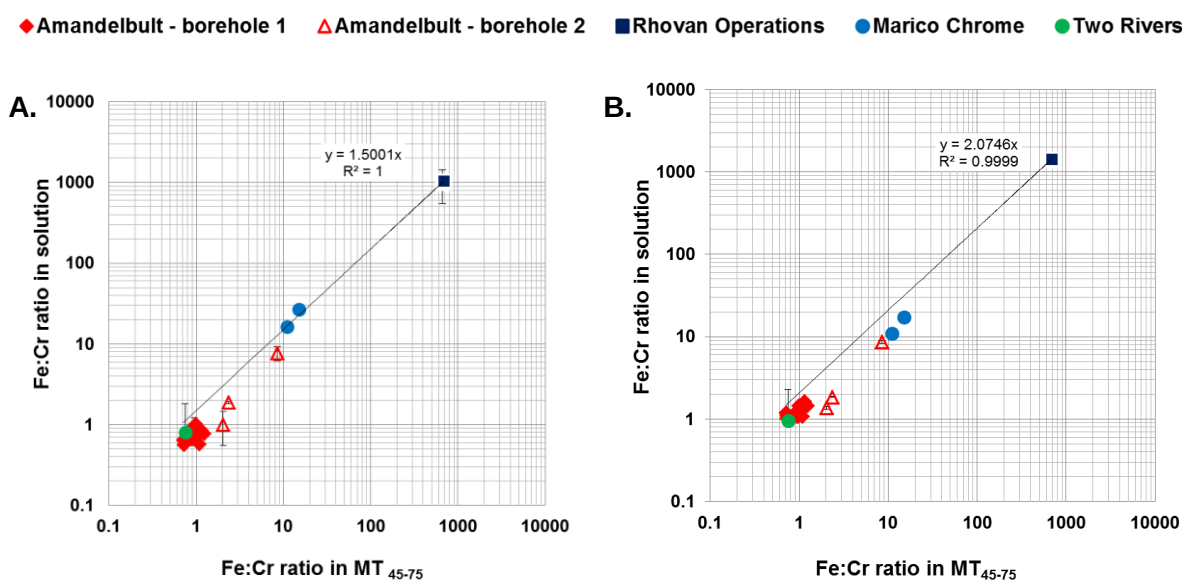


Figure 5.48. Correlation between the elemental Fe:Cr ratio in the starting materials (MT₄₅₋₇₅) and the elemental Fe:Cr ratio in solution (%) following dissolution of MTro (MT: AS of 2:6; 45 minutes) at (A.) 350 °C and (B.) 550 °C under optimal dissolution conditions (3g/500ml; 0.6M HNO₃; 95 °C; 850 rpm, $n=2$) generated from tailings with varying Fe:Cr ratios. Cr content for Rhovan operations samples is < 0.05 wt. % and that for the Marico Chrome samples is < 1.5%.

5.2.2 Characterisation of thermochemically-treated Cr-depleted mine tailings (Rhovan) before and after optimal dissolution

The best Fe extraction (ca. 72 %) was achieved for the Rhovan Operations tailings samples which were depleted in Cr. For this reason, a sample from Rhovan Operations was selected and was characterised using XRF, XRD, FE-SEM, reflected light microscopy and Raman spectroscopy after the thermochemical treatment and optimal dissolution procedure.

5.2.2.1 Characterisation of the thermochemical treated mine tailings (MT_{ro})

Cr-depleted MT from Rhovan Operations and the corresponding MT_{ro} generated using the optimal thermochemical and dissolution procedures (section 3.3.4) were characterised using a range of complementary techniques (XRD, FE-SEM, SEM-EDS, Raman spectroscopy and optical microscopy).

XRD analysis was conducted on MT_{ro} to identify the new mineral phases which have formed as a result of the thermochemical treatment. The XRD diffractograms for MT and MT_{ro} are presented in Figure 5.49 and indicated the presence of a new mineral phase, mikasaite (asterisks) in the treated sample. This confirmed that the silicates and metal oxides present in the MT (Cr depleted) transformed into soluble metal sulphates during the optimal thermochemical treatment. The relative height of the albite peaks present in the MT_{ro} are much lower in comparison to the MT suggesting that the relative abundance of the phase has decreased. Further analysis will be required to identify and quantify the unreacted or partially reacted mineral phases present in the MT_{ro}.

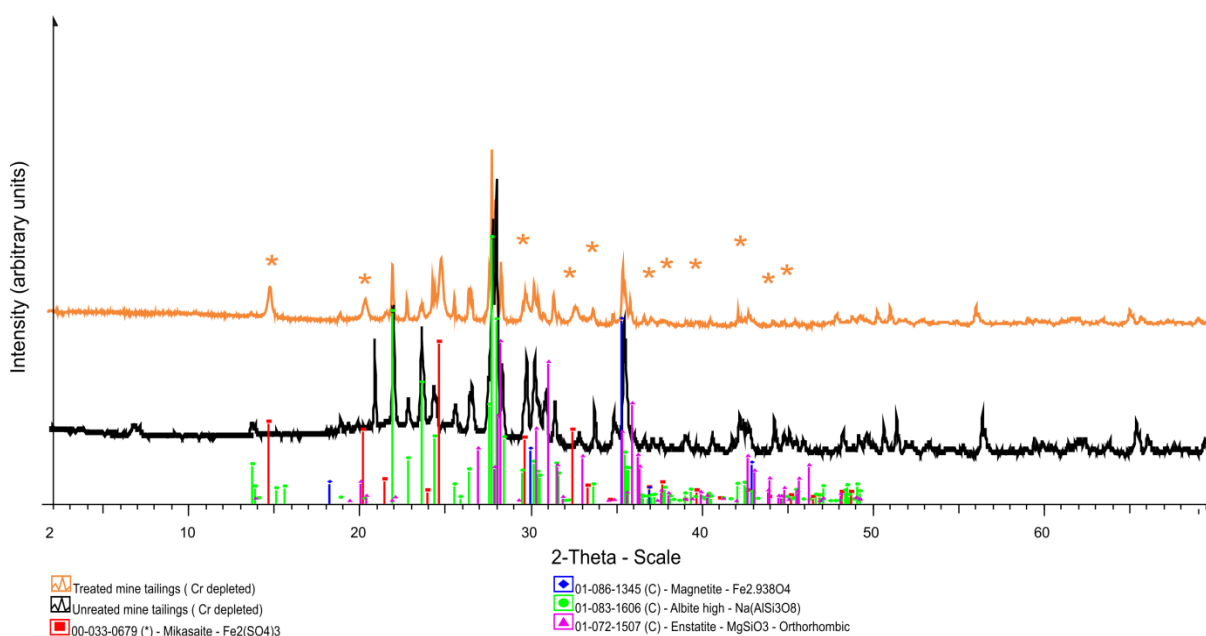


Figure 5.49. XRD patterns for MT (black) tailings from Rhovan Operations and the corresponding MT_{ro} (orange) formed from using the optimal thermochemical treatment (MT: AS of 2:6; 550 °C; 45 minutes). Asterisks (*) indicate the diffraction peaks of the Fe₂(SO₄)₃ (mikasaite) mineral phase.

Raman spectroscopy analysis was also conducted (Figure 5.50). The Raman spectrum for MT_{ro} displayed intense peaks in the spectral regions 150-340 cm⁻¹, 440-510 cm⁻¹ and 1059–1142 cm⁻¹ which correspond to the mikasaite phase. This result was therefore in agreement with the XRD data. The Raman spectrum was also compared to Raman spectra of different Fe sulphates with varying degrees of hydration; and the comparative analysis confirmed that the newly formed phase was an anhydrous Fe sulphate.

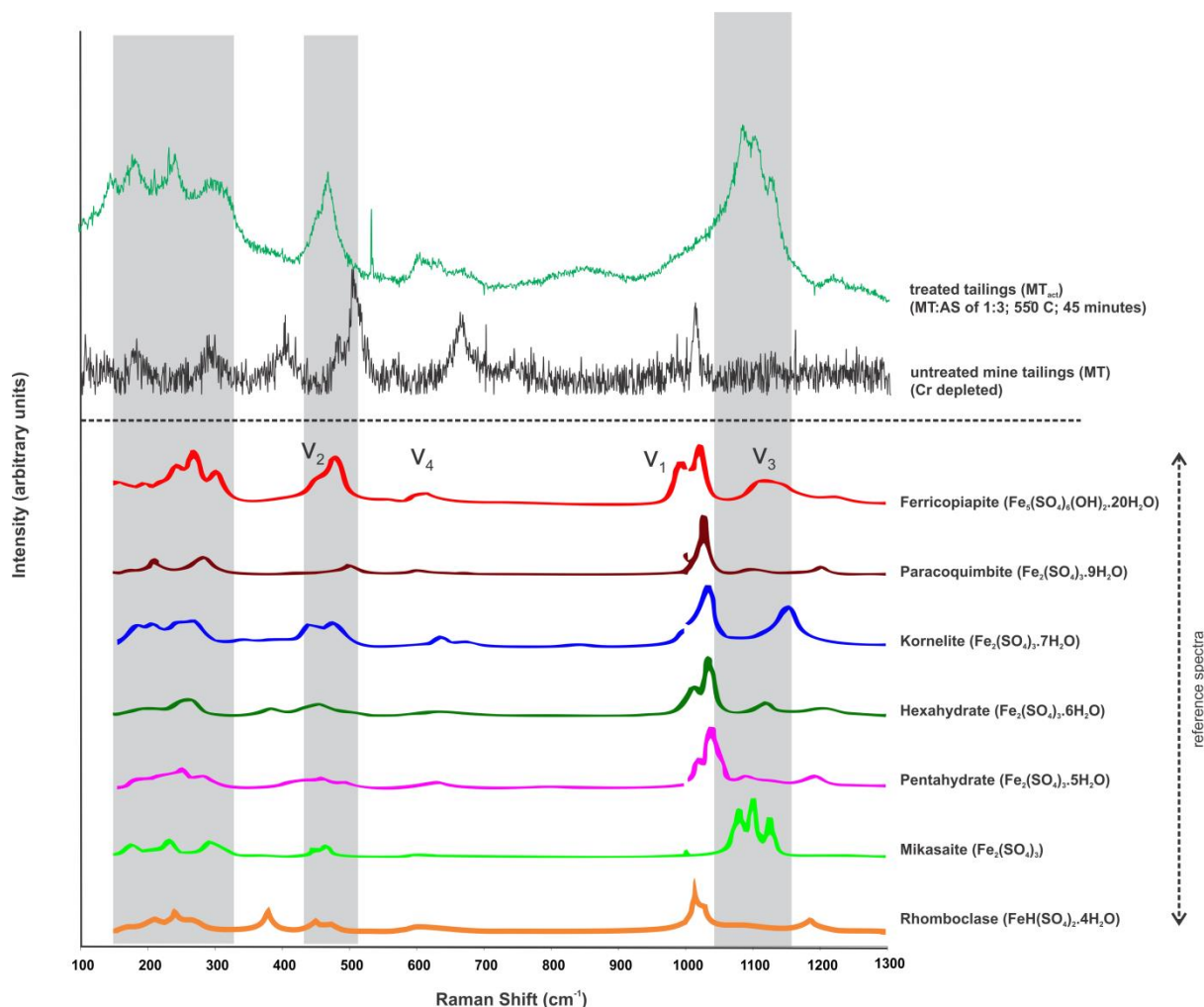


Figure 5.50. Raman Spectra for MT (black) and MT_{ro} (green) formed from Cr depleted MT under the optimal thermochemical treatment (MT: AS of 2:6; 550 °C; 45 minutes) compared to published spectra (Ling and Wang, 2010) of iron sulphate with varying degrees of hydration.

Morphological changes endured by MT were examined using FE-SEM (Figure 5.51). As expected, the FE-SEM micrographs of MT_{ro} showed the distinctive transformation from anhedral MT particles (Figure 5.51A) to euhedral hexagonal crystals (Figure 5.51B). The resulting hexagonal crystals were much smaller ($\pm 4 \mu\text{m}$) than those formed from Cr-enriched MT (Two Rivers; $\pm 10 \mu\text{m}$) and suggest that either the smaller particles are more reactive during the thermochemical treatment or a longer reaction time may be required to improve the sulphation reaction during the thermochemical treatment. The hexagonal particles were seldom identified as individual particles, but were mostly present in larger units comprising of different hexagonal and tabular layers (Figure 5.51C). The hexagonal particles were not completely smooth, and textural features at their surface are shown in Figure 5.51D.

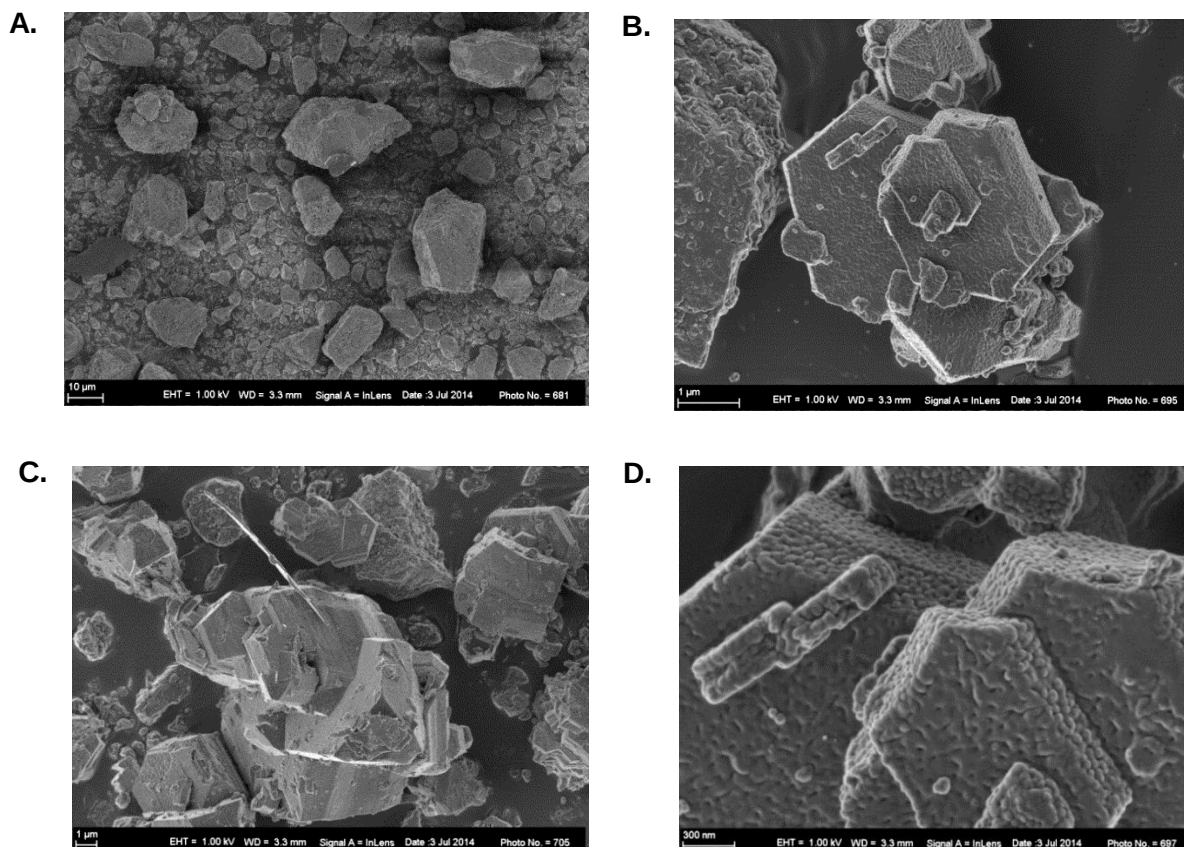


Figure 5.51. FE-SEM micrographs of the Cr depleted MT after the thermochemical treatment (MT₄₅₋₇₅:AS of 2:6; 550 °C;45 minutes) taken at (A.) 2000x, (B.) 35000x, (C.) 12000x and (D.) 100000x magnifications.

SEM-EDS was conducted on the samples in order to obtain a qualitative elemental analysis on a range of selected MT_{ro} particles (Figures 5.52 and 5.53). The first spot analyses were conducted on a single hexagonal crystal (Figure 5.52A and Figure 5.52B) and the second on a larger unit composed of multiple hexagonal crystals (Figure 5.53A and Figure 5.53B). The resulting elemental spectra (Figure 5.52C and Figure 5.53 C) were similar and confirmed the presence of sulphur in the particles. Other elements (Fe, Al, Mg, Ca, Ti, Si) were also identified. The presence of Si suggested the presence of impurities near the analysed spot since it is unlikely to be present in the hexagonal mikasaite-like particles. The hexagonal particles were mostly surrounded by unreacted particles, which made EDS analysis without artefacts challenging.

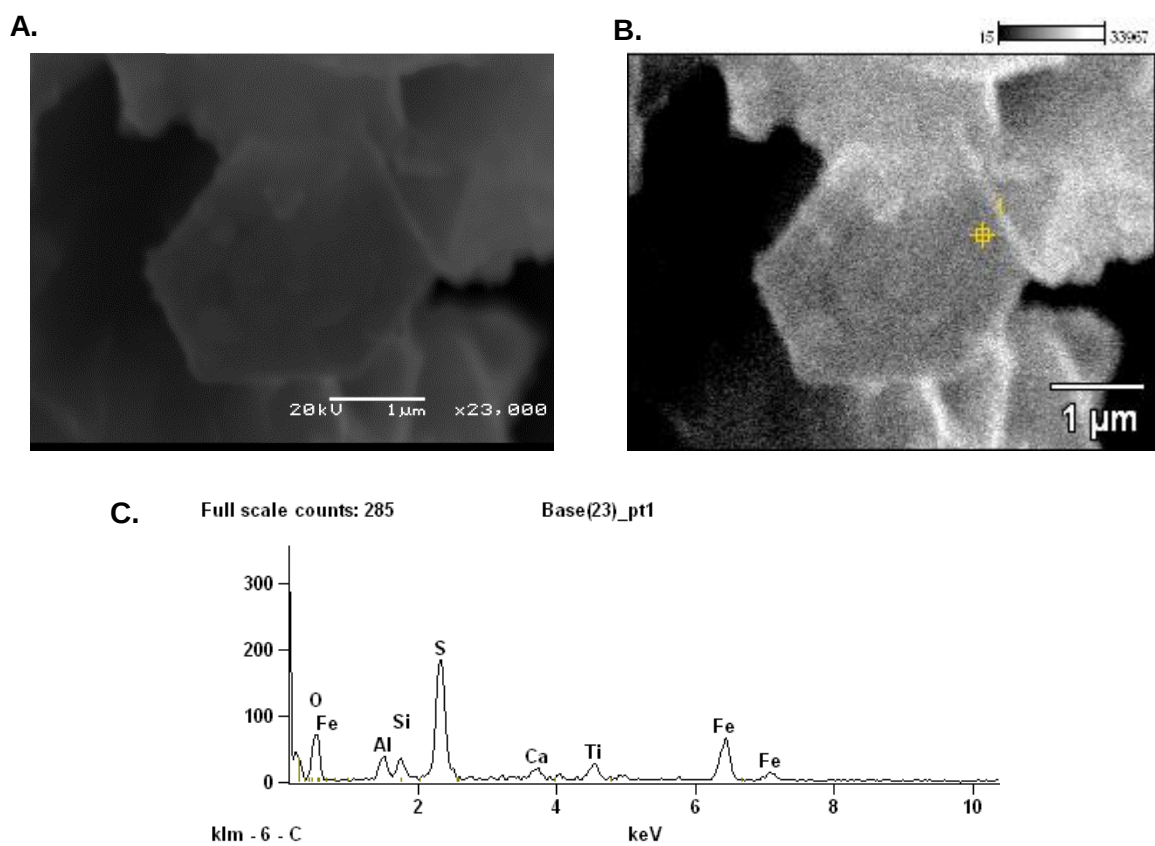


Figure 5.52. SEM-EDS micrographs of the MT_{10} formed from the Cr depleted MT illustrating the formation of hexagonal crystals taken at (A.) 23 000x magnification, (B.) area selected for analysis and (C.) corresponding elemental spectrum.

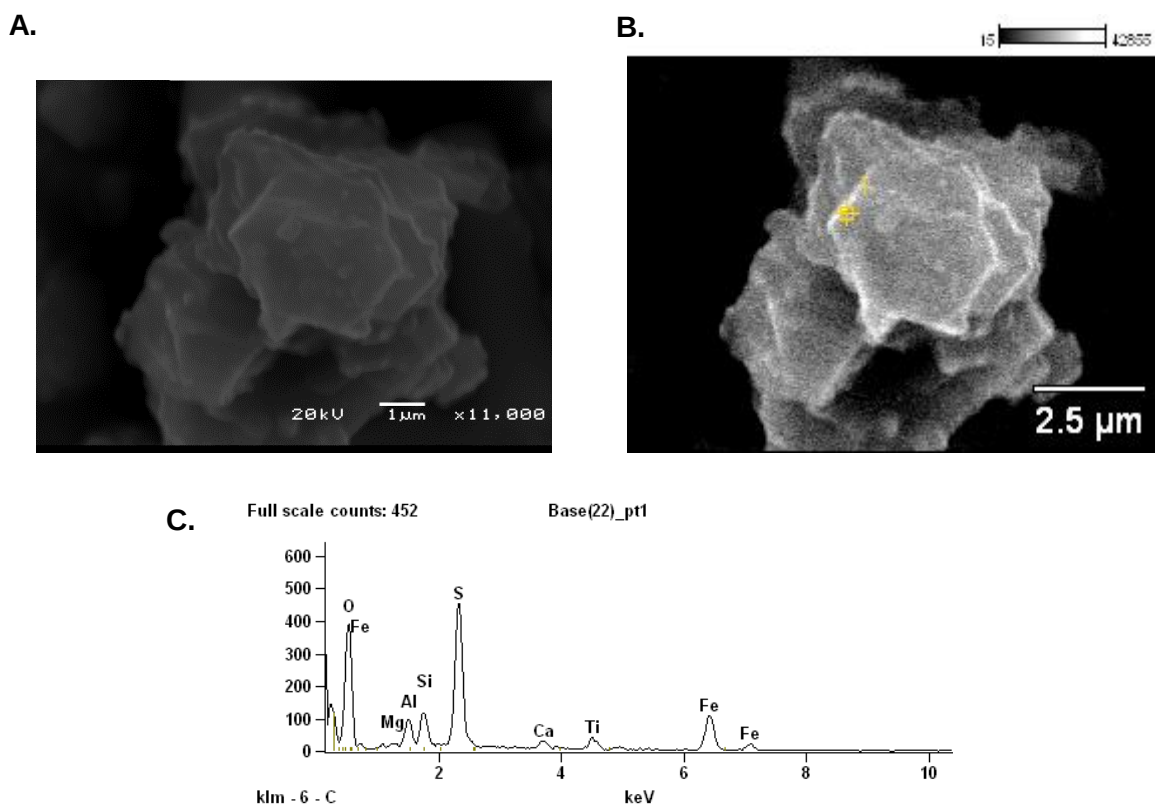


Figure 5.53. SEM-EDS micrographs of the MT_{ro} formed from the Cr depleted MT illustrating the aggregation of hexagonal crystals taken at (A.) 11 000x magnification, (B.) area selected for analysis and (C.) corresponding elemental spectrum.

5.2.2.2 Characterisation of undissolved residue (MT_{res})

The resulting MT_{res} formed following the optimal thermochemical treatment and dissolution procedure described in section 3.3.4 underwent a detailed characterisation using a range of complementary techniques which include XRD, FE-SEM, Raman spectroscopy, optical microscopy and ICP-OES.

XRD analysis was conducted on the MT_{res} as described in section 3.5.1.2 in order to determine the mineral phases which remain unreacted after dissolution of the soluble metal sulphate phases. The XRD diffractograms are presented in Figure 5.54. It was found that the mikasaite phase (asterisks) formed during the optimal thermochemical treatment is absent from the XRD pattern of MT_{res} which indicated that it was soluble under the conditions of dissolution. The XRD spectrum of MT_{res} was similar to that of MT, with no new peaks identified

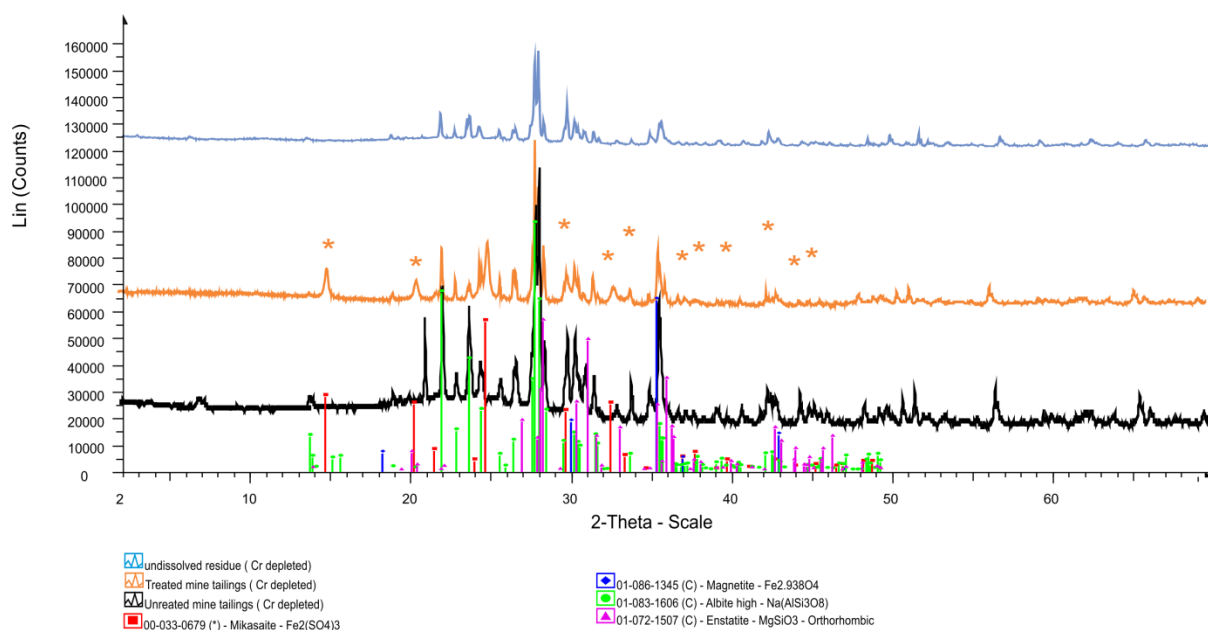


Figure 5.54. Comparative XRD diffractogram for the (Cr depleted) MT (colour), MT_{ro} (colour) and MT_{res} (colour) formed under the optimal thermochemical treatment (MT: AS of 2:6; 550 °C; 45 minutes) and under optimal dissolution conditions (3g/500ml; 0.6M HNO₃, 95 °C, 850 rpm, $n=2$).

Raman spectroscopy was conducted on MT_{res} in order to identify and differentiate the mineral phases which remained unreacted (Figure 5.55). It was also found that the mikasaite phase formed during the optimal thermochemical treatment is absent. The Raman spectrum of MT_{res} was similar to the Raman spectrum of MT with a relatively intense peak at 507 cm⁻¹ indicating the presence of feldspar mineral phases. The absence of augite (662 cm⁻¹) and amphibole and pyroxene (1010 cm⁻¹) peaks which were identified in MT may be ascribed to the laser beam focused on a feldspar-rich particle. These results could be improved by focusing on different particles in the MT of different colour and shape in order to obtain different individual spectra. This may facilitate the identification of additional and minor mineral phases present in the MT.

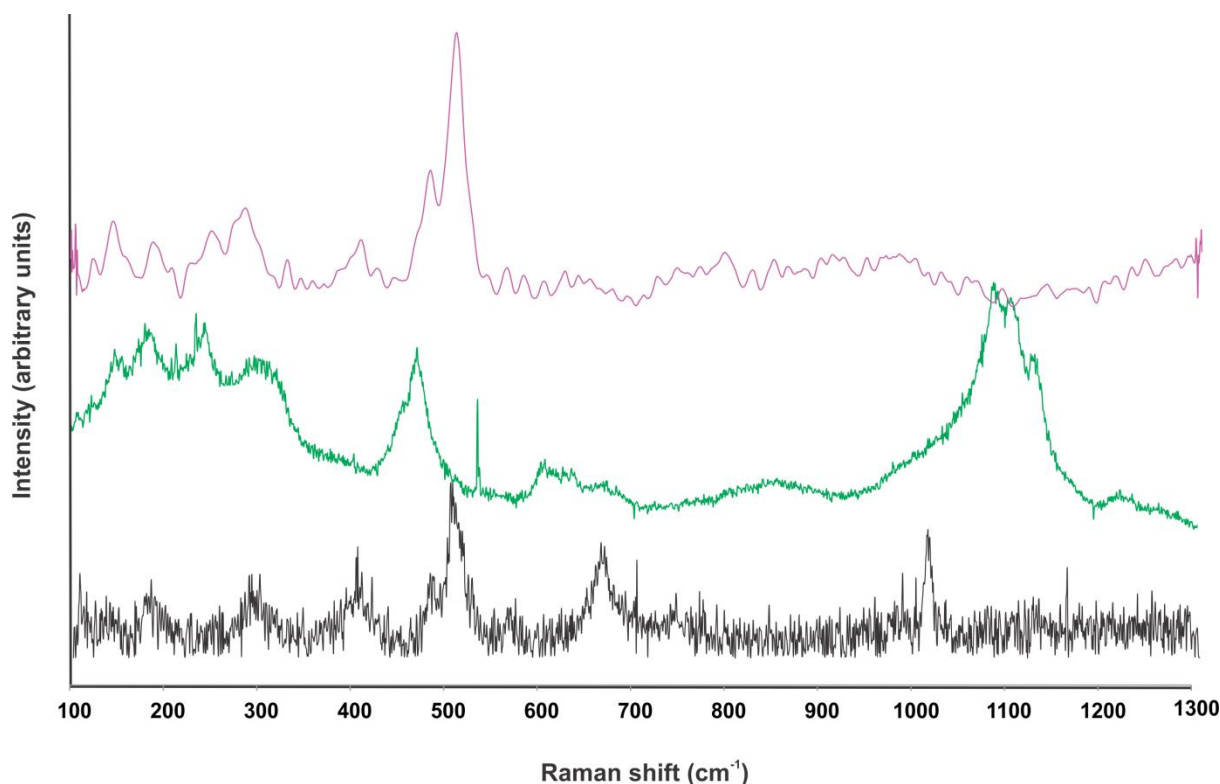


Figure 5.55. Comparative Raman Spectra for the MT (black), MT_{ro} (green) and MT_{res} (purple) formed from Cr depleted MT under optimal thermochemical treatment (MT: AS of 2:6; 550 °C; 45 minutes; $n=2$) and under optimal dissolution conditions (3g/500ml; 0.6M HNO₃, 95 °C, 850 rpm, $n=2$).

The morphology of MT_{res} were examined using FE-SEM (Figure 5.56). The Cr-deficient MT shows similar changes in morphology as observed for the Cr-enriched tailings (section 5.1.5.4). It is evident that the hexagonal particles are no longer present and this confirmed that they were soluble under the conditions of the dissolution experiments. The remaining particles have an anhedral morphology (no well-formed crystal faces) and display a wide distribution in particle size ranging between approximately 200 nm and 15 μ m (Figure 5.57A and Figure 5.56B). The larger particles have an uneven texture (Figure 5.56C) which is either due to etching or coating of smaller particles at the surface (Figure 5.56D).

Optical microscopy was used to visualise the particles contained in MT_{res}. The micrographs were obtained from powder and polished stubs. The optical micrographs of the untreated tailings and undissolved residues are presented in Figure 5.57. As discussed in section 4.2.1.4, the MT (Cr depleted) is predominantly made up of silicates which appear as translucent - yellow crystals, surrounded by darker crystals of spinel, amphibole and pyroxene and under visible light (Figure 5.57A) and in different shades of grey under reflected light (Figure 5.57B). From Figure 5.57C and Figure 5.57D, the MT_{res} contain a large amount of unreacted silicate and crystals of spinel, amphibole and pyroxene. The size reduction observed by FE-SEM is also observed. This confirms the results from the XRD and Raman analyses have shown that MT_{res} still contains some of the primary mineral phases identified in the Cr-depleted MT however in much lower quantities.

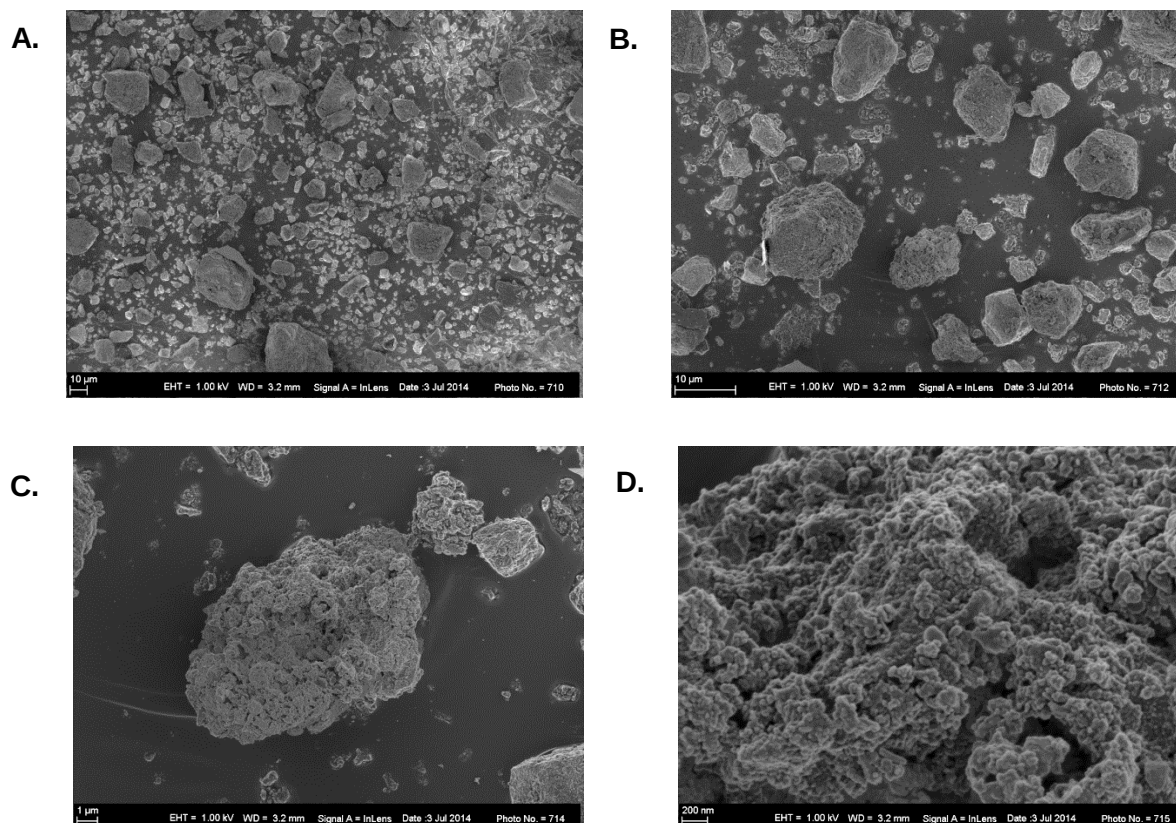


Figure 5.56. FE-SEM micrographs of the MT_{res} (Cr depleted) formed optimal thermochemical treatment (MT: AS of 2:6; 550 °C; 45 minutes; $n=2$) and optimal dissolution procedure (3g/500ml; 0.6M HNO_3 ; 95 °C, 850 rpm, $n=2$). Micrographs taken at (A.) 1000x, (B.) 3500x, (C.) 12 00X, (D.) 75 000x magnifications.

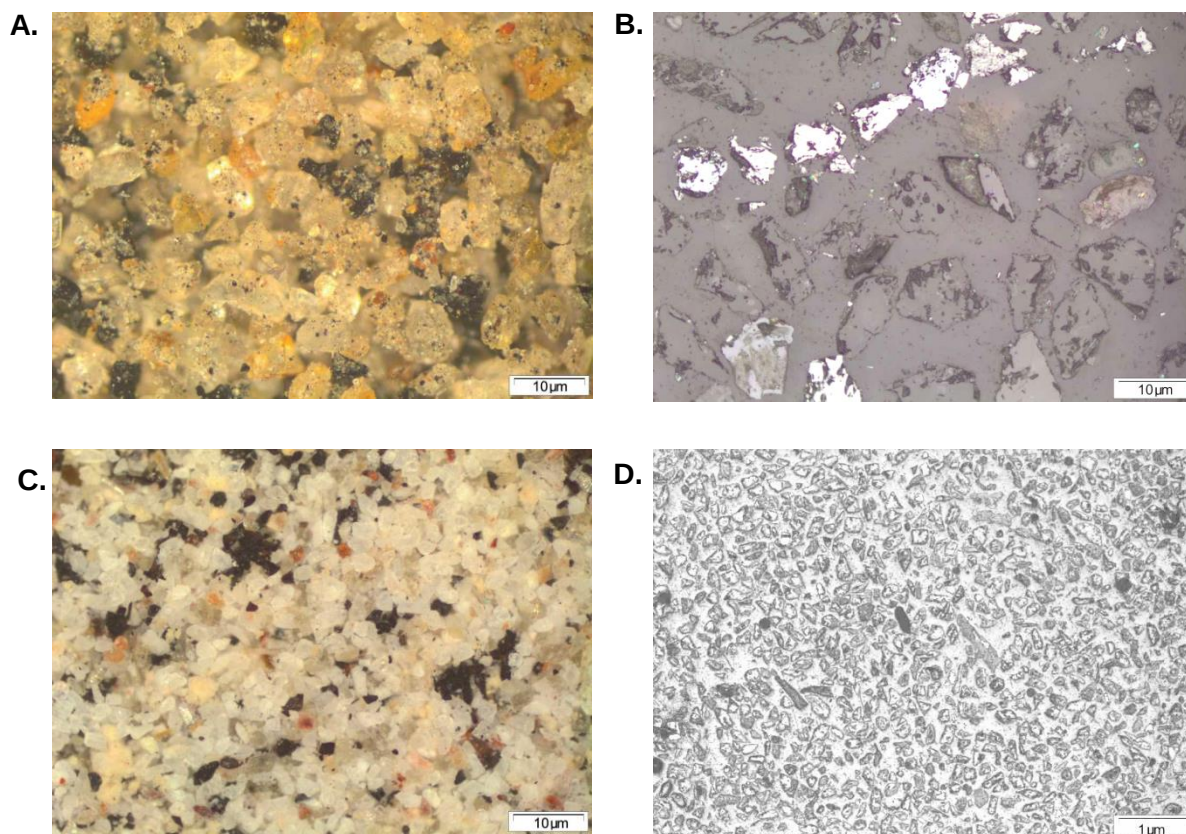


Figure 5.57. Optimal micrographs of the MT (Cr depleted) under (A.) visible light at 10x magnification, (B.) reflected light at 10x magnification and MT_{res} after optimal thermochemical treatment (MT: AS of 2:6; 550 °C; 45 minutes) and optimal dissolution procedure (3g/500ml; 0.6M HNO_3 , 95 °C, 850 rpm) (C.) under visible light at 10x magnification and (D.) reflected light at 40x magnifications.

Results from the XRD and Raman spectroscopy indicate that the mineralogical composition of MT_{res} is similar to the MT and suggests that the mineral phases have not fully reacted in the thermochemical treatment and subsequent dissolution procedure and further optimisation is required. Based on the results discussed in this section it can be concluded that the best extraction results using MT (Cr depleted) were obtained when using a particle size of $45 < x < 75 \mu m$. From the experiments conducted to determine the effect of the Fe:Cr ratio on the elemental extraction efficiency under the optimal thermochemical and dissolution procedure, the presence of elements such as Cr hinders the preferential extraction of Fe. Fe and Al extraction has improved for all conditions investigated in this study however Mg and Si extractions remain relatively low.

Chapter Six – Conclusions and recommendations for future developments

Final conclusions and recommendations for further study are presented.

6.1 Overview

The aim of this study was to demonstrate that PGE mine tailings could be used as a secondary source of major elements (e.g. Fe, Al) for various applications. A multi-step process for the extraction of major elements from silicate-rich PGE mine tailings was developed and entails the combination of a thermochemical solid-solid treatment using ammonium-based reagents followed by aqueous dissolution. The main objectives of this study were to characterise PGE mine tailings in order to identify its potential for additional resource recovery, investigate the use of ammonium sulphate and other ammonium salts as an activator and investigate and optimise a number of process parameters that promotes maximum elemental extraction. Specific focus was given to the extraction of Fe for prospective applications in nanoparticle synthesis and contaminated water remediation. Several analytical techniques such as PSD, XRD, XRF, TGA, TGA-FTIR, Raman spectroscopy, SEM (SEM-EDS, FE-SEM) and optical microscopy were utilised to characterise MT and a selection of MT_{ro} and MT_{res} in order to determine the physicochemical characteristics of MT, phase transformations which have occurred during the thermochemical treatment and the reactivity of the mineral phases present in the MT before and after thermochemical treatment and subsequent dissolution procedures. The results of the thermochemical treatment and subsequent dissolution procedures were integrated in order to determine the reactivity of MT_{ro} formed under varying conditions. The results of the physicochemical characterisation, thermochemical treatment and subsequent dissolution procedures are summarised below.

6.2. General conclusions

6.2.1 Case Study No 1: Two Rivers PGE mine tailings

6.2.1.1 Characterisation

Characterisation of the Two Rivers MT, used to develop the process, was imperative to the understanding of the physical, mineralogical and chemical composition of the starting material. The PSD and chemical composition of the Two Rivers tailings was similar to other PGE tailings previously studied by Amponsah and Reid, (2014); Mohamed, (2012) and Vogeli *et al.*, (2011). The bulk sample was predominantly composed of Cr_2O_3 (ca. 34 wt. %), Fe_2O_3 (ca. 23 wt. %) and SiO_2 (ca. 18 wt. %) with lesser amounts of Al_2O_3 (ca. 11 wt. %), MgO (ca. 12 wt. %) and CaO (ca. 2 wt. %). A similar trend was observed for 45-75 μm size fraction. The Two Rivers tailings are fairly enriched in spinel (ca. 30 %), enstatite (ca. 28 %) and plagioclase (ca. 25 %) with lesser amounts of amphibole (ca. 8 %) and alteration minerals (serpentine, talc, chlorite and calcite; ≤ 3.1 %). Raman spectroscopy confirmed the presence of the enstatite and spinel mineral phases. The mineralogy is consistent with the mining of the UG2 and Merensky reef and consistent with the noritic-leuconortie lithology.

The morphology of the MT₄₅₋₇₅ comprise of anhedral particles with a non-uniform grain size. The Fe is assumed to be trapped within the spinel mineral phases, however further characterisation will be required to confirm this.

6.2.1.2 Thermochemical treatment of tailings using ammonium sulphate, ((NH₄)₂SO₄; AS)

The thermochemical treatment of the MT with AS was successful in transforming the silicates/metal oxide minerals into ammonium-metal-sulphate based compounds. The thermochemical treatment is strongly temperature-dependent resulting in the formation of thermodynamically stable ammonium-metal sulphate compounds at temperatures below 500 °C and metal sulphates at 550 °C. The metal-sulphate phase(s) formed during the thermochemical treatment was identified by XRD as mikasaite (Fe₂(SO₄)₃) which is a rare Fe-rich sulphate formed from a hexagonal unit cell structure in which the isomorphic substitution of Al, Ca, Cr and Mg for Fe during the thermochemical treatment is possible. Further characterisation of the MT_{r0} by Raman spectroscopy, SEM-EDS and FE-SEM confirmed the formation of the mikasaite-like mineral phase from the reaction between the MT₄₅₋₇₅ and AS which was present as hexagonal particles containing Fe, Cr, Al, Mg, S and O. This indicated that a solid solution may exist between Al, Ca, Cr and Fe. The favourable transformation and thermodynamic stability of the mikasaite phase formed from the reaction between MT₄₅₋₇₅ and AS (MT:AS of 2:6) at 550 °C for 45 minutes and was selected as the optimised thermochemical treatment used for all further experiments.

6.2.1.3 Extraction efficiencies under uncontrolled pH conditions of dissolution

Baseline dissolution experiments conducted under uncontrolled pH conditions confirmed the low reactivity of the MT₄₅₋₇₅ prior to the thermochemical treatment. The dissolution of the MT generated a circumneutral pH and low EC ($\leq 29 \mu\text{S cm}^{-1}$) compared to the MT_{r0} which generated a higher EC ($595 \mu\text{S cm}^{-1}$) and lower pH indicating that the generated MT_{r0} was water soluble. The elemental extraction efficiency for the major elements (excluding Si) present in the MT was low (ca. 14 mg/l) in comparison to the MT_{r0} (ca. 70 mg/l) which indicated the efficiency of the thermochemical treatment.

In order to optimise the extraction efficiency, the temperature of the dissolution procedure was increased to 80 °C and investigated over a 64 hour duration. The increase in dissolution temperature increased the rate and extent of dissolution. The pH of the solution decreased to ~ 2 and the EC increased from $2330 \mu\text{S cm}^{-1}$ after 30 minutes to $3778 \mu\text{S cm}^{-1}$ after 10 hours before stabilising at $2883 \mu\text{S cm}^{-1}$ at the end of the experiment. The changes in EC coincided with a change in solution colour which progressed from a murky green to brown over the duration of the experiment. The decrease in EC and colour change as the reaction progressed suggested a secondary precipitation of one or more elements. The temperature-dependent profile of the concentration of dissolved Fe was similar to that of EC, which suggested that Fe was the major element that had undergone secondary precipitation. In order to prevent secondary precipitation, aqueous dissolution was performed under acidic conditions.

6.2.1.4 Extraction efficiencies under acidic conditions of dissolution (0.6 M HNO₃)

In an attempt to improve the elemental extraction efficiency and prevent secondary (Fe) precipitation, dissolution was performed in 0.6 M HNO₃. Baseline dissolution experiments indicated that extraction efficiency remained low for all elements under acidic conditions at ambient temperature. The non-occurrence of the brown suspension indicated that no secondary precipitation of Fe had occurred under these conditions. Higher dissolution temperatures were further examined to improve the extraction efficiency.

The extent of dissolution was shown to be temperature-dependent but Fe and Cr were still leached out at a similar rate irrespective of dissolution temperature. Dissolution at 60 °C yielded much lower elemental extraction efficiencies compared to 80 °C and 95 °C. The highest elemental extraction efficiencies achieved thus far was under acidic conditions at 95 °C for Al (ca. 59 %), Ca (ca. 80 %), Cr (ca. 27 %), Fe (ca. 35 %), Mg (ca. 25 %) and Si (ca. 31 %). The optimal dissolution process parameters identified from these experiments entail an aqueous suspension of 3 g MT_{ro} in 0.63 M HNO₃ solution (500 ml) constantly stirred at 850 rpm using an overhead stirrer at a temperature of 95 °C for 6 hours.

MT_{res} generated under the optimal thermochemical treatment and dissolution procedures were characterised by XRD, Raman spectroscopy, FE-SEM and microscopy. The MT_{res} was comprised of anhedral particles with a reduced particle size. The absence of the mikasaite-like phase was confirmed by XRD, Raman spectroscopy and by the absence of the hexagonal particles from the FE-SEM analysis. XRD indicated that the MT_{res} still contains the primary mineral phases present in the MT₄₅₋₇₅ suggesting that the extent of elemental extraction is limited by the reactivity of the mineral phases in the MT₄₅₋₇₅.

6.2.1.5 Effect of repeated thermochemical treatment on major element extraction efficiencies ('loop experiment')

The effect of repeated thermochemical treatment was investigated to determine whether AS is the limiting reagent during the thermochemical treatment step. The looped experiment improved the elemental extraction efficiencies of Al (ca. 73%), Cr (ca. 40 %), Fe (ca. 48 %) and Mg (31 %), however Si decreased (ca. 20.1 %) and Ca remained unchanged (ca. 77 %). Although the elemental extraction efficiencies were improved using the looped experiment, the multiple steps (5 cycles) will result in substantially higher energy requirements.

6.2.1.6 Thermochemical treatment of tailings using ammonium-based salts

TGA analysis was conducted on the different ammonium salts in order to understand the decomposition mechanisms and their reactivity with MT₄₅₋₇₅. The reaction mechanisms are different for the reaction between the MT and different ammonium salts and is a function of the decomposition temperature, which is lower for NH₄Cl and NH₄NO₃ in comparison to NH₄HSO₄ and (NH₄)₂SO₄. The mineral phases underwent little transformation during the thermochemical treatment with NH₄Cl, NH₄NO₃ and NH₄HSO₄ failing to produce soluble chloride, nitrate and sulphate metal compounds respectively. This was confirmed by the

ICP-OES results. Under the optimal dissolution procedure, the elemental extraction efficiency is strongly dependent on the type of ammonium salt used during the thermochemical treatment. The elemental extraction efficiency using NH_4Cl and NH_4NO_3 was much lower compared to NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ for all elements at the different temperatures tested. NH_4Cl and NH_4NO_3 are fairly selective for Ca compared to all other elements. The extent of elemental extraction using NH_4HSO_4 was much lower compared to $(\text{NH}_4)_2\text{SO}_4$ for all elements. From these experiments it was found that the most suitable ammonium salt for the thermochemical treatment under the optimal conditions is $(\text{NH}_4)_2\text{SO}_4$.

6.2.2 Case Study No 2: Other PGE tailings

6.2.2.1 Characterisation

A series of tailings samples with varying Fe:Cr ratios and mineralogies were selected from the Amandelbult, Marico Chrome and Rhovan TSF's located along the western limb of the BIC. The change in mineralogy coincide with local changes in mineralogy which changes from a harzburgitic rock-type in the North to a pyroxenitic rock-type further south and noritic rock-type further southeast. The Amandelbult MT was generated from the mining of the Merensky and UG2 and additional Cr recovery for Marico and Rhovan Operations respectively. The MT are relatively enriched in Al, Fe, Cr (except for Marico Chrome and Rhovan Operations which are depleted in Cr) and Mg (except for Rhovan Operations which is depleted in Mg) and comprise of varying proportions of spinel, plagioclase and alteration minerals. The variation observed in the bulk chemistry and mineralogy between the different tailings indicates that the major elements are spread amongst different mineral species. The reactivity of the mineral phases present in the tailings is a controlling-factor for the preferential extraction of Fe.

6.2.2.2 Effect of Fe/Cr ratio in PGE tailings on major element extraction efficiencies

The effect of Fe:Cr ratio on the major element extraction efficiencies was studied by applying the optimised thermochemical treatment and dissolution process to the selected tailings from the Amandelbult, Marico Chrome and Rhovan Operations.

Overall, high elemental extraction efficiencies ($\geq 50\%$) were achieved for Al, Ca and Cr compared to Fe, Mg and Si ($\leq 40\%$, except for the Cr-deficient MT from Rhovan Operations (ca. $\geq 50\%$ Fe extraction)). Higher variations in elemental extraction efficiencies were observed for lower temperatures of thermochemical treatment (350°C) which narrowed with an increase in temperature (550°C). This indicated that further optimisation of the thermochemical treatment temperature will be required in order to improve elemental extraction. From these experiments it can be concluded that Cr hinders the preferential extraction of Fe. The correlation between the Fe:Cr ratio in the starting material and elemental ratio in solution following the optimal thermochemical treatment and dissolution procedures follows a linear trend ($R^2 = 1$). This linear correlation was unexpected; given the complex mineralogical composition of the samples originating from different tailings generated from varying mineral deposits, and could not be explained at this stage. The result would suggest that Fe and Cr were co-extracted from similar mineral phases. However, Fe

and Cr are contained in different types of minerals for the different tailings. The mineralogical characterisation provided by XRD was limited; a detailed mineralogical study will be required in order to identify the extraction mechanisms of Fe and Cr from the MT.

The MT_{res} generated from the Cr-depleted MT₄₅₋₇₅ (Rhovan Operations) under the optimal thermochemical treatment and dissolution procedures were characterised by XRD, Raman spectroscopy, FE-SEM and microscopy. The MT_{res} has similar characteristics as the Cr-enriched MT_{res} (Two Rivers) and also comprised of anhedral particles with a reduced particle size. The absence of the mikasaite-like phase was confirmed by XRD, Raman spectroscopy and from the absence of the hexagonal particles confirmed by the FE-SEM analysis. XRD indicated that the MT_{res} still contains the primary mineral phases present in the Cr-depleted MT₄₅₋₇₅, suggesting that the extent of elemental extraction is limited by the reactivity of the mineral phases in the MT₄₅₋₇₅.

6.3 Key Findings

- This study has demonstrated that PGE mine tailings could be used as a secondary source of major elements (e.g. Fe, Al) for various applications. This process, still under development, presents an alternative approach towards beneficiating PGE tailings which may enable the sustainable use of mineral resources in the years to come.
- The physicochemical and mineralogical characteristics of PGE tailings make them suitable to the extractive process studied herein. The mineralogy of the starting material plays an important role in the reactivity of the MT₄₅₋₇₅ during the thermochemical treatment and the extent of elemental extraction following dissolution. The mineralogy of the MT is complex and requires detailed characterisation to further assess the generalized nature and reactivity of the tailings.
- The thermochemical treatment has shown to be an effective process for elemental extraction; however it is not element-selective, and elements such as Fe, Al, Cr and Mg compete for ammonium sulphate during the reaction.
- The preferential ammonium salt, i.e. ammonium sulphate supplements the process with the additional advantage of being able to be captured and re-used in the finalised process.
- Fe extraction appears to be constrained by the Fe:Cr ratio of the starting material. The preferential extraction of Fe for the MT with almost a negligible Cr content is possible under the optimal thermochemical treatment and dissolution conditions.

6.4 Novelty of the findings

- Ammonium-based salts, and in particular ammonium sulphate, can be used as reagents in a thermochemical solid-solid treatment to extract major elements from PGE tailings.
- Thermochemical treatment of PGE tailings using ammonium sulphate was found not to be element-selective, and major elements such as Fe, Al, Cr and Mg compete with the reagent to form water-soluble sulphate-metal species.

- 40 % Mg extraction was achieved in this study using AS as an activator followed by controlled aqueous leaching. This indicates that the process developed in this study may be more suited than the Mg-extraction process under development by Vogeli *et al.*, (2011) and Meyer *et al.*, (2014), who obtained ≤ 3 % Mg extraction using a strong inorganic acid such as HCl, as well as oxalic acid and EDTA. Further optimisation of the process will be required to convert the Mg in $\text{Mg}(\text{OH})_2$ and MgCO_3 for CCMC application.

6.5 Recommendations

The following recommendations are made for future development of the process in order to better understand the mineralogical composition of the PGE tailings, phase transformations during the thermochemical treatment, and improve elemental extraction efficiency for the major elements, particularly Fe. An exergy analysis will be required in order to fully optimise the process and improve the thermodynamic performance of the process. The integration of the process with other secondary beneficiation processes such as Cr recovery or steel and iron manufacture may promote economic infrastructure needed to scale-up the process.

6.5.1 Detailed characterisation of the starting materials

Further characterisation of the PGE tailings is required for its optimum utilisation which can only be achieved with a detailed mineralogical assessment. The complexity and extensive solid solution which exists within the minerals phases, particularly spinel, prevents the preferential extraction of Fe. The identification of the Fe-bearing mineral phases is crucial to the understanding the mineralogical controls during the thermochemical treatment. Additional analytical techniques which may be required to obtain a more detailed characterisation include:

- QEMSCAN bulk mineralogical analysis (BMA) to obtain a detailed quantitative mineralogical composition of the starting material.
- QEMSCAN particle map analysis (PMA) to determine mineral phases and mineral association for selected particles.
- Magnetic separation to attempt to generated iron-rich concentration as a pre-treatment step before thermochemical treatment.
- Mossbauer spectroscopy as a complementary technique to examine the valence state of Fe and qualitative identification of Fe-oxide phases.
- Multipoint analysis using Raman spectroscopy to obtain a representative spectrum of the MT, MT_{ro} and MT_{res} in order to qualitatively identify the reactive and unreactive mineral phases.

6.5.2 Further optimisation of the process under development

Further optimisation of the process under development is required in order to improve elemental extraction efficiency and reduce the overall energy requirements of the process.

Step 1: Thermochemical solid-solid treatment

- Solid-solid ratio: further investigation of the solid-solid ratio of the MT:AS will be required to optimise elemental extraction during the thermochemical treatment. Fagerlund *et al.*, (2011) suggested that increasing the AS component may improve the elemental extraction however if the stoichiometric amount is too high, excess SO₂ would be released which could be detrimental to the recycling of the AS.
- Duration of thermochemical treatment: AS may not be fully decomposed at lower (≤ 400 °C) temperatures. Increasing the duration of the thermochemical treatment will allow for the complete decomposition of AS and may facilitate further reaction with the MT, possibly forming metal-sulphate compounds.
- Fagerlund *et al.*, (2011) has found that the type of reactor used during the thermochemical treatment is an important factor for scaling up the process and is crucial to the reactivity of the process. The use of a rotary oven could resolve the issue of uneven solid mixing and enhance the contact between the MT₄₅₋₇₅ and AS during thermochemical treatment.
- Mossbauer spectroscopy can be used to examine the valence state of Fe and qualitative identification of Fe-oxide mineral phases after thermochemical treatment.
- Thermodynamic modelling of the system in order to identify the thermodynamic stability of the reactants and products formed during the reaction between the MT₄₅₋₇₅ and AS at different temperatures and identify temperature dependent chemical kinetics.

Step 2: The aqueous dissolution of soluble reaction products

- Improve the solid to liquid ratio in order to decrease water consumption and decrease the energy requirement of the dissolution step
- Ultrasonic assisted leaching: the ultrasonic high shear and cavitation forces may improve the rate of dissolution enabling a faster and more complete reaction by overcoming van der Waals's forces and continuously renewing the outer surface particle layers. Ultrasonic leaching may also improve the extent of elemental extraction as well as decrease the dissolution time, dissolution temperature and concentration.

Step 3: Synthesis of Fe nanoparticles

Conversion of dissolved Fe and Al into nanoparticles needs to be developed. The synthesised nanoparticles will need to be tested for the remediation of contaminated waters. Their suitability for this purpose will have to be compared to the efficiency of nanoparticles manufactured from commercial Fe and/or Al salts, as well as of those generated from iron contained in AMD and fly ash.

Step 4: ammonium salt recovery

It has been shown by Nduagu *et al.* (2012) that the AS by-product is recoverable and can be recycled in the process to reduce associated reagent costs. The recovery of the AS from the thermochemical treatment step in this study will need to be investigated in order to identify the controlling factors for the crystallisation and evaporating conditions required to recover the AS component.

References

- African Rainbow Minerals. (2013). 2013 Integrated annual report. [ONLINE] Available at: http://www.arm.co.za/im/r_annual.php. [Accessed 14 August 2014].
- Akcil, A., & Koldas, S. (2006). Acid Mine Drainage (AMD): causes, treatment and case studies. *Journal of Cleaner Production*, 14(12), 1139-1145.
- Alegbe J.M. (2015) Application of reductants and nanoiron in the treatment of acid mine drainage. PhD thesis, University of the Western Cape, pp. 492.
- Amponsah-Dacosta, M. & Reid, D. L. (2014). Mineralogical characterization of selected South African mine tailings for the purpose of mineral carbonation. *China University of Mining and Technology Press*, Xuzhou, ISBN 978-7-5646-2437-8, 686-689.
- Anglo American plc. (2013). Sustainable Development Report 2013. [ONLINE]. Available at < www.angloplatinum.com >. [Accessed 03 March 2014].
- Antonov, L., & Nedeltcheva, D. (2000). Resolution of overlapping UV–Vis absorption bands and quantitative analysis. *Chemical Society Reviews*, 29(3), 217-227.
- Apopei, A. I. & Buzgar, N. (2010). The Raman study of amphiboles. *Analele Stiintifice ale Universitatii Al I Cuza din Iasi Geologie*, 56, 57-84.
- Atkins, P. W., & De Paula, J. (2010). Atkins' Physical Chemistry. Ninth Edition. Oxford University Press. W.H. Freeman and Company, United States, 972 pp.
- Badger, C. L., George, I., Griffiths, P. T., Braban, C. F., Cox, R. A. & Abbatt, J. P. D. (2006). Phase transitions and hygroscopic growth of aerosol particles containing humic acid and mixtures of humic acid and ammonium sulphate. *Atmospheric Chemistry and Physics*, 6(3), 755-768.
- Bai, G., Teng, W., Wang, X., Zhang, H., & Xu, P. (2010). Processing and kinetics studies on the alumina enrichment of coal fly ash by fractionating silicon dioxide as nano particles. *Fuel Processing Technology*, 91(2), 175-184.
- Bayer, G., Kahr, G. & Mueller-Vonmoos, M. (1982). Reactions of ammonium sulphates with kaolinite and other silicate and oxide minerals. *Clay Mineralogy*, 17, 271 – 283.
- Beckhoff, B., Kanngießer, B., Langhoff, N., Wedell, R., Wolff, H. (2007). *Handbook of Practical X-Ray Fluorescence Analysis*. Springer, Heidelberg. ISBN: 10-3-540-28603-9, 902 pp.
- Bian, Z., Miao, X., Lei, S., Chen, S. E., Wang, W. & Struthers, S. (2012). The challenges of re-using mining and mineral processing wastes. *Science*, 337(6095), 702-703.
- Bobicki, E. R., Liu, Q., Xu, Z. & Zeng, H. (2012). Carbon capture and storage using alkaline industrial wastes. *Progress in Energy and Combustion Science*, 38(2), 302-320.

- Bodor, M., Santos, R. M., Van Gerven, T. & Vlad, M. (2013). Recent developments and perspectives on the treatment of industrial wastes by mineral carbonation—a review. *Central European Journal of Engineering*, 3(4), 566-584.
- Brame, J., Li, Q. & Alvarez, P. J. (2011). Nanotechnology-enabled water treatment and reuse: emerging opportunities and challenges for developing countries. *Trends in Food Science and Technology*, 22(11), 618-624.
- Brough, C. P., Warrender, R., Howell, R. J., Barnes, A. & Parbhakar-Fox, A. (2013). The process mineralogy of mine wastes. *Minerals Engineering*, 52, 125-135.
- Brown, M.E. (2001). Introduction to Thermal Analysis: techniques and applications. Kluwer Academic Publishers, Dordrecht, 224 pp.
- Burda, C., Chen, X., Narayanan, R. & El-Sayed, M. A. (2005). Chemistry and properties of nanocrystals of different shapes. *Chemical reviews*, 105(4), 1025-1102.
- Buzatu, A. & Buzgar, N. (2010). The Raman study of single-chain silicates. *Analele Științifice ale Universității "Alexandru Ioan Cuza" Iași, Geologie*, 56, 107-125.
- Cawthorn, R. G. (2011). Geological interpretations from the PGE distribution in the Bushveld Merensky and UG2 chromitite reefs. *Journal of the South African Institute of Mining and Metallurgy*, 111(2), 67-79.
- Cawthorn, R.G., Eales, H.V., Walraven, F., Uken, R. & Watkeys, M.K. (2006). The Bushveld Complex, In: Johnson, M.R., Anhaeusser, C.R., Thomas, R.J. (Eds.), *The Geology of South Africa, Geological Society of South Africa, Johannesburg/ Council for Geoscience, Pretoria*, 261-281.
- Cole, S., & Ferron, C.J. (2002). A review of the beneficiation and extractive metallurgy of the platinum-group elements, highlighting recent process innovations. In: Cabri, L.J. (Ed.), *The Geology, Geochemistry, Mineralogy and Mineral Beneficiation of platinum-group elements. Canadian Institute of Mining and Metallurgy, Special volume 54*, pp. 811–818.
- Cook, S. M. (2009). Assessing the use and application of zero-valent iron nanoparticle technology for remediation at contaminated sites. Prepared for the U.S. Environmental Protection Agency, Washington, DC. [ONLINE]. Available at: <<https://clu-in.org/download/studentpapers/Zero-Valent-Iron-Cook.pdf>>. [Accessed 05 February 2014].
- Crane, R. A., Dickinson, M., Popescu, I. C. & Scott, T. B. (2011). Magnetite and zero-valent iron nanoparticles for the remediation of uranium contaminated environmental water. *Water Research*, 45(9), 2931-2942.
- Crane, R.A. & Scott, T.B. (2012). Nanoscale zero-valent iron: Future prospects for an emerging water treatment technology, *Journal of Hazardous Materials*, 211,112-115.

- Cziczo, D. J., Nowak, J. B., Hu, J. H. & Abbatt, J. P. D. (1997). Infrared spectroscopy of model tropospheric aerosols as a function of relative humidity: Observation of deliquescence and crystallization. *Journal of Geophysical Research: Atmospheres* (1984–2012), 102(D15), 18843-18850.
- de Beer, M., Maree, J. P., Liebenberg, L., & Doucet, F. J. (2014). Conversion of calcium sulphide to calcium carbonate during the process of recovery of elemental sulphur from gypsum waste. *Waste Management*, 34(11), 2373-2381.
- de Faria, D. L. A., Venâncio Silva, S. & De Oliveira, M. T. (1997). Raman microspectroscopy of some iron oxides and oxyhydroxides. *Journal of Raman Spectroscopy*, 28(11), 873-878.
- Department of Mineral Resources. (2011). A beneficiation strategy for the minerals industry of South Africa. [ONLINE]. Available at <http://www.gov.za/sites/www.gov.za/files/Beneficiation%20Strategy%20June%202011%20final%20%283%29_0.pdf>. [Accessed 20 June 2013].
- Department of Mineral Resources. (2015). South Africa's Mineral Industry. [ONLINE] Available at < <http://www.dmr.gov.za/publications/south-africas-mineral-industry-sami.html>>. [Accessed 16 April 2015].
- Doucet F.J. (2011). Scoping study on CO₂ Mineralization Technologies. Contract Report No CGS-2011-007 commissioned by the South African Centre for Carbon Capture and Storage, pp.88. [ONLINE] Available at <http://www.sacccs.org.za/wp-content/uploads/2011/011/Scoping_study_on_CO2_mineralization_technologies_report.pdf>. [Accessed 16 April 2012].
- Doucet, F. J. (2010). Effective CO₂-specific sequestration capacity of steel slags and variability in their leaching behaviour in view of industrial mineral carbonation. *Minerals Engineering*, 23(3), 262-269.
- Downs, R. T. 2006. The RRUFF Project: an integrated study of the chemistry, crystallography, Raman and infrared spectroscopy of minerals. *Program and Abstracts of the 19th General Meeting of the International Mineralogical Association, 03-13 July 2006*, Kobe, Japan.
- DWAF. (1998). Department of Water Affairs and Forestry (DWAF), Waste Management Series. Minimum Requirements for the Handling, classification and disposal of hazardous waste. Second Edition. Department of Water Affairs and Forestry, Pretoria.
- Dzvinamurungu, T., Viljoen, K. S., Knoper, M. W., & Mulaba-Bafubiandi, A. (2013). Geometallurgical characterisation of Merensky Reef and UG2 at the Marikana Mine, Bushveld Complex, South Africa. *Minerals Engineering*, 52, 74-81.
- Eales, H.V. (2014). The Bushveld Complex, An introduction to the geology and setting of the Bushveld Complex. Council for Geoscience,(2) 214pp.

- Echlin, P. (2009). *Handbook of Sample Preparation for Scanning Electron Microscopy and X-ray micro-analysis*. Springer, New York, United States of America. ISBN: 978-0-387-85730-5, 344 pp.
- Edraki, M., Baumgartl, T., Manlapig, E., Bradshaw, D., Franks, D. M. & Moran, C. J. (2014). Designing mine tailings for better environmental, social and economic outcomes: A review of alternative approaches. *Journal of Cleaner Production*, 84, 411-420.
- Erdey, L., Gal, S. & Liptay, G. (1964). Thermoanalytical properties of analytical-grade reagents: Ammonium salts. *Talanta*, 11, 913-940.
- Fagerlund, J. & Zevenhoven, R. (2011). An experimental study of $\text{Mg}(\text{OH})_2$ carbonation. *International Journal of Greenhouse Gas Control*, 5(6), 1406-1412.
- Fagerlund, J., Nduagu, E. & Zevenhoven, R. (2011). Recent developments in the carbonation of serpentinite derived $\text{Mg}(\text{OH})_2$ using a pressurized fluidized bed. *Energy Procedia*, 4, 4993-5000.
- Fagerlund, J., Nduagu, E., Romão, I. & Zevenhoven, R. (2012). CO_2 fixation using magnesium silicate minerals part 1: Process description and performance. *Energy*, 41(1), 184-191.
- Freeman, J. J., Wang, A., Kuebler, K. E., Jolliff, B. L. & Haskin, L. A. (2008). Characterization of natural feldspars by Raman spectroscopy for future planetary exploration. *The Canadian Mineralogist*, 46, 1477-1500.
- Gasmet.(2015). Nitrogen dioxide. [ONLINE] Available at:< <http://www.gasmet.com/technology/spectra/501-nitrogen-dioxide>>. [Accessed 22 June 2015].
- Gerdemann, S. J., O'Connor, W. K., Dahlin, D. C., Penner, L. R. & Rush, H. (2007). *Ex-situ* aqueous mineral carbonation. *Environmental Science & Technology*, 41(7), 2587-2593.
- Glencore Xstrata. (2013). Glencore Xstrata Annual report 2013. [ONLINE] Available at <http://www.glencore.com/assets/investors/doc/reports_and_results/2013/GLEN-2013-Annual-Report.pdf>. [Accessed 22 August 2014].
- Goldstein, L., Newbury, D.E., Echlin, P. & Lyman, C.E. (2003). *Scanning electron microscopy and X-ray microanalysis*. Kluwer Academic/ Plenum Publishers, New York. ISBN: 9781461502166, 690 pp.
- Google Earth 7.1.2.2041. (2014a). Two Rivers tailings storage facility, 24°57'23.27" S, 30°06'20.29" E, elevation 965 m. [ONLINE] Available at: <https://www.google.com/earth>. [Accessed 10 November 2014].
- Google Earth 7.1.2.2041. (2014b). Amandelbult tailings storage facility, 24°48'01.90" S, 27°20'53.03" E, elevation 978 m. [ONLINE] Available at: <https://www.google.com/earth>. [Accessed 10 November 2014].

- Google Earth 7.1.2.2041. (2014c). Marico Chrome tailings storage facility, 25°06'04.98" S, 26°15'08.01" E, elevation 1046 m. [ONLINE] Available at: <https://www.google.com/earth>. [Accessed 10 November 2014].
- Google Earth 7.1.2.2041. (2014d). Rhovan Operations Chrome tailings storage facility, 25°34'15.23" S, 27°35'08.16" E, elevation 1094 m. [ONLINE] Available at: <https://www.google.com/earth>. [Accessed 10 November 2014].
- Guo, C., Zou, J., Jiang, Y., Huang, T., Cheng, Y. & Wei, C. (2014). Thermal activation of coal fly ash by sodium hydrogen sulfate for alumina extraction. *Journal of Materials Science*, 49(12), 4315-4322.
- Guo, X. Y., Li, D., Wu, Z. & Tian, Q. H. (2012). Application of response surface methodology in optimizaing the sulfation-roasting-leaching process of nickel laterite. *International Journal of Minerals, Metallurgy, and Materials*, 19(3), 199-204.
- Guo, X., Li, D., Park, K.-H., Tian, Q. & Wu, Z. (2009). Leaching behavior of metals from a limonitic nickel laterite using a sulfation–roasting–leaching process. *Hydrometallurgy*, 99, 144-150.
- Guo, Y., Li, Y., Cheng, F., Wang, M., & Wang, X. (2013). Role of additives in improved thermal activation of coal fly ash for alumina extraction. *Fuel Processing Technology*, 110, 114-121.
- Hakimi, M., Nezhadali, A., Raissi, H. & Amirabad, M. T. (2008). Study of stability constants of some of the transition metal complexes with β -diketones by spectrophotometry. *Asian Journal of Chemistry*, 20, 5497-5502.
- Halstead, W. D. (1970). Thermal decomposition of ammonium sulphate. *Journal of Applied Chemistry*, 20(4), 129-132.
- Haskin, L. A., Wang, A., Jolliff, B. L., Korotev, R. L., Rockow, K. M. & Viskupic, K. M. (1997). Laser Raman spectroscopic determination of mineral proportions in rocks on planetary surfaces. *Lunar and Planetary Science Conference*, 28, 523.
- Hawthorne, F. C., Krivovichev, S. V. & Burns, P. C. (2000). The crystal chemistry of sulfate minerals. *Reviews in Mineralogy and Geochemistry*, 40, 1-112.
- Highfield, J., Lim, H., Fagerlund, J. & Zevenhoven, R. (2012). Activation of serpentine for CO₂ mineralization by flux extraction of soluble magnesium salts using ammonium sulfate. *RSC Advances*, 2(16), 6535-6541.
- Hitch, M. & Dipple, G. M. (2012). Economic feasibility and sensitivity analysis of integrating industrial-scale mineral carbonation into mining operations. *Minerals Engineering*, 39, 268-275.
- Horiba. (2014). Application note on Raman data and analysis: Raman Spectroscopy for Analysis and Monitoring. [ONLINE]. Available at < <http://www.horiba.com/scientific/products/raman-spectroscopy/raman-academy/raman-tutorial/raman-scattering/>>. [Accessed 15 October 2014].

- Hornsey R. & van der Merwe, P. (2003). Optimization of geological lead-time in a feasibility study drill out-Two Rivers Platinum, Mpumalanga, South Africa. *Application of Computers and Operations Research in the Minerals Industries, South African Institute of Mining and Metallurgy*, 335-343.
- Hosterman, B. D. (2011). Raman spectroscopic study of solid solution spinel oxides. Published PhD Thesis, University of Nevada, Las Vegas. [ONLINE] Available at <<http://digitalscholarship.unlv.edu/cgiviewcontent.cgi?article=2088&context=thesesdissertations>>. [Accessed 26 June 2014].
- Hua, M., Zhang, S., Pan, B., Zhang, W., Lv, L. & Zhang, Q. (2012). Heavy metal removal from water/wastewater by nanosized metal oxides: a review. *Journal of Hazardous Materials*, 211, 317-331.
- Huang, E., Chen, C., Huang, T., Lin, E. & Xu, J.-A. (2000). Raman spectroscopic characteristics of Mg-Fe-Ca pyroxenes. *American Mineralogist*, 85, 473-479.
- Hudson-Edwards, K. A., Jamieson, H. E. & Lottermoser, B. G. (2011). Mine wastes: Past, present, future. *Elements*, 7, 375-380.
- Huisamen, A. (2013). Contaminant mobilisation by fluid-rock interaction and related transport mechanisms in platinum tailings. MSc thesis, University of Pretoria, Pretoria, South Africa.
- Jamei, M. R., Khosravi, M. R. & Anvaripour, B. (2014). A novel ultrasound assisted method in synthesis of n-ZVI particles. *Ultrasonics sonochemistry*, 21(1), 226-233.
- Jamieson, H.E. (2011). Geochemistry and mineralogy of solid mine waste: essential knowledge for predicting environmental impact. *Elements*, 7, 381-386.
- Jiang, Z., Zhang, S., Pan, B., Wang, W., Wang, X., Lv, L. & Zhang, Q. (2012). A fabrication strategy for nanosized zero valent iron (n-ZVI)-polymeric anion exchanger composites with tunable structure for nitrate reduction. *Journal of Hazardous Materials*, 233, 1-6.
- Jiang, K., Jiang, X., Feng, L., Jiang, W., Wang, S., Zhao, L., & Fan, Y. (2013). Study on Self-Catalysis Reduction Leaching of Ocean Co-Mn Polymetallic Ores in Ammonia Solution. International Society of Offshore and Polar Engineers, *In Tenth ISOPE Ocean Mining and Gas Hydrates Symposium*, 22-26 September, Szczecin, Poland.
- Jiang, M., Zhao, Q., Liu, C., Shi, P., Zhang, B., Yang, D., Saxén, H. & Zevenhoven, R. (2014). Sulfuric acid leaching of South African chromite. Part 2: optimization of leaching conditions. *International Journal of Mineral Processing*, 130, 102-107.
- Jin, J. Y., Li, Z. Y. & Wu, Y. (2014). Extraction of Aluminium from High Iron Bauxite by Carbothermal Reduction-Ammonium Sulfate Roasting. *Applied Mechanics and Materials*, 624, 3-7.
- Johnson, D. B. & Hallberg, K. B. (2005). Acid mine drainage remediation options: a review. *Science of the Total Environment*, 338(1), 3-14.

- Kalnicky, D.J. & Singhvi, R. (2001), Field portable XRF analysis of environmental samples. *Journal of Hazardous Materials*, 83, (1-2), 93-122.
- Kar, B. & Swamy, Y. (2000). Some aspects of nickel extraction from chromitiferous overburden by sulphatization roasting. *Minerals Engineering*, 13, 1635-1640.
- Kearey, P.(2001). The New Penguin Dictionary of Geology. Second edition. Penguin Books, Penguin Group, England, ISBN:978-0-14-051494-0, 327pp.
- Kiyoura, R. & Urano, K. (1970). Mechanism, kinetics, and equilibrium of thermal decomposition of ammonium sulfate. *Industrial & Engineering Chemistry Process Design and Development*, 9(4), 489-494.
- Klein, C. & Dutrow, B. (2008). *The 23rd Edition of The Manual of Mineral Science:(after James D. Dana)*, J. Wiley, Hoboken, N.J.. ISBN : 978-0-471-72157-4, 716 pp.
- Klimkova, S., Cernik, M., Lacinova, L., Filip, J., Jancik, D. & Zboril, R. (2011). Zero-valent iron nanoparticles in treatment of acid mine water from in situ uranium leaching. *Chemosphere*, 82(8), 1178-1184.
- Landa, E. R. & Gast, R.G. (1973). Evaluation of Crystallinity in Hydrated Ferric Oxides*. *Clays and clay minerals*, 21, 121-130.
- Lenaz, D. & Lughi, V. (2013). Raman study of $\text{MgCr}_2\text{O}_4\text{--Fe}^{2+}\text{Cr}_2\text{O}_4$ and $\text{MgCr}_2\text{O}_4\text{--MgFe}_2^{3+}\text{O}_4$ synthetic series: The effects of Fe^{2+} and Fe^{3+} on Raman shifts. *Physics and Chemistry of Minerals*, 40, 491-498.
- Li, H., Hui, J., Wang, C., Bao, W., Sun, Z. (2014) Extraction of alumina from coal fly ash by mixed-alkaline hydrothermal method. *Hydrometallurgy*, 147-148, 183-187.
- Ling, Z. & Wang, A. (2010). A systematic spectroscopic study of eight hydrous ferric sulfates relevant to Mars. *Icarus*, 209, 422-433.
- Liu, Z. X., Yin, Z. L., Hu, H. P. & Chen, Q. Y. (2012). Oxidative leaching of low-grade copper ore in ammonia-ammonium sulfate solution with ammonium persulfate. *The Chinese Journal of Nonferrous Metals*, 22(5):1488.
- Liu, Z., Li, Q., Liu, Z., Yang, T., Jiang, B., & Li, Y. (2013). Dissolution behaviour of nickel silicate in ammonia-ammonium sulfate aqueous solution. *Journal of Central South University (Science and Technology)*, 7, 2669-2674.
- Lottermoser, B. G. (2011). Recycling, reuse and rehabilitation of mine wastes. *Elements*, 7, 405-410.
- Ma, B., Wang, C., Yang, W., Yin, F. & Chen, Y. (2013). Screening and reduction roasting of limonitic laterite and ammonia-carbonate leaching of nickel–cobalt to produce a high-grade iron concentrate. *Minerals Engineering*, 50, 106-113.
- Majzlan, J. (2010). Advances and Gaps in the Knowledge of Thermodynamics and Crystallography of Acid Mine Drainage Sulfate Minerals. *CHIMIA International Journal for Chemistry*, 64, (10), 699-704.

- Malvern. (2012). A Basic Guide to Particle Characterization. Inform White Paper, Malvern Instruments Limited. [ONLINE]. Available at < <http://www.malvern.com/en/support/resourcecenter/Whitepapers/WP120620BasicGuidePartChar.aspx>>. [Accessed 13 October 2014].
- McCarty, K. F. & Boehme, D. R. (1989). A Raman study of the systems $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$ and $\text{Fe}_{2-x}\text{Cr}_x\text{O}_3$. *Journal of Solid State Chemistry*, 79(1), 19-27.
- McEwan, N., Courtney, T., Parry, R. & Knupfer, P. (2011). Chromite—a cost-effective refractory raw material for refractories in various metallurgical applications. *Southern African Pyrometallurgy*, 359-370.
- Medvedev, A. S. & Sannikova, O. V. (2012). Recycling tailings from nickel plants that process oxide ores by ammonia-carbonate technology. *Metallurgist*, 56(7-8), 537-545.
- Meyer, N. A., Vögeli, J. U., Becker, M., Broadhurst, J. L., Reid, D. L. & Franzidis, J. P. (2014). Mineral carbonation of PGM mine tailings for CO_2 storage in South Africa: A case study. *Minerals Engineering*, 59, 45-51.
- Meyer, N. A., Vögeli, J. U., Becker, M., Broadhurst, J. L., Reid, D. L. & Franzidis, J. P. (2014). Mineral carbonation of PGM mine tailings for CO_2 storage in South Africa: A case study. *Minerals Engineering*, 59, 45 – 51.
- Miura, H., Kryoaki, N. & Hlrama, T. A. (1994). Mikasaite, $(\text{Fe}^{3+}, \text{Al})_2(\text{SO}_4)_3$, a new ferric sulphate mineral from Mikasa city, Hokkaido. *Mineralogical Magazine*, 58, 649-653.
- Mohamed. S. (2012). Investigating the CO_2 sequestration potential of mine waste tailings through mineral carbonation. Unpublished BSc (Honours) thesis, University of Pretoria, Pretoria, South Africa.
- Mohmood, I., Lopes, C. B., Lopes, I., Ahmad, I., Duarte, A. C. & Pereira, E. (2013). Nanoscale materials and their use in water contaminants removal—a review. *Environmental Science and Pollution Research*, 20(3), 1239-1260.
- Mudd, G. M. (2012). Sustainability reporting and the platinum group metals: a global mining industry leader? *Platinum Metals Review*, 56(1), 2-19.
- Murad, E.U.S., Jerry, M.B. & Carlson, C.L. (1994). Mineralogical characteristics of poorly crystallized precipitates formed by oxidation of Fe^{2+} in acid sulfate waters. *American Chemical Society*, (13), 191-200.
- Murayama, N., Yamamoto, H., & Shibata, J. (2002). Mechanism of zeolite synthesis from coal fly ash by alkali hydrothermal reaction. *International Journal of Mineral Processing*, 64(1), 1-17.
- Murphy, D.B. (2001). *Fundamentals of Light Microscopy and Electronic Imaging*. Wiley-Liss Inc., New York. ISBN: 047125391, 368 pp.

- Nagaishi, T., Ishiyama, S., Matsumoto, M. & Yoshinaga, S. (1984). Reactions between ammonium sulphate and metal oxides (metal=Cr, Mn and Fe) and thermal decomposition of the products. *Journal of thermal analysis*, 29, 121-129.
- Nagaishi, T., Ishiyama, S., Matsumoto, M. & Yoshinaga, S. (1984). Reactions between ammonium sulphate and metal oxides (metal=Cr, Mn and Fe) and thermal decomposition of the products. *Journal of thermal analysis*, 29, 121-129.
- Nakamura, H., Hara, Y., & Osada, H. (1980). The Thermal Decomposition of Ammonium Sulfate and Its Reaction with Iron (III) Oxide. *Nippon Kagaku Kaishi*, 706-710.
- National Institute of Standards and Technology (NIST). (2014a). Ammonia. [ONLINE] Available at: <http://webbook.nist.gov/cgi/cbook.cgi?ID=C7664417&Type=IR-SPEC&Index=1>. [Accessed 10 April 2014].
- National Institute of Standards and Technology (NIST). (2014b). Water. [ONLINE] Available at: <http://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Type=IR-SPEC&Index=1>. [Accessed 10 April 2014].
- National Institute of Standards and Technology (NIST). (2014c). Carbon dioxide. [ONLINE] Available at: <http://webbook.nist.gov/cgi/cbook.cgi?ID=C124389&Type=IRSPEC&Index=1>. [Accessed 10 April 2014].
- National Institute of Standards and Technology (NIST). (2014d). Sulphur dioxide. [ONLINE] Available at: <http://webbook.nist.gov/cgi/cbook.cgi?ID=7446-09-5&Type=IRSPEC&Index=QUANT-IR,8>. [Accessed 10 April 2014].
- National Institute of Standards and Technology (NIST). (2015a). Nitric oxide. [ONLINE] Available at: <http://webbook.nist.gov/cgi/cbook.cgi?ID=C10102439&Mask=80>. [Accessed 22 June 2015].
- Nduagu, E., Bergerson, J. & Zevenhoven, R. (2012a). Life cycle assessment of CO₂ sequestration in magnesium silicate rock—a comparative study. *Energy Conversion and Management*, 55, 116-126.
- Nduagu, E., Björklöf, T., Fagerlund, J., Mäkilä, E., Salonen, J., Geerlings, H. & Zevenhoven, R. (2012b). Production of magnesium hydroxide from magnesium silicate for the purpose of CO₂ mineralization—Part 2: Mg extraction modelling and application to different Mg silicate rocks. *Minerals Engineering*, 30, 87-94.
- Nduagu, E., Björklöf, T., Fagerlund, J., Wärnå, J., Geerlings, H. & Zevenhoven, R. (2012c). Production of magnesium hydroxide from magnesium silicate for the purpose of CO₂ mineralisation – Part 1: Application to Finnish serpentinite. *Minerals Engineering*, 30, 75-86.
- Nduagu, E., Fagerlund, J. & Zevenhoven, R. (2012d). Contribution of iron to the energetics of CO₂ sequestration in Mg–silicates-based rock. *Energy Conversion and Management*, 55, 178-186.
- Nduagu, E., Romão, I., Fagerlund, J. & Zevenhoven, R. (2013). Performance assessment of producing Mg(OH)₂ for CO₂ mineral sequestration. *Applied Energy*, 106, 116-126.

- NEMWA. (2008). National Environmental Management: Waste Act (NEMWA) No 59, of 2008. Department of Environmental Affairs, Pretoria.
- NEMWA. (2014). National Environmental Management: Waste Amendment Act, 2014. Act No. 26 of 2014. Government Gazette No. 37714 (588). [ONLINE] Available at <https://www.environment.gov.za/sites/default/files/legislations/nemwa_actno26of2014.pdf>. [Accessed 06 June 2014].
- Neyaz, N., Siddiqui, W. A. & Nair, K. K. (2014). Application of surface functionalized iron oxide nanomaterials as a nanosorbents in extraction of toxic heavy metals from ground water: A review. *International Journal of Environmental Sciences*, 4(4), 472-483.
- Noubactep, C. & Schöner, A. (2009). Fe₀ based alloys for environmental remediation: Thinking outside the box. *Journal of Hazardous Materials*, 165(1), 1210-1214.
- O'Carroll, D., Sleep, B., Krol, M., Boparai, H. & Kocur, C. (2013). Nanoscale zero valent iron and bimetallic particles for contaminated site remediation. *Advances in Water Resources*, 51, 104-122.
- O'Connor, W. K., Dahlin, D. C., Nilsen, D. N., Rush, G. E., Walters, R. P. & Turner, P. C. (2001). Carbon dioxide sequestration by direct mineral carbonation: results from recent studies and current status (No. DOE/ARC-2001-029). Albany Research Center (ARC), Albany, OR.
- Olszak-Humienik, M. (2001). On the thermal stability of some ammonium salts. *Thermochimica acta*, 378(1), 107-112.
- Pelovski, Y., Petkova, V. & Dombalov, I. (2003). Thermal analysis of mechanoactivated mixtures of Tunisia phosphorite and ammonium sulfate. *Journal of thermal analysis and calorimetry*, 72, 967-980.
- Perkin Elmer. (2013). Atomic Spectroscopy: A guide to selecting the appropriate technique and system. [ONLINE] Available at <http://www.perkinelmer.com/CMSResources/Images/44-74482BRO_WorldLeaderAAICPMSICPMS.pdf> [Accessed 13 October 2014]
- Petrik, L. & Ndungu, P. (2012) Nanotechnology in Water Treatment. *Report to the Water Research Commission*, report number 1897/1/12. ISBN 978-1-4312-0334-5.
- Piatak, N. M., Parsons, M. B. & Seal II, R. R. (2015). Characteristics and environmental aspects of slag: A review. *Applied Geochemistry*, 57, 236-266.
- Prime Resources. (2013). Amandelbult chrome recovery plant, Final scoping report prepared in terms of Regulation 49 (no. R527 of 2004) of the Mineral and Petroleum Resources Development Act, no. 28 of 2002. [ONLINE] Available at <<http://www.sahra.org.za/sites/default/files/additionaldocs/Amandelbult%20CRP%20-%20Final%20Scoping%20Report.pdf>>. [Accessed 11 August 2014].

- Ramsden, J. 2013. Applied Nanotechnology (Second edition): The conversion of research results to products. In Micro and Nano Technologies, edited by Jeremy J. Ramsden, William Andrew Publishing, Oxford, 2014, ISBN 9781455731893, 159pp.
- Rawlins, W. T., Hensley, J. M., Sonnenfroh, D. M., Oakes, D. B. & Allen, M. G. (2005). Quantum cascade laser sensor for SO₂ and SO₃ for application to combustor exhaust streams. *Applied optics*, 44(31), 6635-6643.
- Reardon, E. J. (2014). Capture and storage of hydrogen gas by zero-valent iron. *Journal of Contaminant Hydrology*, 157, 117-124.
- Rice, E. W. (2012). American Public Health Association American Water Works Association. Standard methods for the examination of water and wastewater, Washington, D.C., American Public Health Association.
- Rinaudo, C., Belluso, E., & Gastaldi, D. (2004). Assessment of the use of Raman spectroscopy for the determination of amphibole asbestos. *Mineralogical Magazine*, 68(3), 455-465.
- Rodríguez, J. G., & Uriarte, A. (2009). Laser diffraction and dry-sieving grain size analyses undertaken on fine-and medium-grained sandy marine sediments: A note. *Journal of Coastal Research*, 25, 257-264.
- Romão, I. S., Gando-Ferreira, L. M. & Zevenhoven, R. (2013). Combined extraction of metals and production of Mg(OH)₂ for CO₂ sequestration from nickel mine ore and overburden. *Minerals Engineering*, 53, 167-170.
- Romão, I., Nduagu, E., Fagerlund, J., Gando-Ferreira, L. M. & Zevenhoven, R. (2012). CO₂ fixation using magnesium silicate minerals. Part 2: Energy efficiency and integration with iron-and steelmaking. *Energy*, 41(1), 203-211.
- Romão, I., Gando-Ferreira, L.M. & Zevenhoven, R. (2015). Separation and recovery of valuable metals extracted from serpentinite during the production of Mg(OH)₂ for CO₂ sequestration. *Minerals Engineering*, 77, 25-33.
- RRUFF. (2014). RRUFF Project website containing an integrated database of Raman spectra, X-ray diffraction and chemistry data for minerals. [ONLINE] Available at < http://rruff.info/about/about_general.php > [Accessed 15 October 2014].
- Scheurenberg, R. & Grant-Stuart, D. (2008). South African mine residue disposal practices in a global context: environmental. *Civil Engineering*, 16(8), 19-21.
- Scheurenberg, R. & Grant-Stuart, D. (2012). Tailings facility management design and practice: geotechnical engineering. *Civil Engineering*, 20(3), 54-57.
- Schwertmann, U. (1991). Solubility and dissolution of iron oxides. *Plant and Soil*, 130(1-2), 1-25.
- Scoon, R. & Eales, H. 2002. Unusual fe-ti-cr spinels from discordant bodies of iron-rich ultramafic pegmatite at the amandelbult platinum mine, northwestern bushveld complex. *Mineralogical Magazine*, 66, 857-879.

- Seifritz, W. (1990). CO₂ disposal by means of silicates. *Nature*, 345, 486.
- Shebanova, O. N. & Lazor, P. (2003). Raman spectroscopic study of magnetite (FeFe₂O₄): A new assignment for the vibrational spectrum. *Journal of Solid State Chemistry*, 174, 424-430.
- Shemi, A., Mpana, R.N., Ndlovu, S., van Dyk, L.D., Sibanda, V., Seepe, L. (2012) Alternative techniques for extracting alumina from coal ash. *Minerals Engineering*, 34, 30-37.
- Shemi, A., Ndlovu, S., Sibanda, V., & van Dyk, L. D. (2015). Extraction of alumina from coal fly ash using an acid leach-sinter-acid leach technique. *Hydrometallurgy*, 157, 348-355.
- Song, B., Zhang, Y. R., Di, Y. H., Dai, R. & Zheng, S. L. (2013). Study on Calcination Process of Serpentine Mixed with Ammonium Sulfate. *Applied Mechanics and Materials*, 320, 296-302.
- Song, X., Zhao, J., Li, Y., Sun, Z. & Yu, J. (2013). Thermal decomposition mechanism of ammonium sulfate catalyzed by ferric oxide. *Frontiers of Chemical Science and Engineering*, 7(2), 210-217.
- Spencer, M. 1982. *Fundamentals of light microscopy*. Cambridge University Press, New York. ISBN: 0521-28967, 93pp.
- Struthers, S., Brumle, J. & Taylor, G., 1997. An Integrated System for Recycling Base Metal Tailings. Paper presented at the 1997 Annual Meeting of the American Society for Surface Mining and Reclamation Austin, Texas, May 11, 16, pp. 579-592.
- Sun, Y. P., Li, X. Q., Cao, J., Zhang, W. X. & Wang, H. P. (2006). Characterization of zero-valent iron nanoparticles. *Advances in Colloid and Interface Science*, 120(1), 47-56.
- Szostak, R. (1989). *Molecular sieves, principles of synthesis and identification*. Van Nostrand Reinhold, New York. ISBN: 978-0-7514-0480-7.
- Teir, S., Revitzer, H., Eloneva, S., Fogelholm, C.-J. & Zevenhoven, R. (2007a). Dissolution of natural serpentinite in mineral and organic acids. *International Journal of Mineral Processing*, 83, 36-46.
- Teir, S., Eloneva, S., Fogelholm, C. J., & Zevenhoven, R. (2007b). Dissolution of steelmaking slags in acetic acid for precipitated calcium carbonate production. *Energy*, 32(4), 528-539.
- Tong, W. F., Fan, X. X., Wu, X. F., Zhao, J. C., Li, B. J. & Wu, Y. D. (2013). Extraction of Ni and Co from Laterite-Nickel Ores with Sulfating and Oxidizing Roasting-Water Leaching Process. *Nonferrous Metals (Extractive Metallurgy)*, 7, 9-12.
- University of Washington. (2015). University of Washington Molecular database – Composite spectral images. [ONLINE]. Available at: < University of Washington sulfurmolecules.htm>. [Accessed 10 April 2014].

- Vandenberghe, R. E., De Resende, V. G., da Costa, G. M., & De Grave, E. (2010). Study of loss-on-ignition anomalies found in ashes from combustion of iron-rich coal. *Fuel*, 89(9), 2405-2410.
- Vogeli, J., Reid, D.L., Becker, M., Broadhurst, J. & Franzidis, J. -P. (2011). Investigation of the potential for mineral carbonation of PGM tailings in South Africa. *Minerals Engineering*, 24, 1348-1356.
- Wang, A., Haskin, L. & Jolliff, B. (1998). Characterization of mineral products of oxidation and hydration by laser Raman spectroscopy implications for *in-situ* petrologic investigation on the surface of mars. Twenty-ninth Lunar and Planetary Science Conference, 16 – 20 March, 1998, Houston, Texas.
- Wang, X. & Maroto-Valer, M. (2011a). Integration of CO₂ capture and storage based on ph-swing mineral carbonation using recyclable ammonium salts. *Energy Procedia*, 4, 4930-4936.
- Wang, X. & Maroto-Valer, M. M. (2011b). Dissolution of serpentine using recyclable ammonium salts for CO₂ mineral carbonation. *Fuel*, 90, 1229-1237.
- Wang, M. W., Yang, J., Ma, H. W., Shen, J., Li, J. H., & Guo, F. (2012). Extraction of aluminum hydroxide from coal fly ash by pre-desilication and calcination methods. *Advanced Materials Research*, 396, 706-710.
- Wang, C., Harbottle, D., Liu, Q. & Xu, Z. (2014a). Current state of fine mineral tailings treatment: A critical review on theory and practice. *Minerals Engineering*, 58, 113-131.
- Wang, R. C., Zhai, Y. C., & Ning, Z. Q. (2014b). Kinetics of SiO₂ leaching from Al₂O₃ extracted slag of fly ash with sodium hydroxide solution. *Transactions of Nonferrous Metals Society of China*, 24(6), 1928-1936.
- Waseda, Y., Matsubara, E., Shinoda, K. (2001). *X-Ray Diffraction Crystallography*. Springer-Verlag, Berlin, Heidelberg. ISBN: 978-3-642-16634-1, 310 pp.
- White, W. M. (2013). *Geochemistry*, John Wiley & Sons, ISBN 9781118485255 672 pp.
- Wills, B.A. (2006). Wills' mineral processing technology (Seventh edition): An introduction to the practical aspects of ore treatment and mineral recovery. Edited by Barry A. Wills & Tim Napier-Munn, Butterworth-Heinemann, Oxford, ISBN 9780750644501, 444pp.
- Winter, J.D. (2001). An Introduction to Igneous and metamorphic petrology. Prentice Hall, New York, ISBN 9780132403429, 697pp.
- Xu, P., Zeng, G. M., Huang, D. L., Feng, C. L., Hu, S., Zhao, M. H. & Liu, Z. F. (2012). Use of iron oxide nanomaterials in wastewater treatment: a review. *Science of the Total Environment*, 424, 1-10

- Yao, Z. T., Ji, X. S., Sarker, P. K., Tang, J. H., Ge, L. Q., Xia, M. S., & Xi, Y. Q. (2015). A comprehensive review on the applications of coal fly ash. *Earth-Science Reviews*, 141, 105-121.
- Yibas, B., Netshitungulwana, R., Novhe, O., Mengistu, H., Sakala, E., Thomas, A. and Nyabeze, P.K. (2013). A holistic approach towards best management practices of mine pollution impacts using a catchment area strategy, South Africa. 2013 Annual Conference, International Mine Water Association, IMWA 2013 — Reliable Mine Water Technology, Denver, Colorado, USA, 5–9 August 2013.
- Yu, Z. (2012). Plant Practice of Copper Recovered with Ammonia Heap Leaching from Low Grade Copper Oxidized Ore with High Calcium and Magnesium Content. *Nonferrous Metals (Extractive Metallurgy)*, 6, 14-16.
- Zhang, Wei-xian. (2003). Nanoscale iron particles for environmental remediation: an overview. *Journal of Nanoparticle Research*, 5, 323-332.
- Zhang, Z. M., Chen, S., Liang, Y. Z., Liu, Z. X., Zhang, Q. M., Ding, L. X., & Zhou, H. (2010). An intelligent background-correction algorithm for highly fluorescent samples in Raman spectroscopy. *Journal of Raman spectroscopy*, 41(6), 659-669.
- Zhao, Q., Liu, C., Shi, P., Zhang, B., Jiang, M., Zhang, Q., & Zevenhoven, R. (2014). Sulfuric acid leaching of South African chromite. Part 1: Study on leaching behavior. *International Journal of Mineral Processing*, 130, 95-101.
- Zhao, Q., Liu, C., Zhang, B., Jiang, M., Qi, J., Saxén, H., & Zevenhoven, R. (2015). Study on Extraction of Iron from Chromite. *Steel research International*, 85, 1-7.
- Zuniga, M. & Asselin, E. (2013) Reductive Leaching of Limonitic Laterites Using Ferrous Sulphate, in Ni-Co 2013 (eds T. Battle, M. Moats, V. Cocalia, H. Oosterhof, S. Alam, A. Allanore, R. Jones, N. Stubina, C. Anderson and S. Wang), John Wiley & Sons, Inc., Hoboken, NJ, USA.

Appendices

Appendix A: Standard test methods: Total dissolved solids dried at 180°C (Rice et al., 2012).

SOLIDS (2540)/Total Dissolved Solids Dried at 180°C

2-65

2540 C. Total Dissolved Solids Dried at 180°C

1. General Discussion

a. Principle: A well-mixed sample is filtered through a standard glass fiber filter, and the filtrate is evaporated to dryness in a weighed dish and dried to constant weight at 180°C. The increase in dish weight represents the total dissolved solids. This procedure may be used for drying at other temperatures.

The results may not agree with the theoretical value for solids calculated from chemical analysis of sample (see above). Approximate methods for correlating chemical analysis with dissolved solids are available.¹ The filtrate from the total suspended solids determination (2540D) may be used for determination of total dissolved solids.

b. Interferences: See 2540A.2 and 2540B.1b. Highly mineralized waters with a considerable calcium, magnesium, chloride, and/or sulfate content may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing. Samples high in bicarbonate require careful and possibly prolonged drying at 180°C to insure complete conversion of bicarbonate to carbonate. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue.

c. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Tables 2020.I and II.

2. Apparatus

Apparatus listed in 2540B.2a-h is required, and in addition:

*a. Glass-fiber filter disks** without organic binder.

b. Filtration apparatus: One of the following, suitable for the filter disk selected:

1) *Membrane filter funnel.*

2) *Gooch crucible*, 25-mL to 40-mL capacity, with Gooch crucible adapter.

3) *Filtration apparatus* with reservoir and coarse (40- to 60-μm) fritted disk as filter support.[†]

c. Suction flask, of sufficient capacity for sample size selected.

d. Drying oven, for operation at 180 ± 2°C.

3. Procedure

a. Preparation of glass-fiber filter disk: If pre-prepared glass fiber filter disks are used, eliminate this step. Insert disk with wrinkled side up into filtration apparatus. Apply vacuum and wash disk with three successive 20-mL volumes of reagent-grade water. Continue suction to remove all traces of water. Discard washings.

b. Preparation of evaporating dish: If volatile solids are to be measured, ignite cleaned evaporating dish at 550°C for 1 h in a

muffle furnace. If only total dissolved solids are to be measured, heat clean dish to 180 ± 2°C for 1 h in an oven. Store in desiccator until needed. Weigh immediately before use.

c. Selection of filter and sample sizes: Choose sample volume to yield between 2.5 and 200 mg dried residue. If more than 10 min are required to complete filtration, increase filter size or decrease sample volume.

d. Sample analysis: Stir sample with a magnetic stirrer and pipet a measured volume onto a glass-fiber filter with applied vacuum. Wash with three successive 10-mL volumes of reagent-grade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete. Transfer total filtrate (with washings) to a weighed evaporating dish and evaporate to dryness on a steam bath or in a drying oven. If necessary, add successive portions to the same dish after evaporation. Dry evaporated sample for at least 1 h in an oven at 180 ± 2°C, cool in a desiccator to balance temperature, and weigh. Repeat drying cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight. If volatile solids are to be determined, follow procedure in 2540E.

4. Calculation

$$\text{mg total dissolved solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

where:

A = weight of dried residue + dish, mg, and

B = weight of dish, mg.

5. Precision

Single-laboratory analyses of 77 samples of a known of 293 mg/L were made with a standard deviation of differences of 21.20 mg/L.

6. Reference

1. Sokoloff, V.P. 1933. Water of crystallization in total solids of water analysis. *Ind. Eng. Chem., Anal. Ed.* 5:336.

7. Bibliography

Howard, C.S. 1933. Determination of total dissolved solids in water analysis. *Ind. Eng. Chem., Anal. Ed.* 5:4.

U.S. GEOLOGICAL SURVEY. 1974. Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases. Techniques of Water-Resources Investigations, Book 5, Chap. A1. U.S. Geological Survey, Washington, D.C.

* Whatman grade 934AH; Gelman type A/E; Millipore type AP40; E-D Scientific Specialties grade 161; Environmental Express Pro Weight; or other products that give demonstrably equivalent results. Practical filter diameters are 2.2 to 12.5 cm.
† Gelman No. 4201 or equivalent.

Appendix B: Characterisation of thermochemically-treated mine tailings (MT_{r0}):Elemental mapping and spot analysis

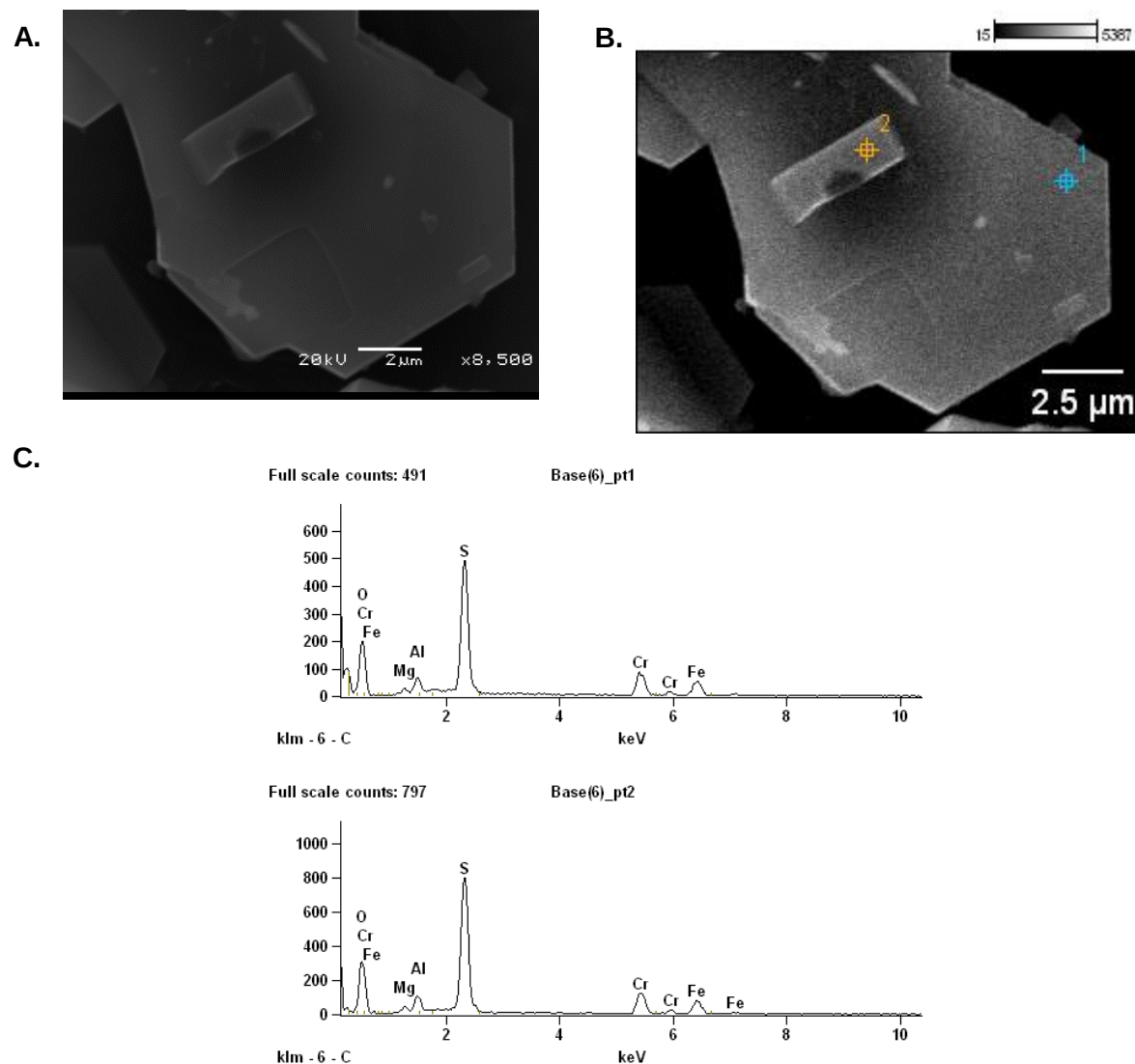


Figure B.1. SEM-EDS micrographs of a hexagonal crystals present in MT_{r0} taken at (A.) 4000x magnification, (B.) the relative location selected for the spot analysis along the grain boundaries and (B.) corresponding elemental spectrum for points 1- 2 respectively.

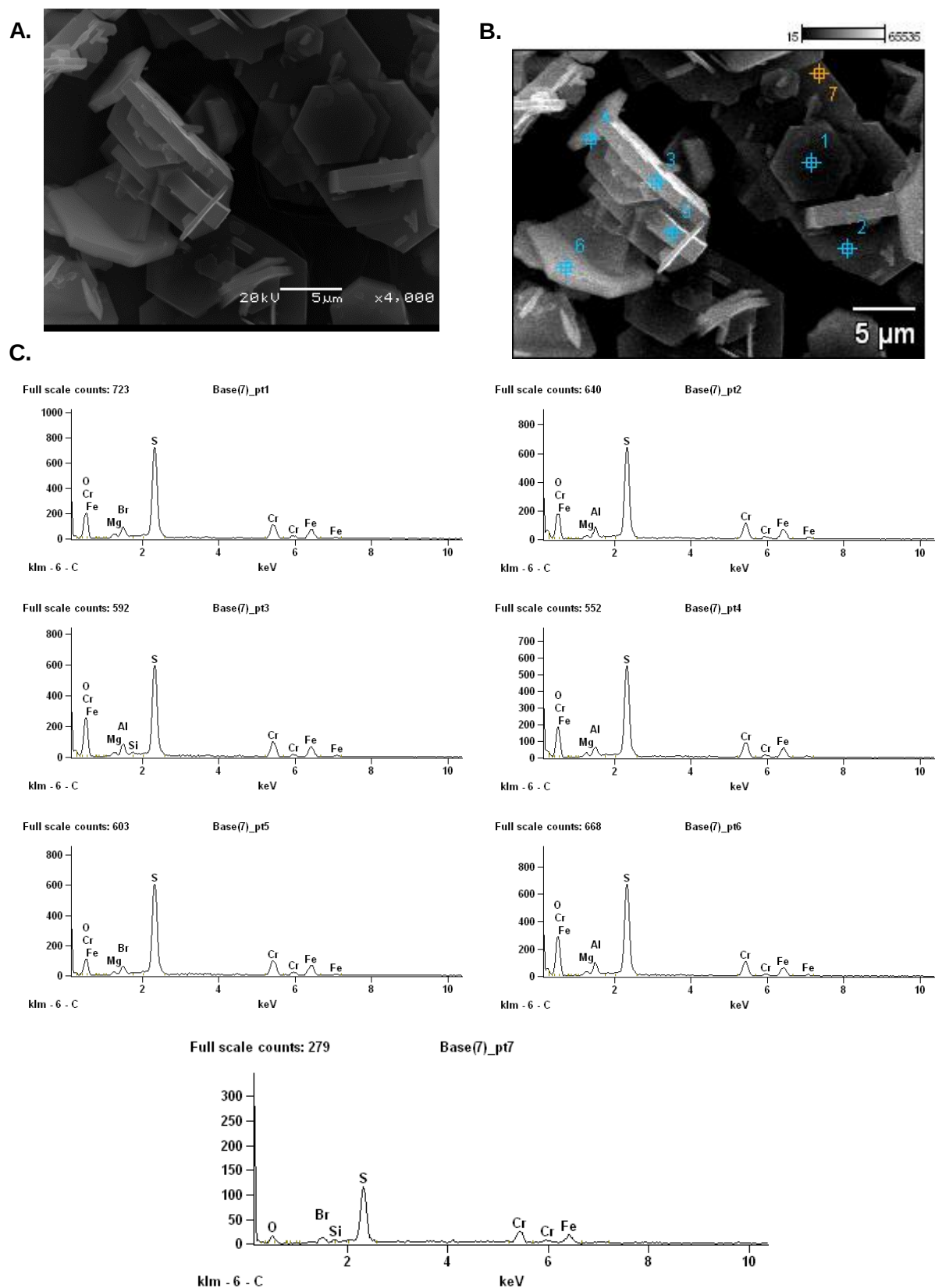
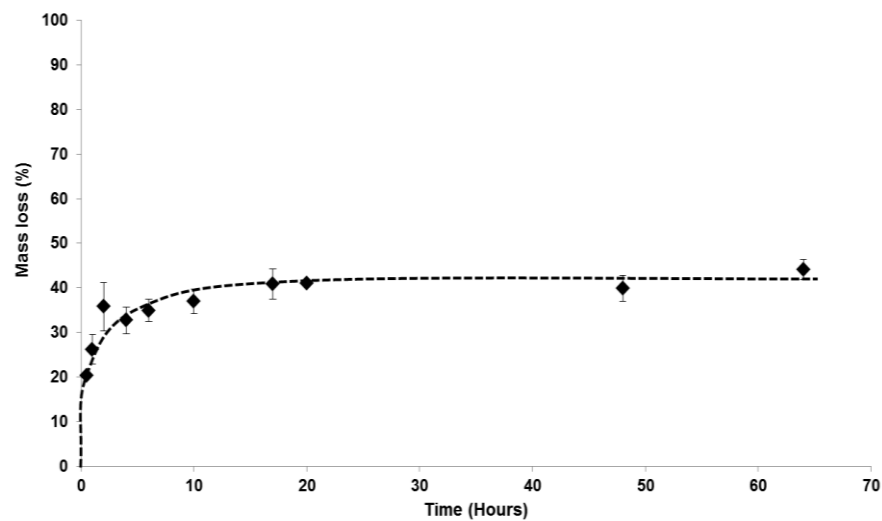


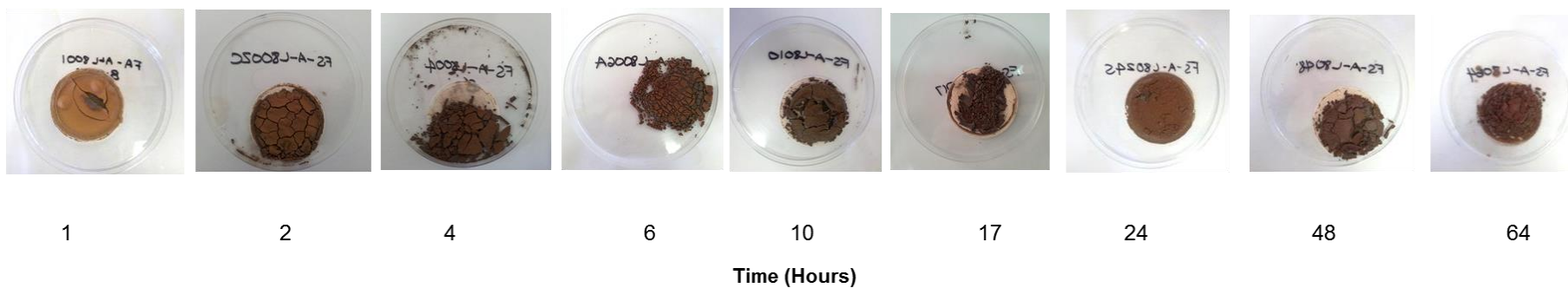
Figure B.2. SEM-EDS micrographs of a hexagonal crystals present in MT_{10} taken at (A.) 4000x magnification, (B.) the relative location selected for the spot analysis along the grain boundaries and (B.) corresponding elemental spectrum for points 1- 7 respectively.

Appendix C: Colour bar created from the colour of the undissolved residues following dissolution under uncontrolled pH conditions

A.



B.



C.



Figure C.1. Temporal changes observed for (A) percentage (%) mass loss, (B.) colour changes of the undissolved residue following dissolution of MT_{10} (MT_{45-75} : AS of 2:6; 550 °C; 45 minutes) under uncontrolled pH conditions (3 g/500 ml; ultrapure water; 80 °C; 850 rpm, $n=3$) and (C.) colour bar illustrating the change in colour over time of the undissolved residues.

Appendix D: UV-Vis Spectroscopic analysis of the leachate following dissolution under uncontrolled pH conditions

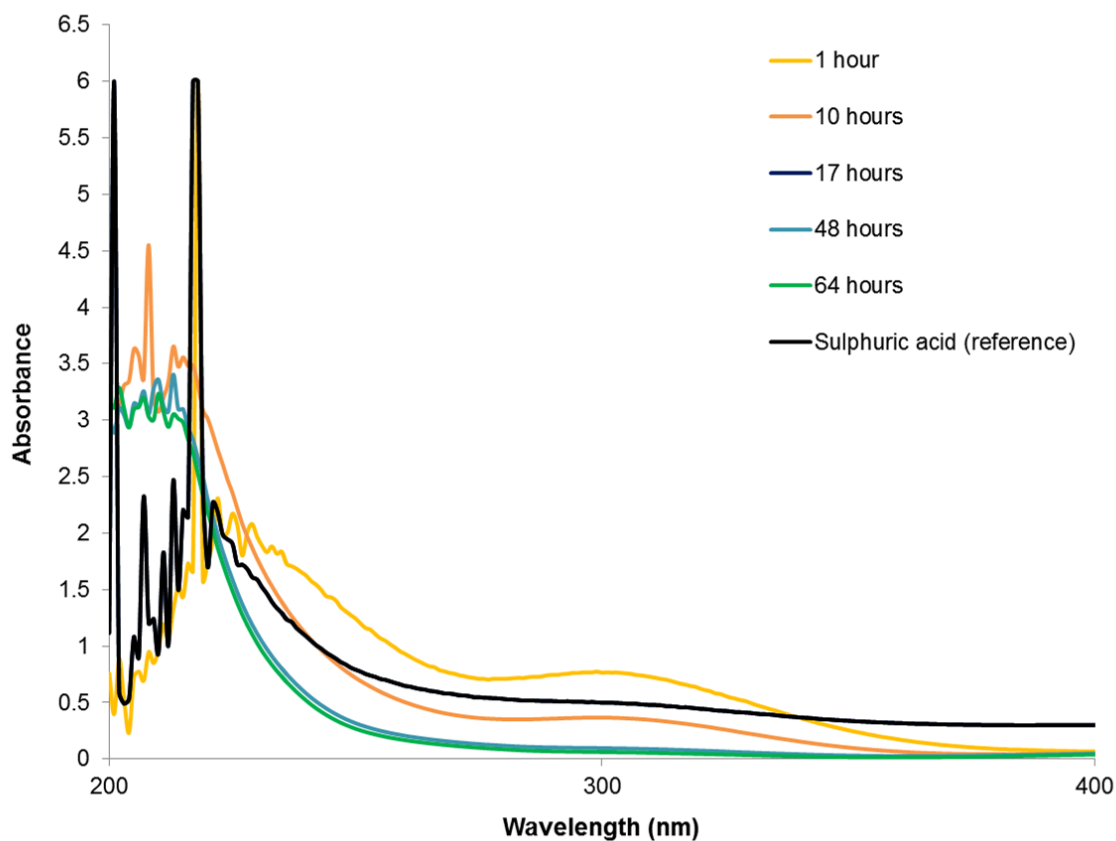


Figure D.1. UV-Vis spectra of the leachate following dissolution of MT_{r0} (MT: AS of 2:6; 550 °C; 45 minutes) under uncontrolled pH conditions (3g/500ml; ultrapure water, 80 °C, 850 rpm, $n=2$) for 1 hour (yellow), 10 hours (orange), 17 hours (dark blue), 48 hours (light blue), 64 hours (green). Sulphuric acid (black) used as a reference.

Appendix E: Elemental extraction efficiencies (mg/l) for mine tailings with different Fe:Cr ratio

◆ Amandelbult - borehole 1 ▲ Amandelbult - borehole 2 ■ Rhovan Operations ● Marico Chrome ● Two Rivers

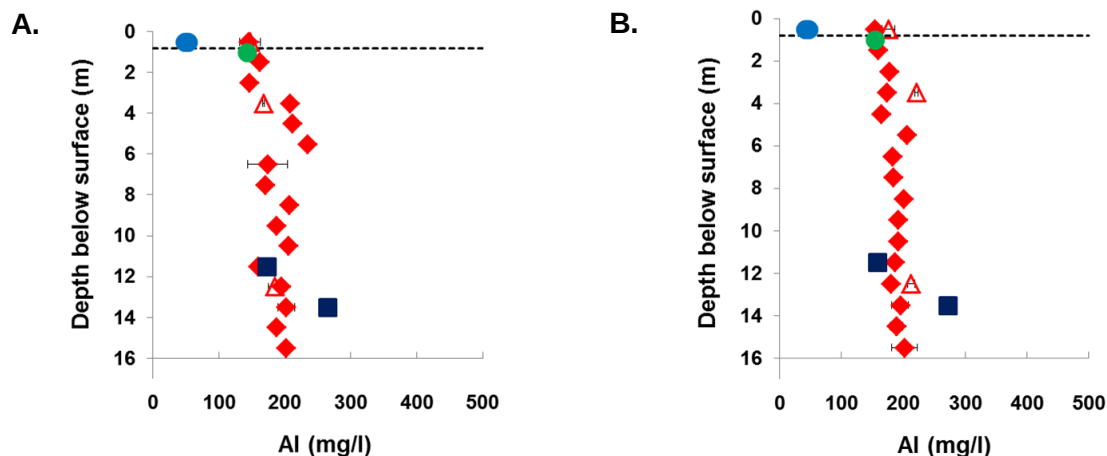


Figure E.1. Differences in concentration of dissolved Al (mg/l) following dissolution of MT_{r0} (MT:AS of 2:6; 45 minutes) at (A.) 350 °C and (B.) 550 °C under optimal dissolution conditions (3g/500ml; 0.6M HNO_3 ; 95 °C; 850 rpm, n=2) generated from tailings with varying Fe:Cr ratios.

◆ Amandelbult - borehole 1 ▲ Amandelbult - borehole 2 ■ Rhovan Operations ● Marico Chrome ● Two Rivers

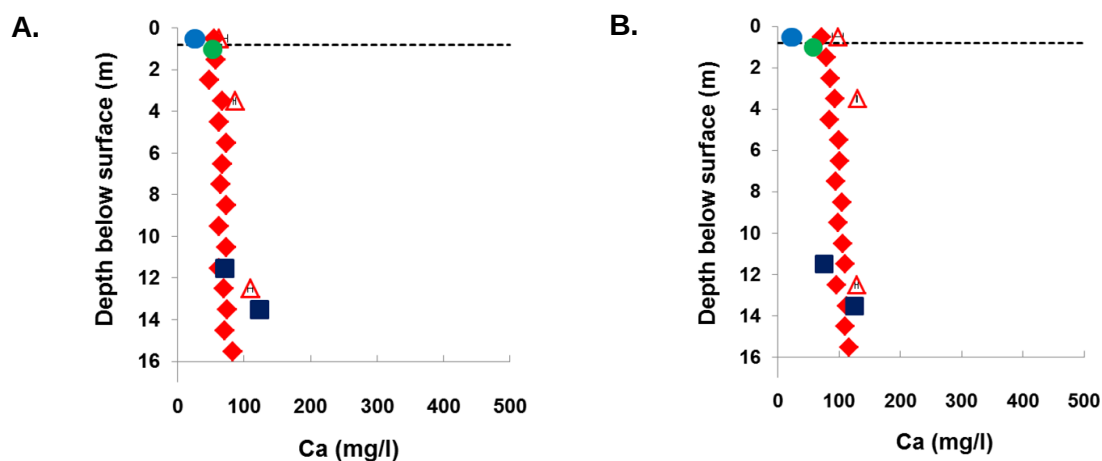


Figure E.2. Differences in concentration of dissolved Ca (mg/l) following dissolution of MT_{r0} (MT:AS of 2:6; 45 minutes) at (A.) 350 °C and (B.) 550 °C under optimal dissolution conditions (3g/500ml; 0.6M HNO_3 ; 95 °C; 850 rpm, n=2) generated from tailings with varying Fe:Cr ratios.

◆ Amandelbult - borehole 1 ▲ Amandelbult - borehole 2 ■ Rhovan Operations ● Marico Chrome ● Two Rivers

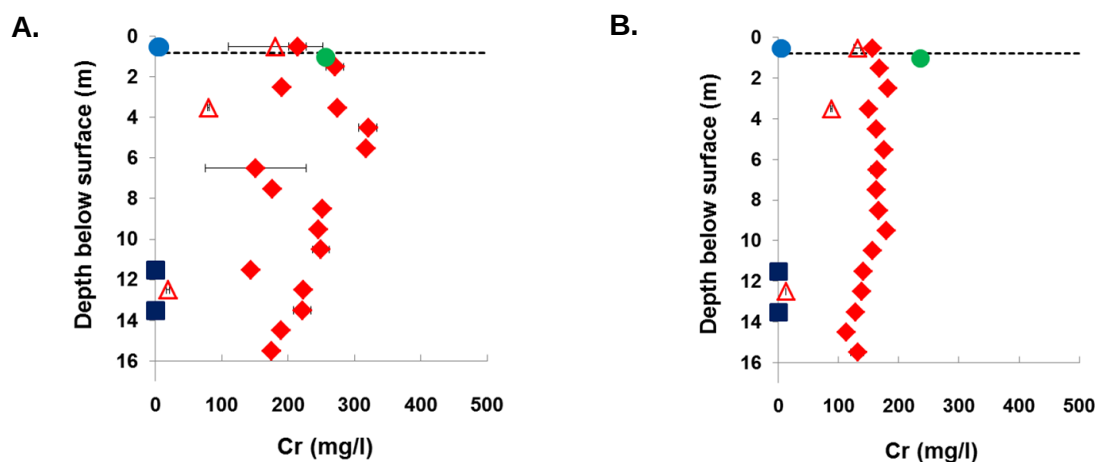


Figure E.3. Differences in concentration of dissolved Cr (mg/l) following dissolution of MT_{ro} (MT:AS of 2:6; 45 minutes) at (A.) $350\text{ }^{\circ}\text{C}$ and (B.) $550\text{ }^{\circ}\text{C}$ under optimal dissolution conditions (3g/500ml; 0.6M HNO_3 ; $95\text{ }^{\circ}\text{C}$; 850 rpm, $n=2$) generated from tailings with varying Fe:Cr ratios.

◆ Amandelbult - borehole 1 ▲ Amandelbult - borehole 2 ■ Rhovan Operations ● Marico Chrome ● Two Rivers

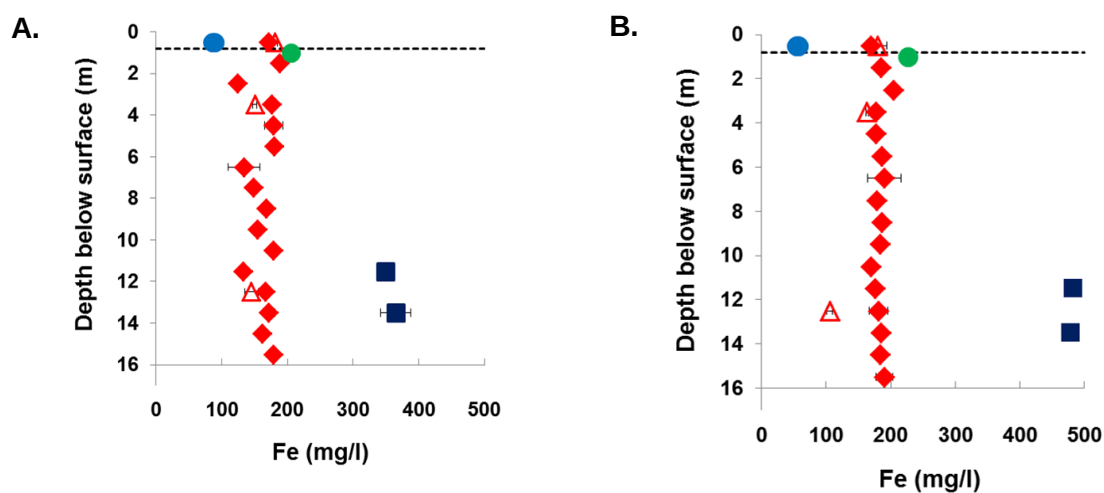


Figure E.4. Differences in concentration of dissolved Fe (mg/l) following dissolution of MT_{ro} (MT:AS of 2:6; 45 minutes) at (A.) $350\text{ }^{\circ}\text{C}$ and (B.) $550\text{ }^{\circ}\text{C}$ under optimal dissolution conditions (3g/500ml; 0.6M HNO_3 ; $95\text{ }^{\circ}\text{C}$; 850 rpm, $n=2$) generated from tailings with varying Fe:Cr ratios.

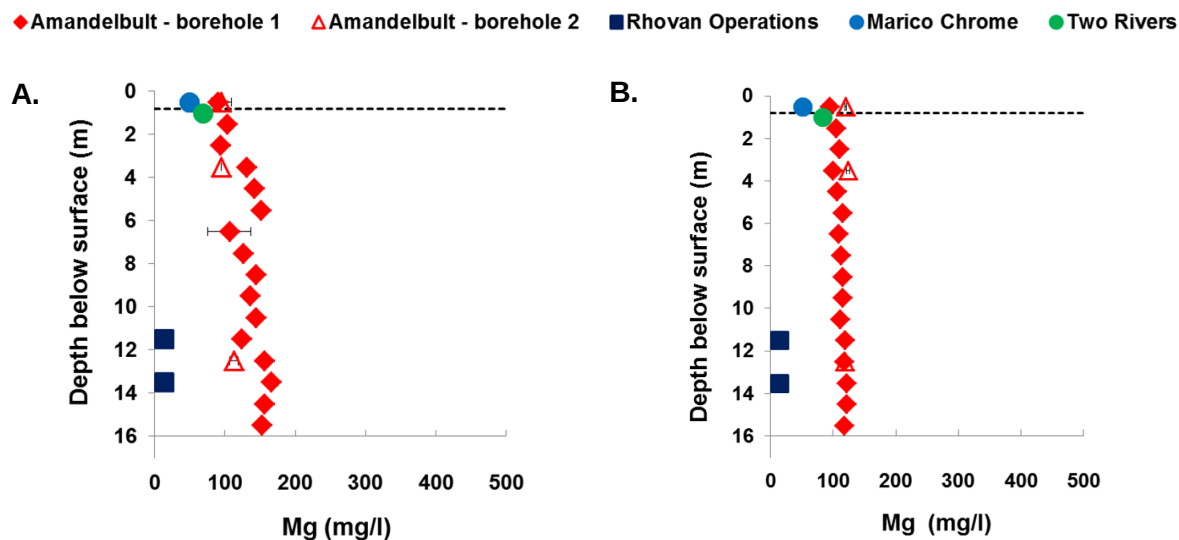


Figure E.5. Differences in concentration of dissolved Mg (mg/l) following dissolution of MT_{r0} (MT:AS of 2:6; 45 minutes) at (A.) $350\text{ }^{\circ}\text{C}$ and (B.) $550\text{ }^{\circ}\text{C}$ under optimal dissolution conditions (3g/500ml; 0.6M HNO_3 ; $95\text{ }^{\circ}\text{C}$; 850 rpm, $n=2$) generated from tailings with varying Fe:Cr ratios.

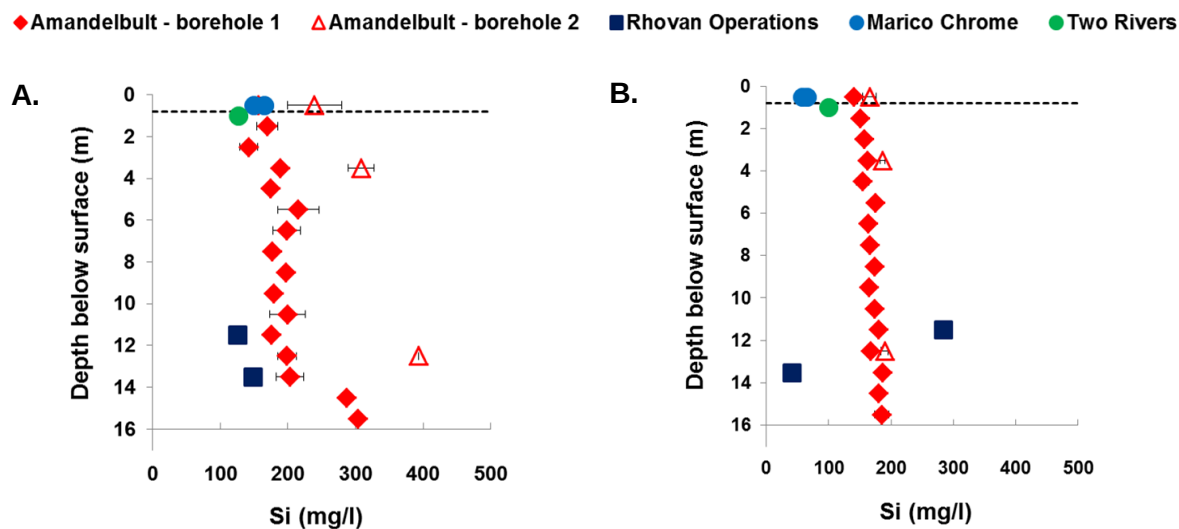


Figure E.6. Differences in concentration of dissolved Si (mg/l) following dissolution of MT_{r0} (MT:AS of 2:6; 45 minutes) at (A.) $350\text{ }^{\circ}\text{C}$ and (B.) $550\text{ }^{\circ}\text{C}$ under optimal dissolution conditions (3g/500ml; 0.6M HNO_3 ; $95\text{ }^{\circ}\text{C}$; 850 rpm, $n=2$) generated from tailings with varying Fe:Cr ratios.

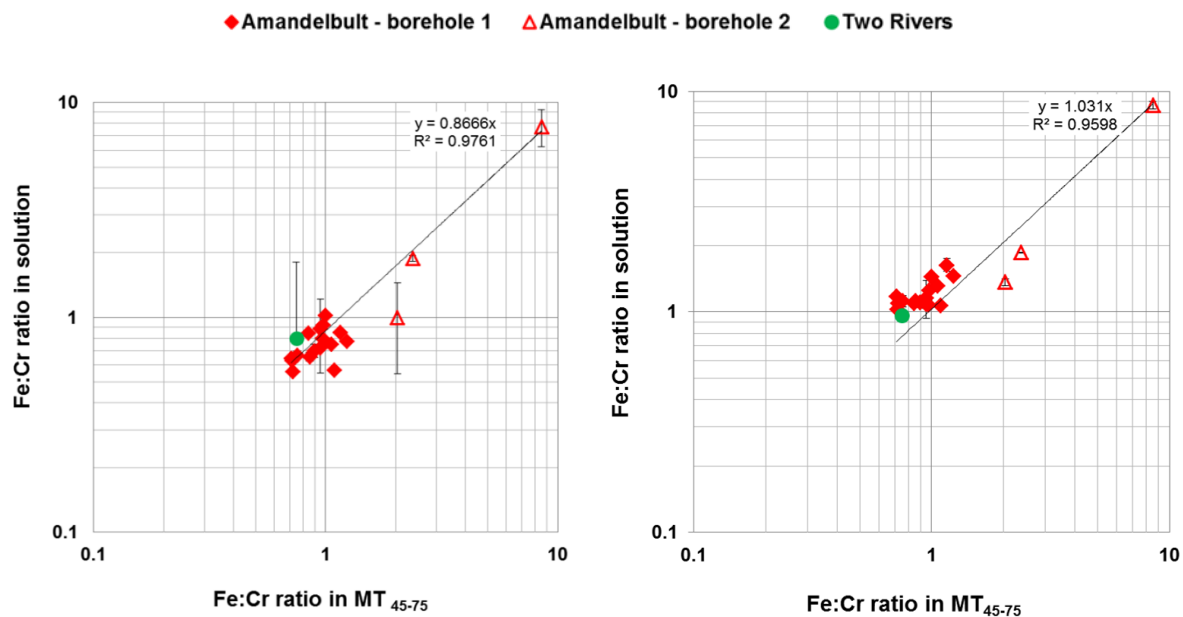


Figure E.7. Correlation between the elemental Fe:Cr ratio in the starting materials (MT₄₅₋₇₅) and the elemental Fe:Cr ratio in solution (%) following dissolution of MTro (MT: AS of 2:6; 45 minutes) at (A.) 350 °C and (B.) 550 °C under optimal dissolution conditions (3g/500ml; 0.6M HNO₃; 95 °C; 850 rpm, n=2) generated from tailings with varying Fe:Cr ratios. Cr-depleted MT from Rhovan operations and Marico Chrome removed from dataset.