

Beneficiation of diamond mine residues for the synthesis of Mg containing compounds

By

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Declaration

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

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Summary

The mining industry plays a vital part in the South African economy. However, its activities are associated with the generation of large quantities of waste mine residues (e.g. tailings, slimes). These residues create major environmental challenges and take up vast amounts of land that could be used for other economic purposes. On the other hand, these same residues may have the potential to be secondary mineral resources that promote sustainability if processed into valuable products.

The aim of this study is to develop a process for the valorisation of diamond mine residues. Thermochemical processing using ammonium sulphate (AS), $(\text{NH}_4)_2\text{SO}_4$, is a promising technology for extracting strategic metals from various mineral-bearing materials. The diamond mine residues used in this study were characterised by a complex mineral matrix, with smectite, talc, phlogopite and diopside being the most common minerals. Mg (13.1 – 15.7% m/m), Fe ($\sim$ 6.6% m/m) and Al (2.8 – 3.0% m/m) were determined to be the most abundant metals. The beneficiation potential of these residues could therefore lie in the extraction and conversion of these elements into valuable products. For instance, Mg is frequently listed as a critical element (i.e., a valuable constituent element of a mineral commodity that is subject to risk of disruption in its supply) owing to its importance and versatility in various industrial applications such as automotive, aerospace, electronics, medical or chemical. The relatively high talc content ($\sim$ 30 wt. %) of the residues have furthermore raised the question whether talc should be regarded as a source of Mg or whether it could be purified and recovered as a value-added product.

In this study, a multistep process entailing the combination of a thermochemical solid-solid reaction between the mine residues and ammonium sulphate was used to achieve maximum extraction of metals and to produce water-soluble metal and ammonium-metal sulphates. This was followed by aqueous dissolution under various conditions, to maximise extraction efficiencies of the soluble metals.

The degree of conversion of extractable metals from the mine residues into soluble sulphate-bearing minerals, during thermochemical treatment with $(\text{NH}_4)_2\text{SO}_4$ between 450 – 550°C, was monitored using a combination of TGA, XRD, FTIR and FE-SEM analyses. The residue:AS ratio of 2:4 was found to provide optimal extraction at a

temperature of 450°C. Increasing the temperature during leaching also improved the extraction of the elements of interest, with 50°C being selected as optimal with regard to extraction and energy efficiencies. Mg (89%), Fe (59%) and Al (62%) were successfully extracted from the roast product of the thermochemical treatment at 450°C using both deionised H₂O and sulphuric acid solutions at 50°C, with the acidic solutions providing superior extraction.

Thermochemical treatment of the mine residues with (NH₄)₂SO₄ was found to be non-selective at a single temperature, with several metals being co-extracted from the residues. This made the production of pure Mg-containing products difficult, as the removal of the Fe-fraction post thermochemical treatment was challenging. TGA data of the products obtained from thermochemical treatment was used to develop a roasting programme to separate Fe from Mg before leaching. By employing an additional roasting step, the soluble Fe content in Mg-bearing leachates could be reduced by up to 90%.

Several products were generated after elemental extraction and separation. Brucite and Mg/Al layered double hydroxides (LDHs) were successfully synthesised from the leachates and characterised by XRD, TGA, FTIR and FE-SEM. The composition of talc, present in the untreated tailings, was not altered during the thermochemical reaction with AS or the dissolution process. The talc content increased from ~30% in the mine residue to ~56% in the leach residue after thermochemical treatment, combined with an improvement in colour clarity. Talc can therefore be considered a valorisation product, although further purification is required.

This study successfully proved that Mg containing products can be formed during the beneficiation of diamond mine residues.

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List of abbreviations and symbols

AS	Ammonium sulphate
ABS	Ammonium bisulphate
ATR	Attenuated total reflection
BET	Brunauer- Emmett Teller analysis
CS	Mine residue slimes
CT	Mine residue tailings
DLS	Dynamic Light Scattering
DSC	Differential Scanning Calorimeter
DTG	Derivative Thermogravimetry
EC	Electrical Conductivity
EDX	Energy-dispersive X-ray Spectroscopy
FE-SEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
LDH	layered double hydroxide
LOI	Loss on Ignition
MMO	Mixed metal oxide
Mg	Magnesium
m/m	mass/mass
m/v	mass/volume

NEWMA	National Environmental Management Waste Act
PGM	Platinum Group Metals
PSD	Particle Size Distribution
rpm	Revolutions per minute
TGA	Thermogravimetric analysis
μm	Micrometre
v/v	volume/volume
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

Chapter 1: Introduction, motivation and scope

1.1 Introduction

This chapter presents a short introduction which provides background information with regard to the comprehensive topic of this study. The overall and individual objectives as well the novelty of this work are described. The scope, methodology and layout are summarised.

1.2 Background

The discovery of the first diamond in 1867, on the banks of the Orange River near Hopetown, initiated the development of mining in South Africa. It also launched a number of other activities, including the establishment of the first stock exchange in Africa in nearby Kimberley in 1881, and the founding of the Witwatersrand and Pretoria universities, which originated from a school of mines set up in Kimberley in 1896 (Kane-Berman, 2017). South Africa's total reserves remain some of the world's most valuable, with an estimated worth of R20.3-trillion. Overall, the country is estimated to have the world's fifth-largest mining sector in terms of GDP value. The mining sector is an important foreign exchange earner, with gold accounting for more than one-third of exports. In 2009, the country's diamond industry was the fourth largest in the world. Although the relative contribution of mining to GDP has shrunk, it still accounts for 8% of gross fixed capital formation, and also for almost a quarter of all foreign direct investment in South Africa (Kane-Berman, 2017; Möncks et al, 2023).

Mining stimulated further development as railways had to be built from the coast to the interior to support the needs of mining. A variety of service and ancillary industries were founded to service the mines, the people who worked in them and everyone else in the towns (Kane-Berman, 2017).

The impact of mining was more extensive than just the development of the manufacturing sector. The establishment and expansion of towns were also stimulated, which provided new and available markets for agricultural products and necessitated

the construction of roads as well as railways. Mining in South Africa has always needed extremely high levels of skill in numerous different fields, ranging from metallurgy to shaft sinking, laboratory work and the more hazardous work deep underground. Importantly, mining also provides employment opportunities for both unskilled and semi-skilled people.

Although the mining industry is an important economic asset for South Africa, mining inevitably has had detrimental effects on the environment. South Africa and other countries face a variety of environmental legacy problems associated with the management of large volumes of solid mine waste residues (Asif and Chen, 2016). The amount of mine waste produced also continues to increase as natural resources become depleted, and lower grade ore with a higher ratio of unwanted material must be extracted (Falagán et al., 2017; Lottermoser, 2011). The major environmental impacts from waste disposal of mining can be divided into two categories: the loss of productive land and possible biodiversity due to it being used as a waste storage area, and contamination of soil, including erosion and formation of sinkholes, as well as contamination of surrounding surface and groundwater by chemicals from mining processes.

Besides creating environmental damage, the contamination resulting from leakage of chemicals may also affect the health and safety of the local population. Erosion of exposed hillsides can cause fine dust dispersal, slope instability and mud slides. Mine residues can also contain leftover processing chemicals or sulphidic minerals, which may combine with rainwater and oxygen to form sulphuric acid which then dissolves uranium and other metals as it flows or seeps into the local groundwater (Falagán et al., 2017; Morin and D'Hugues, 2007). The dumps may also produce airborne radioactive material (Kane-Berman, 2017), although very often people living near them are unaware of the resulting health risks.

Mine dumps, tailings dams and the resultant siltation of drainages and rivers can also significantly impact the surrounding areas. Mine dumps, also known as tailings or slimes dams, are a major distinguishing feature of Johannesburg and adjoining towns. They have also been a major source of pollution for decades. Tailings are finely ground rock and mineral waste products of mineral processing operations, i.e. after the

minerals have been extracted from it, the crushed rock is brought to the surface and deposited onto dumps. Tailings may be deposited in the form of a water-based slurry into tailings ponds (sedimentation lagoons enclosed by dams built to capture and store the tailings), which are known as slimes. The type, amount, and properties of mine waste produced at different mines vary depending on the resource being mined, the process technology used and the geology at the mine site (Bullock et al., 2023; Mervine et al., 2018).

Mine tailings can be considered to be complex material, as parent rock is variable and a combination of various types of wastes is generated. They also undergo continuous weathering changes due to being stored in exposed heaps, which must be managed properly to protect the environment. These wastes could however, represent untapped secondary mineral resources, which could be processed to promote sustainability through their conversion to valuable materials or products (Frändegård et al., 2015; Mohamed et al., 2016), as well as the associated development of treatment technologies to mitigate environmental problems. Due to the heterogeneous composition of mine tailings, the procedures for rehabilitation or beneficiation need to be designed for the specific material. As new sources of minerals become more difficult to find, and grades of most metals and minerals have declined, exploiting waste may become a profitable proposition. In addition, the waste material is already on the surface and available for processing (Falagán et al., 2017; Morin and D'Hugues, 2007).

1.3 Motivation

Beneficiation, by definition, is the treatment of raw material, such as ore, to improve the physical or chemical properties in preparation for further processing. The process is the transformation of a mineral, or a combination of minerals, into a higher-value product, which can either be consumed locally or exported. Unfortunately, South Africa and possibly the African continent in general can be defined as an economy with low levels of beneficiation of minerals, in that most of its minerals are exported as ores or semi-processed minerals rather than high value intermediates or finished products. As the African continent's largest and most mature mining market, South Africa has made beneficiation policies a central pillar of its "New Growth Path" economic development

policy (Dept. Min Resources, 2011). As a result of the three spheres of sustainable development, namely environment, social and economic aspects, stringent environmental legislation has been introduced, which presents opportunities for South Africa to realise the benefits of implementing the beneficiation strategy. In addition, due to developed economies seeking to diversify their supply of critical minerals (CM), South Africa has the potential to become a supplier of CMs.

Various processes are being developed for the recovery of metals from waste materials, including bauxite residue (Liu and Naidu, 2014), copper tailings (Chmielewski et al, 2016; Han et al., 2018), cyanide tailings (Zhang et al., 2012) and the platinum group metal (PGM) tailings (Meyer et al., 2014; Mohamed et al, 2016). While the reuse of mine waste residues is not at the forefront in South Africa, it is one of the central issues of the eco-efficient mining movement, which is gaining momentum in Europe, Australia and Canada. Very little work has been done on diamond mine tailings, but these contain worthwhile amounts of magnesium, as well as iron and aluminium. In addition, no report could be found in the literature on the synthesis of useful products from elements extracted from diamond mine residues. Our interest in magnesium extraction is two-fold. Firstly, we aim to promote environmental benefits by utilising the extensive quantity of mine residues through valorisation. Secondly, our interest in magnesium extraction stems from the fact that it is considered a critical element that has the potential to be transformed into valuable products (European Commission, 2020).

1.4 Problem statement

Although the mining industry is an important economic asset for South Africa, mining inevitably has detrimental effects on the environment. This study proposes to develop a process for the valorisation of diamond mine slimes, which would enable the reduction of piles of waste, the releasing of valuable land that is currently underutilised and the alleviation of a source of soil and water pollution.

In order to ensure the optimum extraction of all possible minerals, a detailed knowledge of the bulk chemical and mineralogical compositions of the mine tailings is required. As the starting material (tailings and slimes) can be considered complex and variable, the

extracted metals and their conversion to produce commercial-grade products will have to be followed in a controlled and reproducible manner.

1.5 Aims and Objectives

Our study aimed to develop a process for the valorisation of diamond mine residues, with the overall goal of reducing waste piles, freeing up currently underutilised land as well as alleviating a source of soil and water pollution. The extraction of three components from the mine residues and their conversion to produce commercial grade products were of particular interest. These include magnesium, iron, aluminium and talc; particularly the extraction of magnesium for the production of magnesium hydroxide and layered double hydroxides. Talc was identified as a major phase in the mine residues, and after excluding it as a contributor of Mg, it was included as a valorisation product. Talc may be used in numerous applications. The extraction of the metals may be attained via a multi-step process of thermochemical treatment with ammonium sulphate (AS) to produce water-soluble metal sulphate species, followed by aqueous dissolution (Nduagu et al, 2012; Mohamed et al, 2016), leaving the talc phase as solid leach residue.

Specific objectives include:

1. To characterise the mine residues with respect to their physical and chemical properties, with the aim of extracting the maximum amount of metals from the raw materials.
2. To investigate the effectiveness of thermochemical treatment using ammonium sulphate (AS) on the physical and chemical properties of diamond mine residues, as compared to untreated materials.
3. To optimise the extraction of the metal sulphates formed from the reaction between the mine residues and AS, using a variety of leaching conditions.
4. To investigate the reactivity of talc during thermochemical treatment with AS. This is to ensure that talc is not contributing to the magnesium being extracted from the mine residues, but can be considered a viable valorisation product.
5. To synthesise and characterise Mg-, Fe- and Al- hydroxide precipitates from the leachates during sequential precipitation with ammonia solution.

6. To synthesise and characterise layered double hydroxides from the leachates, using a variety of different methods.
7. To develop a method to separate the iron from the magnesium and aluminium in the thermochemically treated mine residues, prior to leaching, to improve the purity of the magnesium containing precipitates and layered double hydroxides.

1.6 Research hypotheses

- Diamond mine residues contain valuable elements which can be extracted for subsequent conversion into value-added products.
- Ammonium sulphate is a suitable reagent for the extraction of major elements from diamond mine residues via thermochemical solid-solid treatment.
- The thermochemical treatment is non-selective at a single roasting temperature which may prevent the preferential extraction of specific elements present in diamond mine tailings at a single roasting temperature.
- Selective precipitation may be used to separate the combination of metal ions in the leachate.

1.7 Scope and limitations

The scope of this study was to extract the major elements from the diamond mine residues, with emphasis on the extraction of Mg, which could then be utilised to synthesise Mg-containing products. Characterisation of the raw materials, intermediate products and products produced were analysed using the following analytical techniques: X-ray powder diffractometry (XRD), thermogravimetric analysis (TGA), Fourier Transform infrared spectrometry (FT-IR) and Field-emission scanning electron microscopy (SEM).

The limitations of this study included:

- Due to the complexity of the raw material and to limit variability, only residues from one diamond mine were included in this study.

- The methods followed during product synthesis were not optimised, only the feasibility of producing the products of interest was investigated.
- Optimisation of experimental parameters to improve the physical properties of the products formed was not investigated.

1.8 Structure of thesis

This content of this thesis is divided into the following chapters:

Chapter 1 presents a brief overview of the background to the proposed study, including the problem statement and objectives.

Chapter 2 provides a literature review on mine residues and their environmental impact, as well as background information on the extraction of magnesium using thermochemical treatment and leaching, and the production of precipitates and layered double hydroxides.

Chapter 3 presents and describes the experimental procedures, materials and methods.

Chapter 4 discusses the characterisation of the mine residues.

Chapter 5 covers the thermochemical treatment conditions used to extract magnesium, and other elements, from the mine residues.

Chapter 6 gives an overview on the reactivity of the talc component of the mine residues with the thermochemical treatment utilised.

Chapter 7 provides a report and discussion on the optimisation of the leaching process.

Chapter 8 investigates the removal or reduction of the iron content using a thermal programme.

Chapter 9 presents the Mg containing products synthesised from the mine residues.

Chapter 10 reports on the conclusions from this study and the recommendations for future work.

Chapter 2: Literature Review

2.1 Introduction

This chapter provides a literature review on the environmental impact and physicochemical characteristics of mine residues. Different technological processes for the extraction of metals from mine wastes and other residues are presented. It includes discussions regarding the synthesis of hydroxide precipitates and layered double hydroxides (LDHs), as these were the products of interest in this study.

The information in this chapter furthermore aims to emphasise the need for research into ways to utilise the potential of mine wastes while simultaneously reducing the environmental damage caused by the storage of these residues.

2.2 Mine residues

Globally, due to an ever-growing population, there is an increasing demand for the products of the mining industries. The mining sector can therefore be considered as a facilitator of economic growth worldwide. At the same time, a large amount of waste is produced, with tailings being one of the main waste streams contributing an estimated 5 – 7 billion tons worldwide. This waste increases as natural resources become depleted and ore of lesser grade with a higher ratio of unwanted material is mined (Falagán et al, 2017; Shengo, 2021; Xu et al, 2019). The volume of tailings is therefore generally greater than the desired product and may contain hazardous contaminants, with the ratio of tailings to valuable product being generally 97 – 99%, and up to ~200:1 (Lottermoser, 2011; Xu et al, 2019). However, due to the increasing demand for metals as well as technological advances, waste materials from historic mining enterprises may have greater metal contents than the lesser grade primary ores still available for excavation. Since they are already partly processed in the form of fine particles, and above ground, it may become economically more cost effective to extract the residual metals from the mine wastes rather than mining the primary ore (Asif and Chen, 2016; Chmielewski et al,

2016; Falagán et al, 2017). There may also be metals present, i.e. rare earth elements, that have increased in value since the initial processing, which are therefore worth extracting.

Tailings are mixtures of finely crushed rock and mineral waste products generated during the processing of ore materials to extract the valuable minerals. They are usually stored above ground in tailing impoundments or piles, around or close to the mining site. They may contain left over processing fluids after the extraction of the economically desired metals and minerals, and may be reactive due to waste material content and their small particle size (Asif and Chen, 2016; Falagán et al, 2017). An example is cyanide, used for gold extraction, which is highly toxic to birds, fish and humans.

Tailings may undergo physical and chemical changes after they have been deposited, usually due to weathering effects, and this may allow contaminants to be released into the environment, e.g. pyrite (FeS_2) which forms acidic waste water when exposed to water and oxygen. They may also be deposited into tailing ponds in the form of a water-based slurry, which is then known as slimes (Kossoff et al, 2014). Storing the tailings under water reduces contact with the atmosphere, thus decreasing oxygen-mediated chemical changes. Tailing dam failures, however, result in severe social, economic and environmental impacts with loss of lives and property, as well as extensive environmental pollution (Asif and Chen, 2016; Kossoff et al, 2014; Xu et al, 2019). This is especially prevalent when waste storage is in the vicinity of residential areas (Asif and Chen, 2016; Morin and D'Hugues, 2007).

The mining industry has formed the backbone of the South African economy for over 150 years. Consequently, South Africa and other countries face a variety of environmental problems associated with the management of large volumes of solid mine waste residues (Asif and Chen, 2016; Shengo, 2021). Mine tailings and slimes are a form of environmental pollution through fine dust dispersal, slope instability, mud slides and possible contamination to local surface and ground waters by chemicals from the mining processes. Another major environmental impact is the loss of productive land and possible biodiversity due to the land being used as a waste storage area. The National Environmental Management Waste Act (NEWMA 2014) emphasises the importance of reprocessing and beneficiating mining and industrial waste residues, with the objective of rehabilitating former disturbed environments and the production of renewable

resources. Mine tailings can, therefore, represent untapped secondary mineral resources, which could be processed to promote sustainability through their conversion to valuable materials or products (Frändegård et al, 2015; Mohamed et al, 2016; Pollmann et al, 2010), and the associated development of treatment technologies to mitigate environmental problems.

Currently, mine residues are being used as cemented paste backfill in underground mines or open pits, and in the case of clay-rich tailings, as raw materials for the production of building materials i.e. bricks, concrete and sanitaryware (Lottermoser, 2011; Xu et al, 2019). They may also be used as fill for subsided land, aggregates in roads and embankments or building construction. There is also research into the possibility of using mine tailings for carbon sequestration (Bullock et al, 2023; Lottermoser, 2011; Mervine et al, 2018; Meyer et al, 2014). Metal recovery from mine tailings is not new and has gained increasing interest with the development of a variety of acceptable technologies for different types of mine tailings, i.e. acid leaching, magnetic separation, pressurised leaching or a combination thereof (Table 2.1). Phytoremediation, i.e. establishing a stable vegetative cover by using a selection of plants, is another process that may be used to recover metals (Acosta et al, 2018; Xu et al, 2019). The plant cover simultaneously provides some environmentally sustainable protection by reducing the bioavailability of pollutants, which improves soil fertility and increases the amount of organic matter in the tailings, as well as diminishing the amount of water and wind erosion (Acosta et al, 2018). A disadvantage of phytoremediation is that it is a slow process due to nutritional deficiencies caused by the scarcity of natural topsoil and possibly high levels of heavy metals, which inhibit plant growth.

The optimal solution for mine tailings would be to reprocess them to recover valuable metals and to remove the adverse environmental effects. Understanding the chemical and mineralogical compositions of mine residues is therefore important, as it determines the potential for recovery of the metals.

Table 2.1 provides a summary of major extractable elements from a selection of recent research studies on different tailings types, including the methods utilised.

Table 2.1: Summary of major extractable elements, tailing types and methods utilised for beneficiation from a selection of recent research articles.

Tailing Type	Major extractable elements	Beneficiation method/s	Reference
Cu tailings, Kasese, Uganda	Co, Cu, Fe, Zn	Bioreaching (> 99% Co)	Morin & D'Hugues, 2007
Cu – flotation waste Lubin, Poland	Co, Cu, Mo, U, V, Zn	Hydrometallurgical processes (95% U)	Chmielewski et al, 2016
Cu mine tailings (i) Sevilla, Spain, (ii) Bor, Serbia	Ag, Cu, Fe, Ni, Zn	Bioreaching (i) 99% Ag, 61% Cu; (ii) 76% Ag, 51% Cu	Falagán et al, 2017
Gold – cyanide tailings; Shandong, China	Fe, Si	Reduction roasting, water leaching, magnetic separation 75% Fe	Zhang et al, 2012
Iron ore tailings, China	Al, Ca, Fe	Magnetising roast, magnetic separation (61.3% Fe)	Li et al, 2010
Pb – Zn (after recovery of Fe) Guangdong, China	Ag, Ga, Pb	Roasting, chloride leaching (84.4% Ag, 80.8% Ga, 70.5% Pb)	Lei et al, 2018
Mn tailings, Brazil	Al, Fe, Mn	Sulphuric acid leaching (95.4% Mn)	Santos et al, 2015
PGM tailings, Mpumalanga, South Africa	Al, Cr, Fe, Mg, Si	Thermochemical treatment, leaching (60% Al, 27% Cr, 35% Fe)	Mohamed et al, 2016
Rare Earth, Bayan Obo, China	Ce, La	Supergravity (98.4% Ce, 97.7% La)	Lan et al, 2019

Diamond mine residues are Mg rich and are abundant, with the estimated production using 6 sites in South Africa between 2017 – 2021 being > 200 Mt (Bullock et al, 2023). The extraction of Mg from magnesium-rich rock has been studied as a possible option for CO₂ sequestration (Bullock et al, 2023; Meyer et al, 2014; Nduagu et al, 2012a; Romão et al, 2013). Our interest in magnesium extraction from diamond mine residues is twofold, namely, for the environmental benefit of the valorisation of the extensive quantity of mine tailings and slimes, as well as due to magnesium being considered a critical element which could then be transformed into valuable products (European Commission, 2020; Hayes and McCullough, 2018).

2.3 Location and minerology

The raw materials used in this study were sourced from a South African diamond mine. The primary source of all of South Africa's diamonds is kimberlite found in ancient, vertically dipping volcanic pipes. Many of these pipes are located in the vicinity of the city of Kimberley and were initially amenable to open-cast mining. They were largely discovered in the latter part of the 19th century. Early in the 20th century, the Premier mine's volcanic pipe was discovered near Pretoria and, in the final decades of the century, the Finsch mine's kimberlite pipe was discovered near the town of Lime Acres in the Northern Cape and, later, the Venetia mine's kimberlite near the town of Alldays in Limpopo province. Figure 2.1 (courtesy of Nelson, G, 2013) illustrates the location of diamond deposits (shown in black) in South Africa.

Kimberlite pipes are an ultramafic rock of the peridotite variety, i.e. with less than 45% silica and high in magnesium. The minerals occurring in Kimberlite pipes are predominantly olivine, which is a Mg-Fe silicate, and several of the following minerals: phlogopite, calcite, serpentine, diopside, monticellite, apatite, spinels, perovskite, ilmenite, etc. However, the mineralogy and geochemistry of Kimberlite pipes are heterogenous and may vary between sites, as well as within the deposit. Olivine is extremely abundant relative to the other minerals, which are not necessarily present (Bullock et al, 2023; Field et al, 2008; Mervine et al, 2018).

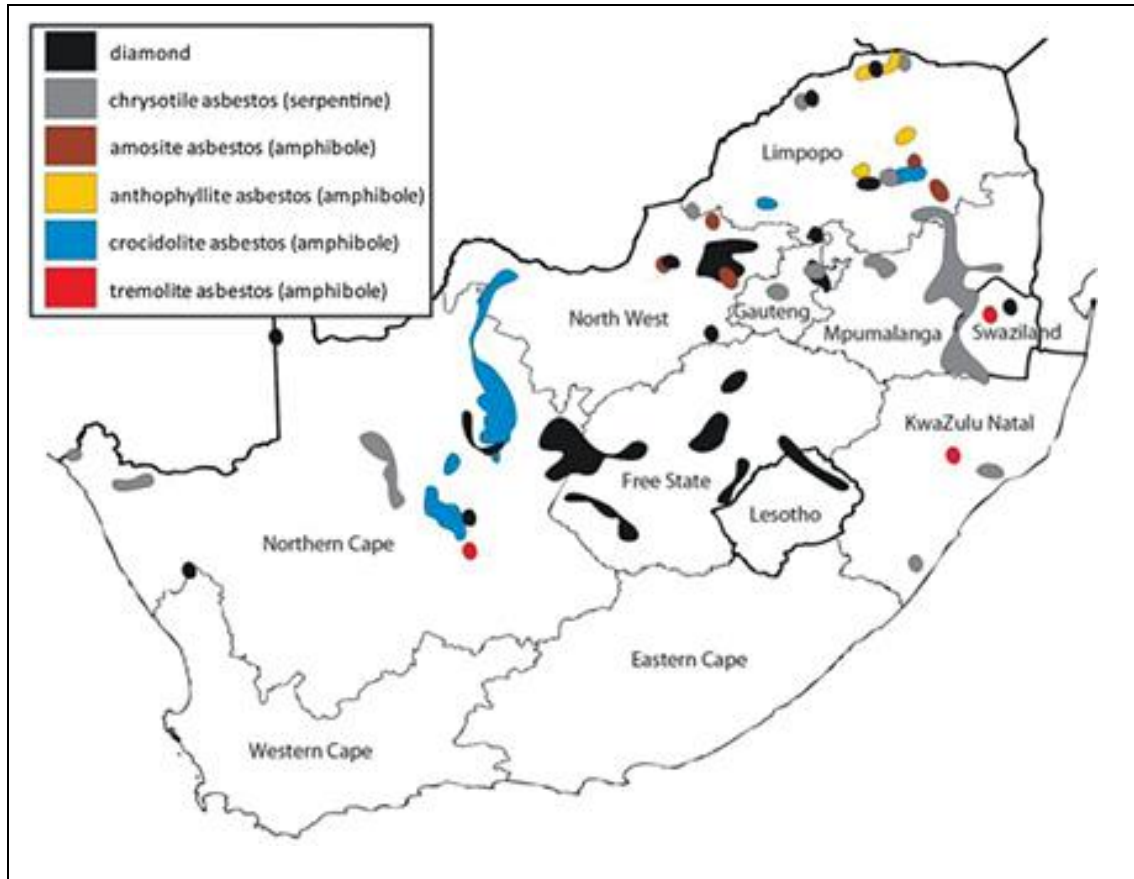
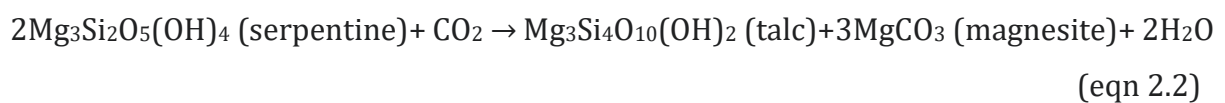
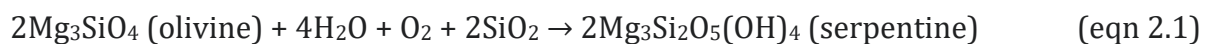


Figure 2.1: Map of South Africa illustrating the availability of various minerals (Courtesy of Nelson, G., 2013).

Generally, in the case of Mg-silicates, olivine is more reactive than serpentine or pyroxene due to differences in the silicate structures (Meyer et al, 2014; Sanna et al, 2014). Olivine is a nesosilicate or orthosilicate, which consists of individual silica tetrahedra, held together by charge-balancing cations, i.e. Mg^{2+} or Fe^{2+} , and undergoes weathering relatively easily. Olivine should also, during hydrothermal action and low-grade metamorphism and weathering, transform into serpentine, which is often associated with talc and magnesite (Nesse, 2000):



The serpentine group of minerals, of which lizardite is the most common mineral, are phyllosilicates, consisting of sheet-like layers which are held together by van der Waals forces.

The pyroxene group, which includes diopside and enstatite, forms inosilicates which consist of chain silicates, i.e. double chains of silica tetrahedra (Nesse, 2000), and are more rigid and less reactive due to their complex structure (Meyer et al, 2014; Sanna et al, 2014).

Extraction of specific minerals from a waste stream necessitates a detailed knowledge of the mineralogy, geochemistry and physical properties of the waste (Lottermoser, 2011). Kimberlite tailings, the fine solid residue generated during the processing of Kimberlite ore to extract diamonds, are a complex mixture of predominantly phyllosilicate minerals (>85% m/m), particularly smectites (2:1 swelling group of clays) and serpentine minerals (Mervine et al, 2018). They display considerable mineralogical diversity (Bullock et al, 2023; Mervine et al, 2018), possibly as a result of the long life of the mines and the weathering of the tailings. Smectites are Mg-rich, with saponite a Mg-Fe containing clay and montmorillonite being Mg-Al bearing. Other minerals generally present include talc, chlorite, plagioclase and amphibole. The mineralogy of the tailings depends on the original kimberlite composition, its alteration history and the mineral processing that it has undergone, as well as the physical characteristics of the surrounding rock (Lavikko and Eklund, 2016b; Mervine et al, 2018). Some minerals present, i.e. diopside, are strongly site specific (Mervine et al, 2018).

Phyllosilicates form a large group of minerals that includes, among others, serpentine, talc, kaolinites, and a variety of clay minerals, such as micas, chlorite, smectites, and vermiculite. They have a two-dimensional, flat layered structure and can be classified according to the condensation of the tetrahedral and octahedral sheets. A 1:1-layer silicate structure, as observed for kaolinite and halloysite, exists if one tetrahedral layer and one octahedral layer are bonded together. If an octahedral layer is sandwiched between two tetrahedral layers, a 2:1-layer silicate is created. Additional subdivisions are made according to the nature of the octahedral sheets. Micas, chlorite, smectite and vermiculite are examples of minerals with a 2:1-layer silicate structure. The layers of cations display weak bonding, often with neutral molecules, i.e. H₂O, trapped between the

layers, which results in soft minerals (Lavikko and Eklund, 2016b). The main thermic reactions of phyllosilicates are dehydration and dehydroxylation. The temperature at which dehydroxylation initiates depends on the structure of the clay, and the cation/s incorporated into the layers (Földvári, 2011; Stevenson, 2016).

Clay minerals, such as kaolinite, illite, smectite, chlorite and vermiculite, are a group of hydrated aluminium phyllosilicates with a very fine particle size, and unique structures (Zhou et al, 2018). Smectite, $\text{Na}_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_{2n}(\text{H}_2\text{O})$, a 2:1 hydrous aluminium phyllosilicate clay mineral group, has substantial interlayer cation exchange capability, swelling ability and a high surface area. Within the smectite group of clay minerals are montmorillonite, saponite, nontronite, and beidellite, with the former two being Mg-containing. The Mg-rich smectites are commonly found in kimberlite (Mervine et al, 2018). The octahedral sites of montmorillonite, the most common dioctahedral smectite, are occupied mainly by Al^{3+} , but also partially by Fe^{3+} and Mg^{2+} . The tetrahedra may have some Al^{3+} substitution for the tetrahedral Si. Saponite is trioctahedral with Mg^{2+} dominating the octahedral sites of the mineral, and pronounced Al^{3+} substitution in the tetrahedral sheet. The extent of hydration of the ions in the interlayer space varies greatly and depends on the nature of the interlayer cations, the composition of the layers and environmental factors i.e. humidity and temperature (Madejová, 2003; Stevenson and Gurnick, 2016).

Various amounts of phlogopite (phyllosilicate mineral within the mica group), kaolinite, lizardite (hydrous magnesium, iron phyllosilicate within the serpentine group), talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, hydrated magnesium silicate) and chlorite may also be present in the Kimberlite tailings. Phlogopite ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$) contains large amounts of silica and alumina, and may also be magnesium rich, although the magnesium may be replaced by ferrous iron (Sreenivasan et al, 2017). The magnesium, which is found in the octahedral layer, may not be easy to extract due to the high silica content and low percentage of crystalline water (Lavikko and Eklund, 2016b). Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) is a 1:1 dioctahedral clay with a 2-dimensional layered structure and low symmetry (Stevenson and Gurnick, 2016). Phlogopite, muscovite and biotite belong to the same mineral group, the micas. Phlogopite may weather, via hydrobiotite, to vermiculite whereas the most common alteration product of biotite is chlorite (Földvári, 2011). They have similar diffraction patterns which makes identification of the exact mineral species difficult using

routine XRD procedures (Zhou, 2018). The same applies to the amphibole minerals, e.g. hornblende and actinolite. Amphiboles are generally stable and only break down at high temperatures (Nesse, 2000).

2.4 Extraction of magnesium from minerals and mine residues

In order to beneficiate the mine residues, one approach is to convert parent minerals into water-soluble compounds, while simultaneously ensuring maximum recovery of the metals and reducing reagent and energy requirements. This has been studied using direct leaching as well as thermochemical treatment combined with leaching.

2.4.1 Direct leaching

Direct leaching can be conducted using a variety of media. Acid leaching, in both inorganic (HCl, HNO₃, H₂SO₄) (Meyer et al, 2014; Sierra et al, 2017; Teir et al, 2007) and organic acids (acetic acid, formic acid, oxalic acid) (Meyer et al, 2014; Teir et al, 2007), as well as ammonium bisulphate (ABS) solutions (Sanna et al, 2014), has been reported. In addition, Teir et al (2007) investigated the dissolution of serpentinite in alkali solutions (NaOH, KOH and NH₃) and ammonium salt solutions (NH₄Cl, NH₄NO₃, (NH₄)₂SO₄). The success of direct leaching is dependent on the starting material (residue or ore) as the mineralogy determines whether the metals are easily extracted, with serpentinites generally producing good results (Teir et al, 2007; Sanna et al, 2013; Sierra et al, 2017), whereas PGM tailings show limited extraction (Meyer et al, 2014).

The temperature employed during the leaching also plays an important role, e.g. the %Mg extracted by Teir et al (2007) using 2M H₂SO₄, increased from 26% at room temperature to 100% at 70°C, and in the study by Sierra et al (2017) from 17% at 20°C to 87% at 100°C using ~4.8M HCl. Sierra et al (2017) also managed to extract 77% Mg from serpentine residues at 20°C using ~7.2M H₂SO₄ indicating that the concentration, and the nature of the acid makes a difference. The use of such high acid concentrations at elevated temperatures is not environmentally friendly and can be quite costly (Sierra et al, 2017). Sanna et al (2013), using NH₄HSO₄ as leaching solution, also reported an increase in Mg

extraction with increasing temperature (28% at 50°C to 75% at 120°C) and increasing solvent concentration (60% in 1 M to 80% in 3 M). Interestingly, although none of the acids extracted Mg selectively, extraction of Fe when using nitric acid was lower than other mineral acids (Teir et al, 2007).

In some cases, the raw material has to be 'activated' before treatment through calcination or thermo-activation (Bayer et al, 1982; Sanna et al, 2013) or grinding (Sanna et al, 2013), which adds to the cost of the process.

Direct dissolution in alkaline solutions had almost no measurable amounts (< 0.5%) of Mg or Fe extracted, and ammonium salt solutions (NH_4Cl , NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$) appeared to extract Mg selectively, although only to a very small degree (0.3 – 0.5%) (Teir et al, 2007).

2.4.2 Solid-solid thermochemical reaction

Thermochemical treatment using ammonium sulphate (AS), $(\text{NH}_4)_2\text{SO}_4$, is an actively researched technology for the extraction of strategic metals from several mineral-bearing materials. Examples include coal fly ash (Wu et al, 2014; Doucet et al, 2016), laterite nickel ore (Li et al, 2018), PGM tailings (Mohamed et al, 2016, 2019), and bauxite residue (Borra et al, 2016; Meng et al, 2020). This method was also used successfully by Bayer et al (1982) to extract aluminium from kaolinite. In addition, it has been used to convert insoluble oxides, e.g. Al_2O_3 (Nagaishi et al, 1982) and Fe_2O_3 (Nagaishi et al, 1984), into soluble sulphates using pure analytical chemicals.

This process can also be effectively applied for the extraction of magnesium from serpentinite rocks in the context of CO_2 mineral sequestration (Nduagu et al, 2012; Romão et al, 2015, 2016). However, different serpentine minerals display varying degrees of reactivity with AS, which is mostly guided by their mineralogical structure, their parent rock, and any possible transformation the rock may have undergone through metamorphism or other type of alteration (Lavikko and Eklund, 2016a). A high Mg content does not guarantee good extraction results as the location of the Mg in the crystal lattice and its bonding to different anions plays a role. For instance, lizardite appears to contain the favourable features more often than antigorite (Sjöblom and Eklund, 2014;

Lavikko and Eklund, 2016b), which generally makes it a more suitable parent material for mineral carbonation. Bayer et al (1982) reported that the micas, e.g. biotite and phlogopite, and feldspars e.g. plagioclase, did not react readily with AS.

The extraction of magnesium from serpentinite rock, a component of diamond bearing rock, has been studied extensively by the research group in Abo Akademi University in Finland, using thermochemical reactions with ammonium salts (Nduagu et al, 2014; Romão et al, 2015). The method used by the Åbo Akademi University (ÅAU) consists of heating the material containing magnesium silicate minerals, mainly serpentinites, with AS, to between 400 – 550°C, in a 2:3 m/m ratio for serpentinite:AS (Fagerland et al, 2012; Nguagu et al, 2012a). Nguagu (2012a) reported that, although it was feasible to extract the Mg from a temperature as low as 200°C, the best extraction was achieved at 450°C. However, for Lithuanian serpentinite, increases in %Mg extraction were obtained at 480 – 535°C (Nguagu, 2012b). The m/m ratio was used due to it being approximately the stoichiometric amounts of the Mg-silicate rock and AS, which would limit the production of SO₃ during the roasting process. The presence of SO₃ appears to reduce the amount of magnesium sulphate (MgSO₄) produced from Finnish serpentinite, favouring the formation of magnesium orthosilicate (Mg₂SiO₄) and magnesium metasilicate (MgSiO₃) (Nduagu et al, 2012a).

The conditions used for thermochemical treatment vary greatly and depend on the starting material and the metals of interest. A large range of m/m ratios, roasting temperatures and roasting times have been used in previous studies and a selection of these are summarised in Table 2.2. The large variation in mass ratios selected could be due to the mineralogy of the residues being relatively complex, e.g. Mohamed et al (2016) found a 2:6 ratio was optimum for PGM tailings. Nduagu et al (2012b) also reported using different mass ratios and temperatures due to elemental composition, specifically the Mg:Fe ratio in Mg-silicate rock, affecting the degree to which Mg and Fe may be extracted.

Table 2.2: Summary of rock:AS ratios (m/m), roasting temperatures and roasting times from selected studies.

Metal	Mineral	Rock:AS m/m ratio	Roasting temperature (°C)	Roasting time	Reference
Fe, Mn	Ferruginous manganese ores	1:1	400 – 500	3 h	Saba et al, 1973
Al	Kaolinite	1:4	420 – 600	20 h	Bayer et al, 1982
Al	Al ₂ O ₃	4:1	400 – 600	30 min	Nagaishi et al, 1982
Mg	Finnish serpentine	2:3	400 – 450	30 min	Nduagu et al, 2012a
Cr, Al, Mg, Fe	PGM tailings	2:6	350 – 550	45 min	Mohamed et al, 2016
Fe, Mn	Pyrolusite residue	1:6	350 – 450	2 h	Deng et al, 2018
Sc, Al, Fe	Bauxite residue	1:1 – 4:1	550 – 750	1 h	Meng et al, 2020

Roasting temperature affects the physical characteristic of the roast product, with lower roasting temperatures being inclined to produce a sintered, hard material whereas higher temperatures produced a softer, more flowable product that is easier to handle (Mohamed et al, 2016, 2019; Romão et al, 2016). This hardness was ascribed, by Mohamed et al (2016), to the presence of excess AS or its decomposition products which had not reacted within the timeframe used.

Additional studies have investigated the extraction of the metals using ammonium bisulphate (ABS) or combinations of AS/ABS (Koivisto et al, 2016; Nduagu et al, 2014; Romão et al, 2016; van der Merwe et al, 2017), as well as with the inclusion of water in

the roast mix (Romão et al, 2016), to improve the efficiency of the extraction. Mohamed et al (2019) included other ammonium salts (NH_4Cl and NH_4NO_3) in their study using PGM tailings, with very limited success. In the study by Koivisto et al (2016) the extraction of Mg improved when using ABS (36.4% to 55.8%), as well as when using the ABS/AS combination (up to 49.8%). The efficiency of the Fe extraction was only improved with the ABS/AS combination (25.8% to 43.5%). Van der Merwe et al (2017) reported that both AS and ABS were suitable extraction reagents, however ABS exhibited superior extraction efficiencies at lower temperatures (400°C). The presence of water also influenced the reaction positively, with a substantial increase in the Mg extraction, which is supported by the study of Romão et al (2016) using AS. This was postulated as due to the water dissolving part of the AS and enhancing contact between the rock and AS. The water vapour emitted also appears to restrict the volatilisation rate of the ammonium salts by stabilising intermediate products (Koivisto et al, 2016; Romão et al, 2016). The disadvantage of using ABS is that the regeneration of AS to form ABS is not energy efficient (Koivisto et al, 2016; van der Merwe et al, 2017), and in South Africa it is considerably more expensive than AS. The advantage of using AS is that it is widely available at relatively low cost, and can be easily recycled (Romão et al, 2015, van der Merwe et al, 2017).

2.4.3 Dissolution of soluble metals from thermochemically treated minerals and mine residues

The solid products, containing ammonium metal- or metal- sulphates, formed after the thermochemical treatment with AS are readily soluble in water at room temperature (Fagerlund et al, 2012; Mohamed et al, 2016; Romão et al, 2015). Extraction of the metals can, however, be enhanced by leaching under controlled pH conditions (Mohamed et al, 2016), and at higher temperatures (Deng et al, 2018; Mohamed et al, 2016). This is particularly relevant for the extraction of Fe. In the studies by Mohamed et al (2016, 2019), increasing the temperature from 25°C to 85°C when leaching in water caused the secondary precipitation of the Fe fraction from the leachate. This was prevented when conducting the dissolution under controlled pH conditions (0.63 M HNO_3), where the degree of the elemental extraction was improved with increasing temperature, although

not to the same extent for all elements. Deng et al (2018) investigated the increase in both the temperature and acid concentration (0.3 M and 0.5 M H_2SO_4) when extracting Fe and Mn from pyrolusite residue, with best results shown at the higher concentration and higher temperature. Working at higher temperatures may also reduce the leaching time required to obtain a high recovery efficiency (Deng et al, 2018; Mohamed et al, 2016).

The solid to liquid ratio during leaching should be considered carefully. While sufficient liquid is necessary to improve dissolution, too large a volume can impact the cost efficiency of the process if AS is to be recovered from the leachate (Romão et al, 2012). Therefore, the volume of water or acid solution needs to be minimised, which may result in a solution with a complex mixture of metals and a wide range of concentrations. Reported ratios vary from 1 g/10 mL (Romão et al, 2015) to 3 g/500 mL (Mohamed et al, 2016, 2019).

2.5 Synthesis and characterisation of Mg containing products from minerals and mine residues

A rapidly emerging research area in the extraction of minerals from rock or tailings is to use the minerals for carbon dioxide sequestration. An example is the recent interest taken in the CO_2 mineralisation potential of PGM tailings due to their Mg-rich mineralogy (Amponsah-Dacosta and Reid, 2014; Meyer et al, 2014). Magnesium could be converted to magnesite (MgCO_3) as a CO_2 sequestration mineral technology or as a feedstock for the synthesis of nano-based materials. This conversion cannot, unfortunately, occur directly from the sulphate form of the metal, and needs to first be converted into magnesium hydroxide ($\text{Mg}(\text{OH})_2$) via selective precipitation (Fagerlund et al, 2012). Magnesium hydroxide could be used as a feedstock for nano-based materials, i.e. MgO which is used in multiple applications and products. It is also finding application in the field of flame retardants (Hanna et al, 2019; Wang et al, 2011). There is also the potential to use the magnesium and aluminium or iron in the metal-rich solution for the production of layered double hydroxides (LDHs) (Wiyantoko et al, 2015). LDHs are most commonly formed by the co-precipitation of divalent (Mg^{2+} , Fe^{2+}) and trivalent (Al^{3+} , Fe^{3+}) metal cations at moderate to high pH. LDHs are a group of clay minerals that have shown potential for a number of applications in several areas i.e., soil remediation, ion exchange,

pharmaceuticals and medicine, flame retardants and heat stabilisers, as well as environmentally friendly catalysts (Balsamo et al, 2012; Benhiti et al, 2020; Labuschagné et al, 2015; Olfs et al, 2009; Theiss et al, 2016).

2.5.1 Production of precipitates from leachates

By increasing the pH of the leachate solution, hydroxides are formed to achieve the selective precipitation of the various metals, i.e. Mg, Fe, Ca, Ni, Cr, Al, released during the process of solid/solid reaction and dissolution. This is most often achieved by using either sodium hydroxide (NaOH) (Hanna et al, 2019; Henrist et al, 2003; Sierra et al, 2017) or ammonia solution (Alvarado et al, 2000; Fagerlund et al, 2012; Henrist et al, 2003; Nduagu et al, 2012a; Romão et al, 2016), although other alkalis may be employed, e.g. urea (ul Haq and Haider, 2010). A disadvantage of using NaOH is the introduction of Na⁺-ions which facilitates the formation of thenardite/mirabilite (Na₂SO₄) from the sulphate-rich leachate (Sierra et al, 2017).

The alkali used as well as the reaction conditions of temperature and concentrations of reactants may also influence the morphology, i.e. shape, particle size and particle size distribution, of the precipitate formed. Morphologies reported include globular (irregular in shape and size), hexagonal platelet-shaped, rod-like and needle-like (Hanna et al, 2019; Henrist et al, 2003; Wang et al, 2011). In the study by Henrist et al (2003), using NaOH as the precipitating agent produced agglomerated clumps of small globular particles, possibly due to the high pH of the NaOH solution, resulting in a rapid nucleation process. In addition, the adsorption of the small Na⁺-cation onto the surfaces of the growing crystals may hinder crystal growth as the shape of the crystal is influenced by the presence of impurities (Wang et al, 2011).

Using ammonia solution produced particles with a thin, platelet-like morphology, which was further improved by utilising lower temperatures (between 25 – 50°C) for synthesis of the Mg(OH)₂. The morphology of Mg(OH)₂ is particularly important when synthesising products for specific applications, i.e. flame retardants or precursors for magnesium oxide (Hanna et al, 2019; Henrist et al, 2003; Wang et al, 2011). Hydrated inorganic compounds, i.e. Mg(OH)₂ and Al(OH)₃ are commonly used flame retardant materials as

they produce water vapour at low temperatures. Furthermore, their oxides (i.e. MgO and Al₂O₃) can act as smoke suppressants by absorbing the evolved CO, CO₂, SO₂ and nitrogen gases at higher temperatures (Hanna et al, 2019). The combination of a favourable morphology, i.e. nanoplatelets, and water release contributes to Mg(OH)₂ being a suitable inorganic filler for fire resistance applications as it also enhances the mechanical properties of the polymer matrix (Hanna et al, 2019; Henrist et al, 2003).

The expected pH ranges reported for the precipitation of selected metal hydroxides from aqueous leachates are presented in Table 2.3.

Table 2.3: Expected pH ranges for the precipitation of metal hydroxides from aqueous leachates.

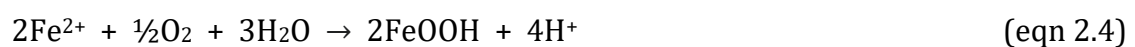
Metal hydroxide	pH range for precipitation	Reference
Fe(OH) ₃	> 4	Romão et al, 2015; Scholtz and Kahler, 2015
FeOOH (Goethite)	~ 3	Georgiev et al, 2020; Scholtz and Kahler, 2015
Al(OH) ₃	> 5.5 – 6.0	Sierra et al, 2017
Fe(OH) ₂	8 – 9	Fagerlund, et al, 2012; Nduagu et al, 2013; Romão et al, 2016; Sierra et al, 2017
Mg(OH) ₂	> 10	Nduagu et al, 2012a; Sierra et al, 2017

In most studies, the Fe-component of the leachate, together with other metals e.g. Al or Cr, was considered to be an impurity (Sierra et al, 2017), which is precipitated off by increasing the pH to approximately 8.5. The precipitate formed at the lower pH values tends to be amorphous (Sujana and Anand, 2010; ul Haq and Haider, 2010), but can be calcined to produce a crystalline product or may be utilised for other purposes. A

combination of iron and aluminium mixed hydroxides was used as a sorbent for removing fluoride from aqueous solutions by Sujana and Anand (2010). The iron hydroxides and oxides can be used in a wide range of applications, i.e. catalysis, pigments or magnetic materials, if separated successfully (ul Haq and Haider, 2010). The Fe component is predicted to precipitate at pH values ranging between 3 to 9, depending on the form of the precipitate, i.e. FeOOH (goethite) from pH $\sim$ 3 (Georgiev et al, 2020; Scholz and Kahler, 2015), Fe(OH)₃ above a pH of 4 (Romão et al, 2015; Scholtz and Kahler, 2015) and Fe(OH)₂ between a pH of 8 – 9, (Fagerlund, et al. 2012; Nduagu et al, 2013; Romão et al, 2016; Sierra et al, 2017). Mg(OH)₂ is expected to precipitate above a pH of 10 (Nduagu et al, 2012a; Sierra et al, 2017). The small difference in pH makes the separation of the Fe and Mg difficult, possibly due to co-precipitation which leads to the formation of mixed crystals, which can form when the radii of the metal ions are relatively similar, Mg²⁺ $\sim$ 79 pm and Fe²⁺ $\sim$ 77 pm (Scholz and Kahler, 2015). The study by Lavikko and Eklund (2016b) measured the concentration of Mg in the leachate by ICP-OES, at the start of the precipitation process, at a pH of 8.5 after filtration of the Fe fraction and at a pH of 11.5. This study illustrated that some Mg is lost after precipitation at 8.5, i.e. has been precipitated together with the Fe fraction, and some Mg is still present after pH of 11.5.

Figure 2.2 (courtesy of Sierra et al, 2017) illustrates the separation of various metals as a function of pH value, by precipitation using NaOH from leachate produced by the dissolution of serpentine residues in H₂SO₄. The presence of Fe (red curve) is apparent up to a pH of approximately 8.5.

The oxidation state of Fe present in leachates is not certain. To overcome this uncertainty, Fe²⁺ can be oxidised to Fe³⁺ by adding a few drops of peroxide. The resulting Fe can then be precipitated at a pH of approximately 4.0, allowing for better separation of the metals (Romão et al, 2015). Goethite (FeOOH) may be formed from both Fe²⁺ and Fe³⁺ ions in aqueous solutions, from a pH $\sim$ 3, according to the following equations (Georgiev et al, 2020):



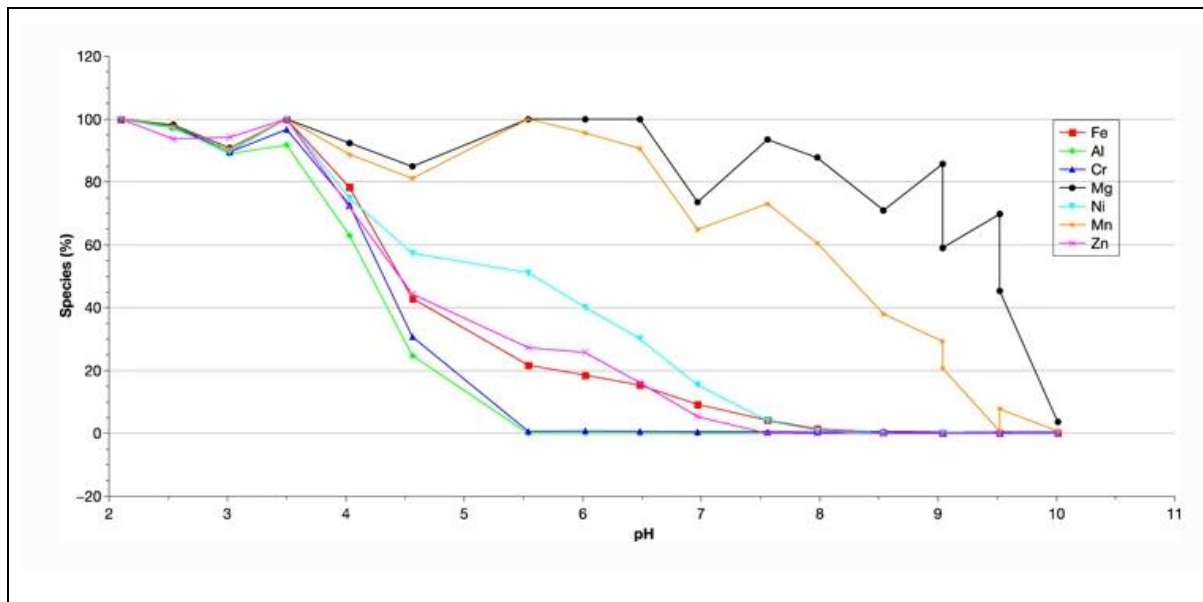


Figure 2.2: Element separation as a function of pH (Courtesy of Sierra et al, 2017).

2.5.2 Production of Layered Double Hydroxides (LDHs)

Naturally occurring mineral hydrotalcites are anionic clays made up of brucite-like ($\text{Mg}(\text{OH})_2$) layers, where some trivalent cations replace the divalent cations, resulting in positively charged sheets. This positive charge is balanced by the inclusion of anions in the hydrated interlayer. They have the formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ (Evans and Duan, 2005; Labuschagne et al, 2015; Salomão et al, 2011). The ion-exchange abilities of hydrotalcites can be attributed to weak chemical interactions between the positive sheet structure and the interlayer anions (Mališová et al, 2018).

Layered double hydroxides (LDHs) are hydrotalcite-like materials with the general formula $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot y\text{H}_2\text{O}$, the structure and properties of which were investigated as early as 1968 (Mishra et al, 2018, Olf et al, 2009; Theiss et al, 2016). The term in the first bracket, $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+}$, describes the composition of the layered double hydroxide layers consisting of divalent (M^{II}) and trivalent (M^{III}) metal cations. The M^{II} and M^{III} cations are connected by OH-units co-ordinated at octahedral positions, allowing the formation of brucite like layers, where some divalent ions have been replaced by trivalent ions (Evans and Duan, 2006; Theiss et al, 2016). The symbol x represents the molar fraction of M^{III} to total metal cations (sum of M^{II} and M^{III}) in the

layered structure, and is in the range $0.1 \leq x \leq 0.5$ (Benhiti et al, 2020; Olfs et al, 2009; Theiss et al, 2016). The net positive charge is balanced by an equal negative charge from the interlayer anions. The term $[(A^{n-})_{x/n} \cdot yH_2O]$ represents the composition of the anionic interlayer, with A being the interlayer anion with charge n^- . The theoretical structure of a layered double hydroxide is illustrated in Fig 2.3.

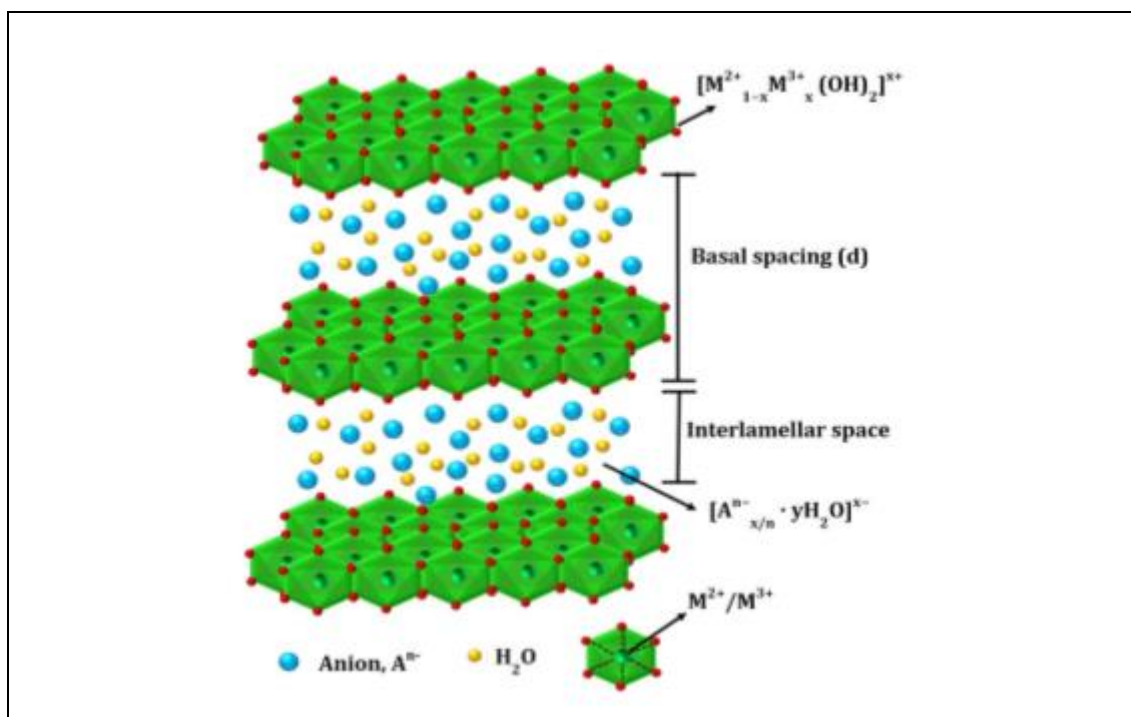


Figure 2.3: Structure of a layered double hydroxide (Courtesy of Mishra et al, 2018).

LDHs are most commonly formed by the co-precipitation of divalent (Mg^{2+} , Fe^{2+}) and trivalent (Al^{3+} , Fe^{3+}) metal cations at moderate to high pH. LDHs are a group of clay minerals that have shown potential for a number of applications. They are well known for their capacity to remove both cationic or/and anionic contaminants via co-precipitation or ion exchange, and can be used for water purification treatment (Evans and Duan, 2006; Douglas et al, 2009). They could also be used for flame retardants or the formation of nano-composite materials (Theiss et al, 2016).

The identities of the divalent and trivalent cations, as well as the interlayer anion and water content, may be varied considerably, allowing for a large range of isostructural

materials (Evans and Duan, 2006). The range of metal cations that can be incorporated into the positively charged sheets is determined by their size, e.g. Fe^{2+} can be substituted for Mg^{2+} or Fe^{3+} for Al^{3+} (Mališová et al, 2018). The ratio of Mg:Al may also be varied and may range from 1:1 to 1:5 (Olfs et al, 2009; Labuschagné et al, 2018). The absence of crosslinking between cation layers is an important feature as the interlayer spacing is then able to contract or expand, allowing a wide range of interlayer anions to be accommodated (Theiss et al, 2016). The interlayer anions could possibly be carbonate (CO_3^{2-}), sulphate (SO_4^{2-}) or nitrate (NO_3^-), amongst others. One of the advantages of LDH materials is the inordinate number of possible compositions and metal-anion combinations that can be synthesised. This allows for the development of numerous LDHs with a variety of properties (Evans and Duan, 2005; Salomão et al, 2011), which leads to the possibility of many potential applications, i.e. flame retardants, additives in polymers, environmental remediation or precursors to magnetic materials (Evans and Duan, 2005; Labuschagné et al, 2015). The low cost and environmentally friendly nature of these materials are an added advantage. The development of LDHs for ion-exchange purposes favours the use of nitrate, hydroxide or chloride as the carbonate anion does not exchange readily due to strong electrostatic interactions (Labuschagné et al, 2015). The structure and surface properties of hydrotalcites and the resulting mixed oxides strongly depend on chemical composition and synthesis procedures utilised (Cavani et al, 1991).

The thermal decomposition of LDHs via calcination is a method for preparing homogeneous mixed metal oxides (MMOs). The use of LDHs and their MMOs as solid catalysts is a promising alternative for the decontamination of soils, groundwater, sediments, and industrial process and effluents (Balsamo et al, 2012).

LDHs may be produced using a co-precipitation method with sodium carbonate (Na_2CO_3), bicarbonate (NaHCO_3), hydroxide (NaOH) or ammonia solution (Douglas et al, 2009; Olfs et al, 2009; Salomão et al, 2011; Theiss et al, 2016), or via a hydrothermal reaction with urea ($\text{CO}(\text{NH}_2)_2$) (Berber et al, 2013; Chaillot et al, 2020). The co-precipitation method is the most widely reported. However, a disadvantage of co-precipitation is that it is difficult to maintain the pH throughout the slurry, regardless of the stirring speed. This leads to product with a large distribution of sizes (Balsamo et al, 2012; Ji et al, 2017; Zeng et al, 2009). It may also be difficult to form LDHs with high crystallinity, therefore thermal

treatment i.e. ageing of the solution is often performed after co-precipitation to improve the crystallinity of the sample (Mishra et al, 2018; Zeng et al, 2009). Advantages of the co-precipitation method is the ability to prepare LDHs with a wide variety of interlayer anions (Theiss et al, 2016) and the production of a good yield (Mishra et al, 2018).

In the case of the urea hydrolysis method, the final products deliver better crystallinity and better control of the particle size because the hydrolysis of urea proceeds very slowly (Mishra et al, 2018; Theiss et al, 2016), but it does have the carbonate anion as the interlayer ion which is difficult to remove for anion exchange (Labuschagné et al, 2015; Thiess et al, 2016).

Control of the structure of LDHs during synthesis is possible by controlling the layer cations and interlayer anions by the selection of the method and starting materials. Table 2.4 gives a summary of the starting materials and methods in a selection of literature articles. In the majority of cases, a soluble salt of the desired M^{II} and M^{III} cations is used in the form of hydrated chloride or nitrate salts.

Although most research into the production of LDHs have used pure analytical chemicals, a study by Douglas et al (2010) precipitated LDHs from waste mine water which was rich in metals, specifically Mg^{2+} , by using sodium aluminate ($NaAl(OH)_4$) together with NaOH or $Ca(OH)_2$. The aluminate was used to increase the Al^{3+} -ion concentration as the Mg:Al ratio in the waste water was typically $\sim 8.7:1$. The waste water was rich in sulphate (SO_4^{2-}) and bicarbonate (HCO_3^-) due to the extraction processes used. Precipitates formed showed some LDH formation, although generally with a lower Mg:Al ratio than was expected and not highly crystalline, together with large amounts of thenardite (Na_2SO_4) when using NaOH and gypsum ($CaSO_4 \cdot 2H_2O$) and dolomite $CaMg(CO_3)_2$ when using $Ca(OH)_2$. This indicates that synthesis of LDHs starting with a waste material containing a range of cations and anions is possible but more complex than using pure chemicals.

Table 2.4: Summary of starting materials and methods used for LDH synthesis from a selection of studies.

Starting materials	Method	M ^{II} :M ^{III} ratio	Reference
Mg(OH) ₂ , Al(OH) ₃ , Mg ₅ (CO ₃) ₄ (OH) ₂ ·4H ₂ O, Na ₂ CO ₃ , NaOH	Hydrothermal co- precipitation	3:1	Misra and Perrotta, 1991
M ^{II} (NO ₃) ₂ ·6H ₂ O M ^{II} = Mg, Zn, Ni; Al(NO ₃) ₃ ·9H ₂ O	Urea	2:1	Yang et al, 2004
Mg(NO ₃) ₂ ·6H ₂ O, KOH, Al(NO ₃) ₃ ·9H ₂ O, NH ₄ OH	Co-precipitation	2:1 and 5:1	Olfs et al, 2009
Mg(NO ₃) ₂ ·6H ₂ O, Al(NO ₃) ₃ ·9H ₂ O	Urea	4:1	Zeng et al, 2009
Mg(NO ₃) ₂ ·6H ₂ O, Al(NO ₃) ₃ ·9H ₂ O	Co-precipitation and urea	2:1	Berber et al, 2012
MgO, Al(OH) ₃ , NaHCO ₃	Green co- precipitation	2:1	Labuschagné et al, 2018
Mg(NO ₃) ₂ ·6H ₂ O, Na ₂ CO ₃ , Al(NO ₃) ₃ ·9H ₂ O, NaHCO ₃ ,	Co-precipitation	3:1 and 2:1	Wiyantoko et al, 2015
Mg(NO ₃) ₂ ·6H ₂ O, KOH, Al(NO ₃) ₃ ·9H ₂ O, NH ₄ OH	Co-precipitation	3:1	Lin et al, 2017
Zn(NO ₃) ₂ ·6H ₂ O, Al(NO ₃) ₃ ·9H ₂ O	Co-precipitation	3:1	Mahjoubi et al, 2017
MgCl ₂ ·6H ₂ O, AlCl ₃ ·9H ₂ O (+Fe, Cu, Co, Ni, Zn)	Co-precipitation	2:1	Gevers et al, 2019
Mg(NO ₃) ₂ ·6H ₂ O, Al(NO ₃) ₃ ·9H ₂ O (+Fe, Co, Ni, Cu, Zn)	Urea	2:1	Naseem et al, 2019
MgCl ₂ ·6H ₂ O, AlCl ₃ ·9H ₂ O, Na ₂ CO ₃ , NaOH	Co-precipitation and urea	3:1	Benhiti et al, 2020

2.5.3 Purification and reactivity of Talc

Talc is a naturally-occurring hydrated magnesium-rich sheet phyllosilicate with the ideal chemical formula $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ (Martin et al, 2019). Although it is the least complex phyllosilicate, natural talc varies greatly in colour, grain size, crystallinity, lamellar-character, softness, and chemical composition, depending on its geological origin (Soriano et al, 2002). Talc deposits can derive from a variety of parent rocks, which include magnesium carbonates, serpentines, aluminosilicate rocks, or magnesium sedimentary deposits (Zussman et al., 2013). As a result, talc ore is found to co-exist with a number of accessory (gangue) minerals, including chlorite, lizardite and carbonates (magnesite, calcite, dolomite). These gangues represent mineral hydrophilic impurities (Castillo et al, 2014), which must be removed before talc can meet the requirements of specific industrial applications such as paints, plastics, medicine or cosmetics.

Lavikko and Eklund (2016b) studied the extraction of Mg from talc with the ÅA route method (i.e. ammonium sulphate process) from two talc samples, but did not ascertain whether the structure and chemical properties of the talc remain unaltered. These authors reported the mineralogical (XRD) and elemental composition (XRF) of their talc samples, % MgO by SEM-EDX before and after roasting and leaching, and ICP-OES of the leachate solution to determine concentration of Mg before, during and after fractional precipitation. They concluded that talc was unreactive as there was almost no difference in the % MgO by SEM-EDX before and after roasting and leaching. Bayer et al (1982) reported that talc showed practically no reaction with $(\text{NH}_4)_2\text{SO}_4$, although reaction conditions are not given. Based on these results, the conclusion was that talc is not reactive. However, Sanchez et al (1996) reported up to 80% extraction of magnesium from talc, after the talc samples were ground for 3 hours and then subjected to acid leaching. This is explained by the talc being transformed from its crystalline state into a disordered state by dry grinding in a planetary ball mill, within about 30 minutes. The structural modification was emphasised by the extended grinding process which altered the environmental structure surrounding the magnesium within the talc crystal. This disordering of the structure allows for relatively easy magnesium extraction by the acid solutions.

The purification of low-grade talc ores represents an area of great interest, owing to the limitations, economics and environmental impacts of current technologies, and the wide array of possible accessory minerals associated with talc and their distinct intrinsic reactivities. Examples of such technologies include flotation, wet attrition, magnetic separation and acid leaching. Table 2.5 summarises the advantages and disadvantages of these purification technologies.

Table 2.5 Comparison of advantages and disadvantages of talc purification methods.

Purification Method	Advantages	Disadvantages
Flotation (Ahmed et al, 2007)	• No chemical changes occur • Carbonate minerals remain intact	• Accessory chemicals required • High cost • Specialised equipment required
Wet attrition (Katircioglu-Bayel, 2020.)	• Likely to produce finer ground products	• Multistep processes, often followed by acid leaching
Magnetic Separation (Piga and Marruzzo, 1992; Hojamberdiev et al, 2010)	• Reduces the iron content	
Chlorination (Orosco et al, 2011)	• Removes Fe_2O_3 efficiently • Improves colour	• Corrosive atmosphere • Specialised equipment required
Acid Leaching (Ahmed et al, 2007; Orosco et al, 2011; Barani and Aghazadeh, 2018)	• Removes carbonate impurities efficiently, and Fe_2O_3 to some degree • No specialised equipment required	• Carbonate minerals are lost

2.6 Conclusions

The literature reviewed in this chapter indicates that the environmental impact of mine residues can be substantially reduced through the recovery of valuable elements and their conversion into value-added products. However, this requires an in-depth understanding of the chemical and mineral compositions of the mine residue of interest before potential products and their synthesis procedures can be identified. Diamond mine residues in South African originate from Kimberlite pipes and are rich in magnesium, which is globally considered a critical element. The mineralogy of the diamond mine tailings depends on the original kimberlite composition, but is predominantly a complex mixture of phyllosilicate minerals. It may also have a significant talc content.

The extraction of valuable elements from mined minerals and mine residues, through thermochemical treatment and/or leaching, has been well described in the literature. The success of the extraction technology applied depends on the physical and chemical properties of the parent material. Various authors have described the extraction of Mg from serpentinite rock via thermochemical treatment with $(\text{NH}_4)_2\text{SO}_4$ as a viable technology. However, the conditions used for thermochemical treatment varied greatly depending on the starting material and metals of interest.

The separation of elements and selective precipitation of $\text{Mg}(\text{OH})_2$ from leachates containing a mixture of various metals have been described in literature. Separation of Mg and Fe has been identified as a potential complication. Although the production of LDHs from pure chemicals is widely discussed in the literature, limited studies are available on their production from sulphate solutions and from leachates containing a mixture of metals.

Chapter 3: Experimental and analytical methods

3.1 Introduction

The purpose of this chapter is to provide background information on the starting materials, chemical reagents and experimental methods used to extract the minerals from the raw materials and generate the products. A process flow diagram for the multistage extraction of minerals from the mine tailings and slimes is given in Fig 3.1. The instrumental characterisation techniques used in the study are also discussed.

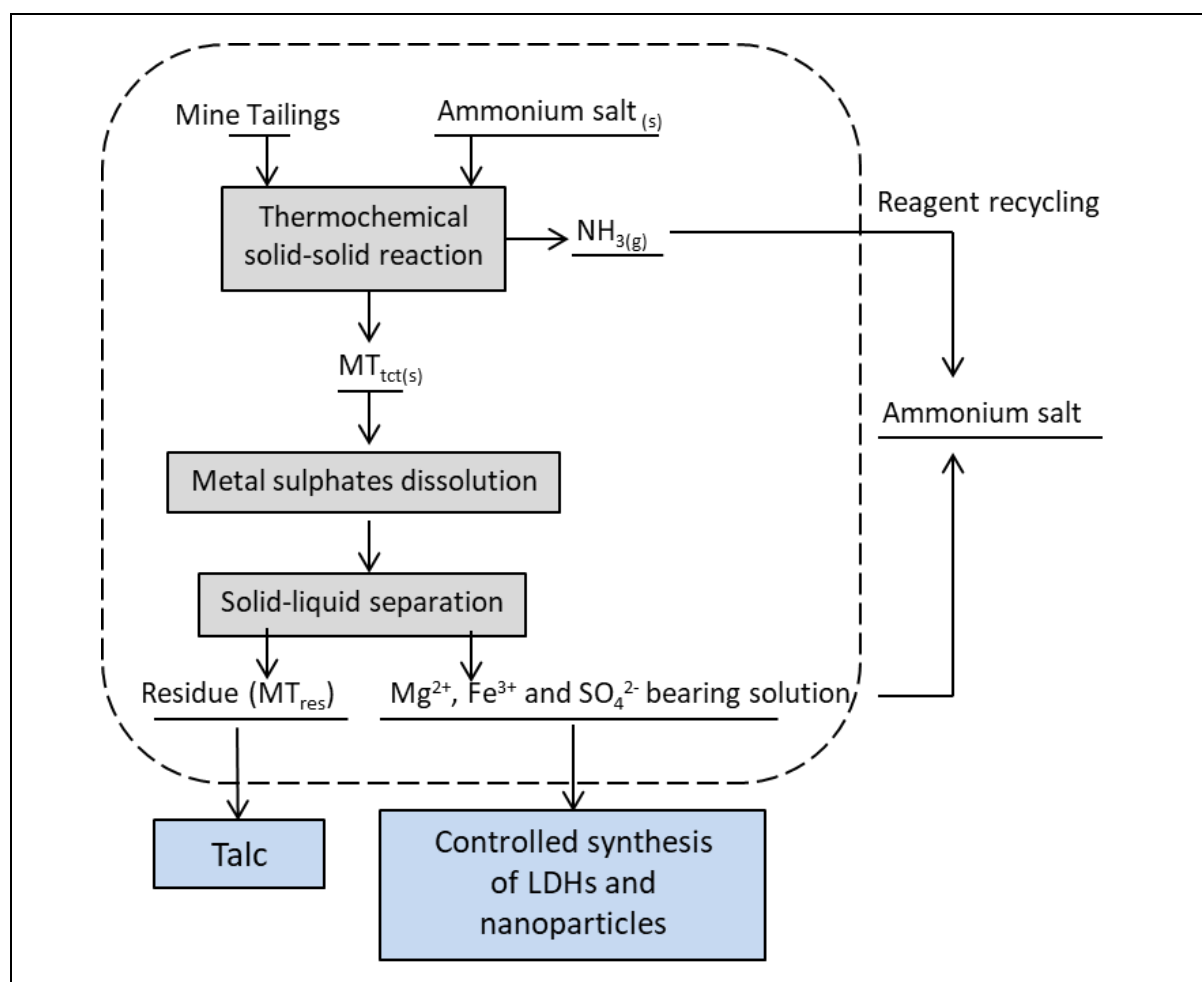


Figure 3.1: Process flow diagram for the multi-stage extraction of minerals from the raw materials and synthesis of products

3.2 Materials tested and chemical reagents

Representative samples of the mine slimes (CS) and mine tailings (CT) were obtained from a diamond mine in South Africa.

A list of chemical reagents used in the study, detailing the supplier and percentage purity of the chemicals is represented in Table 3.1.

Table 3.1: List of chemical reagents used in this study

Chemical	Grade	Supplier	Purity
Aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	AR	Labchem	51.59% as $\text{Al}_2(\text{SO}_4)_3$
Ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$	AR	Merck SA	99.5% m/m
Ammonia solution, NH_4OH		Minema	25% m/m
Deionised water	Analytical grade	Merck SA	Electrical conductivity < $1\mu\text{S} \cdot \text{cm}^{-1}$
Hydrochloric acid, HCl	AR	Merck SA	37% m/m
Hydrogen peroxide, H_2O_2		Dischem	12% m/m
Iron(III) sulphate, $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$	AR	Labchem	>73% as $\text{Fe}_2(\text{SO}_4)_3$
Magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	AR	Labchem	99.0%
Nitric acid, HNO_3	AR	Merck SA	65% m/m
Silicon, Si	AR	Aldrich	99%
Sodium carbonate anhydrous, Na_2CO_3	AR	Saarchem	99.5%
Sulphuric acid, H_2SO_4	AR	Merck SA	98% m/m
Urea, $(\text{NH}_2)_2\text{CO}$	AR	Associated Chemical Enterprises	96%

3.3 Thermal treatment of raw materials

CT and CS were roasted in a muffle furnace at a variety of temperatures, between 420°C and 550°C. This was to investigate the effect of thermal treatment on the composition and mineralogy of the raw materials. These samples were characterised using XRF, XRD, TGA and FTIR, as well as subjected to leaching experiments.

3.4 Thermochemical treatment with ammonium sulphate

CS or CT was mixed thoroughly with ammonium sulphate (AS), $(\text{NH}_4)_2\text{SO}_4$, at various m/m ratios (2:3, 2:4, 3:4, 2:5 and 2:6), using a stainless-steel spatula. The range of mass ratios were used as the mineralogy of the tailings are relatively complex, and Mohamed et al (2016) found a 2:6 ratio was optimum for PGM tailings. Nduagu et al (2012b) also reported using different mass ratios and temperatures due to elemental composition, specifically Mg:Fe ratio in Mg-silicate rock, affecting the degree to which Mg and Fe may be extracted. The particle size of each component is distinctly different (very fine tailings and granular AS), which posed a challenge to produce a homogenous mixture, but the process of mixing was kept constant for each trial, which ensured reliable reproducibility.

The mixtures were placed in fused quartz crucibles and roasted in a muffle furnace set at varying temperatures (400, 420, 450, 480, 500, 520 and 550°C). Initially, the roast was for 45 min, (Nduagu (2012a) used 30 min), as described by Mohamed et al (2016), but was increased to 60 min, as this produced a more workable product (softer and more easily removed from the crucibles). A few trials of 2 h were also conducted at the lower temperatures, to investigate whether that would improve the handling of the product, i.e. produce a softer product.

The initial trials used 2 g of CS or CT for which a 60 min roast time was sufficient, however when scaling up quantities (8 g CS) for the purpose of making products, a longer roasting time was required to ensure the reaction went to completion. Roast ratios of 2:3, 2:4 and 2:6 CS:AS were roasted at 450°C for 2 h, 3h, 4h and 7h.

The samples obtained following roasting were placed in a desiccator and allowed to cool to room temperature, before being reweighed to determine mass loss. The samples were

then ground using a mortar and pestle, before being characterised by TGA, XRD, XRF, sulphur content and FESEM.

3.5 Extraction of soluble minerals

Dissolution was carried out by leaching under a variety of different conditions. The optimisation was initiated using the 2:3 m/m roasting ratio, as this was the experimental procedure optimised by Nduagu et al (2012a) and Romão et al (2014). A picture of the experimental setup is shown in Fig 3.2a.

At the outset, all samples were leached in deionised water, at room temperature, using a ratio of 1:100, i.e. approximately 3.00 ± 0.01 g of roast residue was dispersed in 300.0 mL water. All control and treatment samples were stirred continuously, on a magnetic stirrer (Heidolph MR Hei-Tec), at a constant speed of 750 rpm. The leaching process was followed using a conductivity/ temperature/pH probe (Hanna HI 2829 multi-parameter logger), and leaching was allowed to continue until there was no further change in the conductivity reading. Initially, leaching was run overnight, in a beaker covered by parafilm, to ensure that the process was complete. As the conductivity stabilised within 3 h, the time was reduced to 3 h. Further leaching experiments were conducted, without the conductivity probe, in covered beakers.

To improve the extraction of metal sulphates, leaching was conducted in covered beakers, in deionised water (i.e. uncontrolled pH condition) and under controlled pH conditions (H_2SO_4 , pH 1 and 0.2) at several temperatures (30, 40, 50, 60, 75, 95°C).

The filtrates from the 1:100 m/v ratio were very dilute for the manufacture of products, and needed to be concentrated before products could be made. A range of leaching ratios (1:5, 1:12.5, 1:25, 1:50, 1:75, 1:100 m/v) were therefore investigated, starting at 1:5 m/v (similar to the volume optimised by Romão et al, 2015) to optimise the leaching volume.

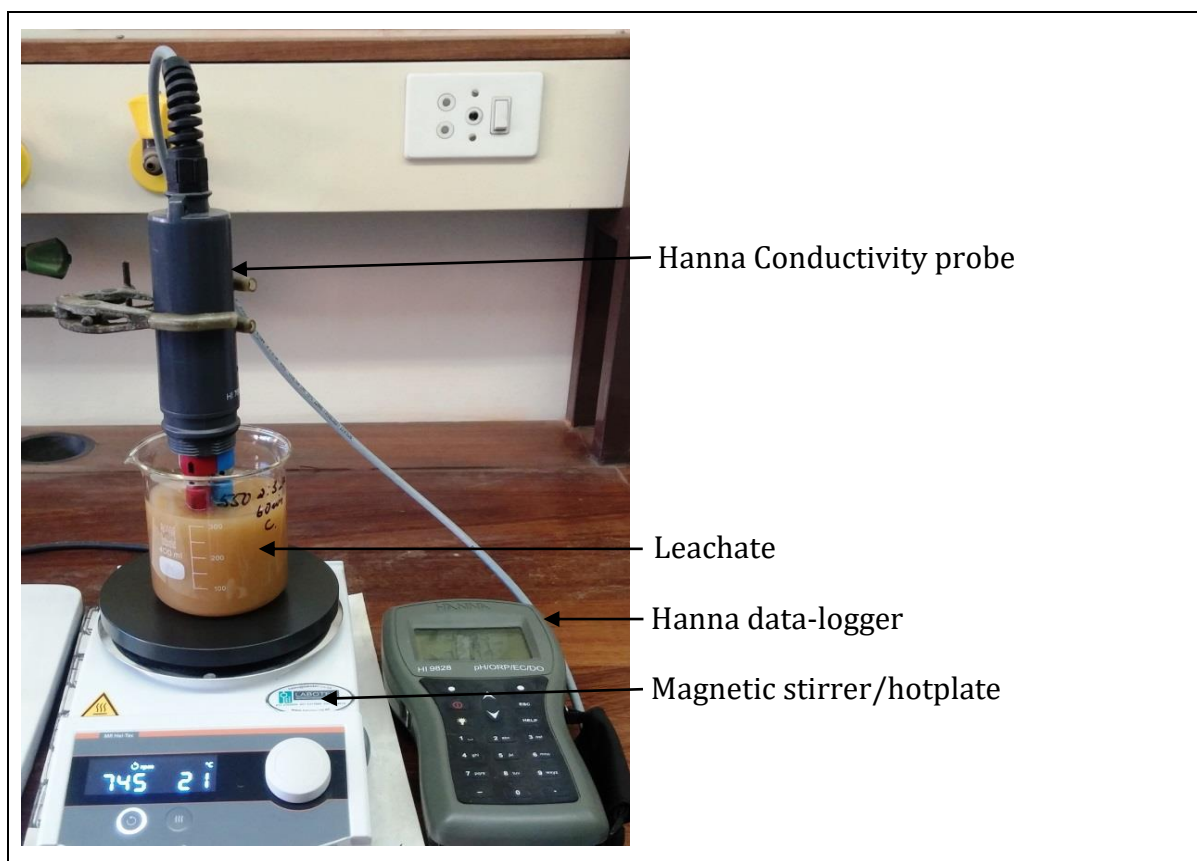


Figure 3.2: Apparatus for following the conductivity during leaching

At the completion of the leaching process, samples were filtered under reduced pressure through 0.4 μm membrane filters (Whatman Nucleopore® Track-Etched polycarbonate, Whatman UK Ltd.) in closed polycarbonate filtration vessels (Sterifil, 47mm Millipore) (Fig 3.3). The filtrates were acidified with nitric acid, HNO_3 , to below pH 2 (when necessary) and were analysed by ICP-OES for all major elements at an accredited laboratory (Waterlab Pty Ltd, Pretoria). As a reference point, leaching of the untreated CS and CT as well as thermally treated CS and CT (at the roasting temperatures of 450°C and 480°C), were also conducted.

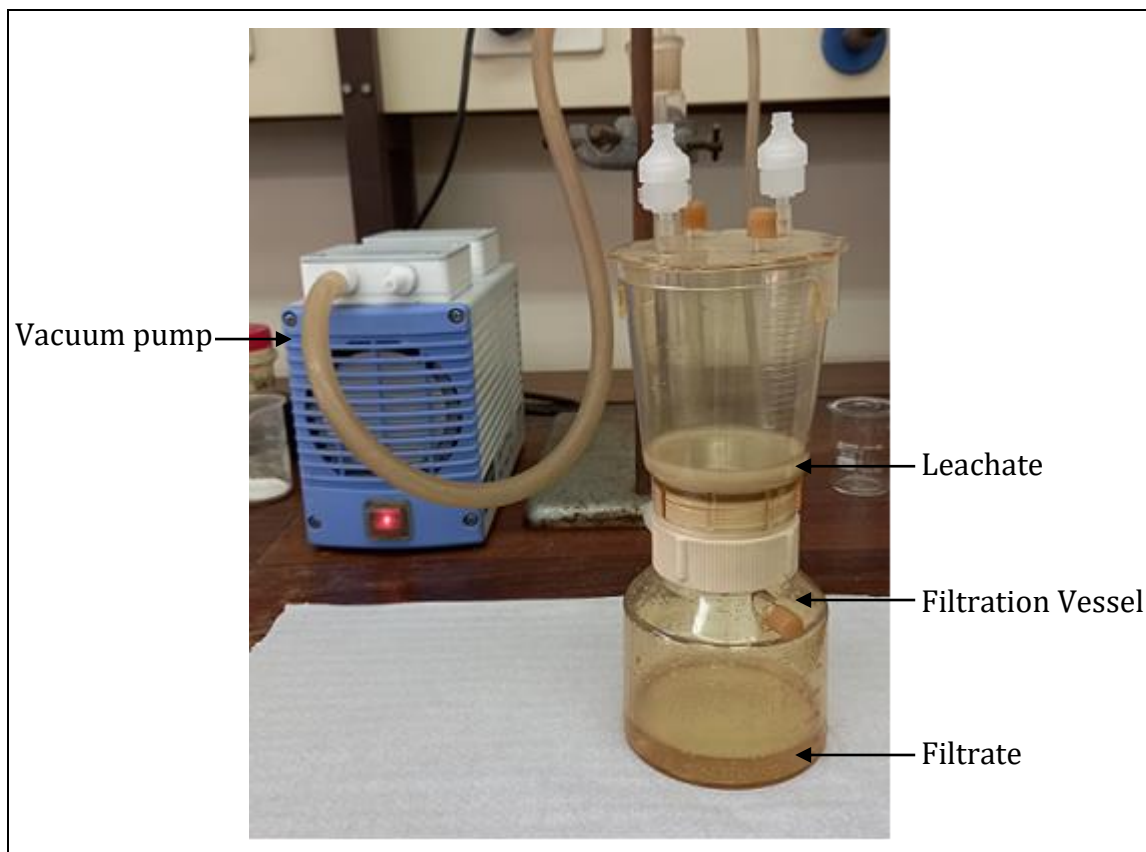


Figure 3.3: Apparatus for the filtering of the leachates

3.6 Separation of iron from magnesium via a roasting program

Pure commercial sulphate chemicals, MgSO_4 , $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Al}_2(\text{SO}_4)_3$ were used to create a solid mixture with analogue composition to that of the minerals of interest in CS, to selectively separate and extract the Mg, Al and Fe. They were initially dried in separate crucibles at 400°C in a muffle furnace for 2 h to remove the water of crystallisation. These salts are all thermally stable at 400°C (Ostroff and Sanderson, 1959; Kloprogge et al, 1992; Ventruti et al, 2020). The pure analytical chemicals were finely ground using a mortar and pestle, and combined in a similar mass ratio to that found in CS, i.e. Mg:Fe:Al at 3:2:1, as determined by XRF. The thermal behaviour and decomposition ranges of each of the individual sulphate salts, as well as the combined sample, were studied during various TGA experiments.

A roasting program was developed from the TGA data, to separate the Fe-fraction in the combined metal sulphate sample from Mg and Al. A summary of the roasting program as

well as the purpose of each roasting step, is provided in Table 8.2 (Chapter 8). The combined metal sulphate sample was roasted at 450°C or 750°C for 2 h. After roasting, the roast products were leached in deionised water at a ratio of 2 g roast product in 50.0 mL distilled water for 2 h, with stirring at 50°C.

To test whether Fe and Al can be recovered from the leach residue, the leach residue obtained from roasting the combined sample at 750°C was re-roasted with AS at 450°C in a 2:4 m/m ratio and then leached in the same way as the previous samples, 2 g roast product in 50 mL distilled water at 50°C. Leachates were analysed by ICP-OES to determine the extent of the extraction and separation.

The roasting program was then applied to CS. A summary of the roasting program applied to CS and the purpose of each roasting step, is summarised in Table 8.3 (Chapter 8). Initially, CS was reacted with AS at ratios of 2:4 m/m at 450°C for 2 h to convert the minerals in CS to soluble sulphates. Additional roasting of AS treated CS was subsequently carried out at 680°C, which was the temperature selected from the pure chemicals study, to separate the Fe-fraction from Al and Mg. Following Fe separation, additional roasting of AS treated CS was carried out at 750°C to retain only the Mg-fraction. CS was also reacted with AS at 680°C for 2 h in a 2:4 m/m ratio in an attempt to convert the Al and Mg containing minerals in CS to soluble sulphates while retaining the Fe-fraction in the leach residue. All roast products were leached at a ratio of 2 g in 50 mL distilled water at 50°C.

The leach residue obtained from roasting CS with AS at 450°C followed by an additional roasting step at 680°C was re-roasted with AS at 450°C in a 2:4 m/m ratio for 2 h and then leached in the same way as the previous samples, at a ratio of 2 g roast product in 50 mL distilled water at 50°C.

The extent of the separation and extraction was followed using TGA, ICP-OES, XRD and FTIR.

3.7 Preparation of products from filtrates

The filtrates were used to produce hydroxide precipitates and layered double hydroxides. Products generated using commercial chemicals vs the experimental filtrates were characterised using XRD, TGA, FTIR and FE-SEM.

3.7.1 Precipitation of hydroxides using NH_4OH solution

Hydroxides were produced by sequential precipitation of the minerals in the filtrate as hydroxides (Henrist et al, 2003; Nduagu et al, 2012a; Wang et al, 2011). The filtered leachate was titrated with a 25% ammonia solution (NH_4OH). A few drops of hydrogen peroxide (12% m/m) was added to the filtered leachate to oxidise any Fe^{2+} ions to Fe^{3+} (Romão et al, 2015). The ammonia solution was added, dropwise, at a rate of 3.0 mL per min (Henrist et al, 2003), with stirring at 300 rpm. The process was followed using a pH meter as $\text{Fe}(\text{OH})_3$ should precipitate between pH 4.0 – 5.0, $\text{Al}(\text{OH})_3$ above pH 5.9 and $\text{Mg}(\text{OH})_2$ above pH 10. The solid material formed at each pH interval was filtered off, washed thoroughly with deionised water and dried at 50°C for 2 h.

3.7.2 Production of layered double hydroxides (LDHs)

Two different methods were used to produce LDHs, namely co-precipitation and urea hydrolysis. Both methods were initially tested by using pure laboratory chemicals, AR grade, to ensure that the desired products were obtained.

Co-precipitation method

Two slightly different co-precipitation methods, i.e. slow, pH-controlled addition (method 1) and rapid addition (method 2) of the metal ion solution to a carbonate solution were used (Cavani et al, 1991). Method 1 started with enough of 0.20 M Na_2CO_3 added to 50 mL water to bring the pH to ~8.0. Using pure laboratory chemicals, 160 mL of a solution containing 0.15 M MgSO_4 and 0.025 M $\text{Al}_2(\text{SO}_4)_3$, i.e. a 3:1 ratio of M(II) to M(III), was added dropwise together with 180 mL of 0.20 M solution of Na_2CO_3 at a rate

to keep the pH at ~ 8 , while stirring at 300 rpm. The rate required was ~ 4.0 mL per min and the final pH 10. The filtered leachate, which contains the divalent and trivalent ions at various concentrations, was treated in the same way. Leachate (100 – 150 mL) was added dropwise together with 60 mL of the 0.2 M solution of Na_2CO_3 into 20 mL of water at pH ~ 8 , with stirring at 300 rpm. Volumes of leachate were determined from the concentrations of Mg and Al as obtained from ICP-OES analysis.

For method 2, using pure laboratory chemicals, 160 mL of a solution containing 0.15 M MgSO_4 and 0.025 M $\text{Al}_2(\text{SO}_4)_3$, i.e. a 3:1 ratio of M(II) to M(III), was added rapidly to 180 mL of 0.20 M solution of Na_2CO_3 (pH ~ 12.0), with stirring at 300 rpm, to form a thick slurry. The filtered leachate, which contains the divalent and trivalent ions at various concentrations, was treated in the same way. Leachate (100 – 150 mL) was added to 60 mL of a 0.2 M solution of Na_2CO_3 very quickly with stirring at 300 rpm. Volumes of leachate were determined from the concentrations of Mg and Al as obtained from ICP-OES analysis.

The slurry formed for both methods was aged at 80°C for 15 minutes, then filtered and washed thoroughly with distilled water adjusted to pH 9. Samples were dried at 100°C overnight (Cavani et al, 1991; Evans and Duan, 2006; Klemkaite et al, 2011; Berber et al, 2013).

Urea hydrolysis method

Using the solution prepared from pure laboratory chemicals, 2.0 g of urea was added to 50 mL of the metal ion solution containing the 3:1 ratio of M(II):M(III), which gives a urea:metals ratio of 3:1, in a Teflon-lined autoclave (Fig 3.4). Samples were heated in an oven at 120°C for 12 h, cooled to room temperature, filtered and washed with deionised water until the rinse water has a pH of 7 (Yang et al, 2004; Berber et al, 2013; Chaillot et al, 2020). Samples were then dried overnight at 80°C .

The filtered leachates were treated in the same way. The Mg^{2+} concentration in 50 mL of the filtered leachate was determined from ICP-OES data (in mmol). When dealing with leachate from the $450^\circ\text{C} + 680^\circ\text{C}$ roast (process 2), additional $\text{Al}_2(\text{SO}_4)_3$ was added to increase the concentration of Al^{3+} ions to the required 3:1 ratio of M(II):M(III). The

amount of urea required to obtain a urea:metals ratio of 3:1 was then calculated and added.



Figure 3.4: Teflon lined stainless-steel autoclaves for production of LDHs using the urea hydrolysis method.

3.8 Reactivity of talc

A talc sample was obtained from the Scotia Talc Mine, which is located near Barberton in the province of Mpumalanga, South Africa. XRD analysis revealed the presence of carbonate minerals (magnesite, calcite and dolomite). The sample (hereafter denoted Talc_{impure}) was therefore pre-treated with 10% m/m hydrochloric acid (HCl) to induce their dissolution (Castillo et al, 2011) and concentrate the talc phase. This pre-concentration step generated the talc-rich solid residue (thereafter denoted Talc_{HCl}),

which was used in all further experiments. The use of a FRITSCH analysette SPARTAN sieve shaker revealed that 83% m/m of Tal_{HCl} was $< 125 \mu\text{m}$.

Tal_{HCl} was then treated in the same way as the mine tailings (CS and CT) samples, to determine whether the extraction of magnesium was possible. This involved using the same multistep process used for the CS and CT, entailing the combination of a thermochemical solid-solid treatment step with AS, using a 2:3 m/m ratio at 450°C for 60 min (Nduagu et al, 2012; Mohamed et al, 2016), followed by aqueous dissolution and filtration. The thermochemical reaction of Tal_{HCl} with AS generated Tal_{AS} as reaction product.

The Tal_{HCl} sample (i.e. not thermochemically treated) was also leached in both deionised water or sulphuric acid, and used as controls.

3.9 Characterisation techniques

The fundamental techniques for characterisation of all solid samples and leachates are discussed in the following subsections.

3.9.1 Particle size distribution (PSD)

The particle size distribution of the bulk tailings and slimes samples was determined by laser diffraction using a Malvern Mastersizer 2000 with Hydro 2000G Dispersion unit. The stirrer was set at 650 rpm, the pump at 1650 rpm and the ultrasound at 20%. Samples were homogenised before adding to the dispersion unit. Each sample was read three times and an average taken of the PSD. Three samples each of tailings and slimes were measured, i.e. a minimum of 9 readings each. Laser diffraction expresses the PSD in terms of volume percent, and is reported in terms of the frequency curve (i.e. volume percent) as well as the undersize (i.e. cumulative volume percent).

3.9.2 X-ray fluorescence spectroscopy (XRF)

The chemical compositions of the solid samples were analysed using XRF (Thermo Fisher ARL Perform'X Sequential XRF instrument), to determine the concentration of major, minor and trace elements. Both the standard fused bead analysis as well as the pressed powder technique were used. This was to enable the comparison of the reacted roasted samples, which should have a high sulphur content, with original raw materials and leach residues, without compromising the sulphur content.

For the standard fused bead analysis, loss on ignition (LOI) was determined by roasting the sample at 1000°C for at least 3 h until a constant weight was obtained. A glass disc was prepared by fusing 1 g of roasted sample together with 6 g of $\text{Li}_2\text{B}_4\text{O}_7$ in a Pt/Au crucible at 1050°C. For trace element analyses, the sample was mixed with PVA binder and pressed in an aluminium cup at 10 tons. Analyses were executed with Quantas/Uniquant software. Blank and certified reference materials were analysed with each batch of samples.

The pressed powder samples were prepared as boric acid briquettes, and the Uniquant software was used for analysis. In both cases, the software analyses for all elements in the periodic table between Na and U, but only elements found above the detection limits were reported.

3.9.3 Qualitative and semi-quantitative X-ray diffraction (XRD) (mineralogy)

The qualitative and semi-quantitative mineralogical compositions of the solid samples were determined by XRD. The samples were prepared according to the standardized Panalytical backloading system, which provides nearly random distribution of the particles. The XRD patterns were collected from 2θ of 5° to 90° .

The samples were analyzed using a PANalytical X'Pert Pro powder diffractometer in θ - θ configuration with an X'Celerator detector and variable divergence- and fixed receiving slits with Fe filtered $\text{Co-K}\alpha$ radiation ($\lambda=1.789\text{\AA}$). The mineralogy was determined by selecting the best fitting pattern from the ICSD database to the measured diffraction

pattern, using X'Pert Highscore plus software. The relative phase amounts (mass %) were identified and estimated, where possible, using the Rietveld method (Highscore Program). Twenty percent silicon (Aldrich 99% pure) was added to the starting material samples, CS and CT, to determine the amorphous content. These samples were micronized in a McCrone micronizing mill before analysis. All other samples were analysed without the addition of silicon and micronisation.

3.9.4 Thermogravimetric Analysis (TGA)

TGA analyses were performed on a TA Instruments SDT Q600 Thermogravimetric Analyzer (TGA) & Differential Scanning Calorimeter (DSC). Approximately 18 mg of sample was placed evenly into a 90 μ L alumina pan and heated from ambient temperature to 1100°C at a heating rate of 10°C/min. Each test was conducted using a flow rate of 100 mL/min of nitrogen (N₂).

3.9.5 Fourier transform infrared spectroscopy (FTIR)

A Bruker Platinum ATR (attenuated total reflection) instrument, with a diamond crystal, was used to record FTIR spectra in the 4000 – 500 cm⁻¹ range. All spectra for the raw materials were collected with 64 scans per background and per sample, and analysed using the OPUS software. These were compared to spectra from pure laboratory chemicals as well as spectra from the literature, stored in the Ruff database (<https://rruff.info>).

3.9.6 Field Emission Scanning Electron Microscopy (FE-SEM)

A Zeiss Ultra PLUS FEG SEM instrument operating at an accelerated voltage of 1 kV was used to obtain information on the morphology and surface features of the samples. Samples were mounted on a metal substrate by means of double-sided carbon tape and subsequently sputter-coated with a thin, conductive layer of carbon, using an Emitech K550X coater (Ashford, England).

3.9.7 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Inductively coupled plasma optical emission spectroscopy was used to measure the concentration of chemical elements present in the filtered leachates produced during the extraction experiments. Filtrates were acidified below pH 2 (when necessary) and were analysed at an accredited laboratory (Waterlab Pty Ltd, Pretoria, South Africa).

3.9.8 Sulphur analysis

Sulphur content, in the form of SO_3 , was determined using a Leco Carbon/Sulphur analyser.

3.9.9 Brunauer- Emmett Teller analysis (BET)

Surface areas were determined by multipoint BET with nitrogen (N_2) adsorption using an Anton Paar Nova 600 Instrument. LDH samples were degassed at 80°C at a rate of 10°C per minute for 180 min

Chapter 4: Characterisation of Untreated Diamond Mine Slimes and Tailings

4.1 Introduction

This chapter provides a detailed characterisation of the diamond mine tailings (CT) and slimes (CS), which were used as the starting materials for the thermochemical and dissolution experiments.

Samples were characterised using a variety of complementary techniques, including PSD, TGA, XRD, XRF, FTIR and SEM-EDX.

4.2 Characterisation of untreated diamond mine tailings and slimes

4.2.1 Physical appearance

The untreated slimes (CS) and tailings (CT) are both dark grey in colour (Fig 4.1)

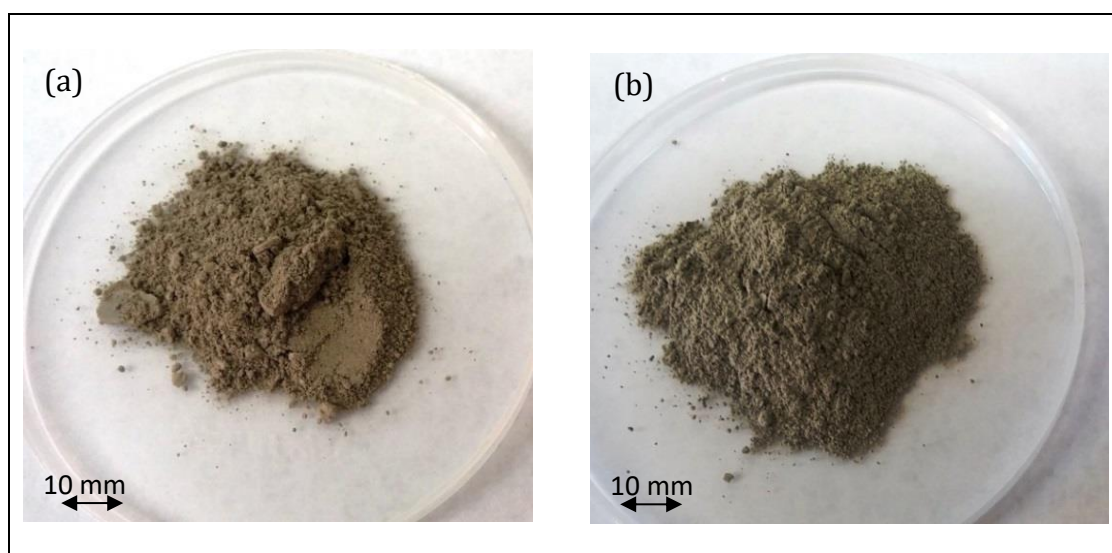


Figure 4.1: Raw materials, (a) slimes (CS) and (b) tailings (CT).

4.2.2 Particle size distribution (PSD)

Laser diffraction expresses the PSD in terms of volume percent, and results are reported in Figure 4.2 in terms of the frequency curve (i.e. volume percent) as well as the undersize (i.e. cumulative volume percent). The calculated percentile diameters are summarised in Table 4.1.

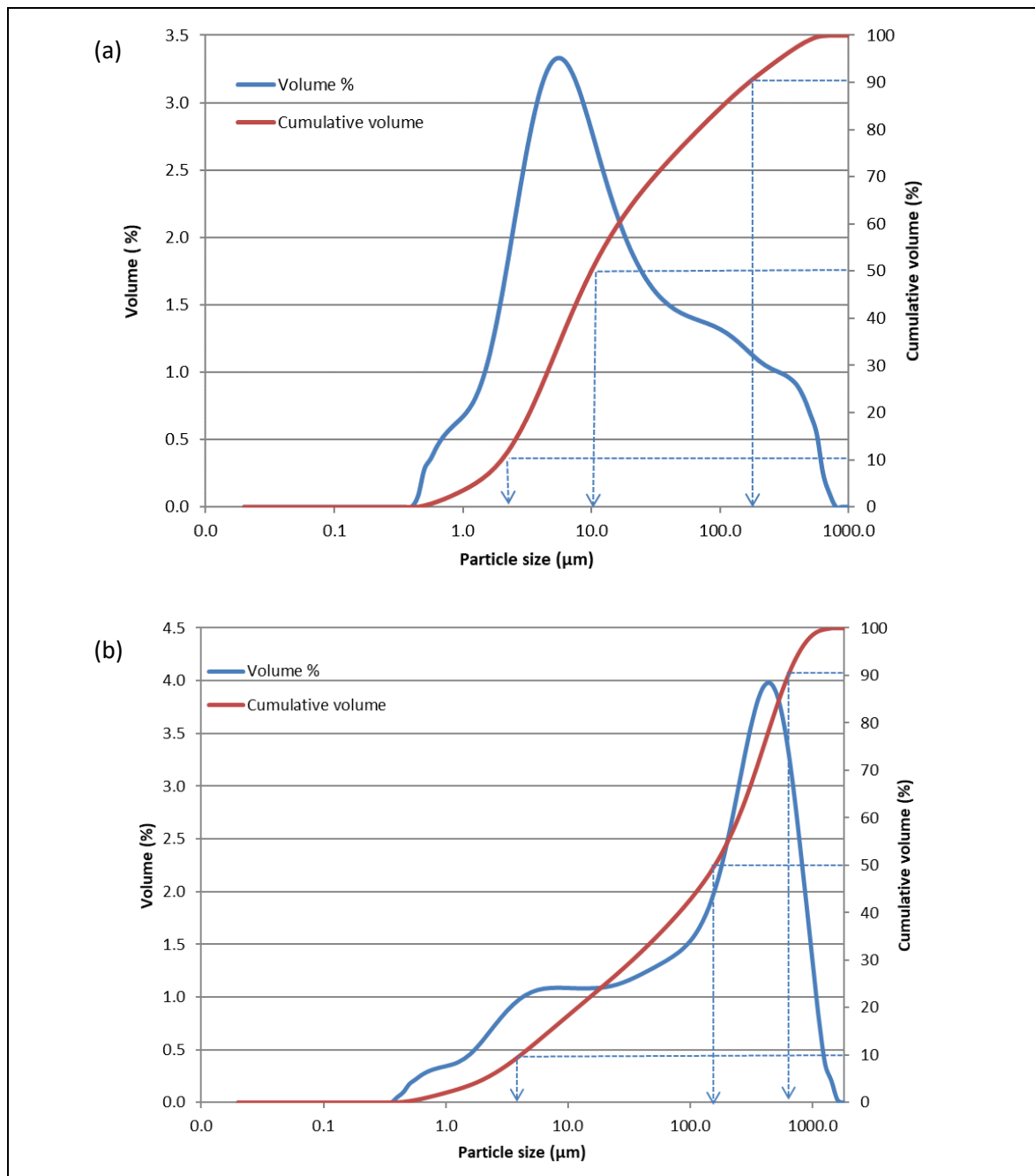


Figure 4.2: Particle size distribution of (a) the bulk diamond mine slimes sample (CS) and (b) the bulk diamond mine tailings sample (CT), expressed as volume percent (blue – primary axis) and cumulative volume percent (red – secondary axis).

Neither of the frequency curves displays a Gaussian-type shape. The slimes curve (CS, Fig. 4.2a) can be considered as having one dominant peak with a tail towards the larger particle sizes. It shows the fine-grained nature of the sample, with the majority of the particles falling between 2.5 and 25.0 μm (60%) and 90 % of the sample having a particle size of less than 161.6 μm (Table 4.1).

The tailings curve (CT, Fig 4.2b) also has one major peak, but with the frequency peak indicating the coarser grained nature of the sample, i.e. having larger particle sizes than the slimes, and with a tail towards the smaller particle sizes. The majority of the particles fall between 90 – 1000 μm (70%), with 90% of the sample having a particle size of less than 641.9 μm (Table 4.1).

The calculated percentile diameters of the CS sample are substantially smaller than that of the CT sample, with the median diameter of CS being 9.6 μm versus 156.9 μm for CT.

Table 4.1: Particle size distribution of the tailings and slimes, expressed as volume percent (%v/v). The calculated percentile diameters $D(v,0.1)$, $D(v,0.5)$ and $D(v,0.9)$ are the size of particles for which 10%, 50% and 90% of the sample is below the specified size ($n=3$).

Sample	Calculated diameters (μm)					
	$D(v,0.1)$	Std dev $D(v,0.1)$	$D(v,0.5)$	Std dev $D(v,0.5)$	$D(v,0.9)$	Std dev $D(v,0.9)$
CS	2.0	0.01	9.6	0.5	161.6	7.8
CT	4.1	0.03	156.9	1.4	641.9	20.1

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

In order to ensure the optimum extraction of all possible minerals, a detailed knowledge of the mineralogical composition of the raw materials is required. The qualitative and semi-quantitative mineralogy of the CS and CT were determined in triplicate, as the material is highly variable due to having a complex mineralogical composition. The XRD patterns for each of the raw materials (Fig 4.3) indicate the presence of talc (T), smectite (S), lizardite (L), kaolinite (K), chlorite (C) and phlogopite (P). At the lower 2θ values, the

high degree of disorder and small particle size (specifically CS), responsible for broad interference maxima, is the reason for the typical feature of clay minerals having poorly defined XRD diagrams (Fig 4.3) (Mervine et al, 2018; Zhou et al, 2018). Samples were also analysed with the inclusion of 20% silicon (Si, 99% pure) for the determination of amorphous content. These samples were micronized in a McCrone micronizing mill before analysis. The Si refined to ~20% for both CS and CT which means that no amorphous material is present in the samples.

The average of the relative phase amounts is reported in Table 4.2. The mineralogy of both samples was dominated by phyllosilicate clay minerals (81.1% and 65.1% for CS and CT respectively). Smectite, (most probably saponite or montmorillonite) and talc are the predominant phyllosilicate clay minerals and occur in almost equal quantities in CS (33.0% and 30.1% respectively), and CT (22.7% and 25.2% respectively). When taking the amount of magnesium present in the slimes and tailings into account, and the relative contributions from the different magnesium containing phases, the smectite fraction must also contribute to the magnesium and, therefore, could be either saponite or montmorillonite, which both contain Mg. CS and CT also contain a fair amount of phlogopite (8.2% and 8.6% respectively). Chlorite, kaolinite, microcline and lizardite are present in quantities less than 5.1%.

Additionally, both samples contain ferrian diopside (6.0% and 11.6%), calcite (4.0% for both) and quartz (3.7% and 3.1%). Plagioclase and the amphibole minerals (actinolite and hornblende) have a noteworthy presence in CT (7.7% and 5.5%) but occur only as minor amounts in CS (1.9% and 2.0%).

With the exception of the kaolinite, all of the phyllosilicate phases, as well as ferrian diopside, contain magnesium, which is considered to be a critical mineral, i.e. metals or non-metals that are considered vital for the world's major industrial economies and for which the supply may be disrupted, due to geological scarcity, geopolitical issues or trade policies. Magnesium, despite being abundant in the upper continental crust, is identified as a critical element due to production being concentrated in China (93%) (European Commission, 2020). This makes the beneficiation of CS and CT, to produce magnesium, a worthwhile initiative.

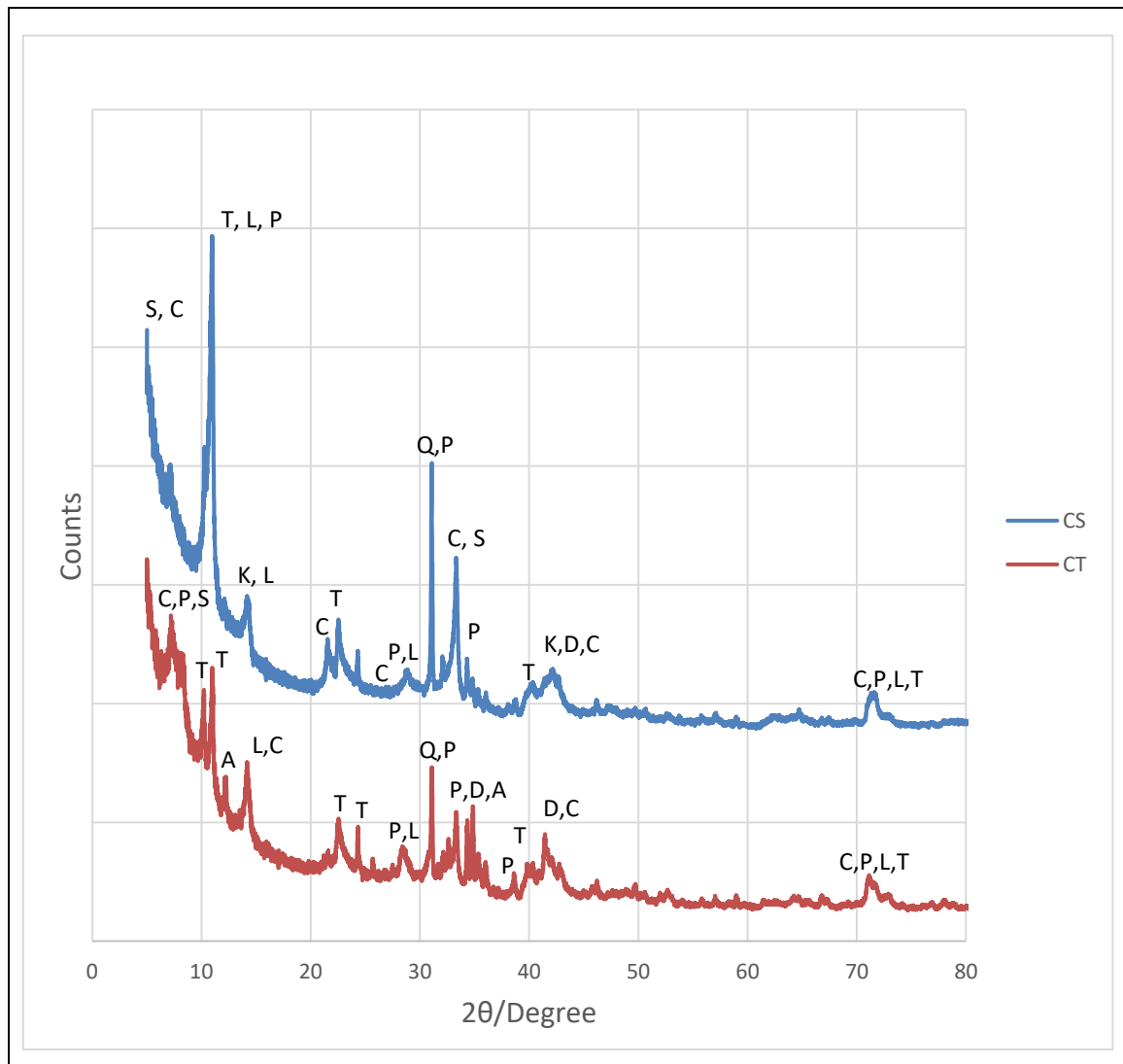


Figure 4.3: XRD patterns comparing the mineralogy of slimes (CS, blue) and tailings (CT, red). T: talc, S: smectite, L: lizardite, K: kaolinite, C: chlorite, P: phlogopite, A: actinolite, D: diopside, Q: quartz.

Table 4.2: Semi-quantitative mineralogy for slimes (CS) and tailings (CT) samples determined by XRD with Rietveld refinement.

Mineral Group	Mineral Name	Approximate Chemical Formula	Abundance (%m/m)	
			CS	CT
Phyllosilicate clay minerals	Smectite	$\text{Na}_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2\text{n}(\text{H}_2\text{O})$	33.0	22.7
	Talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	30.1	25.2
	Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	5.0	5.1
	Lizardite	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	1.1	-
Mica	Phlogopite	$\text{KMg}_3\text{Si}_3\text{AlO}_{10}(\text{F, OH})_2$	8.2	8.6
Chlorite	Clinochlore	$(\text{Fe,Mg,Al})_6(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8$	3.7	3.5
Pyroxene	Ferrian Diopside	$\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$	6.0	11.6
Oxides	Quartz	SiO_2	4.3	3.1
Carbonates	Calcite	CaCO_3	3.8	3.2
Feldspar	Plagioclase	$(\text{Na,Ca})(\text{Si,Al})_4\text{O}_8$	1.9	7.5
	Microcline	KAlSi_3O_8	0.9	4.0
	Actinolite	$\text{Ca}_2(\text{Mg,Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$		5.5
	Hornblende	$\text{Ca}_2(\text{Mg,Fe,Al})_5(\text{Si,Al})_8\text{O}_{22}(\text{OH})_2$	2.0	

4.2.4 Chemical composition by X-Ray Fluorescence Spectroscopy (XRF)

Major oxides and their various proportions were determined using XRF. Magnesium silicate minerals include smectite, talc, biotite, ferrian diopside, phlogopite and chlorite. Both the standard method (fused bead) and the pressed powder method were used for XRF sample preparation, as the high temperatures used for the standard method would destroy the sulphates formed after thermochemical treatment of CS and CT, and the pressed powders could then be used for comparative purposes. In both cases, the software analyses for all elements in the periodic table between Na and U, but only elements found above the detection limits were reported. Results follow in Table 4.3 and Figure 4.4.

Table 4.3: Major element composition of slimes (CS) and tailings (CT) samples as determined by XRF.

Standard method^a (%m/m)											
	SiO ₂	MgO	Fe ₂ O ₃	Al ₂ O ₃	CaO	TiO ₂	K ₂ O	Na ₂ O	P ₂ O ₅	LOI ^b	Total
CS	47.0	23.4	9.4	5.4	3.6	1.3	0.6	0.3	0.1	8.3	99.3
CT	46.0	20.6	8.6	5.0	6.9	1.4	1.7	1.0	0.2	6.8	98.2
Pressed Powders^a (%m/m)											
CS	47.5	25.1	8.8	6.0	3.9	1.7	0.6	0.4	0.2		94.1
CT	48.3	25.8	8.1	5.8	5.8	1.0	1.6	0.9	0.3		97.6

^a Other elements present in minor/trace amounts: MnO, NiO, Cr₂O₃, V₂O₅, ZnO and SrO

^b Loss on ignition

The abundance of phyllosilicate materials in both the slimes (CS) and tailings (CT) samples explains the large amount of SiO₂ (>45%), and as many of them contain magnesium, that could account for the significant amount of MgO (>20%; Table 4.3 and Fig. 4.4). Ferrian diopside, chlorite and actinolite would contribute to the Fe₂O₃ content (>8%), smectite, chlorite, phlogopite, plagioclase and kaolinite to the Al₂O₃ content (>5%) and ferrian diopside, calcite, plagioclase and actinolite to the CaO content (>3%) (Table 4.3).

The loss on ignition can be ascribed to the dehydration and dehydroxylation of smectite, talc, lizardite, chlorite, phlogopite, kaolinite, actinolite and hornblende (Földvári, 2011).

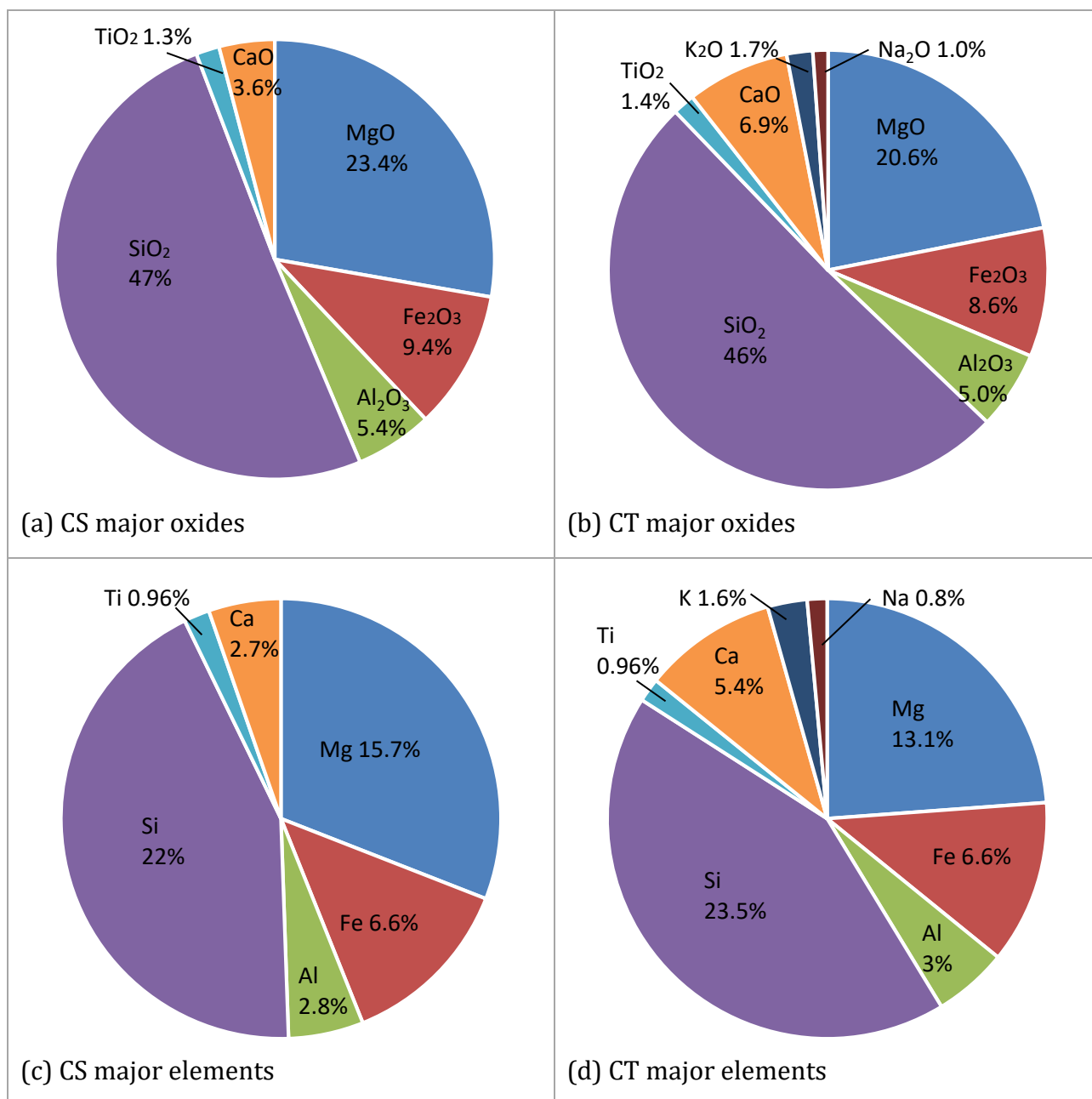


Figure 4.4: Chemical composition of untreated raw materials presented as (a, b) major oxides and (c, d) major elements.

From these results, Mg (13.1 – 15.7%), Fe (~ 6.6%), Al (2.8 – 3.0%) and Ca (2.7 – 5.4%) were identified as the major elements available for extraction in both the slimes and the tailings. The Si, even though most abundant element, is not expected to be extractable using the process of solid-state reaction with ammonium sulphate (Bayer et al, 1982).

4.2.5 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of the raw materials (Figure 4.5) can give an indication of the mineral phases present, and support the data from XRD.

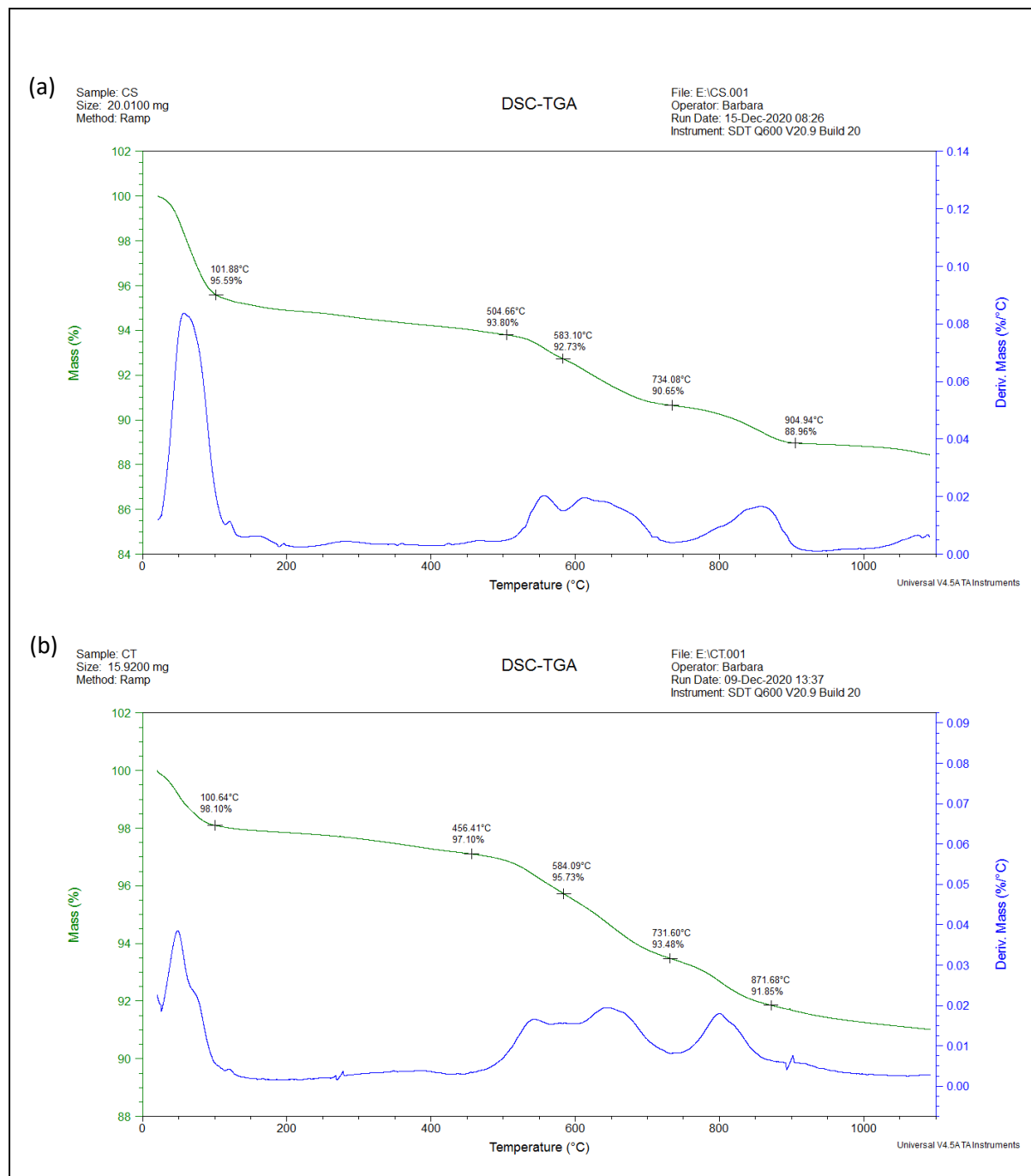


Figure 4.5: Thermogravimetric analysis of (a) CS and (b) CT.

Analysis of Fig 4.5 shows the thermograms have four distinct regions of mass loss. The first region where substantial mass loss occurs is below 200°C (~4.4% for CS and ~1.9% for CT), then in the regions 500 – 580°C (~1.1% for CS and ~1.4% for CT), 600 – 710°C (~2.1% for CS and ~2.3% for CT), and finally, between 750 – 900°C (~1.7% for CS and ~1.6 for CT). The TGA curves obtained for the slimes and tailings showed a total mass loss of 11.2% (CS) and 8.7% (CT) (Fig 4.5), by 1000°C, which are both slightly higher than the LOI values reported by the XRF analyses (Table 4.3).

The main thermic reactions of phyllosilicates are dehydration (loss of both adsorbed water and interlayer free water) below 200°C, and dehydroxylation, which generally occurs at temperatures between 500 – 900°C (Földvári, 2011; Stevenson, 2016). Many also undergo a phase transition at higher temperatures e.g. smectite, talc and chlorite (>850°C), kaolinite and lizardite (>800°C) (de Souza Santos and Yada, 1988; Földvári, 2011).

Quantifying which of the minerals is undergoing dehydroxylation or decomposition in which temperature range is complicated by having a combination of minerals present in the samples, as the mass loss curves may shift when more than one mineral is present (van der Merwe and Strydom, 2004). A further complication during analysis of thermograms of mineral mixtures is that many of the minerals undergo dehydroxylation over a similar temperature range, i.e. kaolinite between 450 – 590°C (Földvári, 2011; Stevenson 2016), the chlorite mineral, clinochlore, between 470 – 650°C (interlayer hydroxide) and lizardite between 600 – 680°C (Földvári, 2011).

The smectite component of CS and CT could be montmorillonite $(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$, or saponite $(\text{Na,Ca})_{0.3}(\text{Mg,Fe}^{2+})_3(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (Table 4.2), which undergo dehydroxylation at 680 – 700°C and 800 – 850°C, respectively (Földvári, 2011).

Some of these dehydroxylation and phase transition reactions are shown in Table 4.4.

Table 4.4: Reactions of some of the clay minerals during thermogravimetric analysis.

Mineral	Reaction	Temp (°C)	Ref
Talc			
(eqn 4.1)	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2(\text{s}) \rightarrow 3 \text{MgSiO}_3(\text{s}) + \text{SiO}_2(\text{s}) + \text{H}_2\text{O}(\text{g})$	850 –	a, b,
	<i>talc</i> <i>enstatite</i> <i>cristobalite</i>	1000	c
Lizardite			
(eqn 4.2)	$2\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4(\text{s}) \rightarrow 2\text{Mg}_2\text{SiO}_4(\text{s}) + 2\text{MgSiO}_3(\text{s}) + 4\text{H}_2\text{O}(\text{g})$	600 –	c
	<i>lizardite</i> <i>forsterite</i> <i>enstatite</i>	670	
(eqn 4.3)	$2\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4(\text{s}) \rightarrow 3\text{Mg}_2\text{SiO}_4(\text{s}) + \text{SiO}_2(\text{s}) + 4\text{H}_2\text{O}(\text{g})$	600 –	c
	<i>lizardite</i> <i>forsterite</i> <i>amorphous</i>	670	
(eqn 4.4)	$3 \text{Mg}_2\text{SiO}_4(\text{s}) + \text{SiO}_2(\text{s}) \rightarrow 2 \text{Mg}_2\text{SiO}_4(\text{s}) + 2 \text{MgSiO}_3(\text{s})$	1050	c
	<i>forsterite</i> <i>enstatite (cryst)</i>		
Kaolinite			
(eqn 4.5)	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{s}) \rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2(\text{s}) + 2 \text{H}_2\text{O}(\text{g})$	500 –	c
	<i>amorphous metakaolinite</i>	590	

(^a)Nakahira and Kato (1963), (^b)de Souza Santos and Yada (1988) and (^c)Földvári (2011)

According to Nakahira and Kato (1963), de Souza Santos and Yada (1988) and Földvári (2011), the dehydroxylation and structural decomposition of talc into enstatite (MgSiO_3) and silica (cristobalite, SiO_2) occurs between 850°C and 1000°C, according to the reaction described by eqn 4.1 in Table 4.4. This provides a theoretical mass loss of 4.75% due to the loss of water.

Lizardite (eqn 4.2, 4.3 and 4.4, Table 4.4) and kaolinite (eqn 4.5, Table 4.4) also undergo dehydroxylation and structural decomposition reactions. The former occurs between 600 and 670°C and 450 – 590°C respectively, and are equivalent to a theoretical mass loss of approximately 13.0% and 14.0% each. The structural decomposition of kaolinite starts at ca. 950°C with the formation of spinel, followed, between 950 – 1000°C, by a transformation to mullite (Stevenson, 2016).

The mica component could be phlogopite, $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$, which undergoes dehydroxylation between 900 – 1200°C, or biotite $\text{K}(\text{Mg,Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$, which undergoes dehydroxylation between 1080 – 1180°C. Phlogopite undergoes simultaneous decomposition to form spinel, leucite and mullite (Földvári, 2011).

The chlorite group of phyllosilicate minerals has four end members based on the elements Mg, Fe, Ni and Mn, and consists of a 2:1 layer with an interlayer hydroxide sheet. Variation in the composition of chlorites leads to variation in the thermal processes. As a result of the two different layers having hydroxyl groups, dehydroxylation generally takes place in two steps, with the interlayer losing its hydroxide between 470 – 650°C. The temperature range of dehydroxylation of the 2:1 layer depends on the major element incorporated into the mineral. The Mg-dominant member of the chlorites is clinochlore $(\text{Mg}_5\text{Al})(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$, which dehydroxylates between 835 – 865°C, the Fe^{2+} -dominant species is chamosite $(\text{Fe}_5\text{Al})(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$, which dehydroxylates between 520 – 580°C. There may also be a combination of Mg^{2+} and Fe^{2+} , in varying ratios, which dehydroxylate between 720 – 800°C. Within ultramafic rocks, the Mg-Fe (15:1 – 30:1) chlorite, $(\text{Mg,Fe}^{2+})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$, is more prevalent, which also undergoes a phase transition at ~ 880°C, to form new minerals, e.g. olivine, spinel and enstatite (Földvári, 2011).

4.2.6. Fourier-Transform Infrared spectroscopy (FTIR)

FTIR spectra of the mine slimes (CS) and tailings (CT) were compared in Figure 4.6, to spectra from literature, selected based on XRD results (Rruff database). As the FTIR data is not available for all minerals, some are not included.

The strong, distinctive band in the slimes, tailings, talc and lizardite spectra, between ca. 950 and 1050 cm^{-1} , with a shoulder towards the higher wave number, is due to the bending and stretching modes of Si – O (Madejová, 2003; Hofmeister and Bowey, 2006, Musić et al, 2011, Sanna et al, 2013), and is also apparent in spectra of kaolinite, montmorillonite and saponite (Madejová, 2003). The variations in shape and positions of this strong band reflects the different arrangement of the layers in the phyllosilicate clays (1:1 or 2:1), as well as the geometry of the minerals (Madejová, 2003).

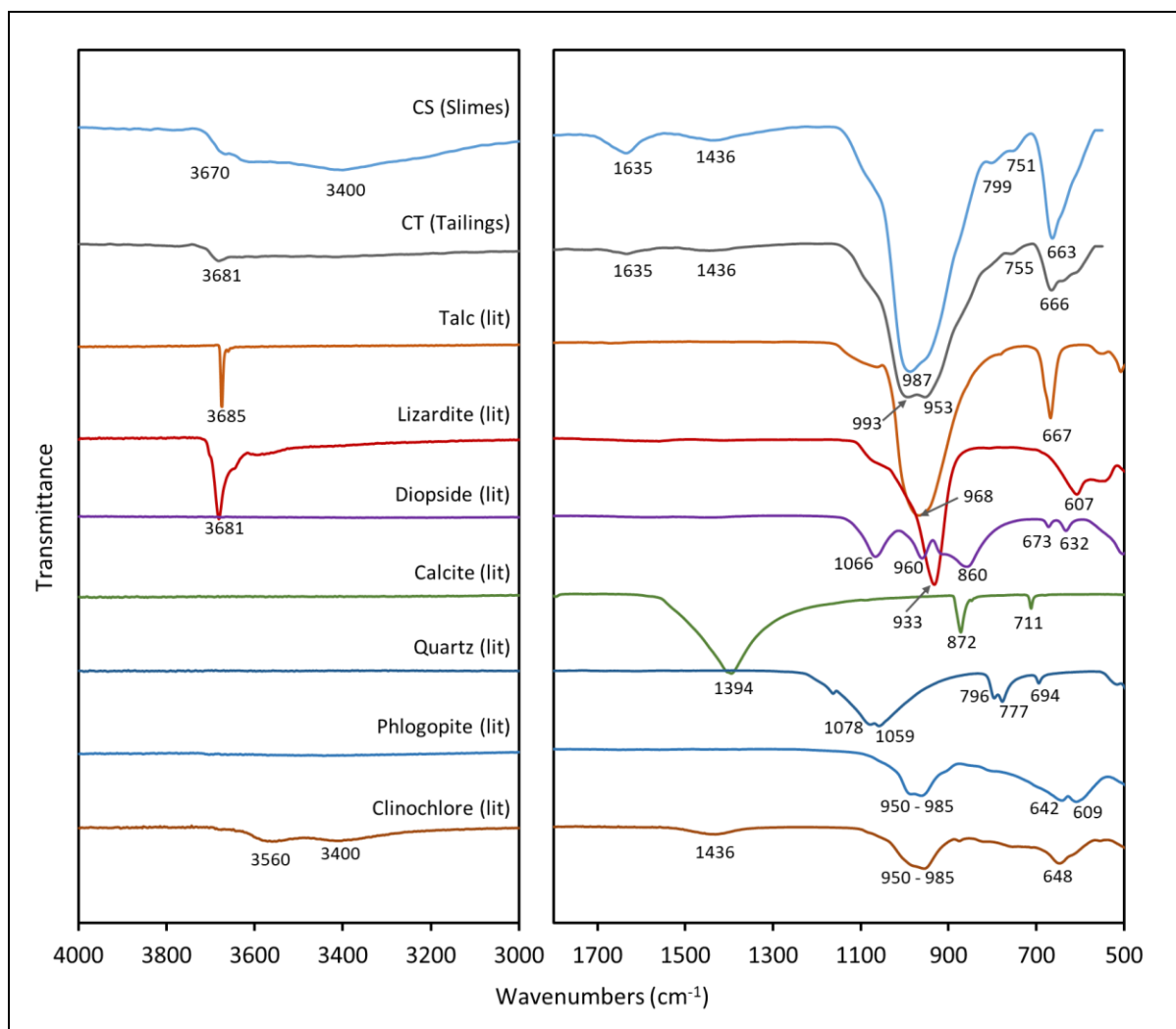


Figure 4.6: FTIR spectra of mine slimes (CS) and mine tailings (CT) compared to spectra of pure minerals from the literature.

The broad band ca. 3200 – 3600 cm^{-1} and low intensity peak at 1635 cm^{-1} in the slimes can be attributed to H – O – H stretching and bending vibrations of adsorbed water (Madejová, 2003), as well as structurally incorporated water (interlayer) molecules (Sanna et al, 2013, Musić et al, 2011). The absence of the broad water band in the CT spectrum, indicates a lower water content which is supported by the TGA thermogram (Fig 4.5). The sharper band at ca. 3681 cm^{-1} , present in talc, lizardite and to a small extent in CT, is due to vibrations of inner hydroxyl groups (Madejová, 2003), and reflects the OH bonded to Mg cations in the octahedral position (Sanna et al, 2013). The band near 660 cm^{-1} (present in CS, CT, talc, lizardite, phlogopite and clinocllore) could be considered Mg–O–H bending (Madejová, 2003; Hofmeister and Bowey, 2006), and Mg–O–H stretching at ca. 3681 in CT, talc and lizardite. The Mg–O–H stretching could also be

included in the broad band between $3400 - 3700\text{ cm}^{-1}$ in CS (Laine et al, 2017). The relatively minor band around 1436 cm^{-1} is also present in clinocllore. This FT-IR data supports the results obtained by XRD analysis and confirmed the presence of talc and other Mg-containing minerals.

4.2.7 Morphology of the raw materials using Field-Emission Scanning Electron Microscopy (FE-SEM)

FE-SEM was used to get an understanding of the morphology of the CS and CT samples. This morphology is illustrated in Figure 4.7 below.

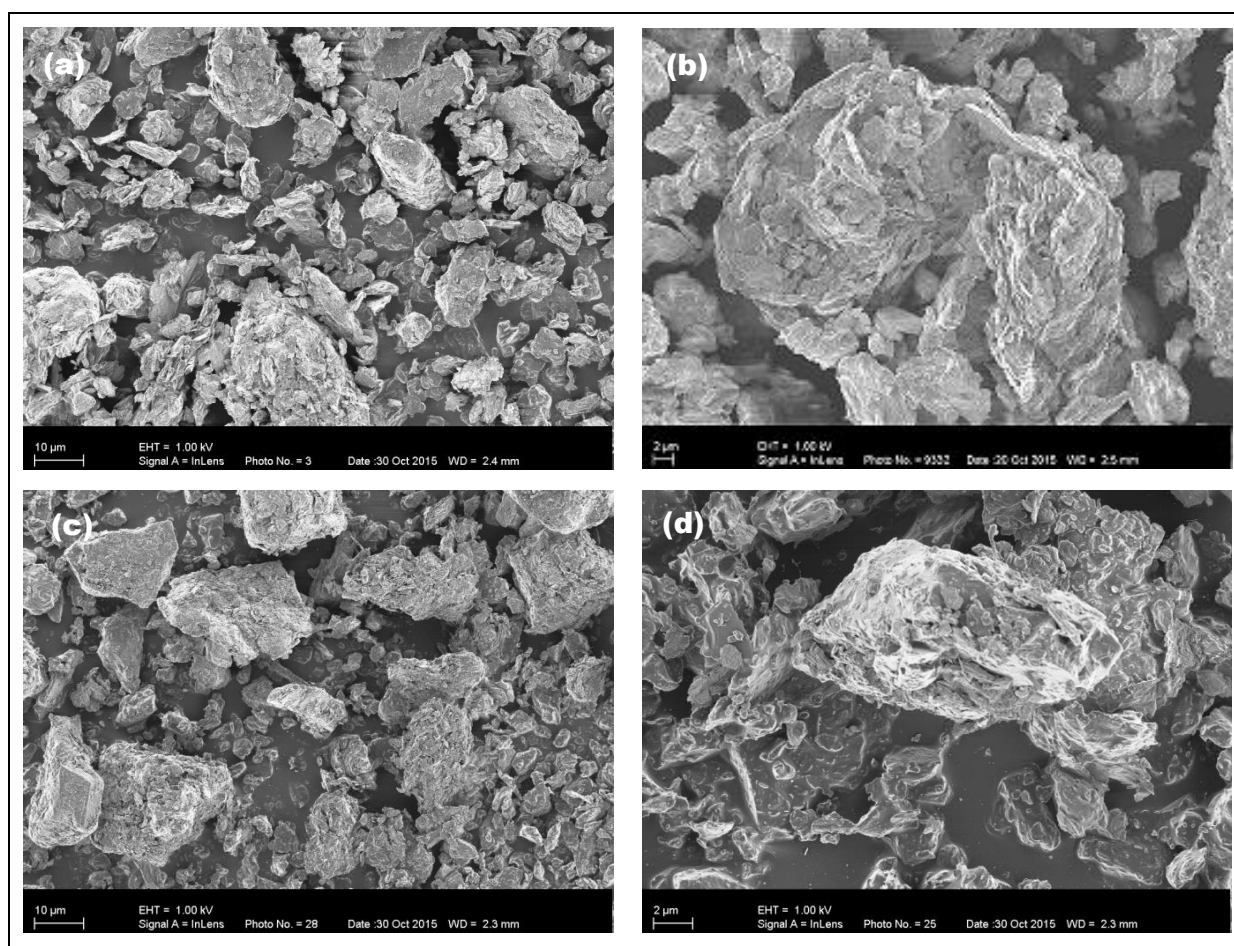


Figure 4.7: FE-SEM images for (a, b) slimes (CS) and (c, d) tailings (CT).

The FE-SEM images of the slimes and tailings revealed that the samples were made up of individual, irregularly shaped particles of varying sizes. The particles have a non-crystalline, platy and irregular appearance. Qualitative elemental analyses determined by

SEM-EDX indicates the presence of magnesium, iron, calcium and aluminium, supporting the results from XRF and XRD.

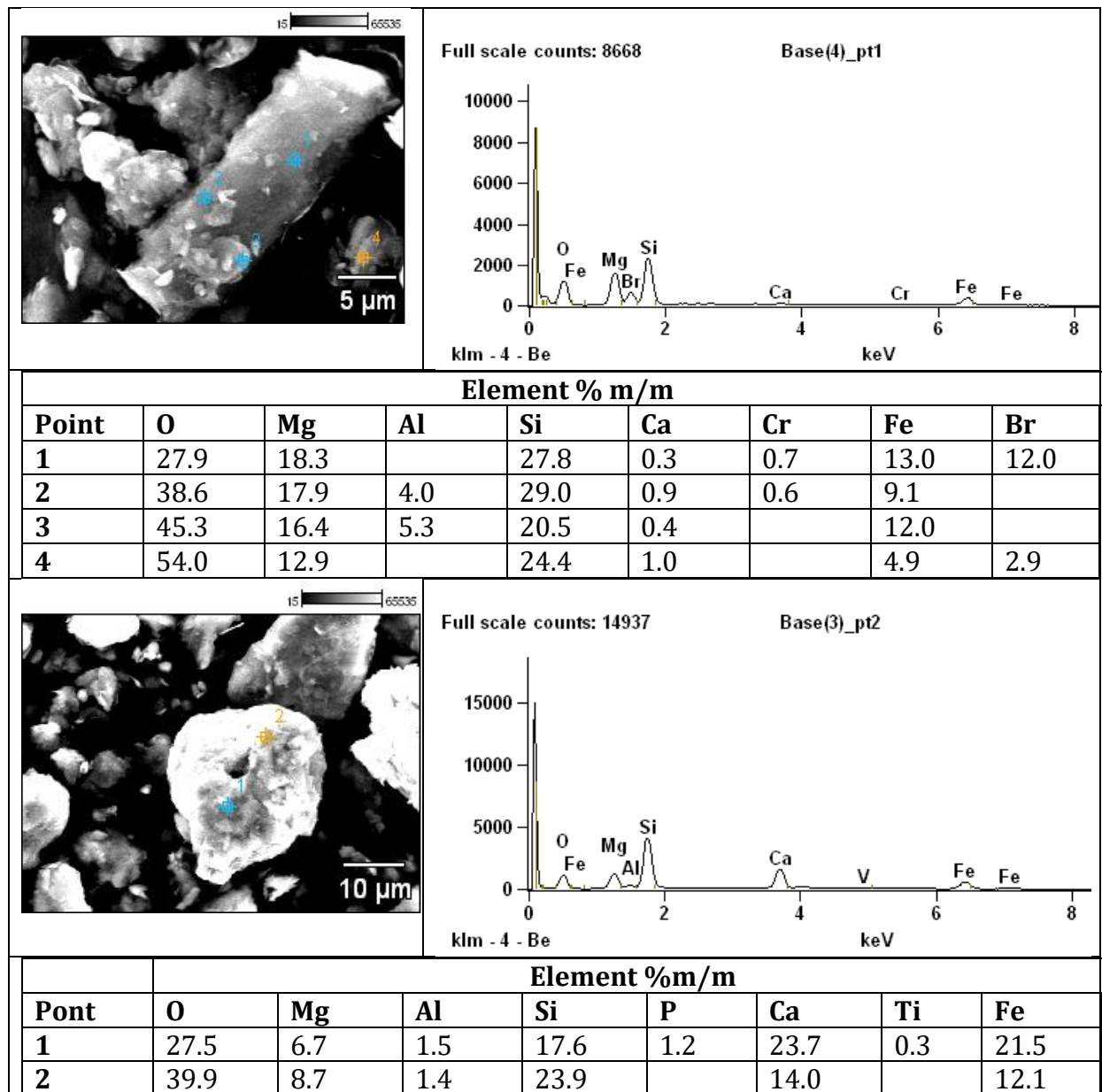


Figure 4.8: An example of SEM-EDX with elemental analysis for slimes (CS).

4.3 Conclusions

The kimberlite mine slimes and tailings are characterised by a complicated matrix of minerals. This is partly due to the long lifetime of the mine, where the composition of the waste changes as the mined ore changes. The material is also stored in exposed heaps, which leads to the material undergoing continuous weathering. In both the CS and CT, the major mineral phases present are smectite, talc, phlogopite (all phyllosilicates) and diopside. From these mineral phases, the most abundant metals are magnesium, iron, aluminium and calcium. The possible beneficiation potential lies in the extraction of these elements from the slimes and tailings, and their conversion to produce commercial-grade products. Co-extraction of elements is highly likely and will be dependant on the differences in reactivity between the minerals present in the samples.

Chapter 5: Thermal and Thermochemical treatment

5.1 Introduction

Thermal (heat only), and thermochemical treatment of the mine tailings and slimes with ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$, were investigated under a variety of temperature conditions, to determine what mineralogical changes occur and to what extent, and at which temperature these changes are most prevalent. The rationale behind this evaluation was to select a treatment temperature, as well as the best mass ratio of slimes or tailings to ammonium sulphate, to enable the optimisation of the extraction process, which is discussed in Chapter 7. The residues generated by thermal and thermochemical treatments were characterised using various methods.

5.2 Thermal treatment of mine tailings and slimes

Before treating the slimes (CS) or tailings (CT) with ammonium sulphate (AS), samples were thermally treated at a variety of temperatures (the same temperatures that were used for thermochemical treatment), to determine whether any significant changes to the starting material could be brought about by heat alone.

5.2.1 Physical appearance and mass change

The untreated slimes and tailings were originally grey in colour (Fig 5.1 a and b), but after heating in the furnace at all temperatures, the colour changed to reddish brown in the case of slimes (Fig 5.1 c) and very dark grey in the case of the tailings (Fig 5.1 d). This colour change was the same for all thermal treatment temperatures.

The mass loss after thermal treatment of slimes (CS) and tailings (CT) at various furnace temperatures is presented in Table 5.1.

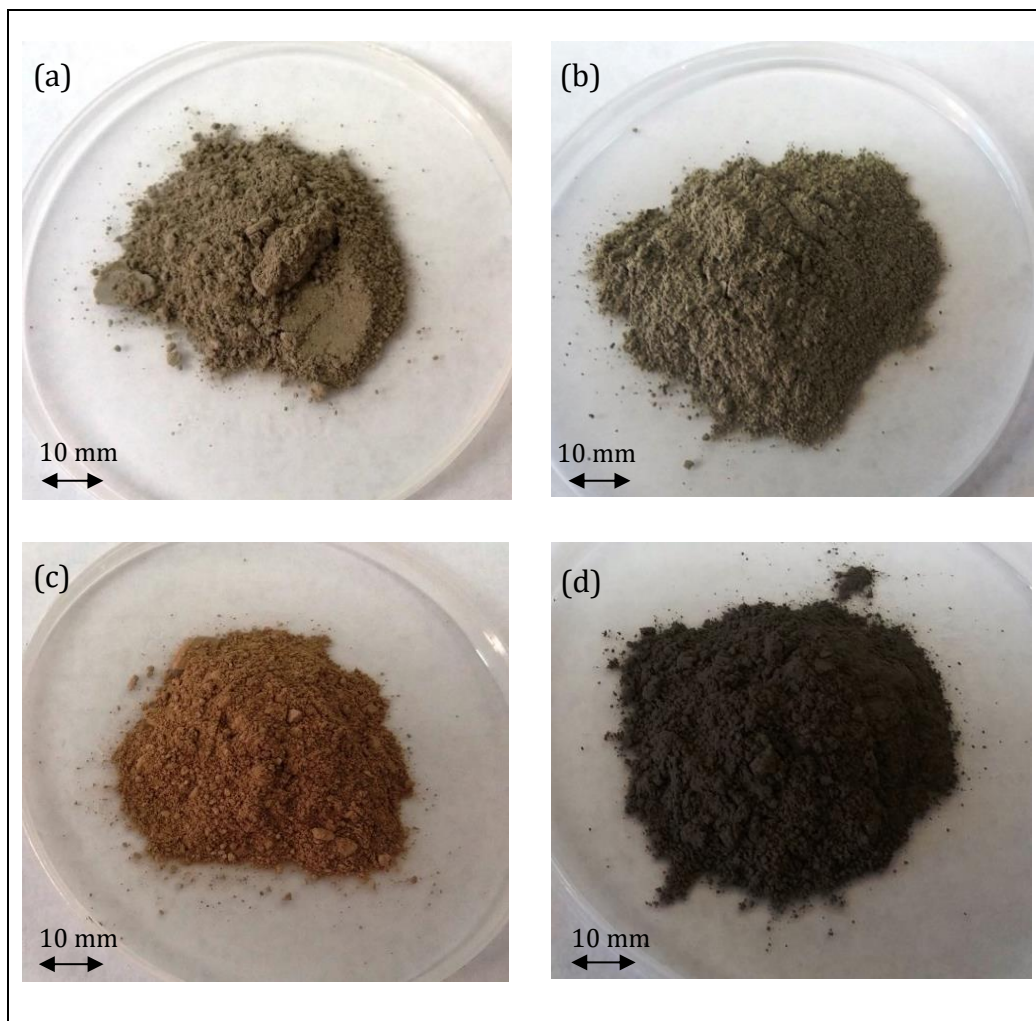


Figure 5.1: Slimes (a) untreated and (c) after thermal treatment at 450°C for 1 h, and tailings (b) untreated and (d) after roasting at 450°C for 1 h.

Table 5.1: Mass loss after thermal treatment of slimes (CS) and tailings (CT) at various furnace temperatures ($n = 2$).

		% Mass loss				
	Time	450°C	480°C	500°C	520°C	550°C
CS	45 min	6.81	6.86	7.00	7.20	7.90
	1 h	6.91	6.96	7.10	7.19	8.19
CT	45 min	2.70	2.75	2.93	3.06	3.37
	1 h	2.73	2.84	2.98	3.11	3.45

The mass losses, for both the CS and CT samples, after treatment at various temperatures (Table 5.1) showed an increasing trend with increasing furnace temperatures. The mass loss for CS was generally around 60% larger than that for CT, with the largest increase in mass loss, in both samples, between 520 and 550°C. This correlated well with the mass losses below 500°C as determined by TGA of the original raw materials (Fig 4.5). Above 500°C, dehydroxylation of some of the mineral phases, i.e. kaolinite or chlorite, could contribute to the increased mass loss (Bayer et al, 1982; Földvári, 2011). The difference between the mass loss at 450°C and 480°C, as well as between 500°C and 520°C, was nominal, and so further characterisation was completed for samples thermally treated at 450°C, 500°C and 550°C. There was also no substantial difference in mass loss between heating the samples at 45 min or 1 h. The 1 h time period produced a more manageable product when samples were thermochemically treated with ammonium sulphate (section 5.3.1), therefore characterisation was continued using thermal treatment for 1 h.

5.2.2 Mineralogical and chemical composition

A comparison of the XRD patterns of the original raw materials and the raw materials thermally treated at 450°C, 500°C and 550°C for 1 h (Figure 5.2), indicates that there is some variability in the raw material after heating, but this could be due to the complexity and variability of the samples, as well as preferred orientation, structural disorders and structural diversity of the clay minerals (Zhou et al, 2018). Structural changes and the formation of new crystal phases generally occur at higher temperatures (Földvári, 2011; Stevenson, 2016).

The approximate quantitative XRD analysis results of the thermally treated slimes and tailings, compared to the untreated raw material, are summarised in Tables 5.2 and 5.3.

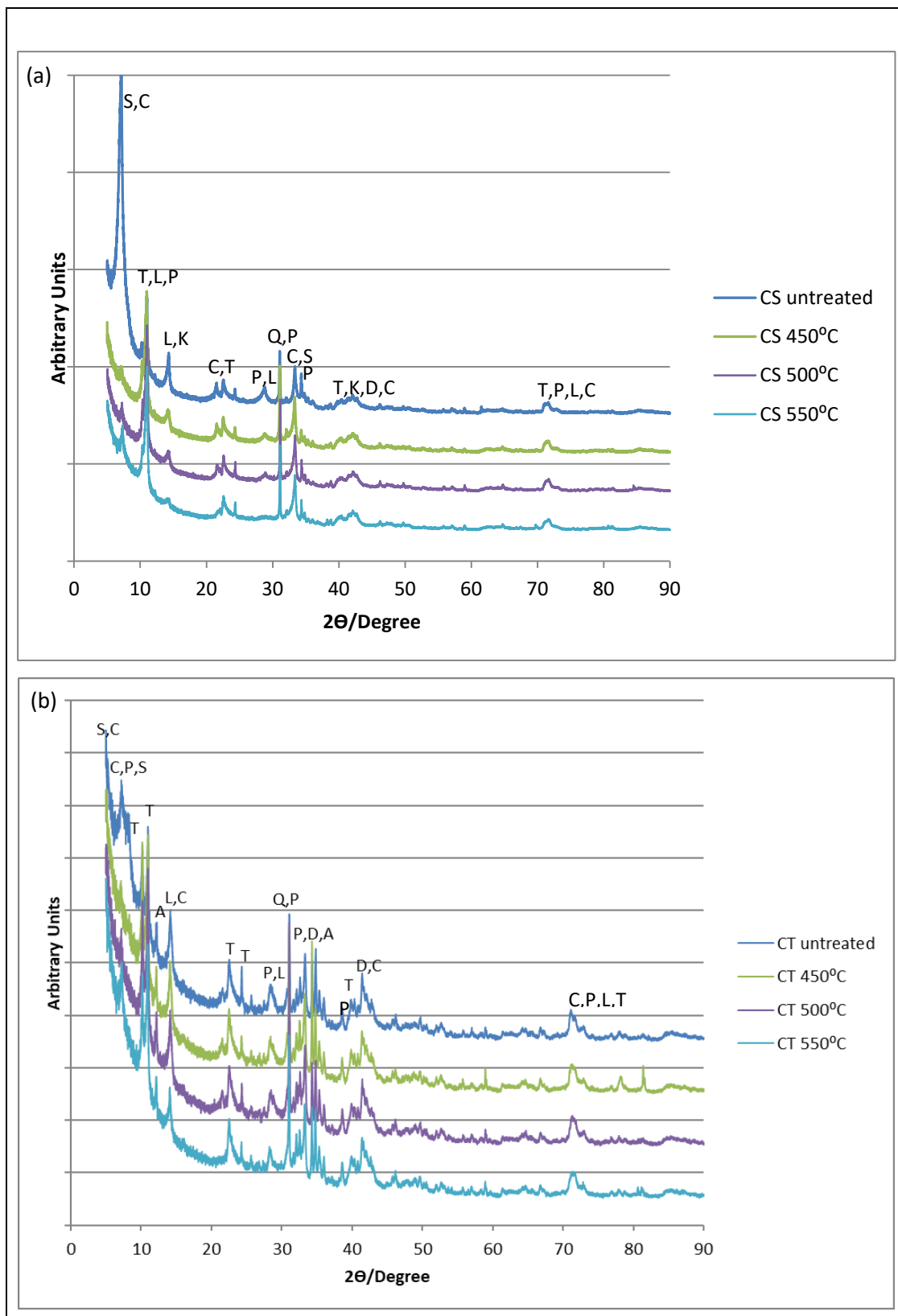


Figure 5.2: Comparison of XRD patterns for CS (a) and CT (b) showing the untreated original raw material and raw material thermally treated at 450°C, 500°C and 550°C for 1 h. T: talc, S: smectite, L: lizardite, P: phlogopite, C: chlorite, Q: quartz, D: diopside, K: kaolinite, A: actinolite.

Table 5.2: Approximate quantitative mineralogy (%m/m) for CS thermally treated at different furnace temperatures for 1 h, determined by XRD with Rietveld refinement.

Mineral Name	Approximate Chemical Formula	Untreated	450°C	500°C	550°C
Calcite	CaCO_3	3.8	4.3	3.9	3.7
Chlorite	$(\text{Fe,Mg,Al})_6(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8$	3.7	7.4	7.5	8.0
Diopside	$\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$	6.0	5.7	7.2	6.8
Hornblende	$\text{Ca}_2(\text{Mg,Fe,Al})_5(\text{Al,Si})_8\text{O}_{22}(\text{OH})_2$	2.0	2.8	3.6	2.4
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	5.0	5.8	5.9	3.9
Lizardite	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	1.1	1.2	1.0	1.0
Microcline	KAlSi_3O_8	0.9	2.8	3.0	3.3
Phlogopite	$\text{KMg}_3\text{Si}_3\text{AlO}_{10}(\text{F, OH})_2$	8.2	9.6	8.8	8.3
Plagioclase	$(\text{Na,Ca})(\text{Si,Al})_4\text{O}_8$	1.9	4.6	5.7	5.6
Quartz	SiO_2	4.3	4.5	4.6	5.2
Smectite	$\text{Na}_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_{2n}(\text{H}_2\text{O})$	33.0	22.9	18.9	21.7
Talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	30.1	28.4	29.9	30.1

Table 5.3: Approximate quantitative mineralogy (%m/m) for CT, thermally treated at different furnace temperatures for 1 h, determined by XRD with Rietveld refinement.

Mineral Name	Approximate Chemical Formula	Untreated	450°C	500°C	550°C
Actinolite	$\text{Ca}_2(\text{Mg,Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	5.5	6.3	6.4	6.6
Calcite	CaCO_3	3.2	3.8	3.8	4.0
Chlorite	$(\text{Fe,Mg,Al})_6(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8$	3.5	8.6	8.1	6.1
Diopside	$\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$	11.6	15.7	13.3	14.0
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	5.1	5.2	6.2	5.9
Microcline	KAlSi_3O_8	4.0	4.2	5.3	5.1
Phlogopite	$\text{KMg}_3\text{Si}_3\text{AlO}_{10}(\text{F, OH})_2$	8.6	7.5	9.1	8.9
Plagioclase	$(\text{Na,Ca})(\text{Si,Al})_4\text{O}_8$	7.5	10.3	9.2	9.0
Quartz	SiO_2	3.1	3.5	3.4	4.3
Smectite	$\text{Na}_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_{2.n}(\text{H}_2\text{O})$	22.7	14.0	14.2	16.9
Talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	25.2	23.0	21.0	19.2

There is a fair amount of variability in the semi-quantitative XRD results due to the samples being complex mixtures of various minerals with a wide range of crystallinity and composition. Because of these complexities the estimation of relative amounts of minerals may often be the most suitable for the given circumstances. The micas and the clay minerals may be slightly overestimated due to preferred orientation and the results may be not as accurate as shown in the table (Zhou et al, 2018).

Major oxides and their various proportions were estimated using XRF and are presented in Table 5.4. There were no noteworthy differences in the proportion of major oxides, in either CS or CT (Table 5.4), after heating at 450°C, 500°C or 550°C for 1 h.

Table 5.4: Bulk chemistry of CS and CT samples (showing major oxides), comparing unroasted samples with samples roasted at 450°C, 500°C and 550°C, as determined by XRF in % m/m using the standard method.

	SiO ₂	MgO	Fe ₂ O ₃	Al ₂ O ₃	CaO	TiO ₂	Na ₂ O	K ₂ O	LOI	Total
CS	47.0	23.4	9.4	5.4	3.6	1.4	0.3	0.6	8.3	99.4
450°C	47.1	24.3	9.4	5.9	2.9	1.3	0.2	0.5	8.1	99.7
500°C	47.7	24.5	8.4	5.5	3.1	1.2	0.3	0.5	8.1	99.3
550°C	47.9	24.7	8.4	5.6	3.1	1.2	0.2	0.5	7.7	99.3
CT	46.0	20.6	8.6	5.0	6.9	1.5	1.0	1.7	6.8	98.1
450°C	47.1	21.2	9.3	5.0	7.1	1.5	1.0	1.6	5.4	99.2
500°C	47.4	21.8	8.0	5.0	6.1	1.3	0.9	1.4	7.3	99.2
550°C	47.6	22.1	8.0	5.1	6.0	1.3	1.0	1.4	6.6	99.1

Minor amounts (<0.15%) of MnO, P₂O₅, Cr₂O₃, NiO, SrO and ZrO₂ were also present.

5.2.3 Thermogravimetric Analysis

A comparison of the TGA and DTG curves for the untreated CS and CT against the samples thermally treated at 450°C is shown in Fig. 5.3.

The primary difference, after heating the samples, is the decrease in the size of the peak below 100°C, i.e. due to the removal of adsorbed and interlayer free water after thermal treatment. The very similar DTG curves for all thermal treatment temperatures indicates that there are no changes in the mineral phases after thermal treatment at the temperatures tested. The lack of the change between 500–550°C for the sample thermally treated at 550°C could be due to the dehydroxylation of kaolinite or loss of interlayer water from chlorite (clinochlore) during the thermal treatment (Bayer et al, 1982; Földvári, 2011).

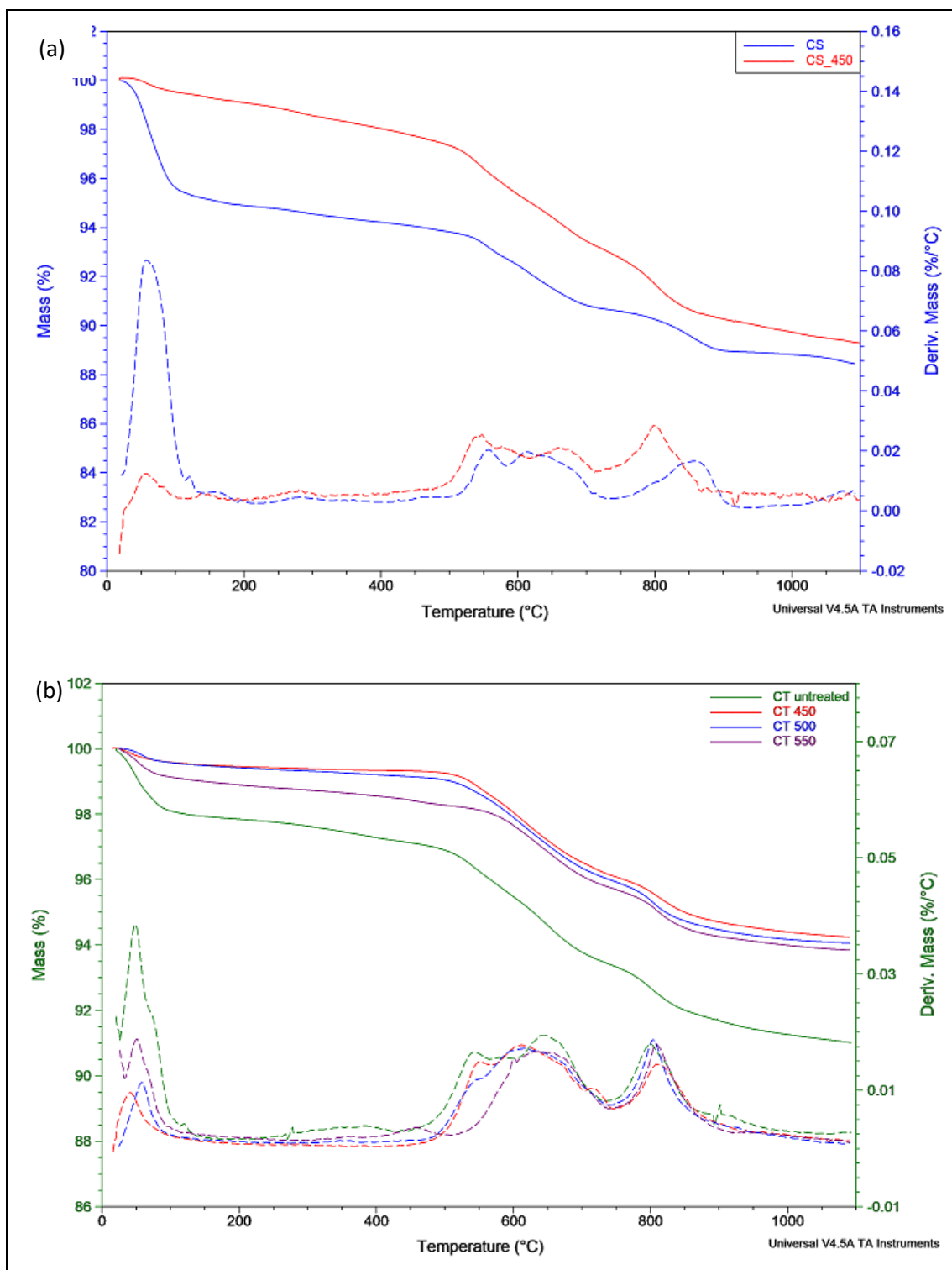


Figure 5.3: Thermogravimetric analysis of (a) CS vs CS roasted at 450 °C for 1 h and (b) CT vs CT roasted at 450 °C, 500 °C and 550 °C for 1 h.

5.2.4 FTIR analyses of thermally treated samples

A comparison of the FTIR spectra for untreated samples of CS and CT against those treated at different temperatures is given in Fig 5.4 and 5.5.

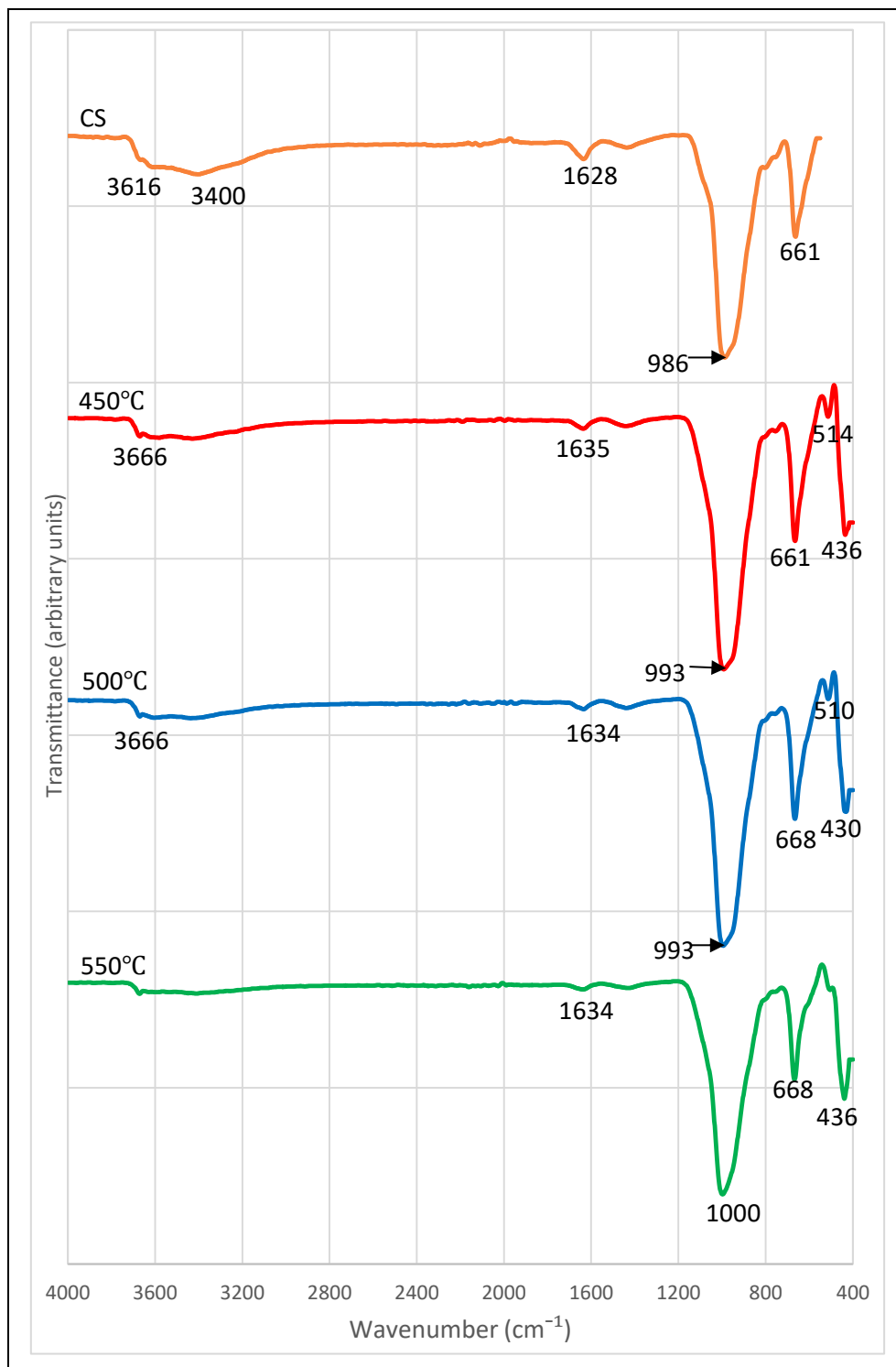


Figure 5.4: Comparison of FTIR spectra for slimes (CS) samples thermally treated at different temperatures for 1 h.

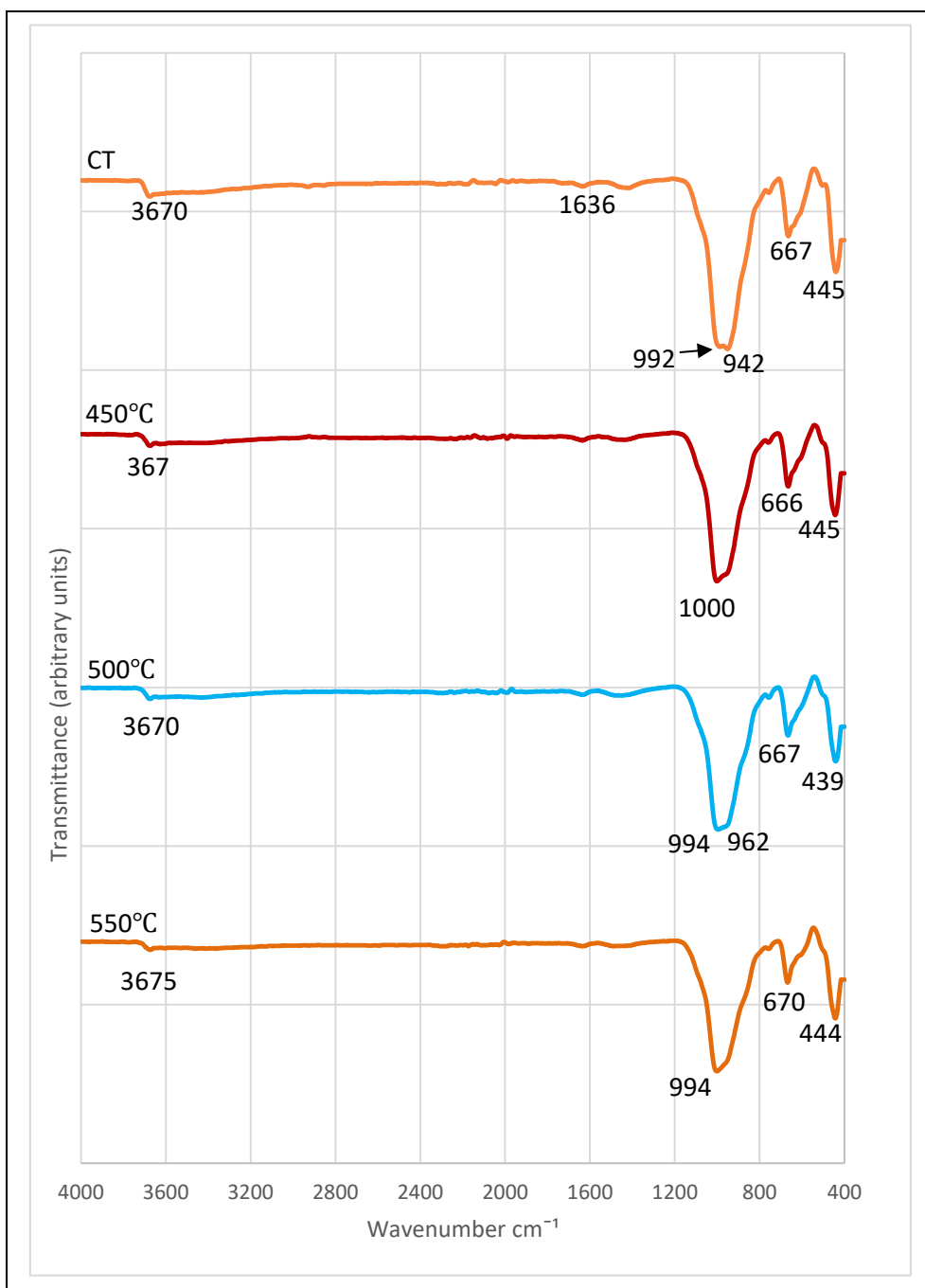


Figure 5.5: Comparison of FTIR spectra for tailings (CT) samples thermally treated at different temperatures for 1h.

There are no discernible differences in the position of the intense Si-O stretching vibrations between 980 – 1000 cm^{-1} or the O-H bending vibrations at 1628 – 1636 and 660 – 670 cm^{-1} . The O – H stretching vibration between 3200 – 3600 cm^{-1} , due to absorbed water in the CS, decreases after thermal treatment, and is absent after treatment at 550°C.

5.2.5 Morphology of CS and CT after thermal treatment

FE-SEM images of the slimes and tailings, before and after thermal treatment at 450°C for 1 h, reveal that the individual, irregularly shaped particles observed in the untreated samples do not change after thermal treatment (Fig 5.6). This supports the observations made using the other characterisation techniques, i.e. XRD, TGA, FT-IR.

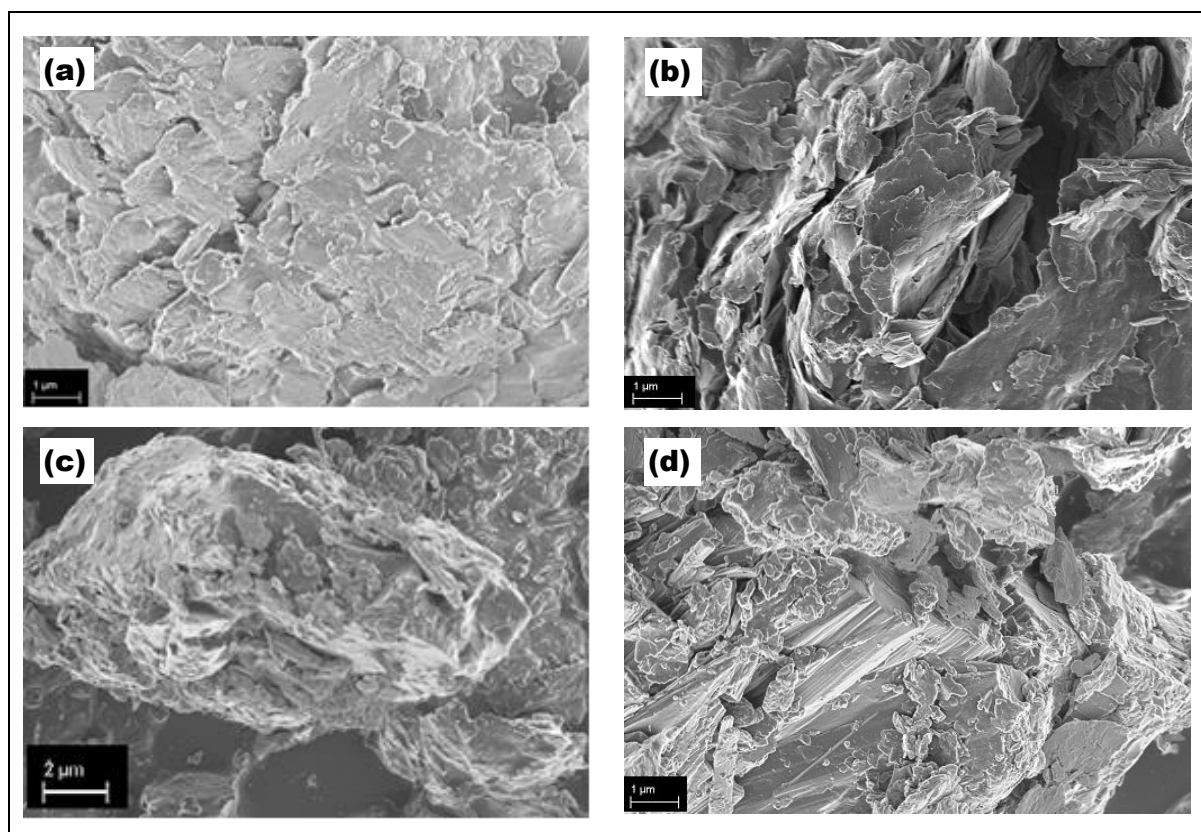


Figure 5.6: FE-SEM micrographs for CS (a) untreated and (b) thermally treated at 450°C for 1 h and CT (c) untreated and (d) thermally treated at 450°C for 1 h.

5.2.6 Summary of thermal treatment results

Thermal treatment of the slimes (CS) and tailings (CT) caused minimal changes in the chemical composition or morphology of the raw materials.

5.3 Thermochemical processing of diamond mine tailings and slimes with ammonium sulphate

The purpose of thermochemical processing with ammonium sulphate is to facilitate the extraction of metals (Mg, Fe and Al) from tailings or slimes via the formation of soluble sulphate compounds. In this section, the extent of the formation of sulphate compounds during thermochemical treatment was investigated. The efficiency of the process can only be quantified by subjecting the product of the thermochemical treatment to an optimised dissolution procedure. The sulphate products formed were subjected to aqueous dissolution to facilitate the optimal extraction of the metals, the results of which are presented in Chapter 7.

Our study was initiated with a range of mass:mass (m/m) ratios for the mine residues (CS and CT) relative to the ammonium sulphate (AS), as well as various roasting temperatures. The range of mass ratios were used due to the mineralogy of the tailings being relatively complex. The reaction conditions were chosen based on data previously reported in the literature. Initially, CS:AS and CT:AS ratios of 2:3 m/m and 3:4 m/m were selected as this was the optimal ratio determined by Fagerlund et al (2012) and Nduagu et al (2012a), working with serpentinite rock. The product obtained from the 2:3 m/m ratio, thermochemically treated at 450°C for 1 h was used as the baseline study, and then expanded to include additional m/m ratios and roasting temperatures, as Mohamed et al (2016) found a 2:6 ratio was optimum for PGM tailings. Nduagu et al (2012b) also reported using different mass ratios and temperatures due to elemental composition, specifically Mg:Fe ratio in Mg-silicate rock, affecting the degree to which Mg and Fe may be extracted. A large range of m/m ratios, roasting temperatures and times have been used in previous studies and a selection of these are summarised in Chapter 2, Table 2.2.

5.3.1 Physical appearance and mass change following AS treatment

The physical properties of the thermochemically treated CS and CT were influenced by the roasting temperature. Images of roast residues after roasting at a mass-to-mass ratio of 2:3 m/m are shown in Figure 5.7.

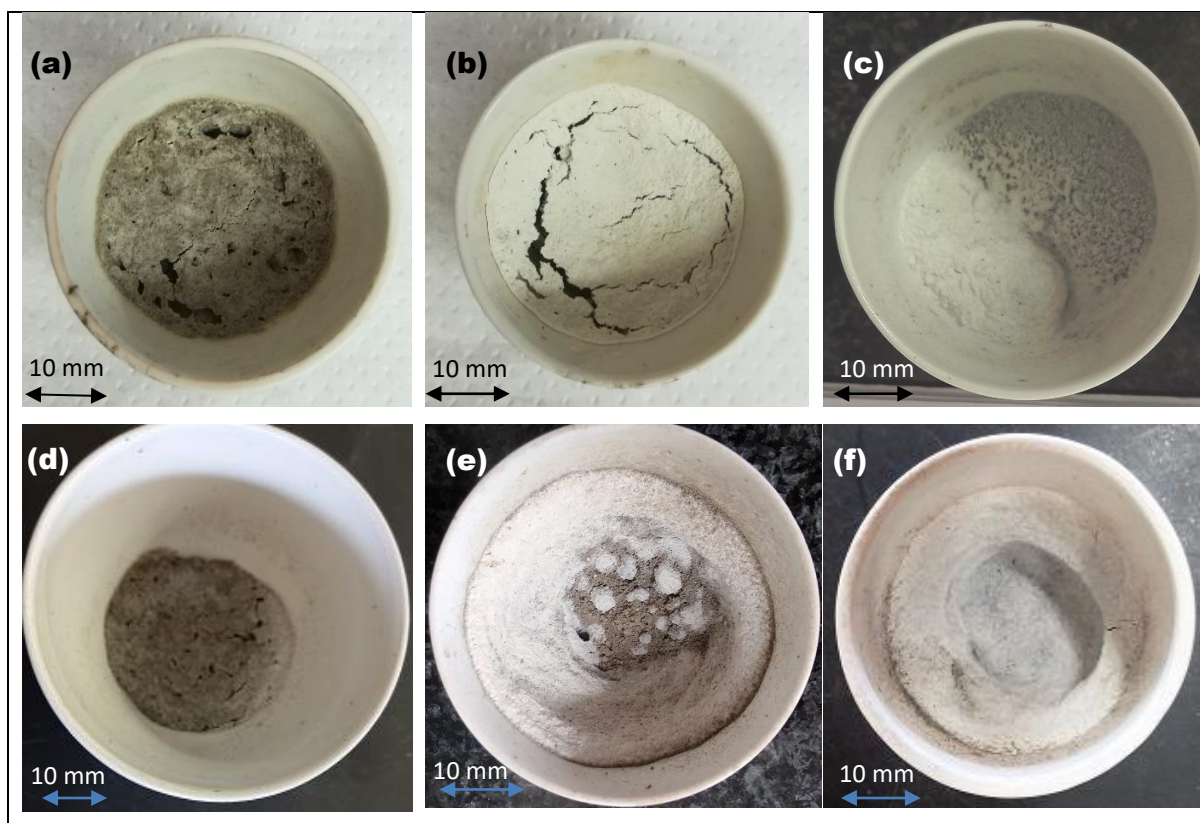


Figure 5.7: Images of roast residues after thermochemical treatment for 1 h at a ratio of 2:3 m/m at (a) 420°C, (b) 450°C and (c) 480°C for CS:AS and (d) 420°C, (e) 450°C and (f) 500°C for CT:AS.

At temperatures below 450°C the product was a hard, dark grey solid, that was difficult to be removed from the crucibles. This was described by Nduagu et al (2012a) as resembling a sintered product, and interpreted by Mohamed et al (2016) as being due to the presence of excess ammonium sulphate and its possible decomposition products which had not reacted completely within the timeframe of the experiments. This interpretation is supported by the XRD results (Table 5.6), where the presence of ammonium bisulphate (NH_4HSO_4) was found at a roasting temperature of 400°C. Higher temperatures ($\geq 450^\circ\text{C}$) produced a lighter, free-flowing powder, which was more easily recovered (Figure 5.7). The CT:AS samples were inclined to rise up the sides of the crucibles and were harder than CS:AS samples at the same temperatures. They also fumed excessively at temperatures below 450°C, indicating that the reaction was incomplete. This could be due to the lower moisture content in CT, as Romão et al (2016) found that the addition of water to the roasting mixture of serpentinite rock and AS improved the extraction of Mg favourably at lower roasting temperatures.

Mass losses after thermochemical treatment at various temperatures for CS:AS and CT:AS at a ratio of 2:3 m/m are presented in Table 5.5.

Table 5.5: Mass loss after thermochemical treatment at various temperatures for CS:AS and CT:AS at a ratio of 2:3 m/m ($n \geq 3$).

	%Mass loss					
	420°C	450°C	480°C	500°C	520°C	550°C
CS	25.3±0.7	39.1±1.2	44.7±0.9	48.3±0.8	49.6±0.6	50.6±0.3
CT	26.9±1.5	41.6±1.8	48.4±0.2	50.2±0.2	51.3±0.1	51.6±0.2

Mass losses after thermochemical treatment increased with increasing temperature, ranging from 25.3 – 53.1% (Table 5.5), with mass losses at 420°C significantly lower than the mass losses after thermochemical treatment at 450°C and higher. This suggests that not all AS has reacted at 420°C to form products due to decreased rate of AS decomposition at lower temperatures. A longer roast duration would be required for complete decomposition. In contrast, the mass losses incurred between 500°C and 550°C increased marginally by 2.3% for CS and 1.4% for CT. This is similar to the observations made by Mohamed et al, 2016. Mass losses were slightly higher for CT compared to CS at all temperatures.

Nduagu et al (2012b) found that Mg extraction was improved above temperatures of 400°C, and reached a maximum between 450 – 480°C. The experimental conditions (temperature and duration) selected for thermochemical treatment should ensure (i) minimal loss of AS during the thermochemical treatment, allowing AS to be recycled at a subsequent stage, (ii) good flowability of the powdered reaction product for ease of removal from the crucible, as well as (iii) the maximum recovery of the metals of interest (Mohamed et al, 2019).

5.3.2 Chemical and mineralogical composition of thermochemically treated tailings (CT) and slimes (CS)

The roast products were characterised using various methods. Major oxides and their various proportions were estimated using XRF. The boric acid pressed powder briquette technique was used for XRF sample preparation to preserve the sulphur content of the samples. The sulphur content, in the form of SO_3 , was also determined for the CS roast products, using a Leco Carbon/Sulphur analyser (Table 5.7). Unfortunately, the two methods do not correlate very well, except for the samples reacted at 450°C and 480°C . This could possibly be attributed to more repeat samples being analysed for those particular temperatures, for both methods. The carbon analyser results are probably more reliable as XRF is generally considered useful for identifying rather than quantifying sulphur content as the correlation of X-ray intensity to reported % sulphur can be poor (Ripley et al, 2011). When comparing the SO_3 content to the TGA mass loss above 550°C (the temperature above which metal sulphates start to decompose), there is a better correlation with the carbon analyser results.

The lower sulphur content, i.e. the decrease in the concentration of sulphate species, at the higher roasting temperatures could be due to the rapid decomposition of the AS leading to the loss of SO_3 during the solid–solid reaction. Modelling performed by Nduagu et al (2012a) found that increased SO_3 formation during the solid-solid reaction decreased the amount of sulphur available to form MgSO_4 , resulting in the production of Mg-orthosilicate (Mg_2SiO_4) and Mg-metasilicate (MgSiO_3).

Due to the sample preparation method used for the XRF analysis, no loss on ignition (LOI) was determined, leading to low total values (Table 5.6). The lower totals at lower temperatures can be explained by the higher content of ammonium species, as light elements, i.e. nitrogen, are difficult to quantify by XRF. At lower temperatures, the decreased rate of AS decomposition results in residual AS and partly decomposed AS in the form of ammonium bisulphate, NH_4HSO_4 (Mohamed et al, 2016).

Table 5.6: Bulk chemistry of CS:AS and CT:AS samples after roasting at a 2:3 m/m ratio at different furnace temperatures, as determined by XRF in % m/m, using boric acid pressed powder briquettes.

	Roasting Temp (°C)	SO ₃	SiO ₂	MgO	Fe ₂ O ₃	Al ₂ O ₃	CaO	TiO ₂	K ₂ O	Na ₂ O	Total
CS	420	31.5	19.8	13.9	7.2	3.2	2.5	1.5	0.4	0.3	80.3
	450	31.4	22.6	14.2	6.3	4.0	2.2	1.0	0.4	0.3	82.4
	480	30.2	24.5	14.6	7.2	3.8	2.8	1.7	0.4	0.3	85.5
	500	32.9	28.2	16.4	6.4	4.1	2.3	1.1	0.4	0.4	92.2
	550	29.3	29.9	16.7	6.6	4.2	2.4	1.1	0.4	0.4	91.0
CT	450	33.8	25.1	13.8	5.0	2.9	3.2	0.7	0.9	0.3	86.2
	500	29.5	29.0	16.6	5.4	3.2	3.6	0.7	1.0	0.4	89.9
	550	28.3	30.3	17.6	5.8	3.6	3.7	0.8	1.0	0.4	92.2

Minor amounts (<0.15%) of MnO, P₂O₅, Cr₂O₃ and NiO were also present.

Table 5.7: Sulphur content (SO₃), %m/m, present in the CS:AS roast products ($n \geq 2$).

Roasting Temperature	420°C	450°C	480°C	500°C	520°C	550°C
%SO ₃	25.7±0.9	31.0±0.3	29.1±0.1	24.2±1.9	23.5±0.8	22.9±0.7

Newly formed phases, including ammonium metal sulphate and/or metal sulphate species, were identified by XRD (Table 5.8), particularly magnesium (Mg), aluminium (Al), and iron (Fe) species, with Mg-species appearing to be the most dominant. At temperatures $\leq 450^\circ\text{C}$, the majority of newly-formed minerals were intermediate double salts, i.e. ammonium-metal sulphate compounds. There were a variety of ammonium-metal sulphates and hydrated metal sulphates present at the lower roasting temperatures (Table 5.8), also reported by Mohamed et al (2016). The existence of ammonium metal sulphates and metal sulphates indicate that the solid – phase reactions between AS and the metals in the mine slimes (CS) and tailings (CT), have occurred. This, in turn, allows the recovery of the metals from the soluble ammonium metal– and metal–

sulphate phases through dissolution. The presence of ammonium bisulphate at lower roasting temperatures caused these samples to have poor workability. Thermochemical treatment should, therefore, be performed under conditions (temperature and duration) where ammonium sulphate is completely converted into metal sulphates.

Table 5.8: List of newly formed minerals present in the roast products following thermochemical treatment between 400°C and 500°C.

Temperature	400°C	420°C	450°C	480°C	500°C
Boussingaultite (NH ₄) ₂ Mg(SO ₄) ₂ ·6H ₂ O	x	x	x		
Efremovite (NH ₄) ₂ Mg ₂ (SO ₄) ₃	x	x	x		
Epsomite MgSO ₄ ·7H ₂ O	x	x			
Hexahydrate MgSO ₄ ·6H ₂ O		x	x	x	x
Kieserite MgSO ₄ ·H ₂ O				x	x
Mikasaite Fe ₂ (SO ₄) ₃	x	x	x	x	x
Sabieite NH ₄ Fe(SO ₄) ₂	x	x	x	x	
Millosevichite Al ₂ (SO ₄) ₃	x	x	x	x	x
Godovikovite (NH ₄)Al(SO ₄) ₂	x	x	x		
Dawsonite NH ₄ Al(OH) ₂ CO ₃	x	x			
Anhydrite CaSO ₄	x		x		
Metaalunogen Al ₂ (SO ₄) ₃ ·4H ₂ O	x				
Ammonium bisulphate NH ₄ HSO ₄	x				

The relative proportion of crystalline phases present in the roasted samples could often not be quantified due to the presence of Sabieite ($\text{NH}_4\text{Fe}(\text{SO}_4)_2$), for which there is no information on crystal structure in the ICSD database. This was generally present in samples roasted at temperatures below 480°C . In addition, due to the samples being complex mixtures of numerous minerals with a wide range of crystallinity and composition, the estimation of relative amounts of minerals is challenging. The exact chemical compositions of some of the formed species could not be unequivocally identified using XRD data only. At temperatures above 450°C , fewer intermediate ammonium-metal sulphate phases were identified.

5.3.3 Thermal analysis of thermochemically treated CT and CS

Thermogravimetric analysis of roast products obtained at different roasting temperatures

Thermogravimetric analysis was used to complement the XRD data. The thermogram of the untreated and thermally treated raw material was relatively constant (Fig. 5.3), with a mass loss of less than 13.0% at 1000°C , due mainly to dehydration and dehydroxylation of the mineral species (Földvari, 2011). After thermochemical treatment, the percentage mass loss increased to between 40 – 52%, depending on the experimental roasting temperature. This can be attributed to the decomposition of the ammonium metal sulphate and metal sulphate species formed during the thermochemical treatment (Table 5.8). The mass loss decreases at higher roasting temperatures due to fewer ammonium metal sulphate species as well as fewer hydrated species being formed at higher roasting temperatures. These values were similar to the LOI determined during sample preparation for XRF measurements, using the standard method, for thermochemically treated samples (Table 5.9).

Table 5.9: Comparison of % mass loss for samples of CS, untreated, thermally treated at 450°C (CS₄₅₀) and thermochemically treated with AS, as determined by TGA and LOI.

	% mass loss				
	CS _{untreated}	CS ₄₅₀	450°C	500°C	550°C
TGA@1000°C	12.9	8.3	48.3	36.3	32.3
XRF LOI	11.7	8.0	48.6	38.2	35.7
	CT _{untreated}	CT ₄₅₀	450°C	500°C	550°C
TGA@1000°C	9.0	4.5	35.8	28.1	25.3
XRF LOI	6.8	5.4	34.5	27.5	23.3

The curves show that the thermal decomposition occurred in several stages (Fig. 5.8a & 5.9). The first step, below 200°C, corresponds to the loss of adsorbed and interlayer free water. This occurred, at varying degrees, for all thermochemically treated samples. The higher mass loss below 200°C, for samples roasted at higher temperatures, can be explained by the hygroscopic nature of the metal sulphates formed. To compare the remaining mass losses for CS, the mass loss percentage was recalculated from 200°C (Fig 5.8 b), which illustrates clearly that there are fewer regions of mass loss for samples roasted above 500°C. This is indicative of fewer hydrated and ammonium containing metal sulphates present in these samples, supporting the data in Table 5.8. Samples roasted at 420°C and 450°C have distinctive mass losses between 400 - 550°C, where the ammonium metal sulphate phases would dissociate (Bayer et al, 1982; Mohamed et al, 2016), supporting the XRD findings (Table 5.8). At a roast temperature of 480°C, these mass losses are smaller, indicating that there are fewer ammonium metal sulphates present.

The dissociation of the metal sulphate species starts from 550°C (Bayer et al, 1982; Mohamed et al, 2016), with the onset of decomposition of iron and aluminium sulphates around 575°C (Kolta and Askar, 1974, Siriwardane et al, 1999) and 650°C (Bayer et al, 1982) respectively, and magnesium sulphate from 850°C (Földvári, 2011).

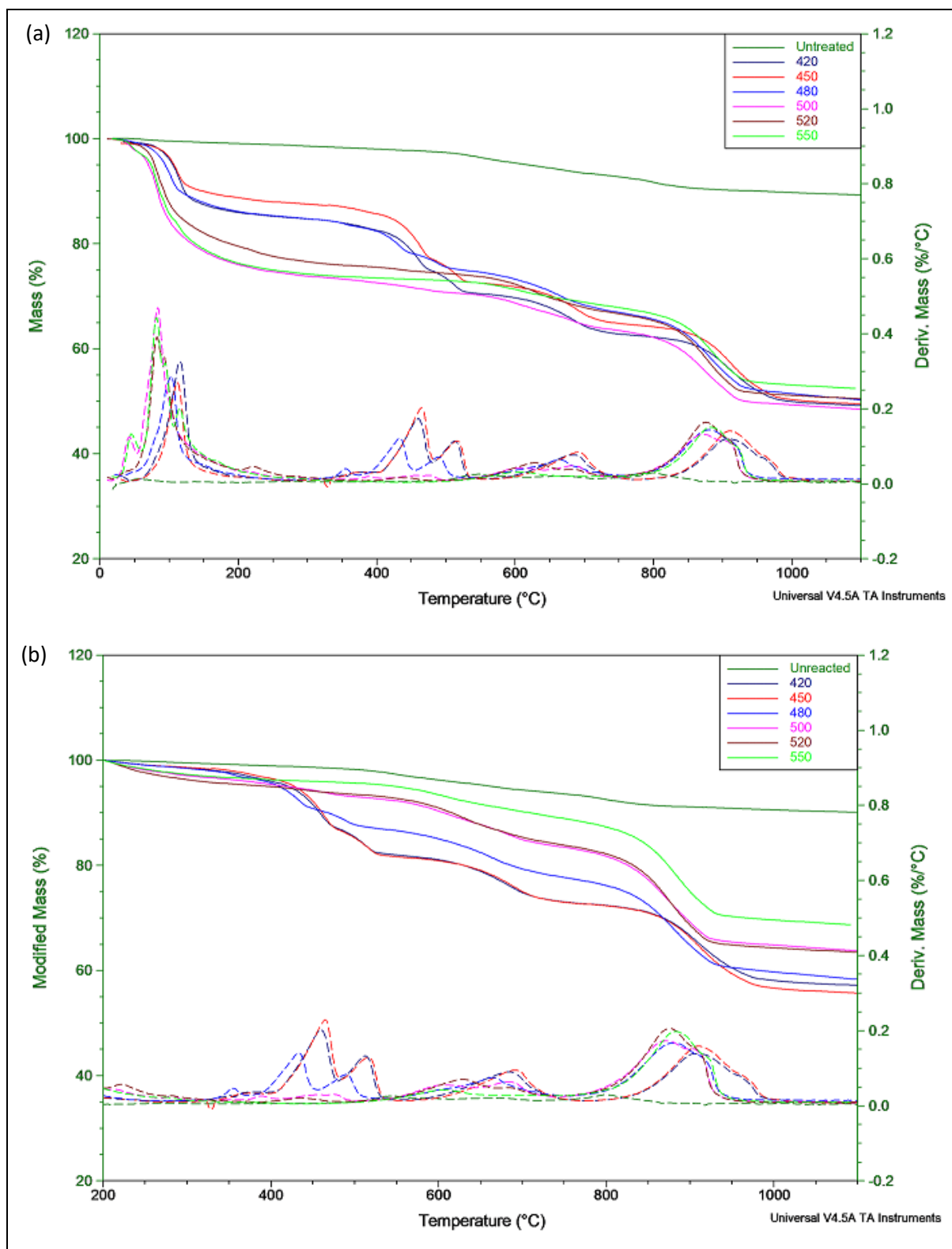


Figure 5.8: Comparison of TGA results (a) ambient – 1100°C and (b) recalculated from 200 - 1100°C for slimes (CS) reacted at a ratio of 2:3 CS:AS m/m at various furnace temperatures for 1 h.

Roast products formed above 500°C contained very few, or no ammonium species, as confirmed by the very small or absence of mass loss between 350 – 450°C. The samples roasted at 520°C and 550°C have a major mass loss above 800°C, indicating the presence of MgSO_4 as the main phase.

Comparisons of the tailings (CT) reacted at a ratio of 2:3 CT:AS, and roasted at different temperatures for 1 h are illustrated in Fig. 5.9.

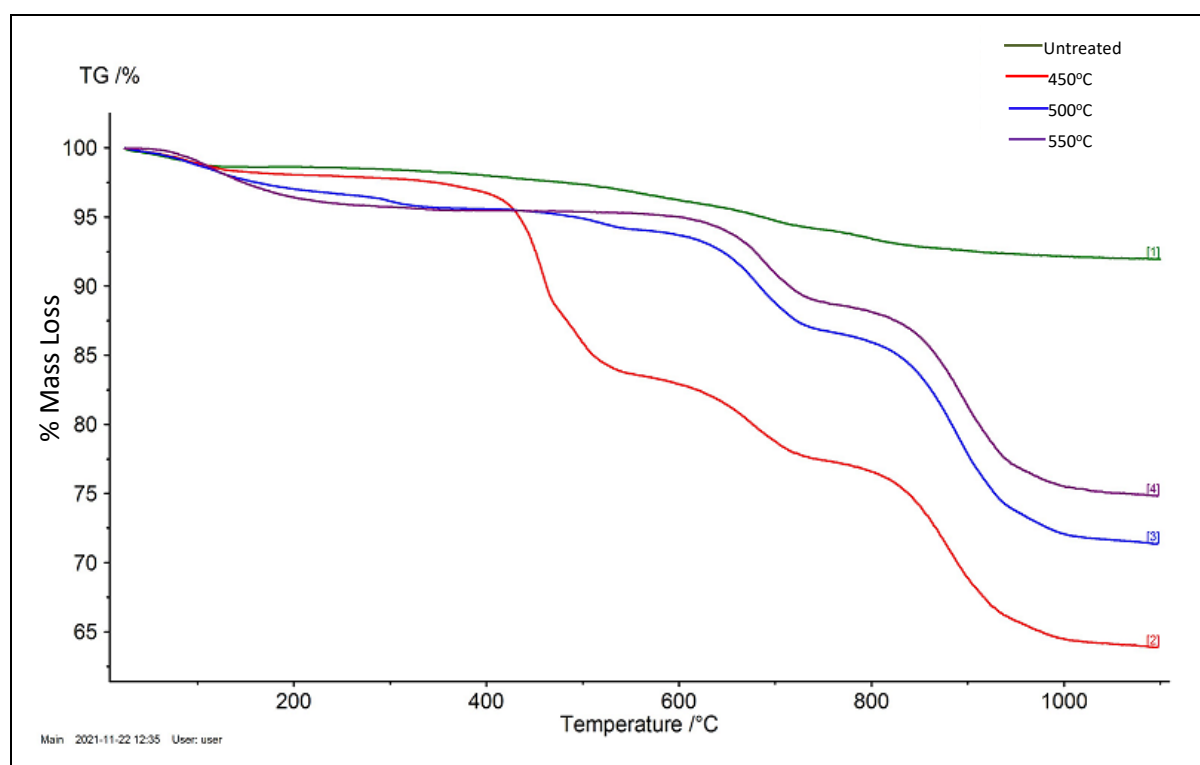


Figure 5.9: Comparison of tailings (CT) reacted at a ratio of 2:3 CS:AS for 1 h at various furnace temperatures.

Similar to the CS:AS thermograms, the CT:AS samples generated at the lower temperature (450°C) show a large mass loss between 350 – 450°C, corresponding to the presence of more ammonium-metal sulphate species, and supporting the XRD data (Table 5.8). This mass loss is absent in the samples roasted at 500°C and 550°C. Total mass loss also decreased with increased furnace temperature, indicating fewer hydrated and intermediate double salts. The major mass loss above 800°C is indicative of the presence of MgSO_4 , which supports the XRF data showing the mine tailings are rich in magnesium. The onset of decomposition of iron and aluminium sulphates occurs at temperatures

ranging between 500 – 600°C (Kolta and Askar, 1975; Bayer et al, 1982; Mohamed et al, 2016).

Thermogravimetric analysis of roast products obtained at different m/m ratios

When comparing different roast ratios for CS:AS, roasted at 450°C for 1 h (Fig 5.10a), the CS:AS of 2:6 had the greatest mass loss between 300°C - 450°C, indicating the thermal decomposition of ammonium sulphate, as well as the decomposition of the ammonium metal sulphates. This is not unexpected as it has the largest excess of AS relative to slimes, and several ammonium metal sulphates species were formed at a roasting temperature of 450°C (Table 5.8).

For the CT:AS thermograms (Fig 5.9b), the 3:5 ratio had the greatest mass loss between 300 – 450°C, which is unexpected as this ratio is only slightly greater than the 2:3 ratio (i.e. 2:3.33), which was calculated to be the required stoichiometric ratio. It could possibly be explained by the variability of the raw material and the small mass used to determine the thermograms (~20 mg).

The efficiency of the process and selection of the appropriate m/m ratio can only be quantified by subjecting the product of the thermochemical treatment to an optimised dissolution procedure.

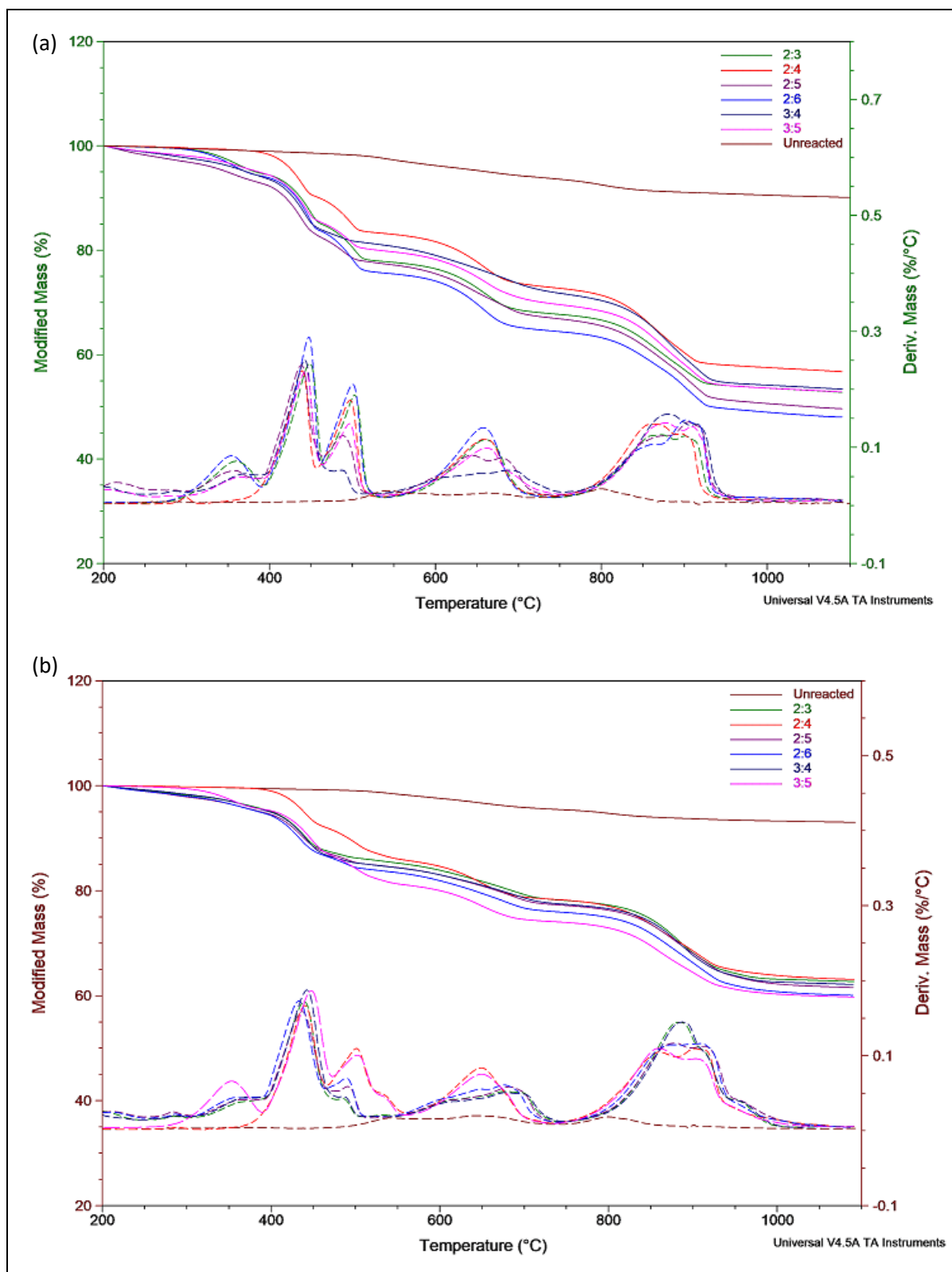


Figure 5.10: Comparison of various ratios of (a) CS:AS and (b) CT:AS, roasted at 450°C for 1 h.

Thermogravimetric analysis of roast products obtained at different m/m ratios after scaling up the starting masses of CS and AS

As larger volumes of leachate were required for the production of Mg containing products, to be reported in Chapter 9, the effect of upscaling the amounts of CS and AS during the roasting step was studied by TGA. The initial sample mass of CS was increased from 2 g to 8 g for these experiments, and CS:AS m/m ratios of 2:3, 2:4 and 2:6 were tested.

When scaling up the starting masses of CS and AS, after 1 h of roasting the samples were still fuming profusely. This was particularly evident with the 2:6 m/m ratio of CS:AS, which was not unexpected due to the AS being in considerable excess. Samples were therefore roasted until a constant mass was reached, with the mass of the samples being recorded after 1, 3, 4 and 7 h to determine the applicable duration for each m/m ratio. A comparison of the TGA curves of the products obtained after a 3 h roast and a 7 h roast is illustrated in Fig. 5.11.

The thermograms indicate clearly that the 3 h roast samples (Fig 5.11, solid lines) retained a substantial amount of AS, with mass losses ranging between 9.3% and 15.9% in the temperature range 300 – 450°C for the different m/m ratios (Mohamed et al, 2016). These mass losses decreased substantially to between 1.0% and 3.5% for the samples roasted for 7 h (Fig 5.11, dashed lines).

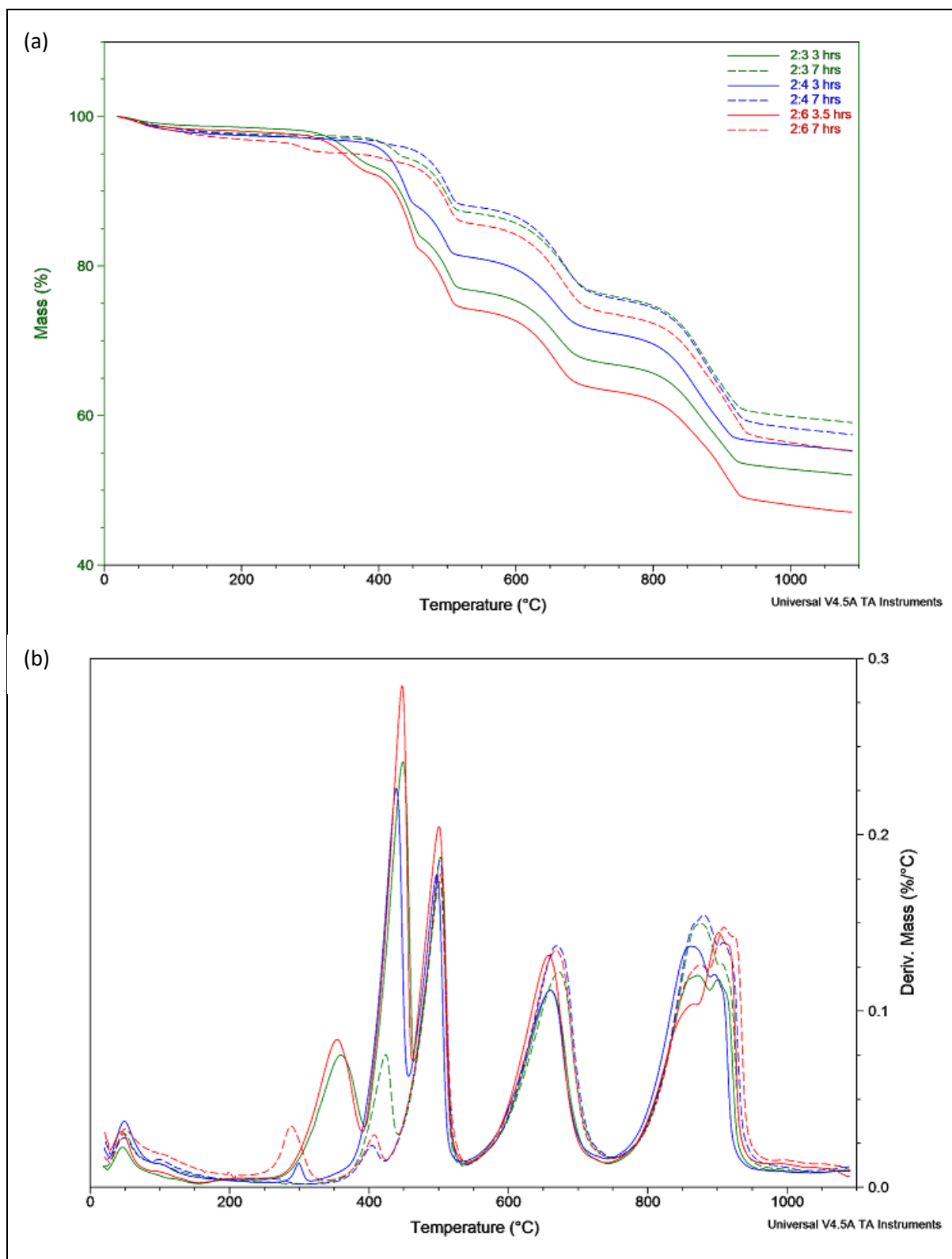


Figure 5.11: Comparison of (a) the %mass loss and (b) the derivative mass loss for 2:3, 2:4 and 2:6 CS:AS mass ratios upscaled to an initial mass of 8 g CS after roasting for 3 h and 7 h at 450°C.

The % mass loss for the various roast times when using 8 g CS compared to the mass loss of the original 1 h roast when using 2 g of CS is shown in Table 5.10.

Table 5.10: Comparison of mass losses after roasting at different ratios of CS:AS at 450°C when upscaling the reaction quantities vs the original mass loss for a small sample after 1 hr roast.

Ratio	% Mass Loss			
	Original 1 h	3 h roast	4 h roast	7 h roast
2:3	39.1 ± 1.2	35.3 ± 0.9	38.5 ± 0.8	39.7 ± 0.4
2:4	47.8 ± 0.9	38.2 ± 0.9	46.8 ± 0.3	49.2 ± 0.01
2:6	55.3 ± 1.6	53.2 ± 0.7	57.7 ± 0.2	60.6 ± 0.2

It is apparent that the 4 h roast samples had lost substantially more of the AS fraction than the 3 h roast, and the mass losses were not that different to the original 1 hr roast. The additional mass loss after 7 h was not large enough to justify an additional 3 h of roasting.

From these results, the duration of upscaled roasting experiments were increased to 4 h.

5.3.4 FTIR

FTIR analysis of products obtained at different roasting temperatures

The infrared analysis of the thermochemically treated samples, using a ratio of 2:3 CS:AS and 2:3 CT:AS at different temperatures are presented in Fig 5.12 and 5.13.

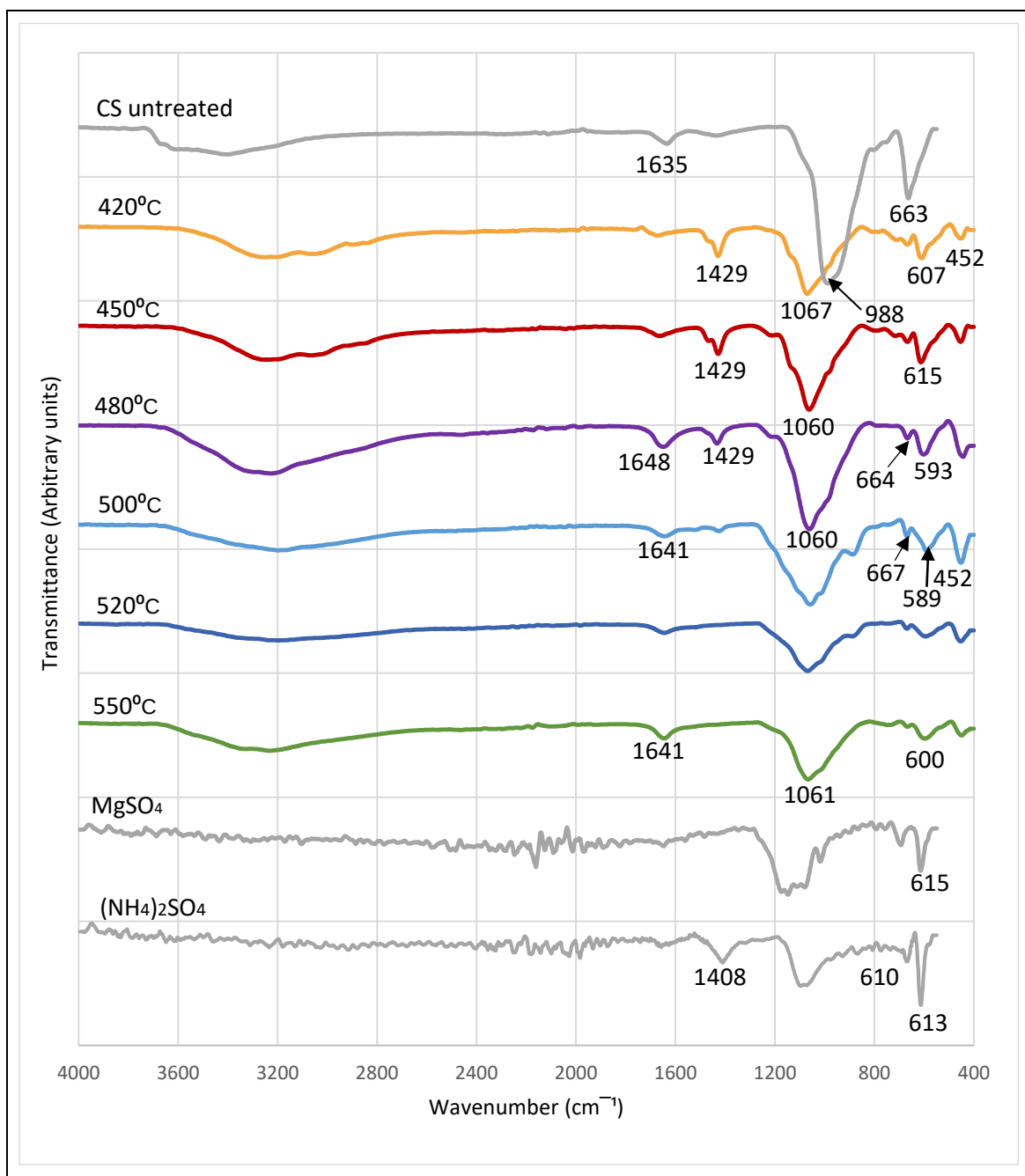


Figure 5.12: FTIR spectra comparing various roasting temperatures for CS:AS at a 2:3 m/m ratio.

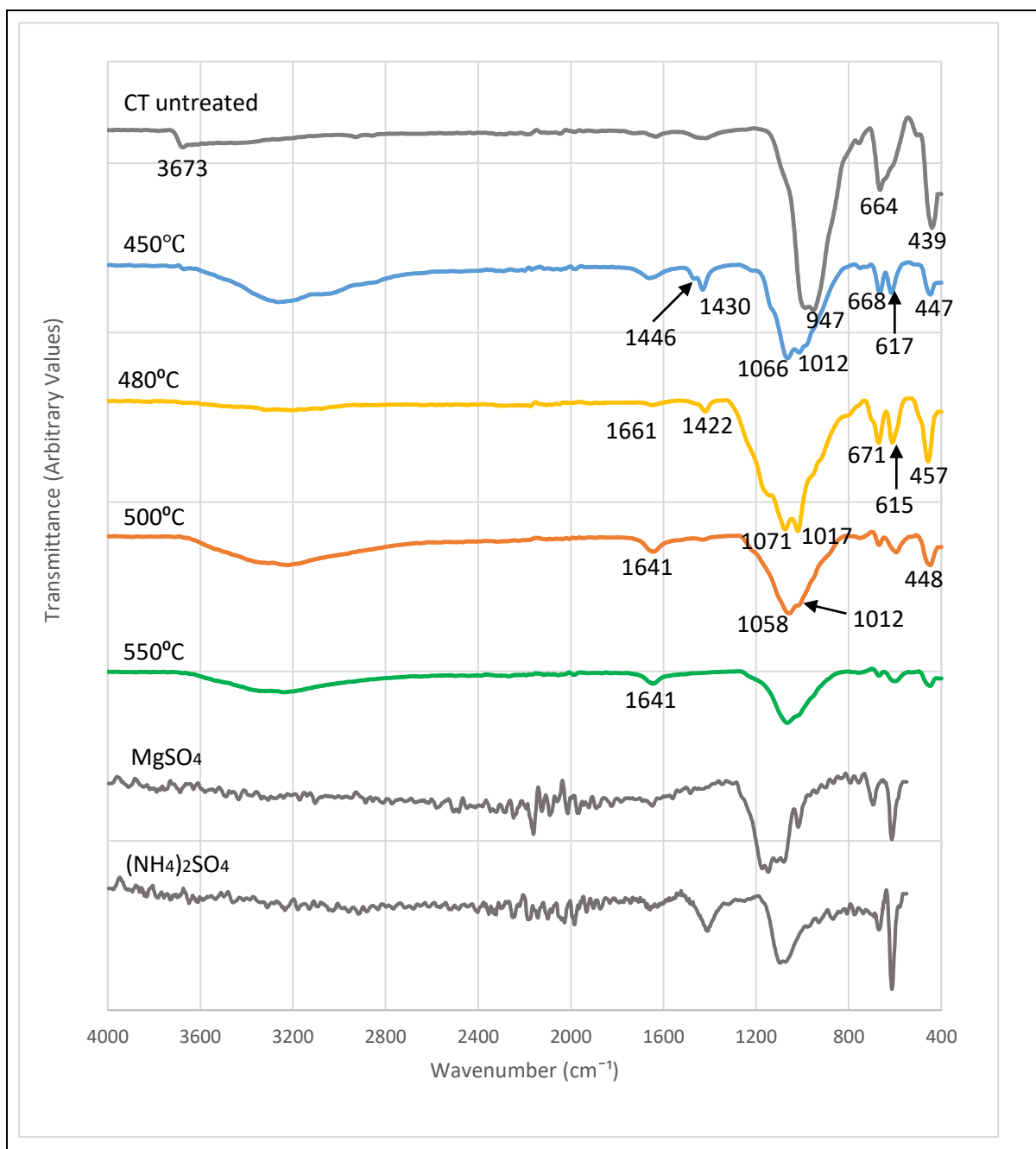


Figure 5.13: FTIR spectra for CT:AS at a 2:3 m/m ratio, roasted for 1 h at various temperatures.

The infrared analysis of the thermochemically treated samples, using a ratio of 2:3 CS:AS and 2:3 CT:AS at different temperatures (Fig 5.12 and 5.13), all show a distinctive peak in the region $1060 - 1067 \text{ cm}^{-1}$, which together with the peak at around 610 cm^{-1} , can be ascribed to the vibrations of the sulphate ion (Castleman et al, 2021), which is also illustrated by the pure MgSO_4 spectrum. The band observed at ca. 1429 cm^{-1} can be attributed to N – H bond movement (scissoring, bending) from hydrated ammonium metal sulphate species formed during the thermochemical treatment. This band is no longer visible at furnace temperatures of 500°C and above, which supports the XRD analysis (Table 5.8).

FTIR analysis of products obtained at different m/m ratios

The infrared analysis of the thermochemically treated samples, using different m/m ratios at a temperature of 450°C for 1 h are presented in Fig 5.14 and 5.15.

There are no apparent differences in the FT-IR spectra (Fig 5.14 and 5.15) when comparing CS:AS and CT:AS, thermochemically treated at 450°C for 1 h using different m/m ratios. The band associated with N – H bond movement (scissoring, bending) from hydrated ammonium metal sulphate species formed during the thermochemical treatment, observed at ca. 1430 cm^{-1} , is visible at all the different ratios, as is expected at a furnace temperature of 450°C .

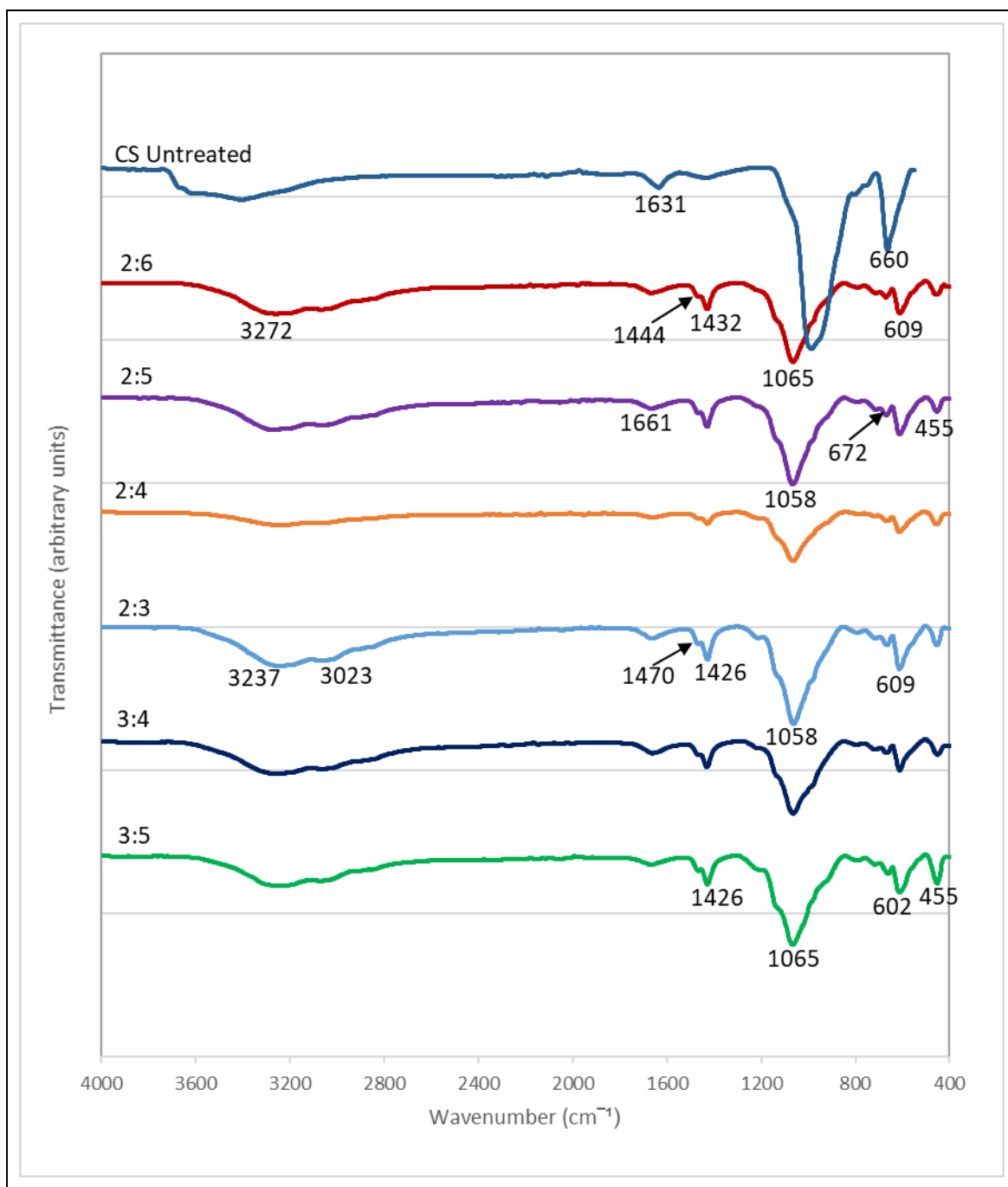


Figure 5.14: FTIR spectra comparing different ratios of CS:AS roasted at 450°C for 1 h.

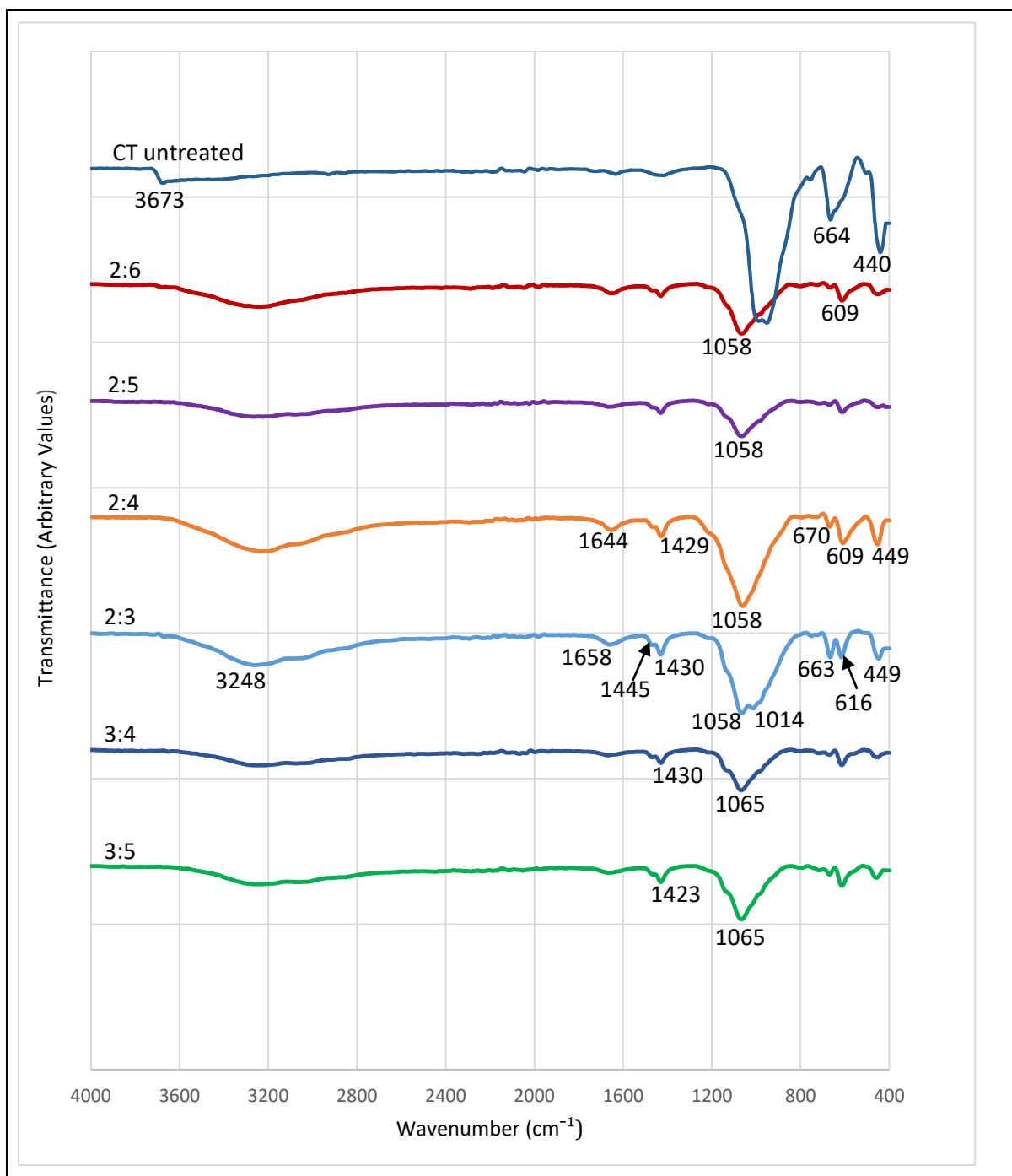


Figure 5.15: FTIR spectra comparing different ratios of CT:AS roasted at 450°C for 1 h.

5.3.5 Morphology of the thermochemically treated samples using FE-SEM

FE-SEM images of the untreated slimes (CS) and tailings (CT) and thermochemically treated samples are illustrated in Fig 5.16. SEM-EDX of thermochemically treated samples are shown in Fig 5.17.

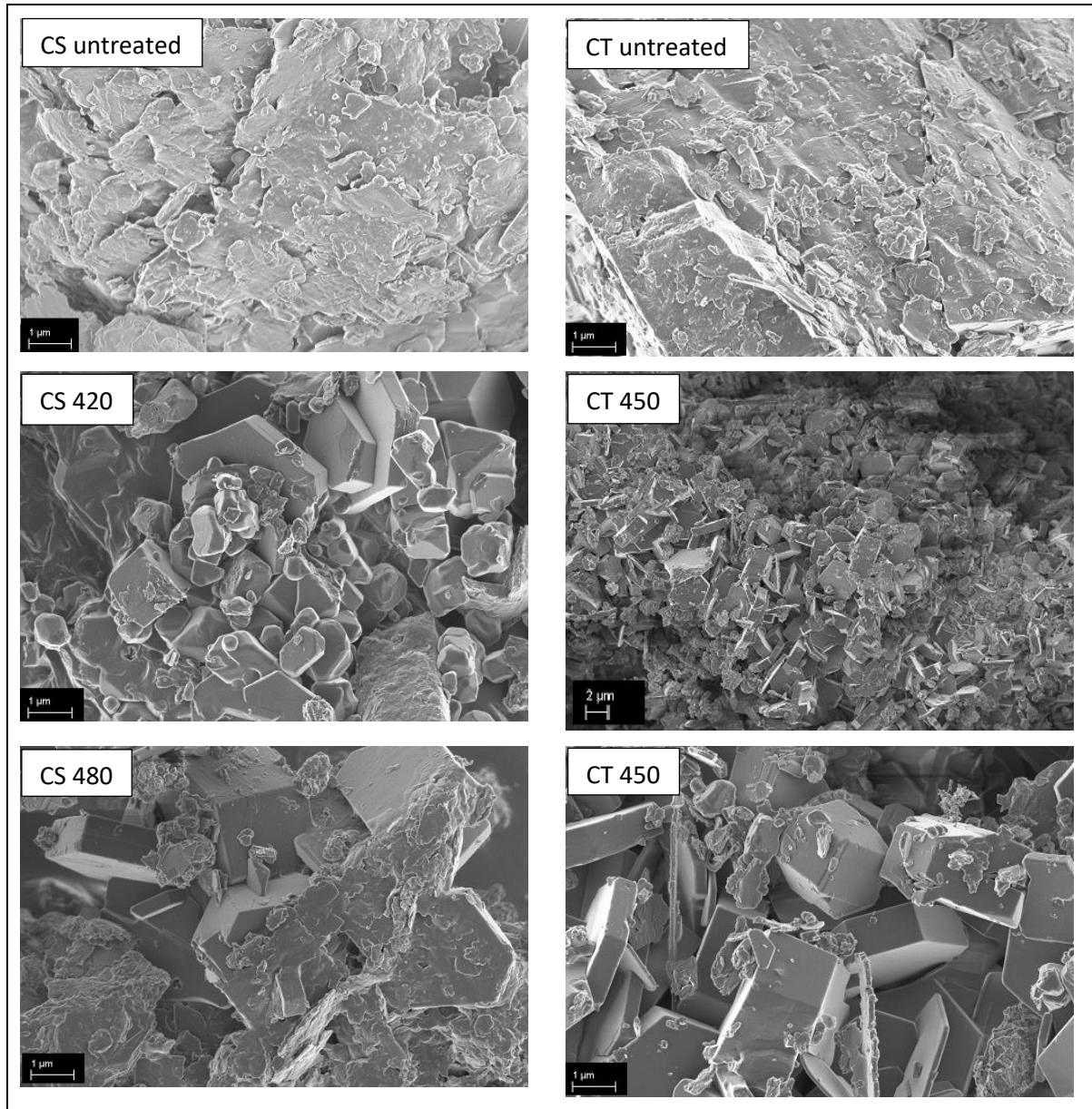


Figure 5.16: FE-SEM micrographs of untreated and thermochemically treated slimes (CS) and tailings (CT).

FE-SEM images of the untreated slimes (CS) and tailings (CT) showed that the samples were made up of individual, irregularly-shaped particles of varying sizes. The thermochemically treated samples however, revealed very different characteristics. The

unreacted, smooth irregularly-shaped particles were interspersed with numerous well-defined hexagonal structures (Fig. 5.16). These were either in clusters of variable sizes or found individually. Since metal sulphate crystals generally exhibit hexagonal shapes (Doucet et al, 2016), these can be considered to be metal (Mg, Al or Fe) sulphates, formed after thermochemical treatment with AS. This is supported by the elemental analyses determined by SEM-EDX (Fig 5.17), which indicate a large presence of the elements, sulphur (S) and oxygen (O).

At lower temperatures, the presence of some globular structures is also apparent (CS 420). These are possibly precursors to similar hexagonal structures, but requiring longer thermochemical reactions to convert into fully-shaped hexagons.

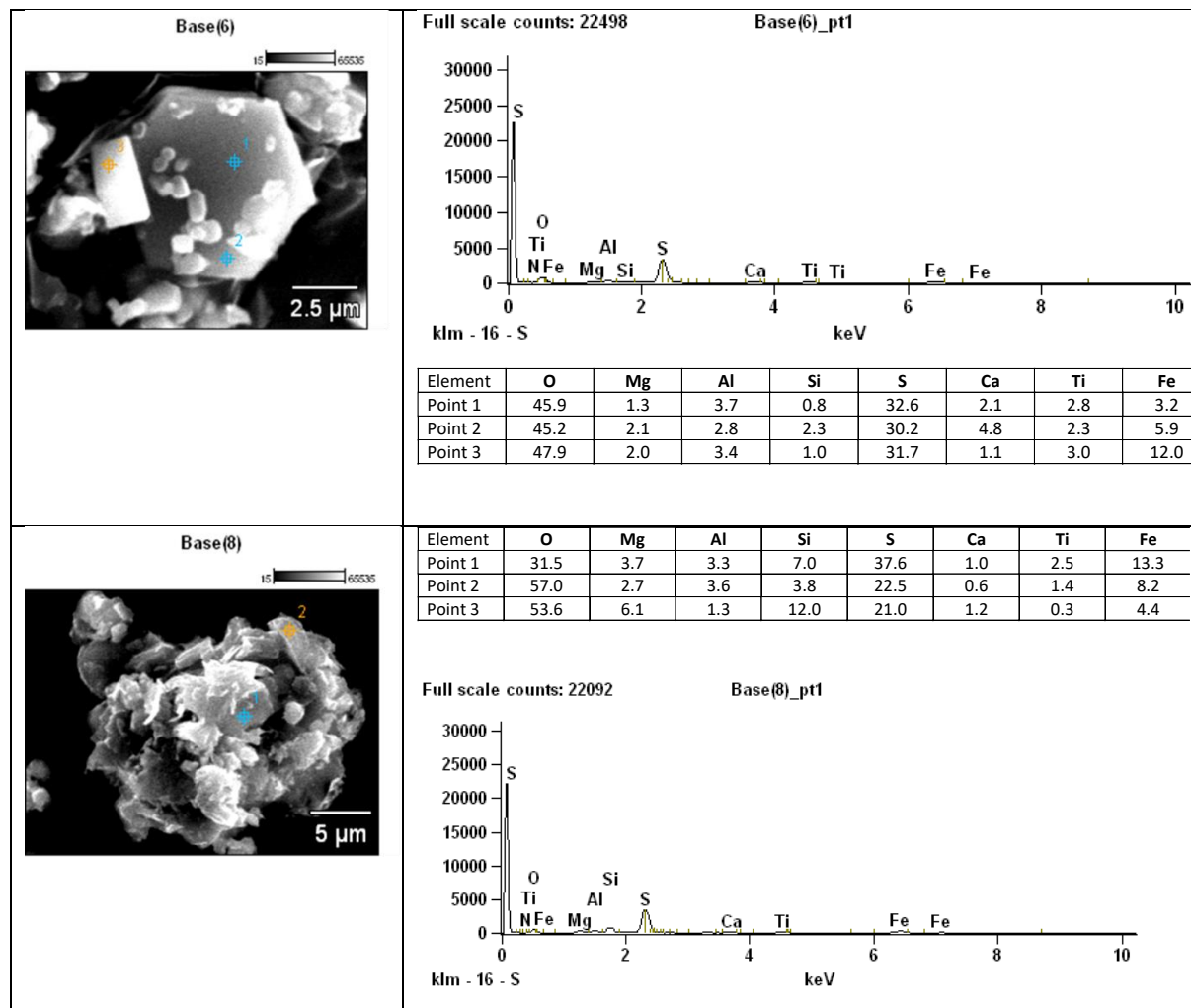


Figure 5.17: SEM-EDX of CS samples thermochemically treated at 450°C at a CS:AS ratio of 2:3 m/m for 1 h.

5.4 Conclusions

The results show that ammonium metal- and metal- sulphates are formed during the thermochemical treatment of slimes and tailings with ammonium sulphate, indicating the potential for extracting major elements from the tailings and slimes. Treatment at lower temperatures produced a hard product, which was difficult to remove from the crucibles, reducing possible yield. Treatment at higher temperatures produced fewer ammonium-metal sulphates and a softer, free-flowing product, but also indicated a decrease in sulphur content.

There were no major changes when the tailings and slimes were only treated thermally.

During the characterisation of the diamond mine tailings and slimes, it was noted that there was a relatively high concentration of talc, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, in the raw material (Table 4.2). As a possible product of the valorisation process of the slimes and tailings, talc could also be a source of magnesium. Although some studies have concluded that the talc does not react with the ammonium sulphate (Bayer et al, 1982; Lavikko and Eklund, 2016b), other studies have reported the extraction of Mg from talc (Sanchez et al, 1996). This led to the investigation into whether the talc in the tailings and slimes could be included as a source of magnesium, and if not, whether it remains structurally intact and can be recovered as a valorisation product with useful properties and quality.

Chapter 6: Investigation into the reactivity of talc when subjected to thermochemical treatment with ammonium sulphate

Sections of this work have been published by Castleman et.al., "Thermochemical purification of talc with ammonium sulphate as chemical additive", Minerals Engineering, 164 (2021) 106815. Available online <https://doi.org/10.1016/j.mineng.2021.106815>.

6.1 Introduction

During the characterisation of the diamond mine tailings and slimes, it was noted that there was a relatively high concentration of talc, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, in the raw material (Table 4.2). As a possible product of the valorisation process of the slimes and tailings, talc could also be a source of magnesium. Lavikko and Eklund (2016b) studied the extraction of Mg with the ÅA route method (i.e. ammonium sulphate process) from two talc samples, but did not ascertain whether the structure and chemical properties of the talc remain unaltered. These authors reported the mineralogical (XRD) and elemental composition (XRF) of their talc samples, % MgO by SEM-EDX before and after roasting and leaching, and ICP-OES of the leachate solution to determine concentration of Mg before, during and after fractional precipitation. They concluded that talc was unreactive as there was almost no difference in the % MgO by SEM-EDX before and after roasting and leaching. Bayer et al (1982) reported that talc showed practically no reaction with $(\text{NH}_4)_2\text{SO}_4$, although reaction conditions are not given. Based on these results, the conclusion was that talc is not reactive. However, Sanchez et al (1996) reported up to 80% extraction of magnesium from talc, after the talc samples were ground for 3 h and then subjected to acid leaching. This is explained by the talc being transformed from its crystalline state into a disordered state by dry grinding in a planetary ball mill, within about 30 min. The structural modification was emphasised by the extended grinding process which altered the environmental structure surrounding the magnesium within the talc crystal. This disordering of the structure allows for relatively easy magnesium extraction by the acid solutions.

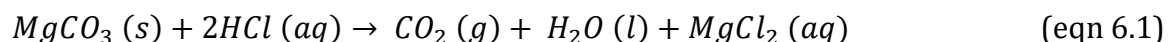
In this part of the study, the reactivity of talc was investigated to exclude it as a potential contributor of magnesium and to ensure that the structure of the talc was not compromised during the process used. Due to the high talc content of the diamond tailings and slimes (25 – 30%), if the talc does not react with AS to extract the Mg, it would remain as part of the solid residue after dissolution. This would have a negative effect on the extraction efficiency of magnesium. On the other hand, if the talc contained in the tailings and slimes remains unaltered following the thermochemical treatment with AS and leaching, it could be considered a possible product of the beneficiation process. As talc finds many applications in the plastic, ceramic, paint and paper industries, it would need to be purified to be considered a product of the beneficiation process. It was therefore necessary to determine, using the thermochemical process with AS, whether talc would be a source of Mg, or a possible product of valorisation. If the latter, the thermochemical processing of talc could provide a means to purify the talc.

Due to the complexity of the mine tailings and slimes, a talc sample, containing fewer phases, was sourced commercially for this investigation.

6.2 Material tested and process overview

The talc sample (Talc_{Cimpure}) was sourced from the Scotia Talc Mine, which is located near Barberton in the province of Mpumalanga, South Africa, and was characterised by a variety of complementary analytical techniques, i.e. XRD, TGA, FTIR and SEM. The XRD analysis revealed that Talc_{Cimpure} contained 33.5% m/m talc and a substantial amount of accessory (gangue) minerals, including chlorite, lizardite and carbonate containing minerals, in the form of magnesite, calcite and dolomite (Table 6.1). These are common impurities found in industrial talc although their combination and concentrations depend on the origin of the sample (Alonso et al, 1991, Castillo et al, 2014). The talc content of Talc_{Cimpure} was too low to ascertain its reactivity with AS during thermochemical treatment, and the carbonate containing phases would react with AS. The carbonate containing minerals were therefore removed by pre-treating the sample with an excess of 10% HCl solution (Fig 6.1), until there was no further evidence of effervescence. All three minerals should react completely (Abali et al, 2006; Castillo et al, 2011; Özdemir et

al, 2009; Pokrovsky et al, 2009) to form the chloride salt of the metal, and carbon dioxide (Eqn. 6.1).



Using the data from the XRD analysis (Table 6.1), it was anticipated that approximately 52% of the sample mass should be lost. The residue was filtered, rinsed thoroughly with distilled water and dried at 100°C, which resulted in a mass loss of 52.4%. This concentrated the talc in the sample to 67.8%. This sample was labelled Tal_{HCl}.



Figure 6.1: Impure talc reacting with 10% HCl solution to remove carbonate minerals.

Tal_{HCl} was then treated in the same way as the mine tailings (CS and CT) samples, to determine whether the extraction of magnesium was possible. This involved using the same multistep process used for the mine slimes, entailing the combination of a thermochemical solid-solid treatment step with ammonium sulphate (AS), using a 2:3 m/m ratio at 450°C for 60 min (Nduagu et al, 2012; Mohamed et al, 2016), followed by aqueous dissolution and filtration. The thermochemical reaction of Tal_{HCl} with AS generated Tal_{AS} as reaction product.

The quantity of AS used represented a stoichiometric excess in relation to the total content of magnesium in the Tal_{HCl} and lizardite, and Al in kaolinite. The temperature was selected to ensure that AS loss was minimised during thermochemical treatment, allowing AS to be recycled at a subsequent stage. The selected duration of the thermochemical treatment ensured good flowability of the powdered reaction product after the thermochemical treatment.

At completion of the thermochemical treatment, the product of the reaction (Tal_{AS}) was leached in deionised water or aqueous sulphuric acid solution (pH 1) at a solid: liquid ratio of 3 g/100 mL for 3 h at 50°C. The Tal_{HCl} sample (i.e. not thermochemically treated) was also leached in both deionised water or sulphuric acid, and used as controls.

A summary of the treatment process is shown in Figure 6.2. The solid phases highlighted in grey were analysed by XRD, XRF, TGA, FTIR and FE-SEM.

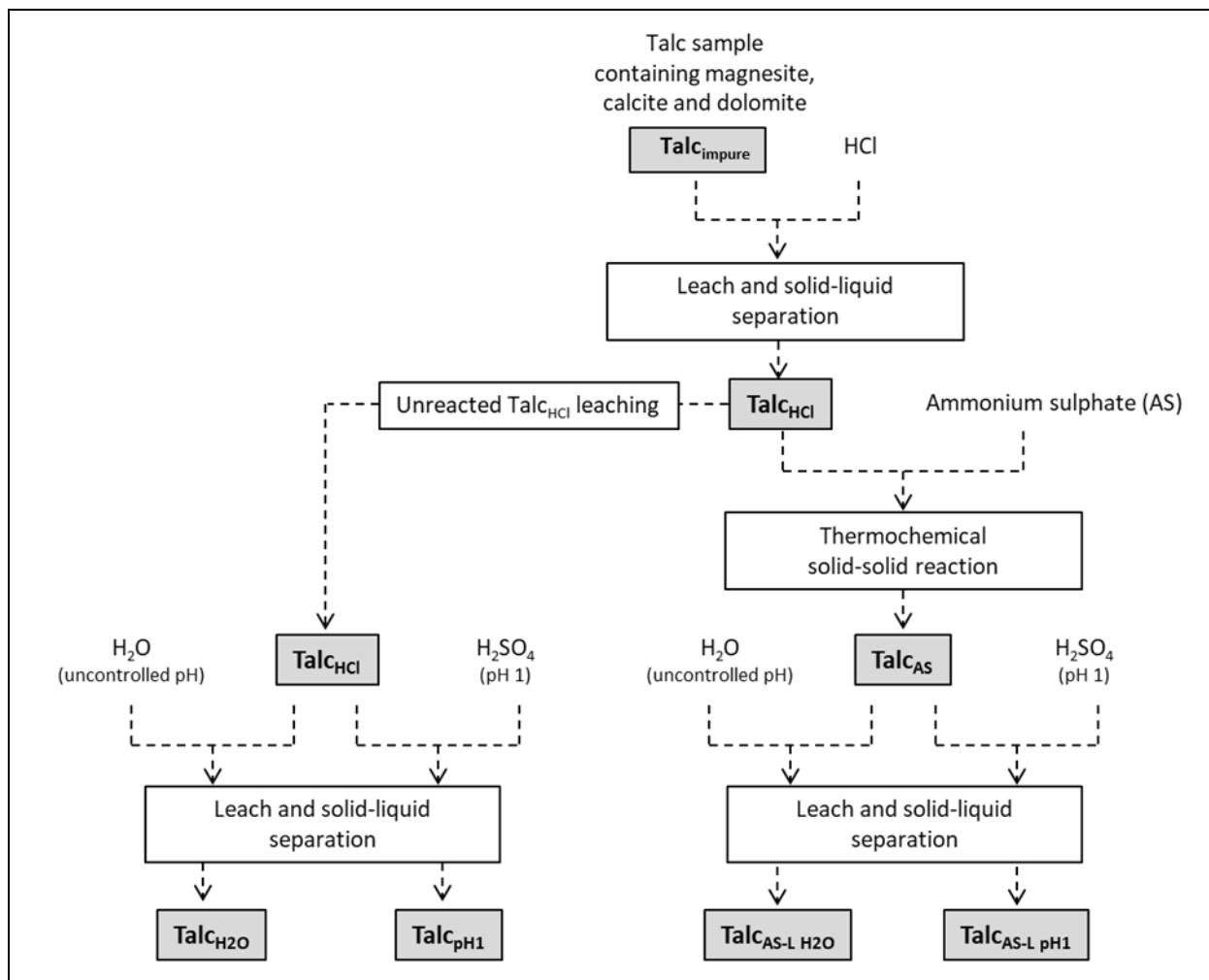


Figure 6.2: Process flow diagram for pre-concentration, direct leaching (Control) and thermochemical treatment followed by leaching (Treatment) of talc-bearing samples. Aqueous phases are not included.

6.3 Chemical and Mineralogical compositions of parent talc, Talc_{HCl}, Talc_{AS} and leach residues

The chemical and mineralogical compositions of the parent talc sample (Talc_{impure}), concentrated parent talc sample (Talc_{HCl}), Talc_{HCl} thermochemically treated with AS (Talc_{AS}), the leach residues generated from leaching Talc_{AS} in water or H₂SO₄ (Talc_{AS-L H2O} and Talc_{AS-L pH1}), and the 'control' leach residues following leaching of Talc_{HCl} in either water or H₂SO₄ (Talc_{H2O} and Talc_{pH1}) are presented in Figure 6.3 and Tables 6.1 and 6.2.

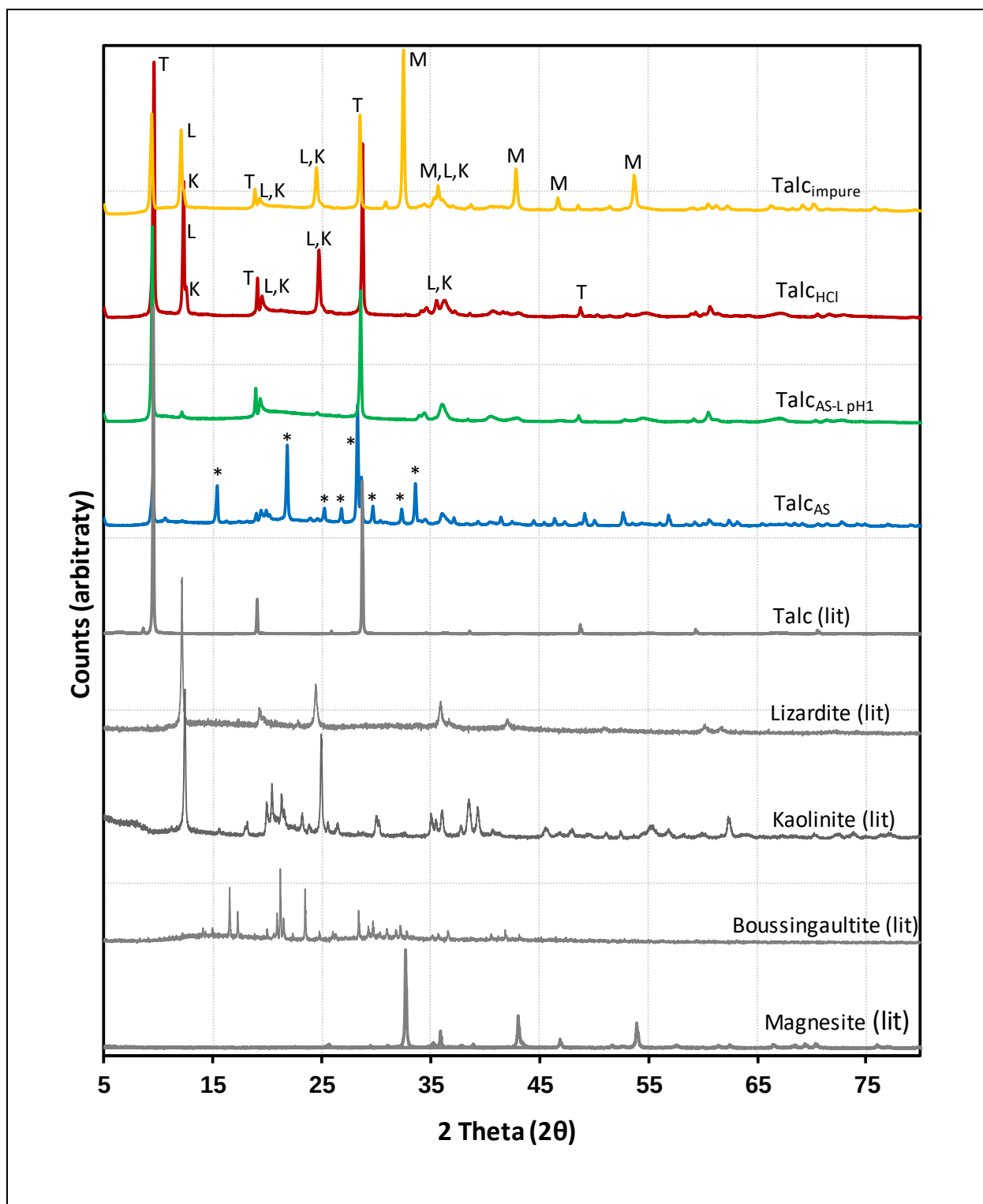


Figure 6.3: XRD patterns of Talc_{impure} (yellow), Talc_{HCl} (red), Talc_{AS} (blue) and Talc_{AS-L pH1} (green). Theoretical patterns of individual phases are also included (grey). T: talc, M: magnesite, L: lizardite, K: kaolinite. Peaks attributed to formation of sulphate species during thermochemical reaction are indicated with asterisks (*).

Table 6.1: Semi-quantitative mineralogical compositions (%m/m) of Talc_{Cimpure}, Talc_{HCl}, Talc_{CAS-L pH 1}, Talc_{H2O} and Talc_{pH1}.

Mineral	Chemical Composition	Talc _{Cimpure}	Talc _{HCl}	Talc _{CAS-L pH 1}	Talc _{pH1}	Talc _{H2O}
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	33.5	67.8	98.8	80.2	67.7
Magnesite	MgCO ₃	47.0	-			
Lizardite	Mg ₃ Si ₂ O ₅ (OH) ₄	8.3	17.2	1.2	17.0	21.6
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	3.9	11.0	-	2.3	7.6
Dolomite	CaMg(CO ₃) ₂	3.3	-			
Quartz	SiO ₂	1.4	2.9	-	0.5	2.1
Calcite	CaCO ₃	1.2	-			
Magnetite	Fe ₃ O ₄	0.9	1.8	-	-	1.1

Table 6.2: Chemical composition (%m/m) of Talc_{Cimpure}, Talc_{HCl}, Talc_{CAS}, Talc_{CAS-L pH 1} and Talc_{pH1}, as determined by XRF using the standard fused bead analysis.

Elements detected	Mass %					
	Theoretical pure Talc	Talc _{Cimpure}	Talc _{HCl}	Talc _{CAS}	Talc _{CAS-L pH1}	Talc _{pH1}
SiO ₂	63.4	27.6	58.6	31.6	70.1	59.0
MgO	31.9	36.5	30.2	16.6	20.5	30.3
Fe ₂ O ₃		4.1	1.8	1.1	1.8	1.8
Al ₂ O ₃		0.1	nd	0.02	nd	0.05
CaO		0.6	0.01	0.1	0.01	nd
TiO ₂		0.01	0.02	0.01	0.01	0.02
Total	95.3	97.2	99.3	100.0	99.6	100.0
LOI	4.8	28.2	8.7	50.6	7.2	8.8

nd = below the analytical detection range, does not imply zero %

Minor amounts (<0.06%) of K₂O, Na₂O, P₂O₅ and MnO were detected in Talc_{Cimpure}

The parent talc sample (Talc_{impure}) obtained from the Scotia Talc Mine contained 33.5% m/m talc and a substantial amount of carbonate materials (47.0% magnesite, 3.3% dolomite and 1.2% calcite), as well as 8.3% lizardite, 3.9% kaolinite and minor quantities of quartz and magnetite (Table 6.1 and Fig. 6.3). The XRF analysis of Talc_{impure} reported 27.6% SiO₂, 36.5% MgO and 4.1% Fe₂O₃ and a loss on ignition (LOI) of 28.2% (Table 6.2). The high LOI value was due to the loss of CO₂ and H₂O upon heating to 1000°C. The loss of CO₂ from the decomposition of the carbonate phases (51.5% m/m in total, as determined by XRD), would amount to approximately 26 – 27%. The remaining mass loss can be attributed to dehydroxylation of the lizardite, kaolinite and talc (Bayer et al, 1982; Földvári, 2011).

The diffraction patterns with the identified phases are illustrated in Fig. 6.3, which clearly indicate that there was magnesite in the Talc_{impure} sample, which was then removed by reaction with hydrochloric acid to form the talc concentrate (Talc_{HCl}). The presence of lizardite, Mg₆Si₄O₁₀(OH)₈ and kaolinite, Al₂Si₂O₅(OH)₄ is also apparent in Talc_{impure}, and remain after treatment with HCl (Talc_{HCl}). This was confirmed by the FT-IR spectra in Fig 6.6, where Talc_{impure} is also compared to spectra from the literature.

XRD analysis of the talc concentrate (Talc_{HCl}), shows that the carbonate phases, originally present in Talc_{impure}, have been removed following HCl treatment (Table 6.1; Fig 6.3).

Its mineralogy consisted of talc (Mg₃Si₄O₁₀(OH)₂; ~68%), with smaller quantities of lizardite (Mg₃Si₂O₅(OH)₄; ~17%) and kaolinite (Al₂Si₂O₅(OH)₄; ~11%). From XRF, Talc_{HCl} was composed of approximately 58.6% SiO₂, 30.2% MgO and 1.8% Fe₂O₃, and had a LOI of 8.7% (Table 6.2). The 30.2% MgO corresponds to the magnesium content of the lizardite (contributes ~7.5% MgO) and talc (contributes ~21.7% MgO) phases.

Thermochemical treatment of Talc_{HCl} with AS generated Talc_{AS} as reaction product (Fig. 6.2). The mineralogical analysis of Talc_{AS} revealed talc as the main mineral phase (Fig. 6.3). The XRD pattern exhibited the presence of new peaks, which were attributed to metal sulphate (hexahydrate, MgSO₄·6H₂O: millosevichite, Al₂(SO₄)₃) and/or ammonium metal sulphate species (efremovite, (NH₄)₂Mg₂(SO₄)₃; boussingaultite, (NH₄)₂Mg(SO₄)₂·6H₂O). The lizardite and kaolinite reflections at 2θ values of 12° and 25° were nearly absent from the XRD pattern, which suggested that these phases had reacted with AS to produce the newly formed sulphate species. Semi-quantitative XRD analysis

could not be performed on Talc_{AS} due to the unavailability of suitable powder diffraction files (JCPDF) for some of the ammonium metal sulphate species, e.g. *sabieite* (NH₄)Fe(SO₄)₂. From XRF, the large LOI for Talc_{AS} (Table 6.2) can be attributed to the loss of ammonia and sulphate (as SO₃) during the decomposition of the ammonium - metal and metal sulphate containing phases, as well as the dehydroxylation of talc. This LOI was supported by the TGA mass loss at 1000°C (Fig. 6.5).

XRD analysis of the leach residue (Talc_{AS-L pH1}) obtained from the dissolution of Talc_{AS} in H₂SO₄ at pH = 1 (Table 6.1, Fig 6.3) and the Talc_{AS-L H2O} obtained from its dissolution in deionised water, featured distinctive reflections at 2θ values of 10°, 19° and 29°. These reflections indicated the composition of talc (> 98%), with traces of lizardite and kaolinite, and the absence of the sulphate species identified in Talc_{AS}. These results showed that the talc content in the parent sample could be further concentrated from 68% in Talc_{HCl} to 98% in Talc_{AS-L pH1} or Talc_{AS-L H2O}. Talc_{AS-L H2O} results are not shown in Table 6.1 as they were very similar (talc 98.0%; lizardite 2.0%) to those of Talc_{AS-L pH1}. This degree of purification could not be achieved with the pre-concentration step in 10% m/m HCl performed on the original talc sample.

The XRF result for Talc_{AS-L pH1} or Talc_{AS-L H2O} has a higher SiO₂ content than would be expected from the 98% talc reported by XRD. This could be due to the Si from lizardite (3.4%) and kaolinite (2.4%), which does not form soluble sulphates (0.9 – 3.2 mg/L from ICP-OES data, n = 6) and should remain in the leach residue.

6.4 Thermogravimetric analysis of parent talc, Talc_{HCl} , Talc_{AS} and leach residues

A comparison of the thermogravimetric analysis of the parent talc ($\text{Talc}_{\text{Cimpure}}$) and concentrated parent sample (Talc_{HCl}), is given in Fig. 6.4.

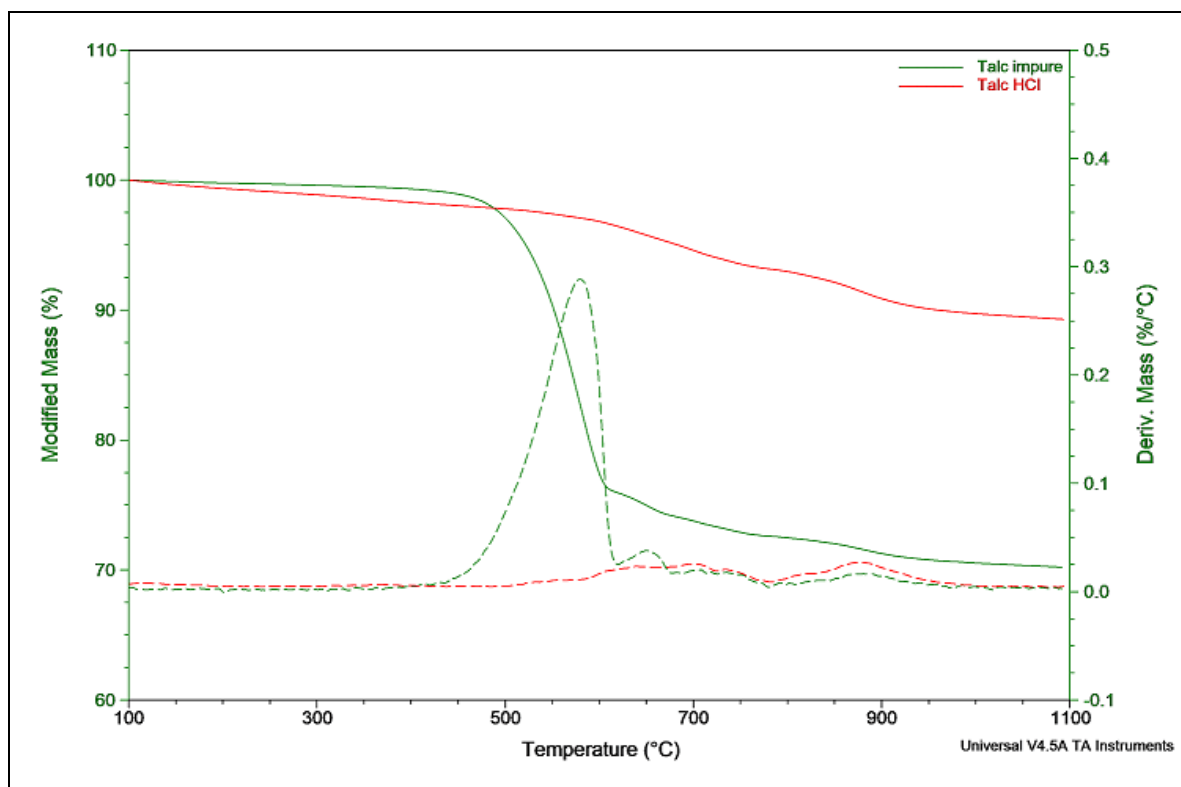


Figure 6.4: Comparison of TGA analyses of $\text{Talc}_{\text{Cimpure}}$ and Talc_{HCl} .

Thermogravimetric analysis of $\text{Talc}_{\text{Cimpure}}$ produced a total mass loss of 29.8% at 1000°C, which correlates well with the LOI obtained from XRF (Table 6.2). The major mass loss of 23.7% between 450 – 620°C can be attributed to the decarboxylation of magnesite, and translates into a magnesite content of 45% in the $\text{Talc}_{\text{Cimpure}}$ sample, which supports the XRD results (47%, Table 6.1).

The smaller mass losses of 2.5% between 620 – 680°C and 1.6% between 680 – 780°C can be assigned to the dehydroxylation of kaolinite plus the first decarboxylation of dolomite, and the dehydroxylation of lizardite respectively. The mass loss of 2.0% between 780 – 950°C represents the second decarboxylation of dolomite and the

dehydroxylation of talc (Földvári, 2011). The temperature ranges for these mass losses are not quite where that of the pure phases would occur due to the curves shifting when there is a combination of minerals in a sample (Van der Merwe and Strydom, 2004), making it difficult to differentiate between these minerals.

Thermogravimetric analysis of Tal_{HCl} (Fig 6.4) indicated a total mass loss of 8.1% between ambient temperature and 1000°C, which confirmed the LOI value of 8.7% (Table 6.2). It also showed a mass loss of 3.3% between 792 and 894°C, which was attributed to the dehydroxylation and structural decomposition of talc into enstatite (MgSiO_3) and cristobalite (SiO_2), as shown by Eq. (2) (Nakahira and Kato, 1963; de Souza and Yada, 1988; Földvári, 2011).



The theoretical mass loss for the dehydroxylation of talc according to Eq. (2) is 4.75%. The mass loss associated to dehydroxylation of talc in Tal_{HCl} (3.3%) therefore corresponds to a talc content of 68.8%. This result supports the XRD analysis (68%, Table 6.1). A combined mass loss of 3.8% was also observed between 550 – 650°C and 600 – 780°C. These two regions correspond to the dehydroxylation of kaolinite (500 – 590°C) and lizardite (600 – 700°C) (Bayer et al, 1982; Földvári, 2011), which indicates a total content of 29.4% for these two mineral phases. The mineralogical compositions of Tal_{HCl} , derived from TGA and XRD were therefore similar.

TGA analysis of Tal_{CAS} , $\text{Tal}_{\text{CAS-L pH1}}$ and $\text{Tal}_{\text{CAS-L H}_2\text{O}}$ were also performed, to complement the XRD results. The results were compared to the TGA curve of Tal_{HCl} (Fig. 6.5A).

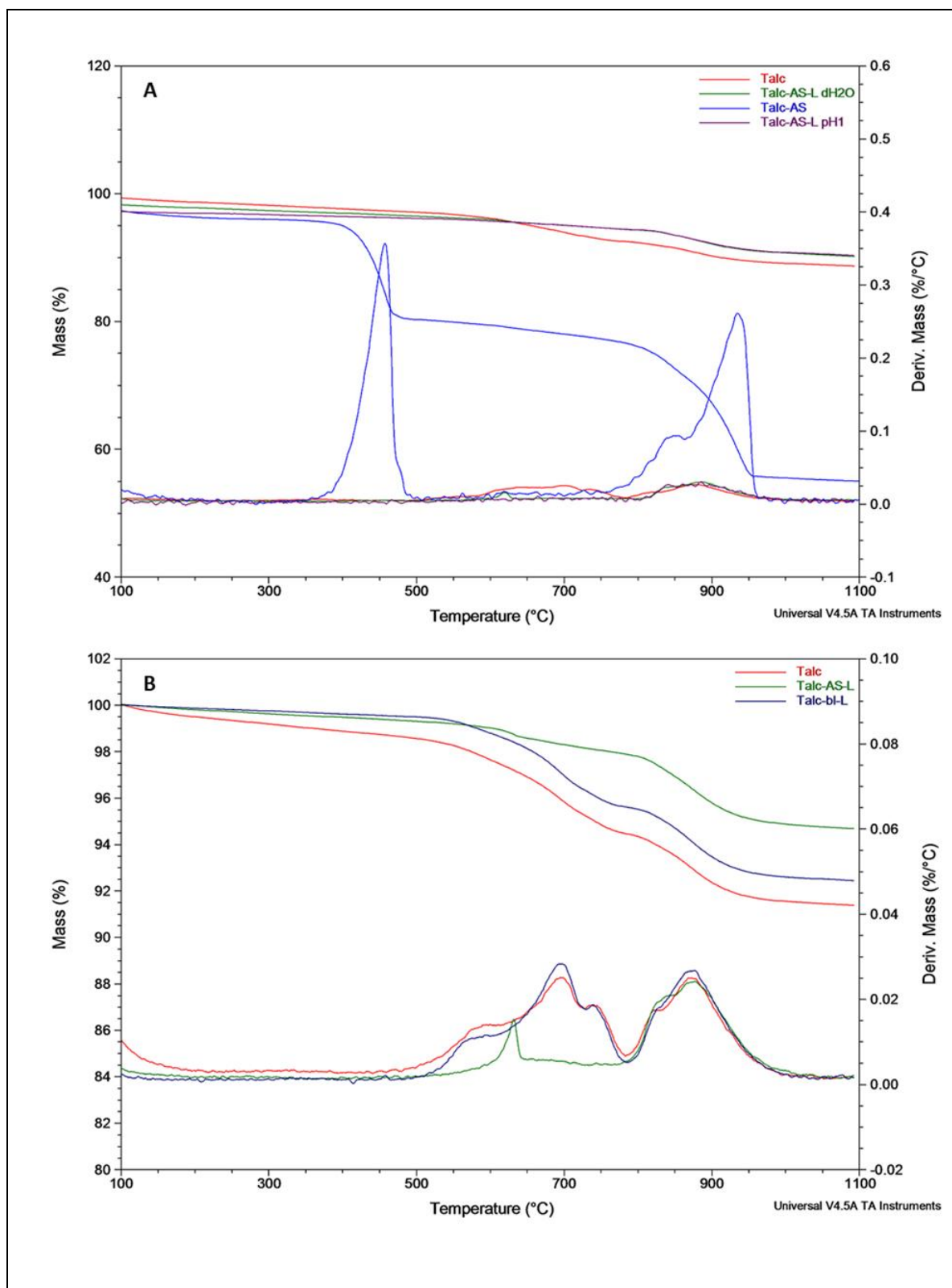


Figure 6.5: (A) Comparison of TGA of Talc_{HCl} (red) with Talc_{AS} (blue), Talc_{AS-L H₂O} (green) and Talc_{AS-L pH1} (purple), and (B) comparison of TGA of Talc_{HCl} (red) with Talc_{AS-L H₂O} (green) and Talc_{H₂O}, (control; navy).

The mass losses for $\text{Talc}_{\text{AS-L pH1}}$ and $\text{Talc}_{\text{AS-L H2O}}$ were identical (Fig. 6.5A), and are therefore discussed jointly. The mass loss observed between 400 – 470°C for Talc_{AS} (Fig 6.5A) was caused by the thermal decomposition of excess, unreacted AS remaining in the sample (Mohamed et al, 2016). Mass losses obtained between 800 and 1000°C correspond to dehydroxylation of talc and the loss of SO_3 (Scheidema and Taskinen, 2011), from the decomposition of the metal and ammonium-metal phases formed from the lizardite and kaolinite during thermochemical treatment with AS.

Fig. 6.5B illustrates the thermal behaviour of Talc_{HCl} vs $\text{Talc}_{\text{AS-L H2O}}$ vs Talc_{H2O} (Talc_{HCl} leached in H_2O control sample). All TGA curves showed an identical mass loss between 850°C and 1000°C, which is the temperature at which talc dehydroxylation occurs. This demonstrated that the amount of talc in Talc_{HCl} and Talc_{H2O} had not been altered by the thermochemical treatment with AS and leaching process, i.e. that talc had not reacted with AS under the thermal condition tested. The finding was further confirmed by the identical DTG curves obtained for these three samples between 850°C and 1000°C. This mass loss of ca. 3.8% indicated a talc content of ca. 80%, which agreed with the recorded mass of the leach residues, which represented 80.5% of the original Talc_{HCl} sample mass before reaction with AS. The curves for Talc_{HCl} and Talc_{H2O} also displayed a small mass loss between 550 – 600°C and 600 – 750°C, which is the region in which kaolinite (500 – 590°C) and lizardite (600 – 700°C) are known to dehydroxylate (Bayer et al, 1982; Földvári, 2011).

6.5 FTIR analyses of parent talc, Talc_{HCl} , Talc_{AS} and leach residues

Comparison of the FTIR spectra of $\text{Talc}_{\text{Cimpure}}$, Talc_{HCl} , Talc_{AS} , and $\text{Talc}_{\text{AS-L}}$ to reference spectra from the literature is presented in Fig. 6.6 and 6.7.

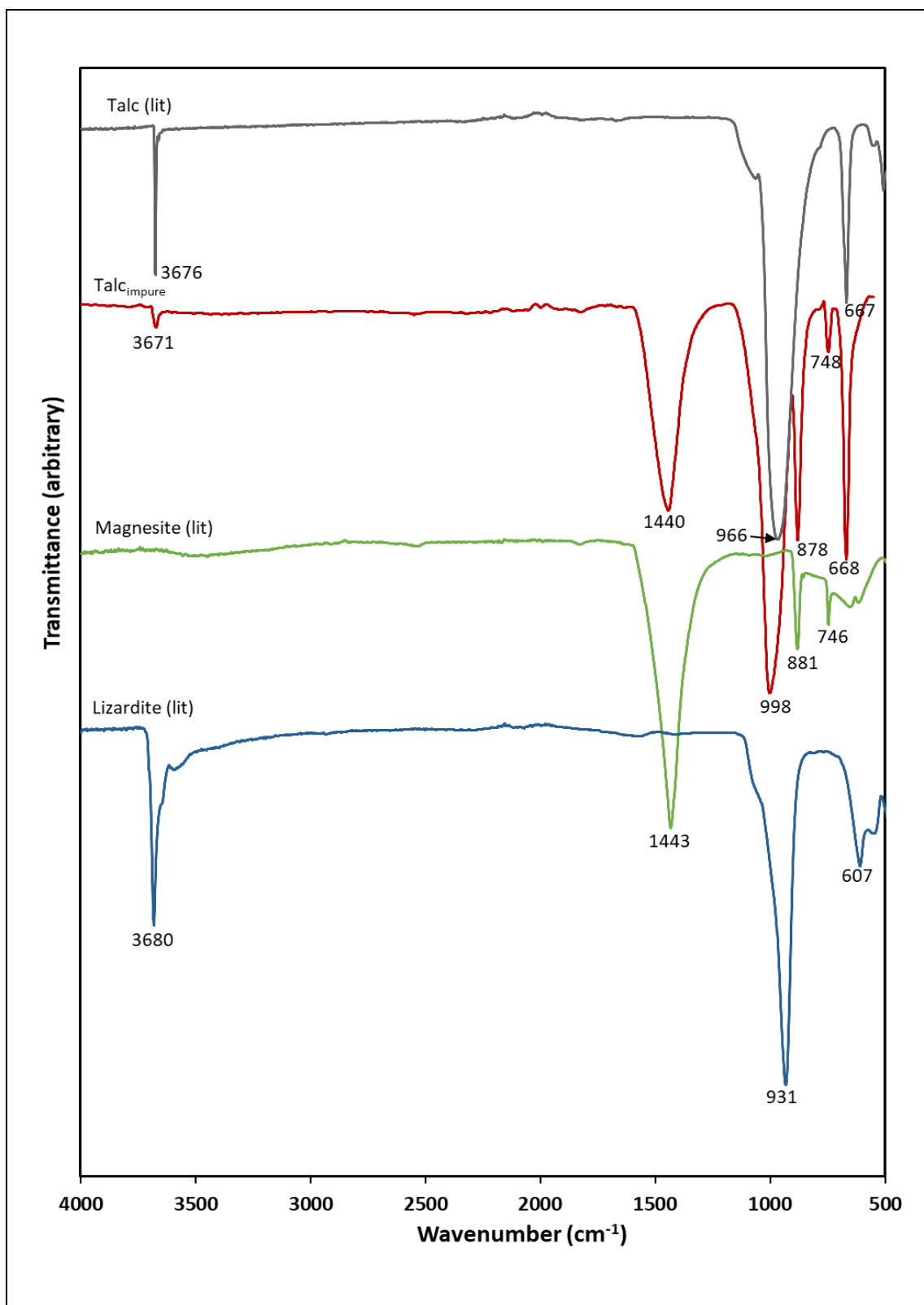


Figure 6.6: Comparison of FT-IR spectra for Talc_{impure} compared to spectra from the literature.

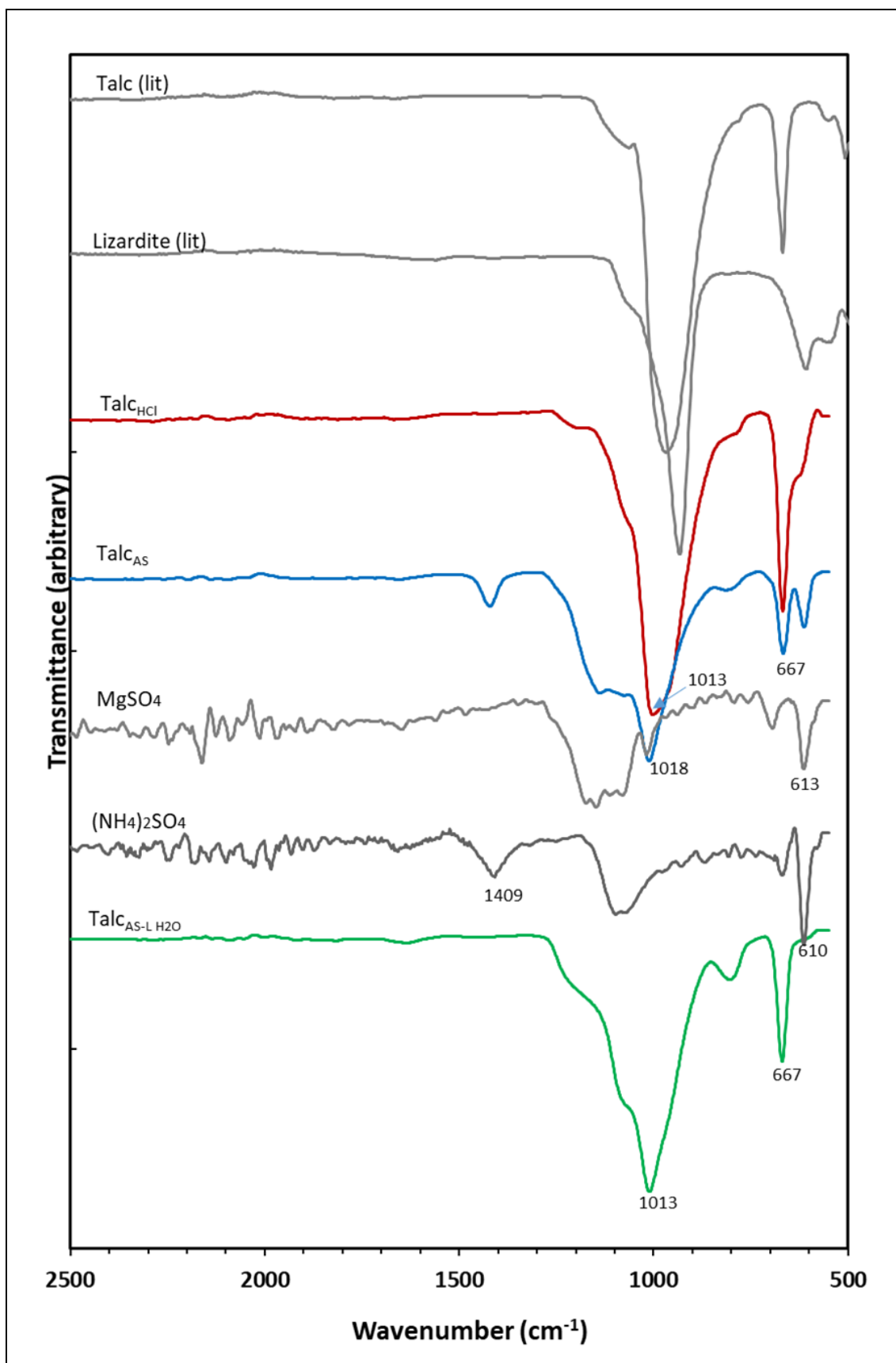


Figure 6.7: FTIR spectra for Talc_{HCl} (red), Talc_{AS} (blue), Talc_{AS-L} (green) and pure salts (grey).

A strong band at around 1440 cm^{-1} can be observed in the $\text{Talc}_{\text{impure}}$ and magnesite spectra (Fig. 6.6), which is characteristic of carbonate asymmetric stretching vibrations. The bands at 748 cm^{-1} and 878 cm^{-1} are characteristic of CO_3^{2-} bending vibrations (Botha et al, 2003; Castillo, 2011; Lanas, 2004). The absence of these three bands in Talc_{HCl} (Fig 6.7) confirms the removal of the carbonate minerals from the $\text{Talc}_{\text{impure}}$ sample which was observed in the XRD data (Fig. 6.3) and TGA analysis (Fig 6.4).

The mineralogy of Talc_{HCl} was confirmed by FTIR (Fig. 6.7), which exhibited well-defined bands, specifically between 950 and 1050 cm^{-1} , where bending and stretching modes of the SiO_4^{2-} tetrahedron occurs (Hofmeister and Bowey, 2006), and which were consistent with the occurrence of talc, lizardite and kaolinite (Table 6.1).

The FTIR scan of Talc_{AS} had distinct bands between 1050 and 1150 cm^{-1} , which are not present in Talc_{HCl} or the leached Talc_{AS} sample, $\text{Talc}_{\text{AS-L H}_2\text{O}}$ (Fig. 6.7). These, as well as the band at 600 cm^{-1} , correspond to the vibrations of the sulphate ion. The band observed at 1409 cm^{-1} was attributed to N - H bond movement (scissoring, bending) from hydrated ammonium metal sulphate species formed during the thermochemical reaction with AS. The sulphate bands were not present in the $\text{Talc}_{\text{AS-L}}$ spectrum, which strongly suggested the complete dissolution of sulphate phases to solution.

6.6 Scanning Electron Microscopy (FE-SEM)

FE-SEM was used to get a clear understanding of the morphology and surface features of the samples (Fig. 6.8). Images of the Talc_{HCl} revealed that the parent sample was made up of individual, irregularly shaped and plate-like particles with varying sizes (Fig 6.8a). Talc_{AS} exhibited distinctly different features. It consisted of unreacted, irregularly-shaped talc-rich particles similar to those found in Talc_{HCl} , which were surrounded by numerous globular structures (Fig 6.8b). These globular particles were different from the perfectly formed hexagonal structures of metal- and ammonium-metal sulphate species reported previously (Doucet et al, 2016; Mohamed et al, 2016, 2019). They were most likely precursors to similar hexagonal structures, but had nevertheless developed crystalline lattices that could be identified by XRD. Longer thermochemical reactions may have induced the growth and conversion of the globular particles into fully-shaped hexagons.

Talc_{AS-L} (Fig 6.8c) consisted of platy and irregular particles, similar to those observed in Talc_{HCl}. No globular morphologies were identified, which indicated their complete dissolution following leaching, as already shown by XRD and TGA.

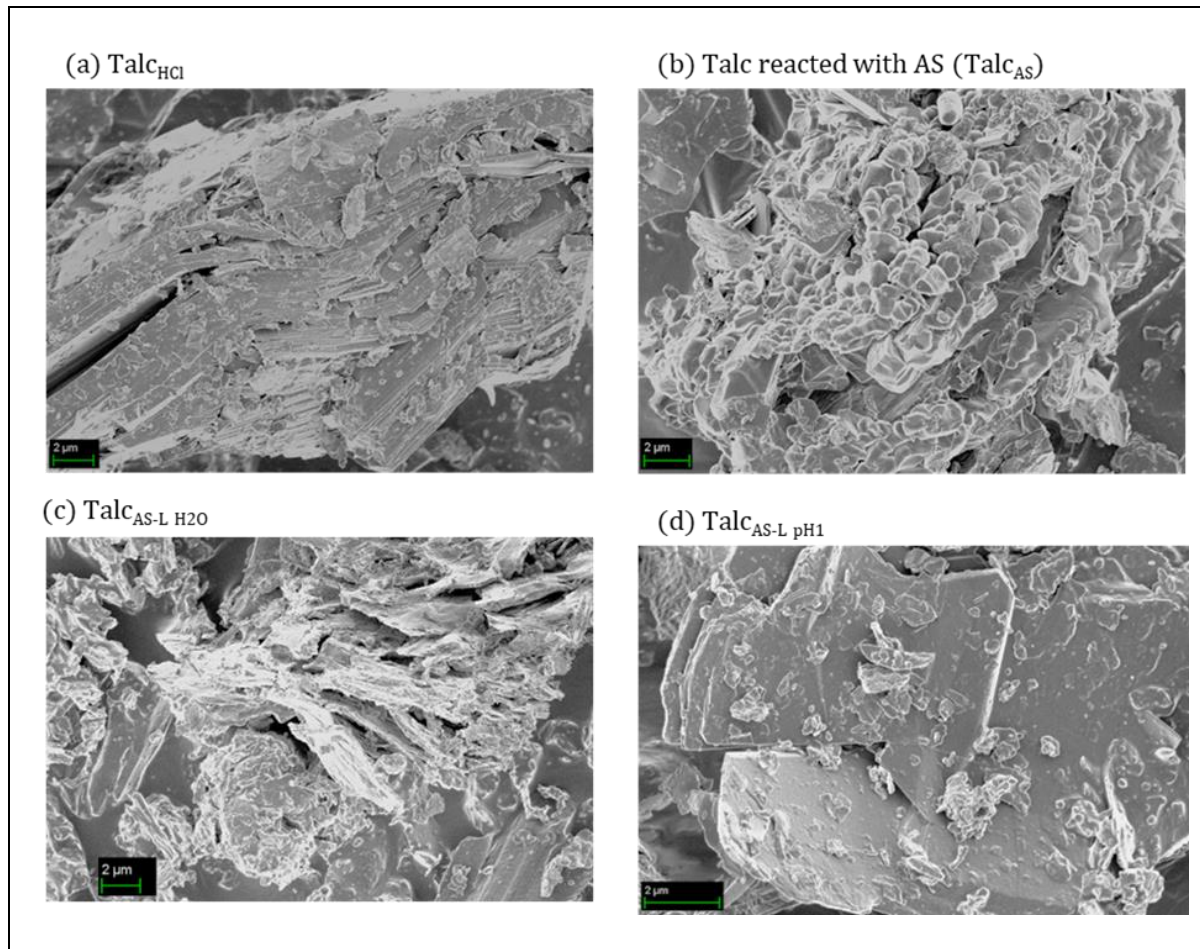


Figure 6.8: Representative SEM images of Talc_{HCl}, Talc_{AS}, Talc_{AS-L} H₂O and Talc_{AS-L} pH1.

6.7 Conclusions

This study showed that talc exhibits very limited, if any, reactivity with AS to form sulphate minerals when subjected to thermochemical processing under the experimental conditions tested. This thermochemical process of talc with AS may therefore find applications in the field of purification of low-purity talc ore or other talc-bearing materials under the right market conditions, provided the mineral co-exists with phases featuring a high degree of reactivity with AS under thermal conditions, i.e. the diamond mine residues.

Magnesium is not extracted from the talc during the thermochemical processing, which implies that the Mg in the talc of the slimes and tailings must not be considered when optimising the extraction process.

The composition of talc is not altered during the thermochemical reaction with AS or the dissolution process, therefore the talc content of the diamond mine slimes and tailings can be considered a valorisation product.

Chapter 7: Extraction of Soluble Minerals (Leaching)

7.1 Introduction

Thermochemical treatment of the mine tailings (CT) and slimes (CS) with ammonium sulphate (AS) indicated the potential for extraction of major elements through the formation of water-soluble ammonium metal- and metal-sulphates (Chapter 5). The mine residues contained substantial amounts of talc (25-30% m/m, Table 4.2) which showed limited, if any, reactivity with AS (Chapter 6). Keeping these results in mind, this chapter will discuss subsequent extraction of major elements from thermochemically treated CS and CT. This was accomplished by leaching/dissolving the roast products under different leaching environments, to optimise the extraction of the metals of interest (Mg, Fe and Al). It was also important to ascertain which furnace conditions, i.e. roast temperature and mine residue to AS roast ratio, provided the maximum extraction of the metals of interest. Optimal dissolution is also crucial for the successful recovery of ammonium sulphate. Based on the results of Fagerlund et al (2012) and Nduagu et al (2012b), which suggested that maximum Mg was extracted with a 2:3 m/m roast ratio between 450 – 480°C, initial optimisation experiments were carried out on samples with a mine residue to AS ratio of 2:3 m/m, thermochemically treated at 480°C. This temperature was specifically chosen as the product at 480°C was slightly softer and easier to remove from the crucibles than the product obtained after roasting at lower temperatures (Chapter 5.3.1).

7.2 Leaching in deionised water

7.2.1 Baseline dissolution

Baseline dissolution experiments were conducted initially to compare the behaviour of the untreated CS or CT (control 1) vs thermally treated samples (480°C; control 2) vs thermochemically treated samples (2:3 m/m ratio at 480°C). Samples were leached overnight in deionised water (3 g in 300 mL), at ambient temperature with stirring at 750rpm. The process was monitored using a Hanna HI 2829 conductivity/pH probe. The

control samples exhibited minimal dissolution, with little change in conductivity and a small decrease in pH values (Table 7.1).

The pH of the control samples remained alkaline. The untreated CS changed from an initial pH of 9.50 to a final pH of 9.12, and untreated CT from an initial pH of 9.47 to a final pH of 9.13. Both had a small increase in conductivity, CS being from 96 to 145 $\mu\text{S}/\text{cm}$ and CT from 86 to 142 $\mu\text{S}/\text{cm}$, possibly as a result of the slight dissolution of the calcite (CaCO_3) and other slightly soluble ions (Table 4.2). These results provided the first indication that little or no major elements were released into solution from the control samples. Mass losses sustained by the control samples during leaching were also very low (<5.5%). Thermochemically treated samples had a low initial pH (<3) and showed substantial changes in conductivity (>1200 $\mu\text{S}/\text{cm}$) and mass loss (>47%) due to the dissolution of the soluble sulphate phases (Table 7.1).

Table 7.1: Solution pH, change in electrical conductivity (ΔEC) and % mass loss after leaching untreated CS and CT (control 1), thermally treated CS and CT (control 2) and thermochemically treated CS and CT samples. Thermochemical treatment: 2:3 m/m ratio; 480°C; 1 h. Leaching: 3 g in 300 mL; 25°C, 750 rpm in water. ($n \geq 2$)

	Solution pH	ΔEC ($\mu\text{S}/\text{cm}$)	% mass loss
Untreated CS	9.50	49	5.5
Untreated CT	9.47	56	4.2
Thermally treated CS	8.87	46	4.2
Thermally treated CT	8.76	48	3.4
Thermochemically treated CS	2.82	1742	48.0
Thermochemically treated CT	2.56	1214	47.9

The concentrations of selected dissolved elements (mg/L) and the corresponding extraction efficiency (%) following the leaching of the control samples compared to thermochemically treated samples (2:3 m/m ratio; 480°C; 1 h) are illustrated in Table 7.2. These results indicate that limited or no major elements were released from the control samples during the leaching period, which supports the conductivity data.

Table 7.2: Concentrations of dissolved elements (mg/L) and corresponding elemental extraction efficiency (%) after leaching untreated CS and CT (control 1), thermally treated CS and CT (control 2) and thermochemically treated CS and CT samples. Thermochemical treatment: 2:3 m/m ratio; 480°C; 1 h. Leaching: 3 g in 300 mL; 25°C, 750 rpm in water. ($n \geq 2$)

	Mg		Fe		Al	
	mg/L	%	mg/L	%	mg/L	%
Untreated CS	4.0 ±0.4	0.3 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0
Untreated CT	2.5 ±0.7	0.2 ±0.1	0.2 ±0.0	0.03 ±0.0	0.2 ±0.0	0.1 ±0.0
Thermally treated CS	3.0 ±0.2	0.2 ±0.1	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0
Thermally treated CT	7.0 ±0.3	0.6 ±0.2	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0
Thermochemically treated CS	478 ±10	63.2 ±2.1	173 ±8.5	32.7 ±3.1	105 ±7.0	44.8 ±3.2
Thermochemically treated CT	358 ±2.1	57.1 ±0.4	62 ±1.4	13.6 ±0.3	66 ±5.6	33.4 ±2.8

As the CT sample produced a harder and less workable roast product (Fig 5.7) and had a lower Mg content as determined by XRF (Table 4.3), the CS sample was used for the majority of the optimisation.

7.2.2 Dissolution after thermochemical treatment at different furnace temperatures

Dissolution after thermochemical treatment of CS reacted with AS at 2:3 m/m and 3:4 m/m ratios for 1 h at different furnace temperatures were studied by leaching in deionised water (dH₂O). The dissolution process was followed through changes in conductivity, pH, percentage mass loss, and the extraction of Mg and Fe during leaching.

A summary of the results obtained for the conductivity and pH readings is given in Table 7.3. Initial measurements refer to the solution data collected within the first 30 seconds of leaching.

Table 7.3: Summary of electrical conductivity (EC) and pH readings during leaching of thermochemically CS treated at different furnace temperatures for 1 h. Leaching conditions: 3 g in 300 mL; 25°C, 750 rpm in water.

T(°C)	CS:AS 2:3 m/m					CS:AS 3:4 m/m				
	EC (µS/cm)			pH		EC (µS/cm)			pH	
	Initial	Final	ΔEC	Initial	Final	Initial	Final	ΔEC	Initial	Final
420	9180	9913	733	1.77	1.58	8017	8726	709	1.91	1.76
450	5100	6750	1650	2.37	2.10	4953	6350	1397	2.38	2.16
480	3216	4958	1742	2.82	2.30	3910	5343	1433	2.79	2.40
500	3277	4239	962	2.72	2.40	3258	4484	1226	2.75	2.32
520	3539	4014	475	2.56	2.35	3423	3999	576	2.68	2.45
550	3320	3952	632	2.68	2.41	3248	3790	542	2.63	2.38

A comparison of the changes in electrical conductivity (ΔEC) indicated that the highest concentrations of soluble ions were obtained after roasting at 480°C, followed by 450°C. The pH of the leachate decreased during the leaching process, with lower roasting temperatures having lower initial pH values. This could be due to the presence of ammonium-metal sulphates in the residues from lower temperatures (Table 5.8). Final pH values were similar to those obtained by Romão et al (2015), i.e. 1.5 – 2.5, and lower than those reported by Mohamed et al (2016), i.e. 2.9 – 3.5. The largest decrease in pH was observed for the 2:3 ratio sample at 480°C.

A comparison of changes in the solution electrical conductivity with time after thermochemical treatment at different furnace temperatures for the CS:AS 2:3 m/m and 3:4 m/m ratios is illustrated in Fig 7.1.

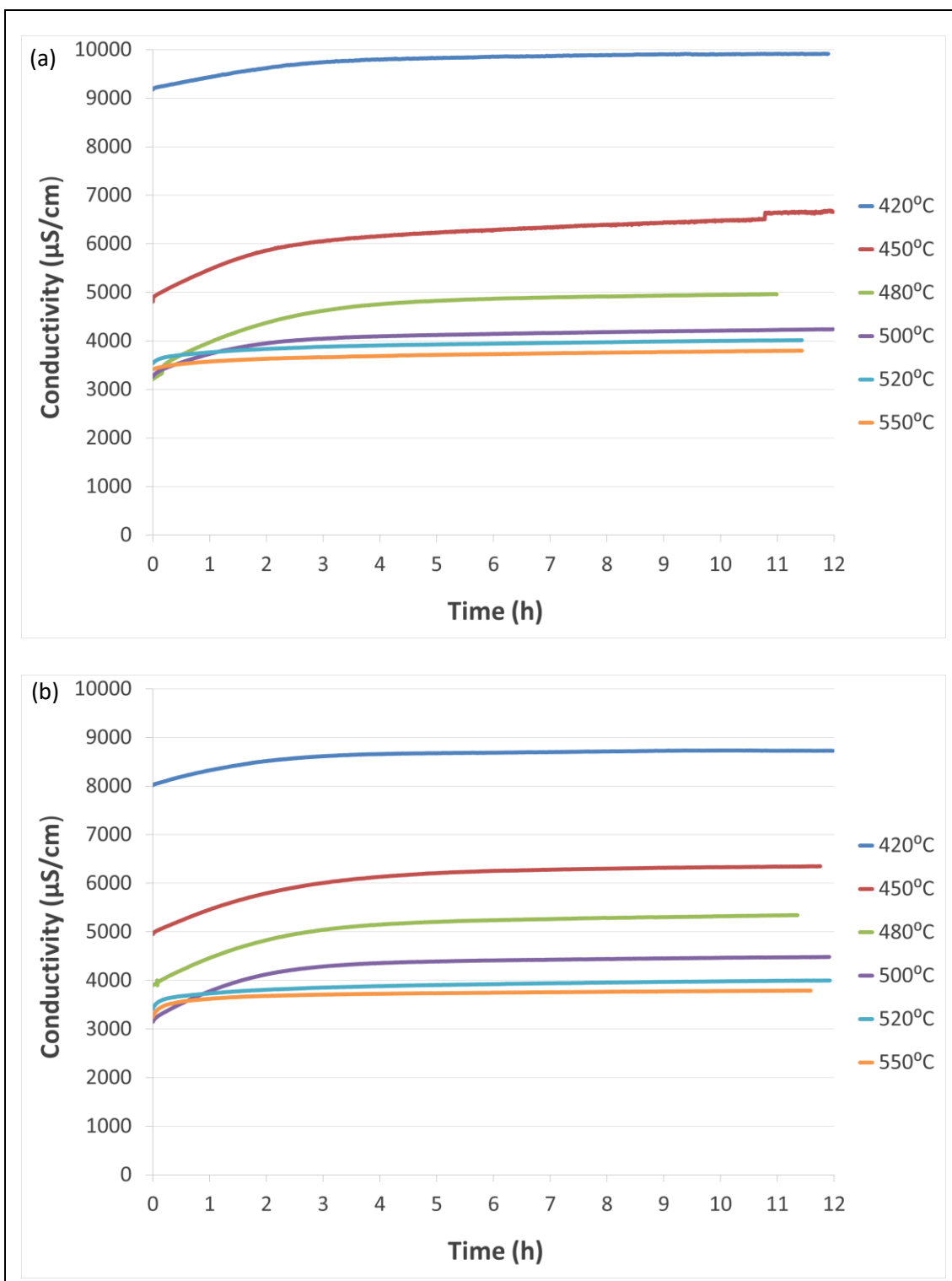


Figure 7.1: Comparison of conductivity during leaching for CS:AS samples at (a) 2:3 m/m and (b) 3:4 m/m ratio after roasting at different furnace temperatures for 1 h. Leaching conditions: 3 g in 300 mL; 25°C, 750 rpm in water, 12 h.

The conductivity of the leachates all increased by varying degrees. The higher initial values for the suspensions thermochemically treated at lower temperatures could be attributed to the formation of more ammonium metal sulphates in these samples which contribute a larger number of ions, compared to samples treated at higher temperatures which contained mostly metal sulphates (Table 5.8). The samples thermochemically treated at lower temperatures consequently released more ions into solution. The greatest change in conductivity (1742 $\mu\text{S}/\text{cm}$) was observed for the 2:3 ratio at a furnace temperature of 480°C (Table 7.2). This prompted further dissolution trials using these parameters. The decrease in the change in conductivity (ΔEC) at higher roast temperatures could be ascribed to no ammonium metal sulphates being present in the roasting product (Table 5.8) as well as a decrease in Fe extraction in the leachate, as seen by the ICP results (Fig 7.2). The solid residue after leaching, for the samples thermochemically treated at higher furnace temperatures, also had a distinctive red-brown colour, pointing to the presence of iron.

Dissolution of the control samples was minimal as observed by the low changes in conductivity and pH (Table 7.1), as well as the lack of major elements released to solution (Table 7.2). The percentage mass loss after dissolution of the CS:AS roast products is presented in Table 7.4.

Table 7.4: Comparison of percentage mass loss after leaching for CS:AS samples thermochemically treated at various mass ratios and furnace temperatures ($n \geq 2$).

	% mass loss					
T (°C)	420	450	480	500	520	550
2:3 ratio	58.7 $\pm$ 2.0	49.7 $\pm$ 0.1	48.0 $\pm$ 1.1	46.6 $\pm$ 1.0	42.7 $\pm$ 0.6	40.7 $\pm$ 0.7
3:4 ratio	59.3 $\pm$ 0.1	51.9 $\pm$ 0.2	50.3 $\pm$ 0.3	48.1 $\pm$ 0.4	41.8 $\pm$ 0.3	41.3 $\pm$ 0.1

Mass losses decreased with an increase in furnace temperature, and ranged from 58.7 to 40.7% (18.0% difference) for the 2:3 mass ratio and 59.3 to 41.3% (18.0% difference) for the 3:4 mass ratio. Higher mass losses at lower roast temperatures can be explained by the aqueous solubility of residual AS or ammonium bisulphate that was present in the

roast residues, as well as the higher number of ammonium-metal sulphates and hydrated metal sulphates present in the roast residues (Table 5.8).

The percentage extraction of magnesium and iron from CS after thermochemical treatment at different furnace temperatures was subsequently determined. Fig 7.2a illustrates the percentage extraction relative to the total Mg content, as determined by XRF (Table 4.3), while Fig 7.2b illustrates the percentage extraction when excluding the Mg contained in the 30.1 % m/m talc phase present in CS (Table 4.2).

When comparing the extraction of magnesium and iron at the different furnace temperatures, the iron concentration decreased substantially with an increase in furnace temperature. This agrees with the results obtained by Deng et al (2018), working with pyrolusite absorption residue, who reported maximum extraction of Fe between 350°C and 450°C, after which there was a decrease. Decreased Fe extraction can be explained by the conversion of soluble Fe sulphates into insoluble Fe oxide, which will be discussed further in Chapter 8. In contrast to these findings, Saba et al (1973) reported an increase in Fe extraction from 31% at a roasting temperature of 400°C to 55% at 500°C, from ferruginous manganese ores. This suggests that there is a strong effect of the Fe mineralogy in parent materials.

The experiments performed at 450°C and 480°C extracted 61% and 63% of magnesium and 37% and 33% of iron (Fig 7.2). The magnesium extraction was not considerably different (~60%) at the various furnace temperatures, with the exception of the leachate obtained from the 420°C roast, which was approximately 10% lower. This differs from the findings of Nduagu et al (2012b), who reported an increase in the amount of Mg extracted from serpentinite when roasting temperatures are increased above 400°C, reaching a maximum between 450 – 480°C, but a decrease at temperatures greater than 520°C, possibly due to the formation of insoluble magnesium metasilicate (MgSiO_3).

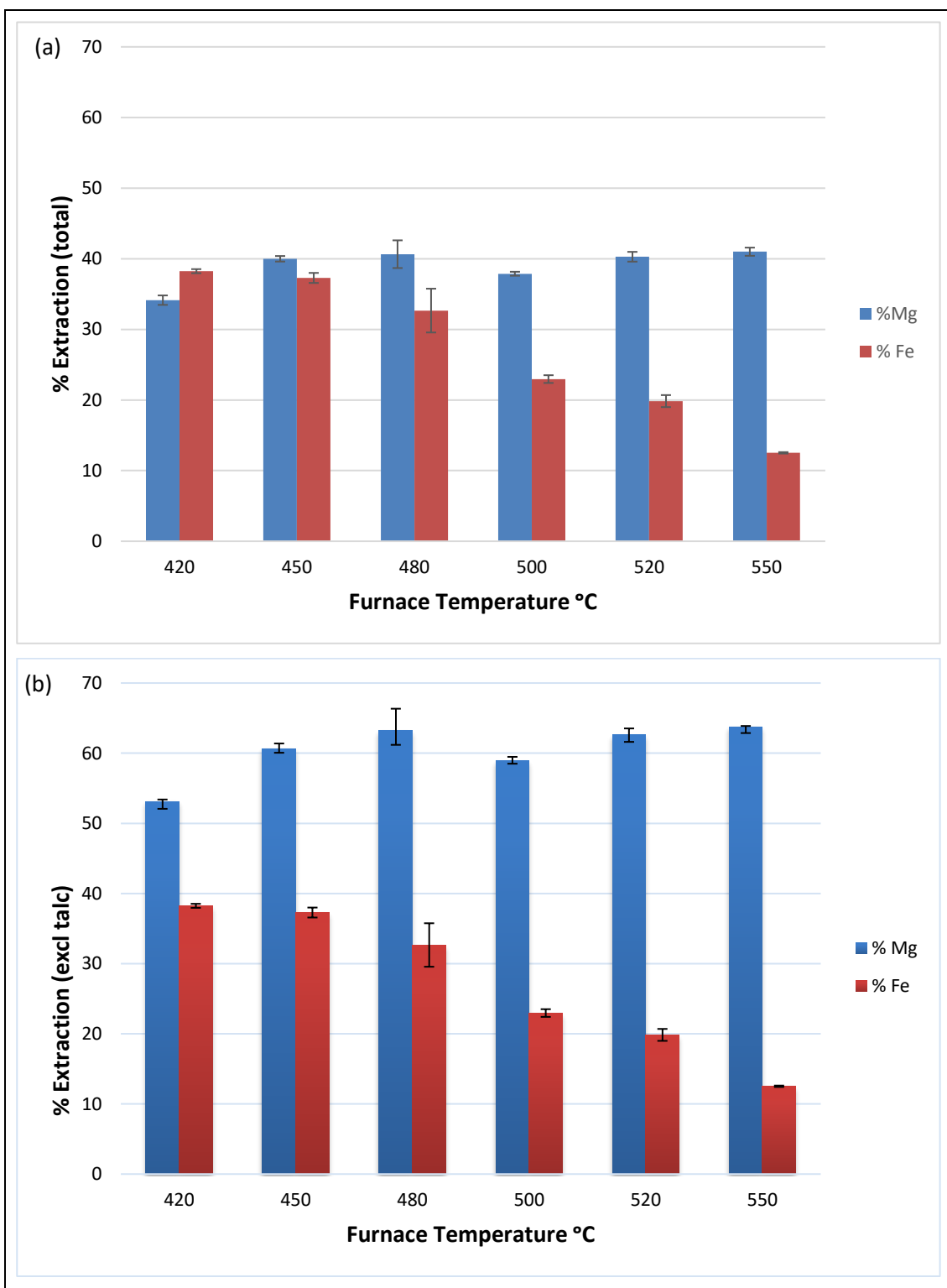


Figure 7.2: Magnesium and iron extraction from the product of the CS + AS thermochemical reaction at a mass-to-mass ratio of 2:3 after roasting at various furnace temperatures for 1 h, expressed as (a) a percentage of total Mg content, and (b) a percentage of readily extractable Mg, i.e. excluding the Mg available in talc. Leaching conditions: 3 g in 300 mL water at 25°C, 750 rpm. ($n \geq 2$)

A comparison of the Mg extraction using a CS:AS 2:3 m/m ratio vs a 3:4 m/m ratio is illustrated in Fig 7.3. The remainder of this chapter will report Mg extraction as a percentage of extractable Mg, excluding the Mg available in talc.

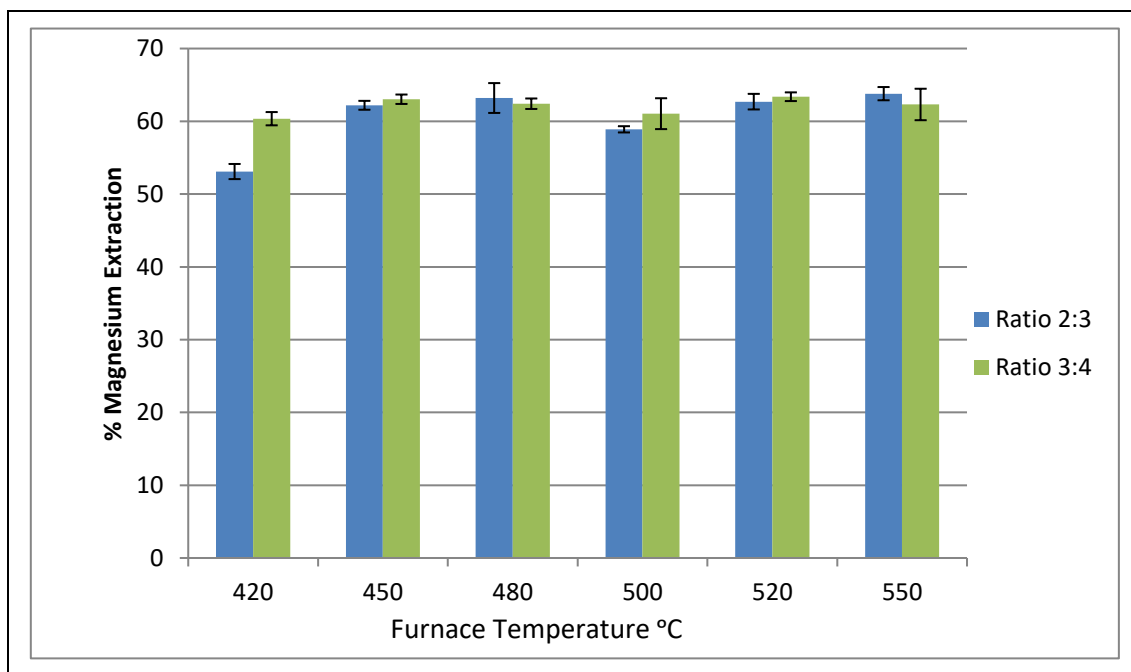


Figure 7.3: Magnesium extraction (as a percentage of extractable Mg) from the product of CS + AS thermochemical reaction at a mass-to-mass ratio of 2:3 vs a ratio of 3:4 after roasting at various furnace temperatures for 1 h. Leaching conditions: 3 g in 300 mL water at 25°C, 750 rpm. ($n = 2$)

There were also no major differences when comparing the 2:3 m/m ratio and 3:4 m/m ratio for magnesium extraction except at 420°C. There was slightly better Mg extraction using the 3:4 m/m ratio compared to the 2:3 m/m ratio when roasting at 420°C.

Comparable extraction efficiencies for magnesium were obtained for roasting at 450°C and 480°C at both mass-to-mass ratios tested (63.2% vs 62.2%; Fig 7.3). Iron extraction was slightly better when a furnace temperature of 450°C was used (Fig 7.2). Further optimisation was conducted using a furnace temperature of 450°C to facilitate maximum extraction of both Mg and Fe as well as to reduce energy usage.

7.2.3 Dissolution after thermochemical treatment at different m/m ratios at a temperature of 450°C.

In an effort to improve the Mg extraction and energy efficiency of the roasting process, various other mass-to-mass ratios of CS:AS were investigated at a roast temperature of 450°C. The CT sample was included in this study to determine whether a different m/m ratio would produce a more workable product. The results are illustrated in Fig 7.4.

This experiment indicated that for CS, a 2:5 or 2:6 CS:AS m/m ratio would possibly also improve the extraction of the minerals of interest. These ratios were investigated further when quantities were scaled up to make products.

A limited study was also conducted using the CT:AS at different ratios, which indicated there were no substantial differences between the different CT:AS m/m ratios for Mg extraction. In general, the extraction from CT was lower than the extraction from CS. These results, together with the CT samples being harder and less workable after roasting, determined that further optimisation would be conducted using only the CS samples.

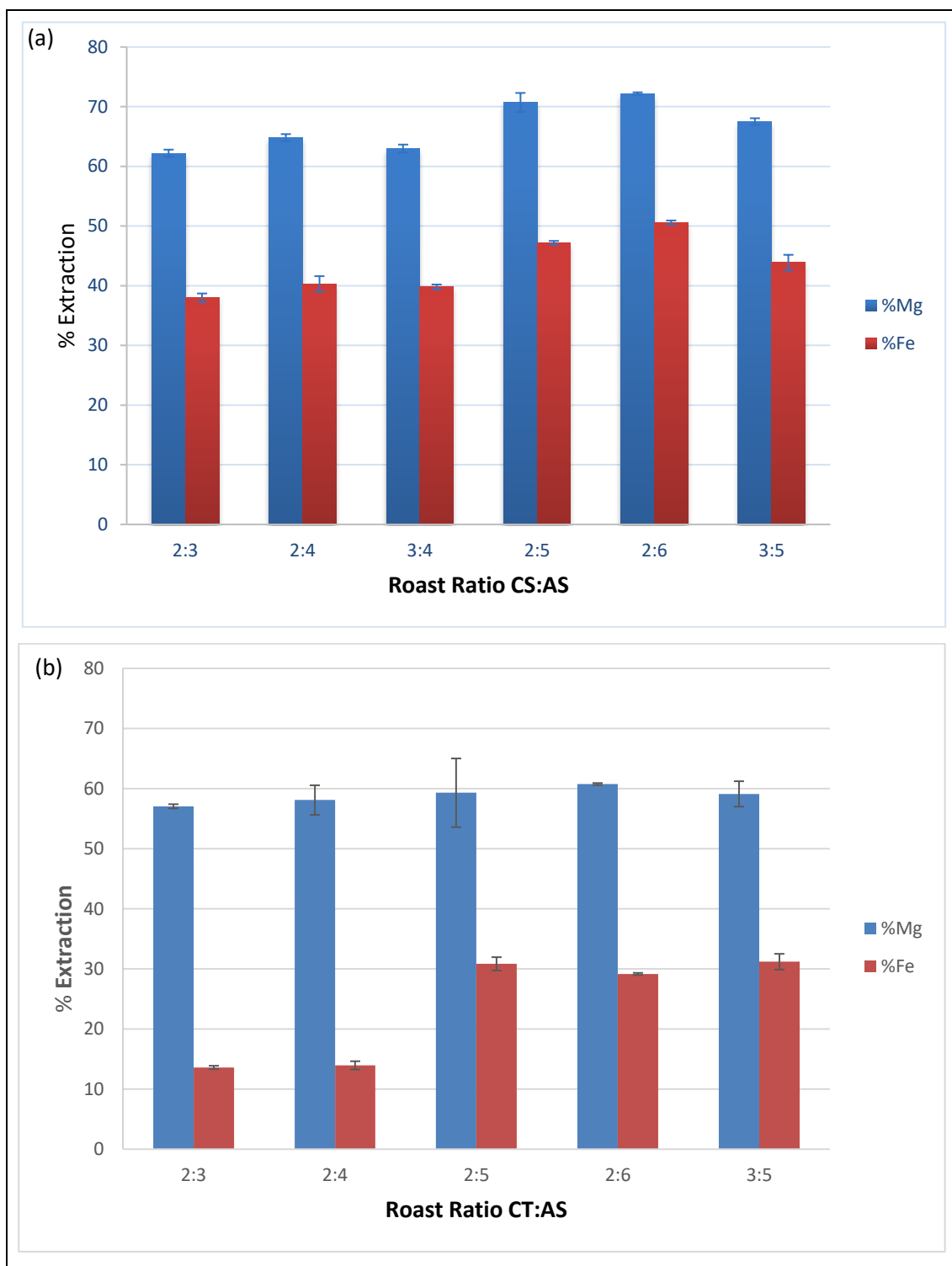


Figure 7.4: Comparison of different mass-to-mass ratios of (a) CS:AS and (b) CT:AS roasted at 450°C for 1 h. Leaching conditions: 3 g in 300 mL water at 25°C, 750 rpm. ($n=2$)

7.2.4 Leaching at different temperatures

Using the CS:AS 2:3 m/m sample roasted in the furnace at 450°C, leaching was carried out using a ratio of 1:100 m/v, at a variety of temperatures between ambient and 95°C, to ascertain whether the magnesium extraction could be improved by increasing the leaching temperature. The extraction was followed using the Hanna HI 2829 conductivity/pH probe, but the time period was shortened to 3 h, as the conductivity readings remained constant after 3 h, indicating that the extraction was complete.

As the temperature was increased, the colour of the leaching solution changed from grey to reddish-brown, possibly an indication of iron precipitating out of solution (Fig 7.5), which was also observed by Mohamed et al (2016).

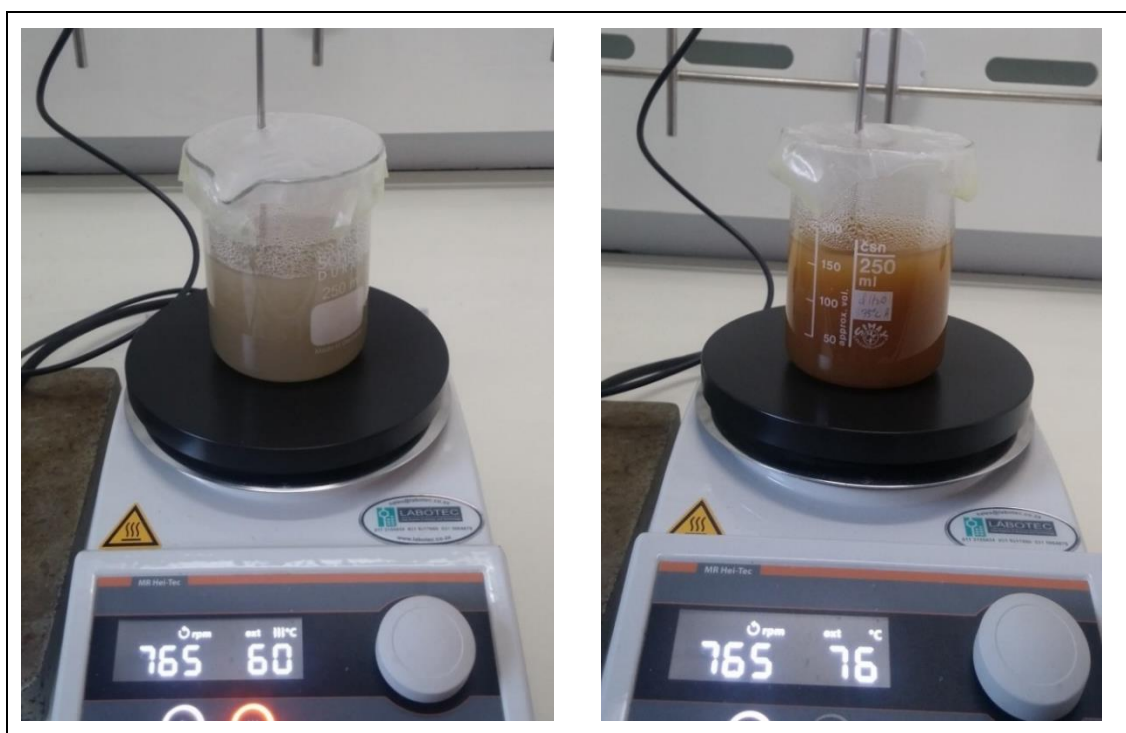


Figure 7.5: Leaching at different temperatures in deionised water at (a) 60°C and (b) 75°C, showing the colour change with the increase in temperature.

This observation was supported by the ICP-MS results for the leachate (Fig 7.6), which indicated a substantial decrease in iron concentration with an increase in leaching temperature. The extraction of magnesium was mostly constant with increasing temperature (63.9 – 65.4%), but the iron extraction was adversely affected by the

temperature increase, and showed a steady decline from 32.7 % when leaching at 20°C to 6.5 % at 95°C (Fig 7.6). Mohamed et al (2016) ascribed similar observations to secondary precipitation of Fe-containing phases, which was also supported by the colour change of the suspension (Fig 7.5).

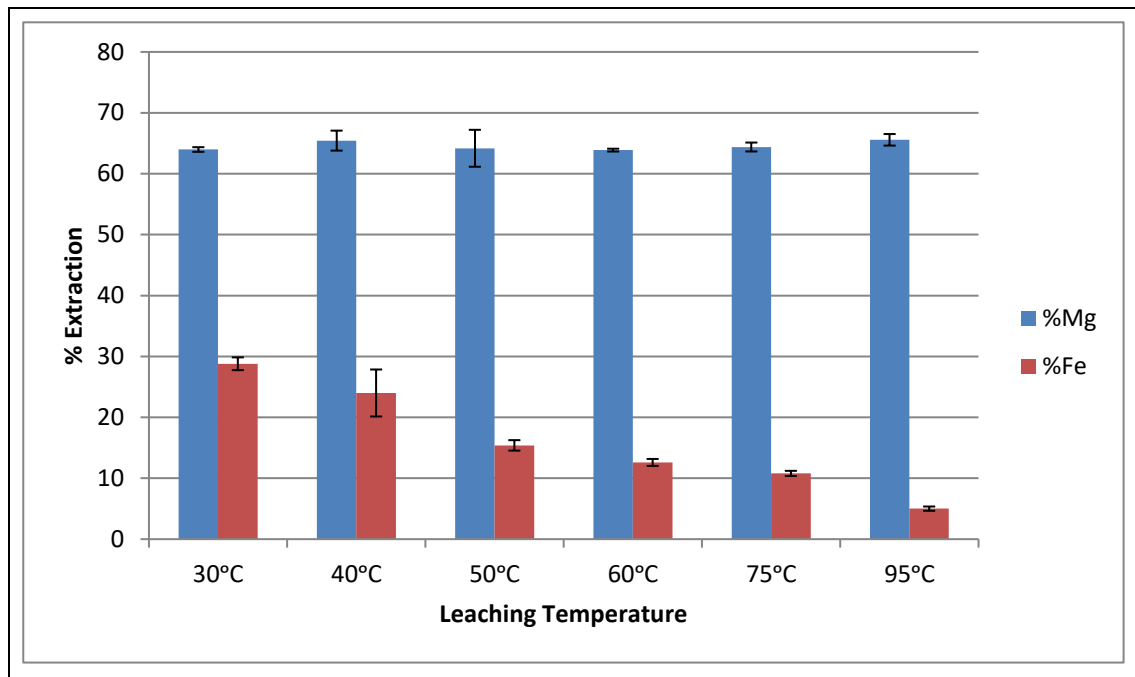


Figure 7.6 Magnesium and iron extraction from the CS roast residue using different leaching temperatures. Other leaching conditions: 1:100 m/v in deionised water, 750 rpm. Thermochemical treatment: CS:AS 2:3 m/m roasted at 450°C for 1 h. ($n \geq 2$)

7.3 Extraction efficiencies under controlled pH conditions

In an attempt to prevent secondary precipitation of iron during extraction (Fig 7.6), dissolution was carried out under controlled pH conditions. Mohamed et al (2016) found an improvement in the extraction of Fe when leaching under acidic conditions over uncontrolled pH conditions (dH₂O), and Deng et al (2018) reported good Fe recovery when leaching in a 0.5 M solution of sulphuric acid. The leaching process at different temperatures was repeated using 0.05 M (pH 1) and 0.63 M (pH 0.2) solutions of sulphuric acid. The results of the extraction under controlled pH conditions are illustrated in Fig 7.7.

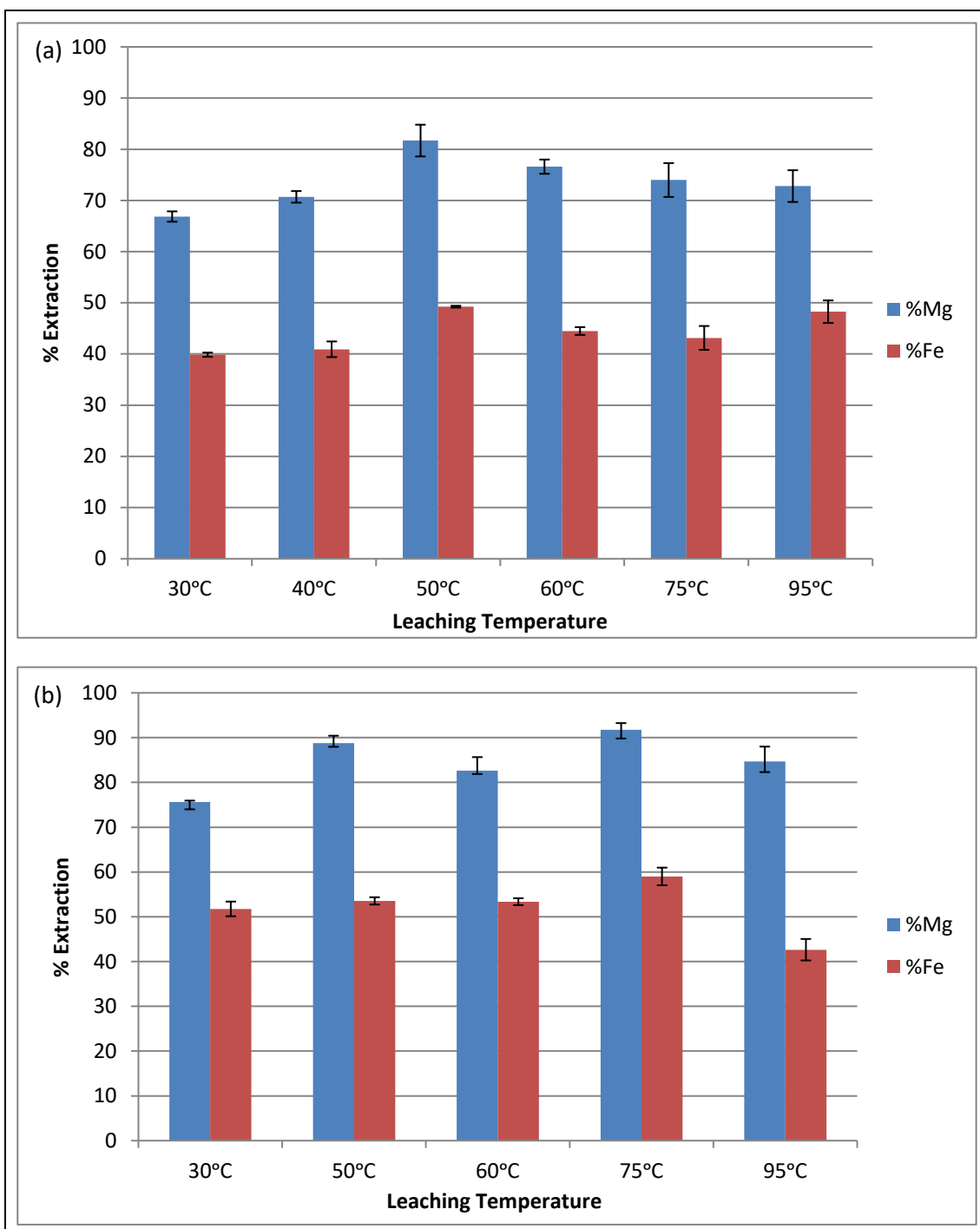


Figure 7.7: Magnesium and iron extraction from the CS roast residue when leached at different temperatures in (a) 0.05 M (pH 1) and (b) 0.63 M (pH 0.2) H_2SO_4 . Other leaching conditions: 1 g in 100 mL H_2SO_4 , 750 rpm. Thermochemical treatment: CS:AS 2:3 m/m roasted at 450°C for 1 h. ($n = 2$)

The concentration of Fe in the solution improved when leaching under controlled pH conditions. The colour of the solution remained grey when leaching at higher temperatures, rather than becoming reddish brown. At a pH of 1 (Fig 7.7a), both

magnesium and iron extraction were improved compared to water leaching (Fig 7.6), with the most efficient Mg extraction obtained at a temperature of 50°C (64.2% in dH₂O vs 81.7% at pH 1). At ambient temperature, there was already an improvement in the extraction of Fe, i.e. 39.8% at pH 1 vs 31.9% in dH₂O. At 50°C, the Fe extraction increased from 14.8% in dH₂O to 49.2% in the pH 1 solution. This improvement in iron extraction was evident when comparing the appearance of the leach residues after leaching at 50°C (Fig 7.8).

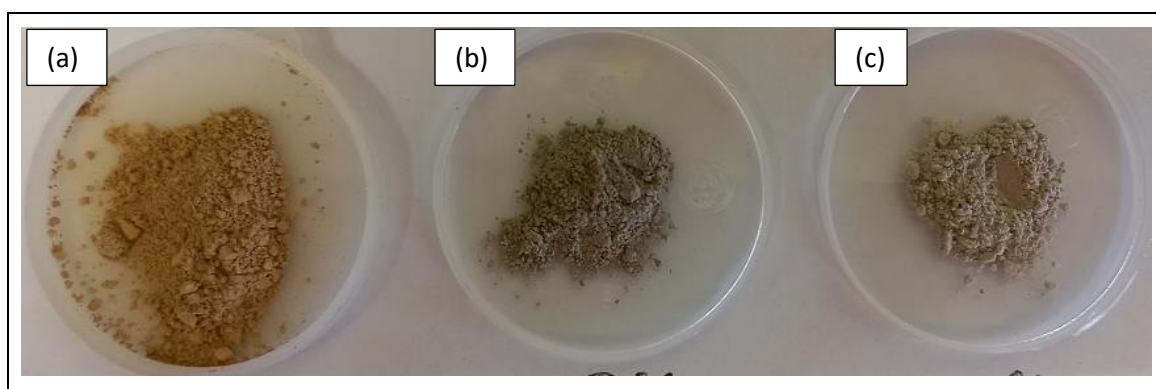


Figure 7.8: Leach residues after leaching the roast product at 50°C in (a) dH₂O, (b) H₂SO₄ at pH 1 and (c) H₂SO₄ at pH 0.2.

The improvement in the extraction of Mg during controlled leaching could be due to the dissolution of minerals (e.g. Hornblende and Diopside) that did not react during the thermochemical treatment, and did not dissolve in water. Teir et al (2007) reported successful extraction of Mg and Fe from serpentine using leaching in H₂SO₄ solutions.

In general, Mg and Fe extraction efficiencies were improved when leaching was performed at a pH of 0.2 (Fig 7.7b), which supported the findings of Teir et al. (2007), who reported increased extraction of Mg and Fe with increased acid concentration. The best extraction was achieved at 75°C (Mg 91.8%, Fe 59.0%), although not substantially higher than the extraction at 50°C (Mg 88.8%, 53.5%). Based on these results, and in an attempt to maintain energy efficiency, further leaching optimisation was performed at 50°C.

Figure 7.9 compares the extraction efficiencies of Mg and Fe after leaching CS:AS 2:3 m/m roasted at 450°C at 50°C using deionised water and sulphuric acid solution at both pH = 1 and pH = 0.2.

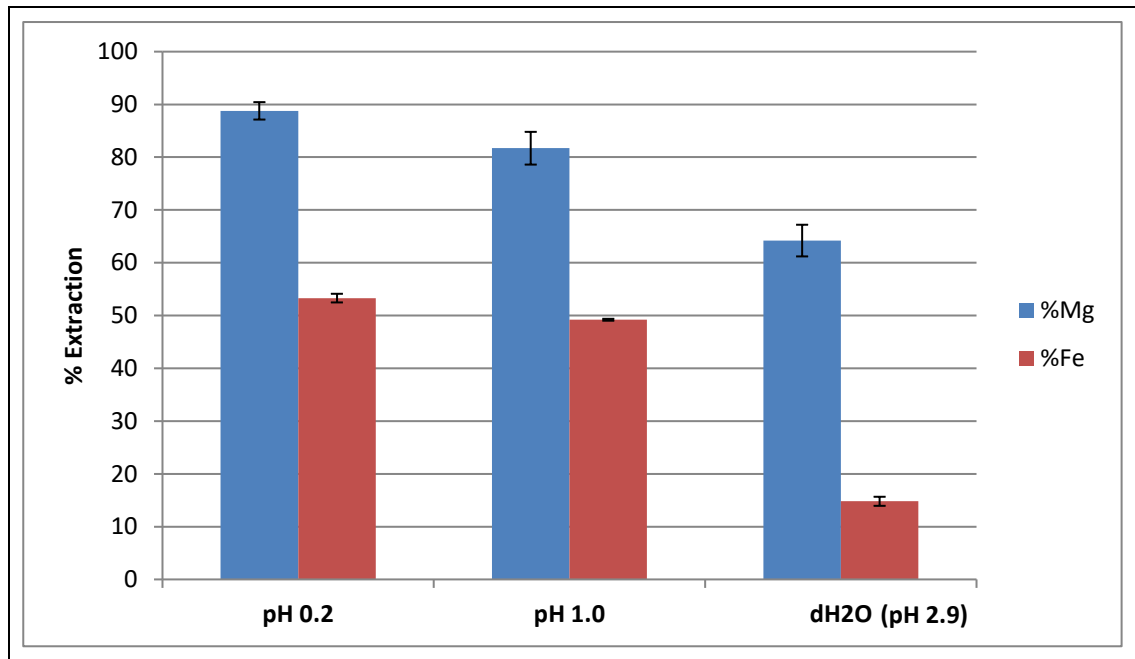


Figure 7.9: Comparison of magnesium and iron extraction from the CS roast residue leached at 50°C under uncontrolled and controlled pH conditions. Thermochemical treatment: CS:AS 2:3 m/m roasted at 450°C for 1 h.

The most efficient Mg extraction for leaching at 50°C was obtained in H₂SO₄ at pH 0.2 (64.2% in dH₂O vs 81.7% at pH 1 and 88.7% at pH 0.2). Leaching under controlled pH conditions appeared to prevent secondary precipitation of the Fe phases, with the subsequent increase in the concentration of Fe in the solution. This translated into substantially improved extraction of Fe during leaching in H₂SO₄ (14.8% in dH₂O vs 49.2% at pH 1 and 53.3% at pH 0.2). In order to keep the process more environmentally acceptable, it was decided to select a pH of 1 instead of pH 0.2 for further optimisation.

7.4 Optimisation of the extraction at different liquid to solid leach ratios

At the leaching ratio of 1:100 m/v roast residue to either dH₂O or sulphuric acid solution, the concentration of the metal sulphates was generally very low (typically 480 – 600 mg/L for Mg and 200 – 250 mg/L for Fe obtained from leaching in H₂SO₄ at pH 1). This resulted in the leachate needing to be concentrated before products could be made, which again, reduced the energy efficiency of the process. Leaching at a variety of different liquid to solid ratios was conducted in an attempt to maximise the concentrations of magnesium and iron without compromising the extraction. Due to the complexity of the mine residues, this study was conducted using pure laboratory chemicals, i.e. MgSO₄, Fe₂(SO₄)₃ and Al₂(SO₄)₃ combined in the mass-to-mass ratio of 3:2:1, i.e., similar to that found in the mine residues. Samples were roasted in the muffle furnace at 450°C for 1 h before leaching, to mimic the process being used for CS and CT, as well as leached without roasting to act as a control. The % mass loss due to the roasting was minimal, with an average of 1.06% ±0.08 for 12 samples.

Fig 7.10 compares the % mass loss after leaching for 2.0 g of the solid mixture in the different leach volumes at 50°C in deionised water.

Theoretically, the samples should have dissolved completely in all of the volumes tested, as in 2.0 g of the solid mixture there would be 1.0 g MgSO₄, 0.66 g Fe₂(SO₄)₃ and 0.33 g Al₂(SO₄)₃ and at 20°C the solubility of MgSO₄ is ~0.71 g/mL, Fe₂(SO₄)₃ is ~0.26 g/mL and Al₂(SO₄)₃ is ~0.36 g/mL in water. The smallest leach volume used was 10 mL, which should have been sufficient to dissolve all of the salts in the sample.

The mass losses of the control and roast samples were similar and varied from 91.5% for 2.0 g of the roast sample leached in 10 mL dH₂O to 98.4% for 2.0 g of the control sample leached in 25 mL dH₂O. An increase in mass loss with decreasing leach volume was observed from leaching in 200 mL dH₂O up to leaching in 25 mL dH₂O (i.e. a 1:12.5 solid to liquid ratio). This supports the findings of Romão et al (2015), who used 1 g of roasted material in 10 mL water. The dissolution decreased at the 1:5 ratio, possibly due to the very small volume, which was difficult to stir effectively. The difference in mass loss for the roast sample between the 1:12.5 and 1:25 solid to liquid ratio was nominal (98.1% vs 97.7%).

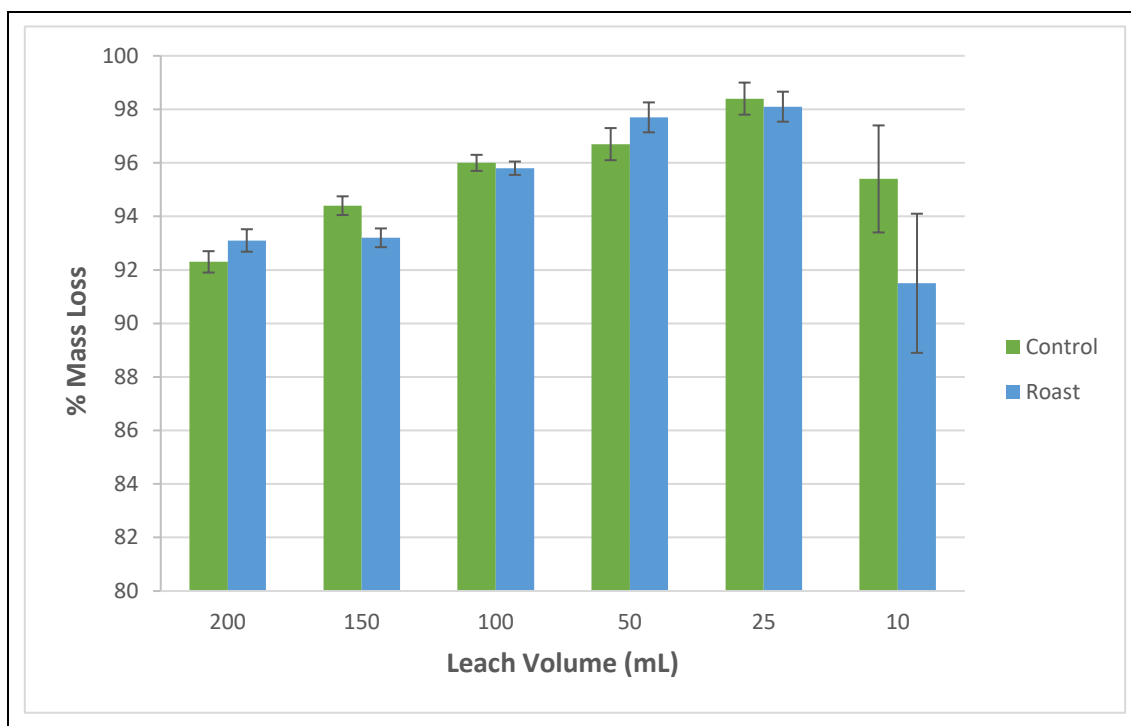


Figure 7.10: Comparison of % mass loss after leaching 2.0 g of the solid mixture of MgSO_4 , $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Al}_2(\text{SO}_4)_3$ combined in a mass-to-mass ratio of 3:2:1 in various volumes of dH_2O at 50°C . ($n = 2$)

The extent of the extraction was measured by ICP-OES and was found to be 100% for Mg, between 74.9% (1:5) and 97.3% (1:25) for Fe, and 72.8% (1:5) and 99.8% (1:75) for Al. What is more important is the values of the concentration of the elements in the leachate, which is illustrated in Table 7.5. The higher concentration of elements in the leachate allows for the more efficient production of Mg containing compounds.

Table 7.5: Comparison of the concentration of Mg, Fe and Al (in mg/L) at the different solid to liquid ratios after leaching 2.0 g of a solid mixture of MgSO_4 , $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Al}_2(\text{SO}_4)_3$ in various volumes of dH_2O at 50°C . ($n = 2$)

S:L ratio	Concentration of Elements (mg/L)					
	1:100	1:75	1:50	1:25	1:12.5	1:5
Mg	1084 ± 42	1399 ± 15	2134 ± 92	4393 ± 225	8767 ± 150	20400 ± 142
Fe	716 ± 106	1149 ± 37	1495 ± 22	3379 ± 142	7104 ± 138	17370 ± 124
Al	256 ± 2.1	362 ± 17	479 ± 1.2	934 ± 33	2011 ± 88	3989 ± 96

From these results, when leaching for the purpose of generating sufficient leachate for the production of Mg containing compounds, a solid to liquid ratio of 1:25 m/v in dH₂O or sulphuric acid solution at pH 1 was proposed for leaching of the CS roast residues as this ratio allowed for higher concentrations of the elements in the leachate and a useful leach volume to utilise during product development.

Application of this solid to liquid leach ratio was subsequently used for leaching CS samples that had been roasted at different CS:AS m/m ratios in an effort to produce a more concentrated leachate for the creation of Mg containing products. As larger volumes of leachate were required, the amounts of CS and AS used were upscaled to use 8 g of CS during the roasting step, which required longer roasting times when roasting at 450°C, as illustrated previously (Fig 5.11).

Table 7.6 compares the extraction results after roasting the upscaled samples to the results of a smaller sample (2 g of CS) after roasting for 1 h and leaching in dH₂O at a 1:100 solid to liquid ratio (Fig 7.4). There was generally improved extraction for all elements for the leachates obtained from the upscaled sample after the longer roasting time with the 1:25 solid to liquid leaching ratio in dH₂O at 50°C.

Table 7.6 Comparison of the % extraction of elements from CS after roasting for 1 h (2 g of CS) and 7 h (8 g of CS) at 450°C using CS:AS m/m ratios of 2:3, 2:4 and 2:6 after leaching in dH₂O at 50°C at solid to liquid ratios of 1:100 and 1:25.

Ratio	2:3		2:4		2:6	
Roast time	1 h	7 h	1 h	7 h	1 h	7 h
m/v ratio	1:100	1:25	1:100	1:25	1:100	1:25
Mg	62.2 ± 0.6	71.2 ± 6.2	64.8 ± 0.6	89.1 ± 4.7	72.2 ± 0.2	89.7 ± 4.5
Fe	37.3 ± 0.7	48.6 ± 5.7	40.4 ± 1.3	58.7 ± 3.6	50.6 ± 0.3	63.6 ± 1.4
Al	42.4 ± 0.6	52.3 ± 4.8	44.7 ± 1.1	62.4 ± 5.6	53.1 ± 0.6	66.1 ± 3.4

Figure 7.11 exemplifies the % extraction of Mg, Fe and Al after roasting CS:AS at various mass to mass ratios at 450°C for 7 h, using dH₂O as the solvent. The magnesium extraction is relative to the Mg in CS as determined by XRF, excluding the amount of Mg that would be due to the talc content.

When using dH₂O as the solvent, the 2:4 and 2:6 m/m ratios gave similar extraction of Mg, with the 2:6 ratio being slightly higher. As additional roasting time was required to remove all the excess AS from the 2:6 sample, which then affects the energy efficiency of the process, it was decided to use the 2:4 ratio to produce the leachate required for the manufacturing of Mg containing compounds.

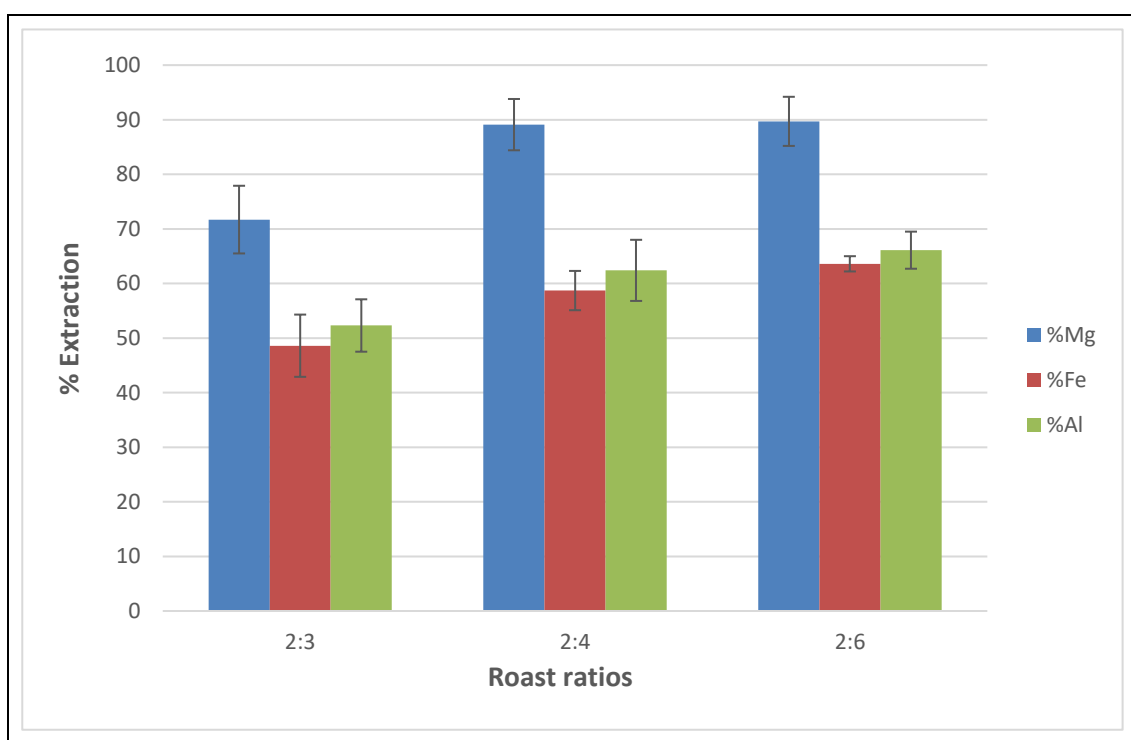


Figure 7.11: Comparison of the extraction of Mg, Fe and Al after roasting at 450°C at 2:3, 2:4 and 2:6 m/m ratios of CS:AS for 7 h, using 3 g roast product in 75 mL dH₂O at 50°C.

7.5 Conclusions

Mg, Fe and Al were successfully extracted from the roast product of the thermochemical treatment at 450°C using both dH₂O and sulphuric acid solutions, with the acidic solutions providing superior extraction.

Increasing the temperature during leaching also improved the extraction of the elements of interest, with 50°C being selected as the optimum with regard to extraction and energy efficiencies.

When testing various solid to liquid leach ratios, the 1 g solid to 25 mL liquid combination provided an increased concentration of elements in solution with sufficient volume for the synthesis of the desired products.

Although the majority of the optimisation was conducted using the 2:3 m/m ratio, when scaling up the quantities, the 2:4 m/m ratio gave the better extraction. This ratio was then used when producing leachate for the synthesis of the desired products.

Initially, when attempting to extract the maximum amounts of Mg, Fe and Al, the sulphuric acid solution of pH 1 was selected as the best option. However, dH₂O would be the more environmentally friendly option, and with the improvement in extraction when using the 1:25 solid to liquid ratio, this can be considered a viable choice.

Having the combination of elements in the leachate made the production of pure Mg(OH)₂ difficult, as the separation of the Fe-fraction from the leachate, post treatment, was challenging. This led to the development of a thermal program to separate the iron from the Mg and Al, prior to leaching. This is expanded on in Chapter 8.

Chapter 8: Separation of Fe from Mg during thermochemical treatment of mine residues

8.1 Introduction

The overall aim of this study was to develop a process for the valorisation of the diamond mine residues, particularly the extraction of Mg. The thermochemical treatment with AS is non-selective at a single temperature, with several metals being co-extracted from the residues. This was acceptable initially, as the goal was the maximum extraction of metals available in the residues. Results presented in Chapters 5 and 7 led to the selection of 450⁰C as roasting temperature, as it gave good extraction, a manageable product as well as being more energy efficient than higher temperatures. However, having the combination of metals in the leachate made the production of pure Mg-products difficult, as the removal of the Fe-fraction post treatment, via methods such as selective precipitation using pH was challenging, as the Fe appeared to be ubiquitous. Another route to remove the Fe, before leaching, was therefore pursued.

Thermochemical treatment of CS and CT with AS at 450⁰C produced a variety of water-soluble ammonium metal- and metal-sulphate species (Table 5.8) which led to the co-extraction of Mg, Al and Fe (Fig 7.9; Fig 7.14). However, extraction of some of these metals could possibly be prevented by thermally decomposing and thereby converting some of the water-soluble ammonium metal- and metal-sulphate species into water-insoluble metal oxides. This may be done by carefully controlling the temperature of the thermal treatment in a subsequent roasting step. From the earlier roasting treatments, it was apparent that Fe extraction was decreased at higher thermochemical treatment temperatures (Fig 7.2). When using AS to extract the manganese from low grade ore which contained 27.5% Fe, Saba et al (1973) found that soluble Fe extraction decreased at temperatures above 700⁰C. Similar results were reported by Meng et al (2020) who found that no Fe was extracted at temperatures above 650⁰C during the extraction of scandium from bauxite ore. From this, a roasting program was developed using pure analytical chemicals at first, with the aim of separating the Fe-fraction from the Mg and Al via decomposition of soluble Fe sulphates to insoluble oxides.

This chapter reports on the development of a method to thermally separate Fe from Mg and Al using mixtures of pure metal sulphate salts. The resultant experimental conditions were then applied to separate Fe from Mg in thermochemically treated mine residues prior to leaching.

8.2 TGA study using pure analytical chemicals

Dehydrated pure chemicals (MgSO_4 , $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Al}_2(\text{SO}_4)_3$) were used as a synthetic analogue that mimics the parent material to demonstrate the selective separation and extraction of Mg, Al and Fe via thermal treatment of a mixture of these salts. A roasting program was developed from TGA data, using the decomposition temperature ranges of the pure metal sulphates as well as a mixture thereof, combined in a similar mass ratio to that found in CS, i.e. Mg:Fe:Al at 3:2:1 as determined by XRF (Fig 4.4). It was important to also investigate the thermal behaviour of a combination of the metal sulphates as the decomposition temperatures of the respective metal sulphates may shift considerably when combined (van der Merwe and Strydom, 2004).

The decomposition reactions and theoretical mass losses expected during TGA analysis of the dehydrated pure metal sulphates and the metal mixture are summarised in Table 8.1, while a comparison of the decomposition behaviour of the pure single metal sulphates vs the mixture is illustrated in Fig 8.1. The mass loss was recalculated from 200°C to eliminate any loss due to adsorbed water which allowed an enhanced comparison.

Table 8.1: Decomposition reactions and theoretical mass losses expected for pure metal sulphates and the metal mixture.

Decomposition reaction	Composition of metal mixture (% m/m)	Theoretical TGA mass loss (%)	
		Pure	Mixture
$\text{MgSO}_4 (\text{s}) \rightarrow \text{MgO} (\text{s}) + \text{SO}_3 (\text{g})$	50.0%	66.5%	33.3%
$\text{Fe}_2(\text{SO}_4)_3 (\text{s}) \rightarrow \text{Fe}_2\text{O}_3 (\text{s}) + 3\text{SO}_3 (\text{g})$	33.3%	60.1%	20.0%
$\text{Al}_2(\text{SO}_4)_3 (\text{s}) \rightarrow \text{Al}_2\text{O}_3 (\text{s}) + 3\text{SO}_3 (\text{g})$	16.7%	70.2%	11.7%

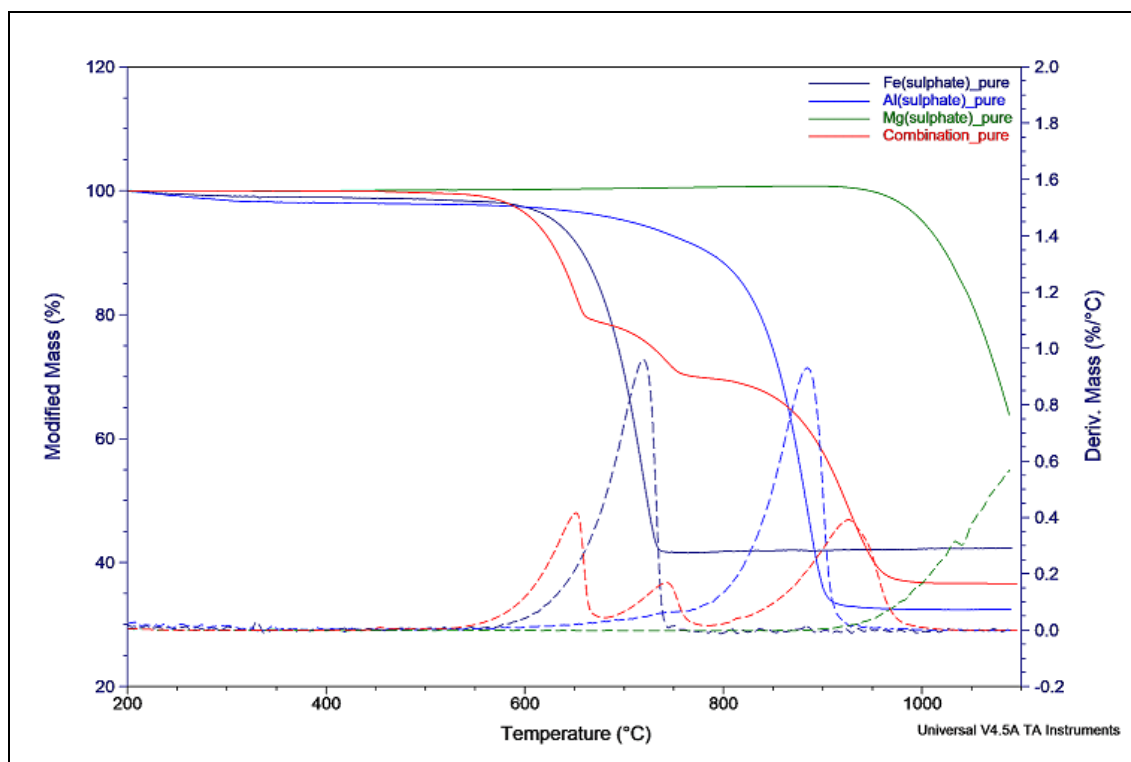


Figure 8.1: Comparison of TGA decomposition temperatures for pure MgSO_4 , $\text{Al}_2(\text{SO}_4)_3$ and $\text{Fe}_2(\text{SO}_4)_3$ vs the metal mixture.

The TGA mass losses obtained for pure $\text{Al}_2(\text{SO}_4)_3$ (70.7%) and $\text{Fe}_2(\text{SO}_4)_3$ (57.8%) agreed well with the calculated values (Table 8.1). Pure MgSO_4 was not completely decomposed over the temperature range studied. Duplicate TGA measurements indicated that the mass losses for the mixture were 19.8 – 19.9% between 550 and 700°C ($\text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{Fe}_2\text{O}_3$), 8.9 – 9.1% between 680 – 775°C ($\text{Al}_2(\text{SO}_4)_3 \rightarrow \text{Al}_2\text{O}_3$) and 32.6 – 33.6% between 780 – 1050°C ($\text{MgSO}_4 \rightarrow \text{MgO}$), which corresponded well to the expected values (Table 8.1). A shift in decomposition temperatures for the metal sulphates in the combined sample was clearly shown by the TGA results. All metal sulphates in the combined sample had decomposition temperature ranges lower than those of the pure metal sulphates, with that of $\text{Fe}_2(\text{SO}_4)_3$ shifting from 600 – 750°C to 580 – 680°C, $\text{Al}_2(\text{SO}_4)_3$ from 750 – 925°C to 680 – 780°C and the largest shift for MgSO_4 from 900 – 1200°C to 800 – 950°C.

The thermal stabilities of the pure dehydrated $\text{Fe}_2(\text{SO}_4)_3$, $\text{Al}_2(\text{SO}_4)_3$ and MgSO_4 used in this study are summarised in Figure 8.2.

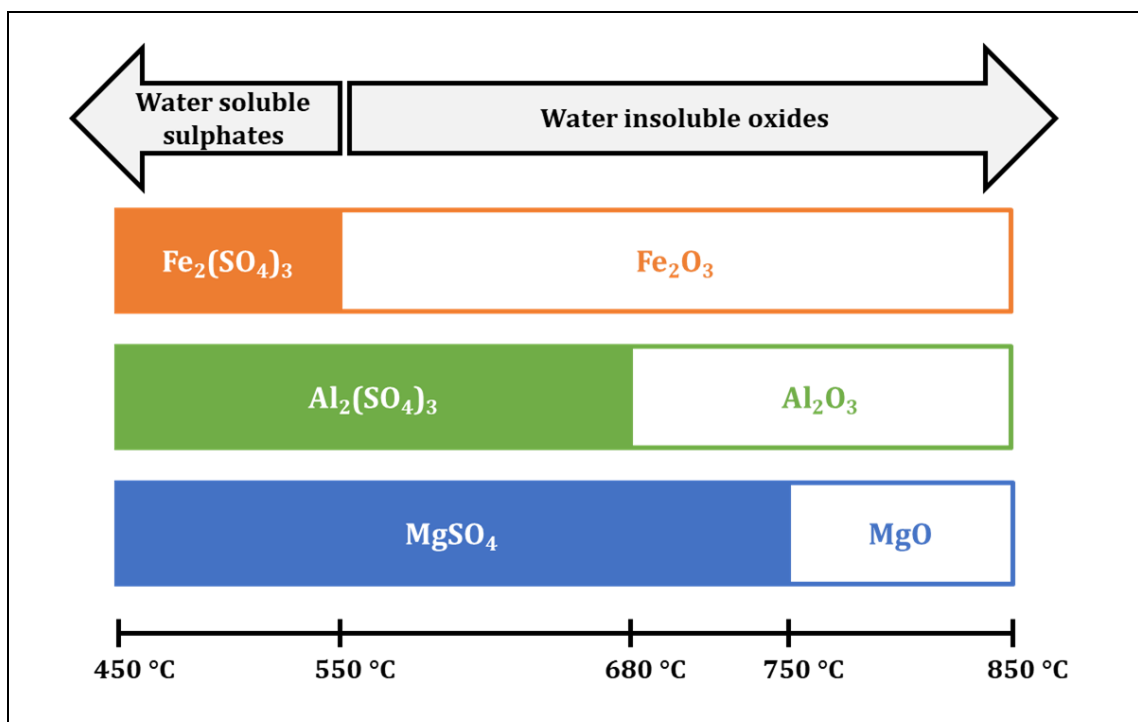


Figure 8.2: Thermal stabilities of water-soluble metal sulphates and conversion into insoluble metal oxides relevant to the metal sulphate mixture.

The results in Fig 8.2 indicate that separation of Fe from Al and Mg in a mixture of their sulphate salts may be achieved by thermal treatment of the mixture at temperatures where water soluble $\text{Fe}_2(\text{SO}_4)_3$ is decomposed to insoluble Fe_2O_3 while $\text{Al}_2(\text{SO}_4)_3$ and MgSO_4 should be kept in the soluble sulphate form, i.e. between 550 – 680°C. Similarly, if both Fe and Al are to be separated from Mg, thermal treatment of the mixture should occur at temperatures between 680 – 750°C. Leaching of the thermally treated mixture is expected to yield the soluble metal sulphate in the leachate and the insoluble metal oxide in the solid leach residue. Re-roasting of the solid leach residue with AS at 450°C is anticipated to convert the remaining insoluble metal oxides back into soluble metal sulphates, which can again be recovered by leaching. Applying these results, the roasting program used to investigate selective separation of Fe, Al and Mg from a mixture of their pure sulphate salts is summarised in Table 8.2.

Table 8.2: Roasting programs used for selective separation of Fe, Al and Mg from the metal sulphate mixture

Sample	Roasting program	Purpose
Metal sulphate mixture	450°C	Test thermal stability of the metal sulphates at the temperature used for thermochemical treatment of mine residues with AS
	750°C	Separate Fe and Al (insoluble oxides, leach residue) from Mg (soluble sulphate, leachate)
Leach residue obtained from 750°C thermal program	Re-roast at 450°C with AS	Recovery of Fe and Al (soluble sulphates, leachate) from the leach residue

The mixture was subjected to the various roasting programs presented in Table 8.2, followed by leaching in distilled water, for 2 h at 50°C. When comparing the colour of the roast residues obtained from roasting at 450°C and 750°C, as well as the 750°C leach residue, the presence of Fe-oxides in the both residues of the 750°C roast was indicated by the dark red colour (Fig 8.3).

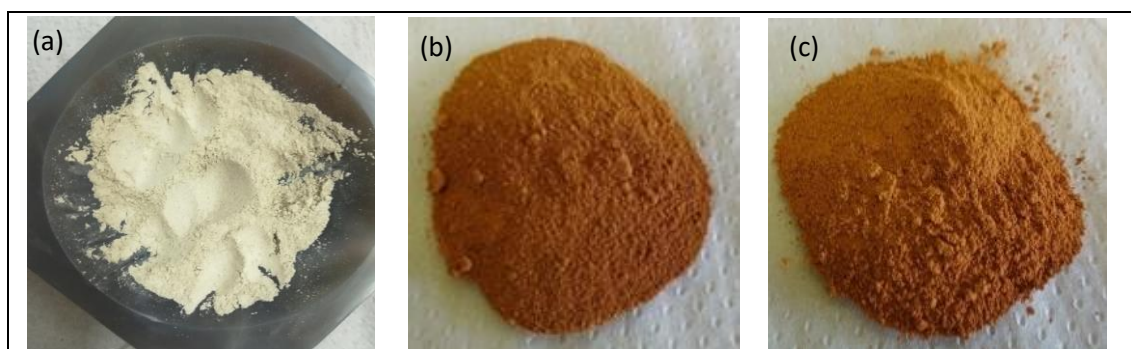


Figure 8.3: Roast residues of the metal sulphate mixture roasted at (a) 450°C and (b) 750°C; and (c) leach residue after leaching of 750°C roast.

This was supported by XRD data for the leach residue, which confirmed that hematite (Fe_2O_3) was the major Fe-containing phase (Fig 8.4), with strong reflections at 2θ of 28.5°,

38.5°, 41°, 48°, 64°, 74° and 76°. Particulate hematite, which has neither crystal faces nor cleavage planes, is typically red in nature (Georgiev et al, 2020; Rock&Gem, 2022)

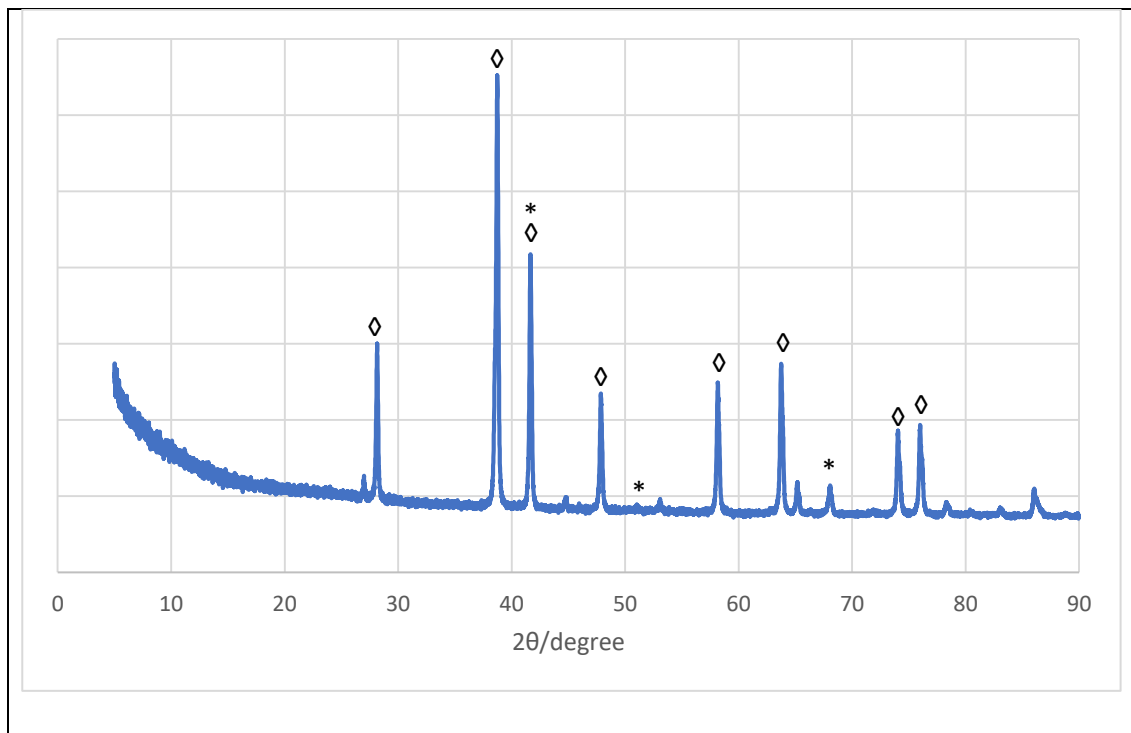


Figure 8.4: XRD pattern for the leach residue of the 750°C roast with ◊ indicating the reflections for hematite (Fe_2O_3) and * for alumina (Al_2O_3).

TGA analysis of the roasting products obtained from roasting at 450°C and 750°C is illustrated in Figure 8.5. The leach residue from the 750°C roast was re-roasted at 450°C with AS to determine whether Fe and Al could be recovered from their respective oxides (Fe_2O_3 and Al_2O_3). TGA analysis of this product is also shown in Figure 8.5.

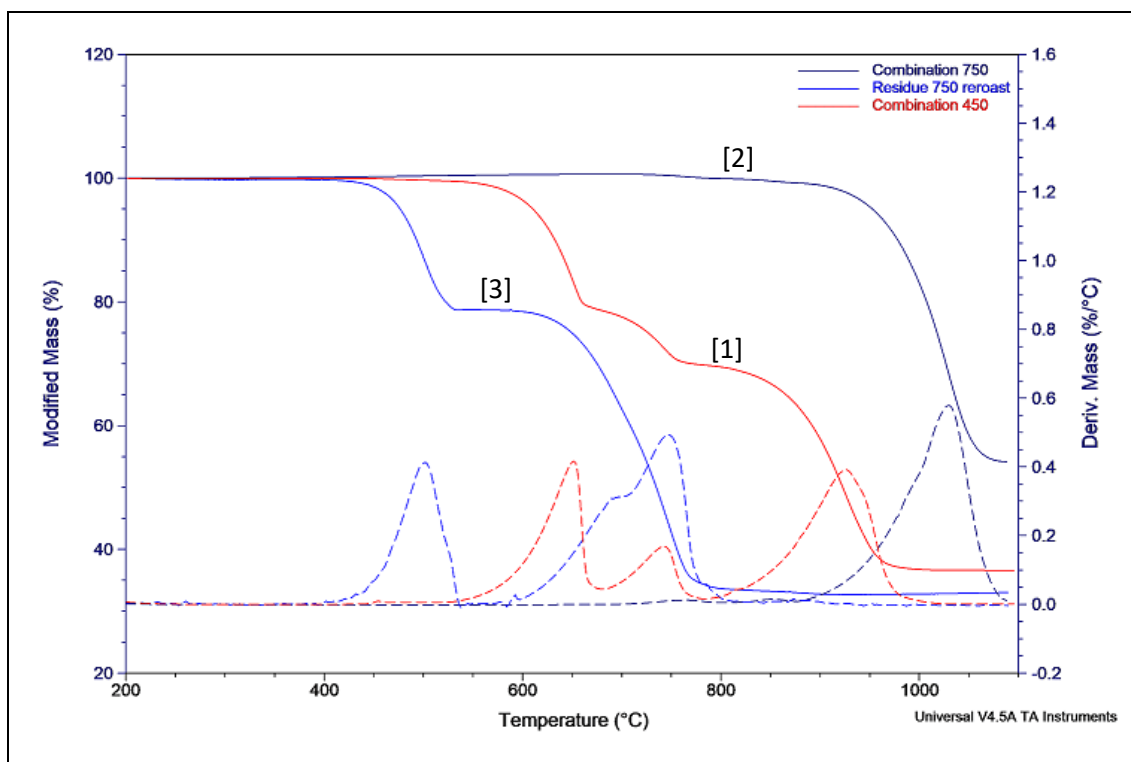


Figure 8.5: Comparison of roasting products after roasting the metal sulphate mixture at [1] 450°C, [2] 750°C and [3] re-roasting the 750°C leach residue with AS at 450°C.

Thermogram 1 showed that Mg, Fe and Al all remain in the soluble sulphate form after roasting at 450°C. All three metals can therefore be extracted from the roasting product by aqueous leaching. Thermogram 2 was similar to that reported for pure MgSO_4 (Fig. 8.1), indicating that only Mg remains in the sulphate form after roasting at 750°C. This was supported by the ICP-OES data (Fig 8.6). The presence of $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Al}_2(\text{SO}_4)_3$ in the roasting product obtained from re-roasting the 750°C leach residue with AS at 450°C (thermogram 3), illustrated that both Fe and Al locked in oxide forms can be recovered into water-soluble metal sulphate forms from the 750°C leach residue after re-roasting with AS at 450°C. Decomposition of the $\text{Fe}_2(\text{SO}_4)_3$ formed during re-roasting with AS overlapped with that of the $\text{Al}_2(\text{SO}_4)_3$ between 600 - 800°C, as indicated by the shoulder in the DTG curve. Excess AS is also apparent (400 - 550°C, thermogram 3), as was observed previously for thermochemical treatment with AS at 450°C for 1 h (Doucet et al, 2016; Mohamed et al, 2016; Castleman et al, 2021) (Fig 5.9 and Fig 6.5a).

From these results (Fig 8.5, thermogram 1), the decomposition of $\text{Fe}_2(\text{SO}_4)_3$ to Fe_2O_3 appears to be complete at 680°C for all samples tested. This temperature was similar to

the temperature reported by Meng et al (2020), i.e. $\geq 650^{\circ}\text{C}$ when working with bauxite residues, and was therefore selected as the roasting temperature to retain Mg and Al as soluble sulphates when applying this program to CS. The rationale behind this was that to produce layered double hydroxides (LDHs), one of the products of interest, both Mg and Al would be required in solution.

The TGA results were supported by the ICP-OES data (Fig 8.6), as Mg, Al and Fe are extracted from leaching of the roasting product obtained at 450°C . The ICP data furthermore indicated that there was still a very small amount of Fe and Al in solution after leaching the 750°C roast (0.3% and 2.4% of the original amount respectively), even though $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Al}_2(\text{SO}_4)_3$ were not visible on the thermogram (Fig 8.4, thermogram 2). Fe and Al were also successfully recovered and extracted from the 750°C leach residue after re-roasting at 450°C with additional AS.

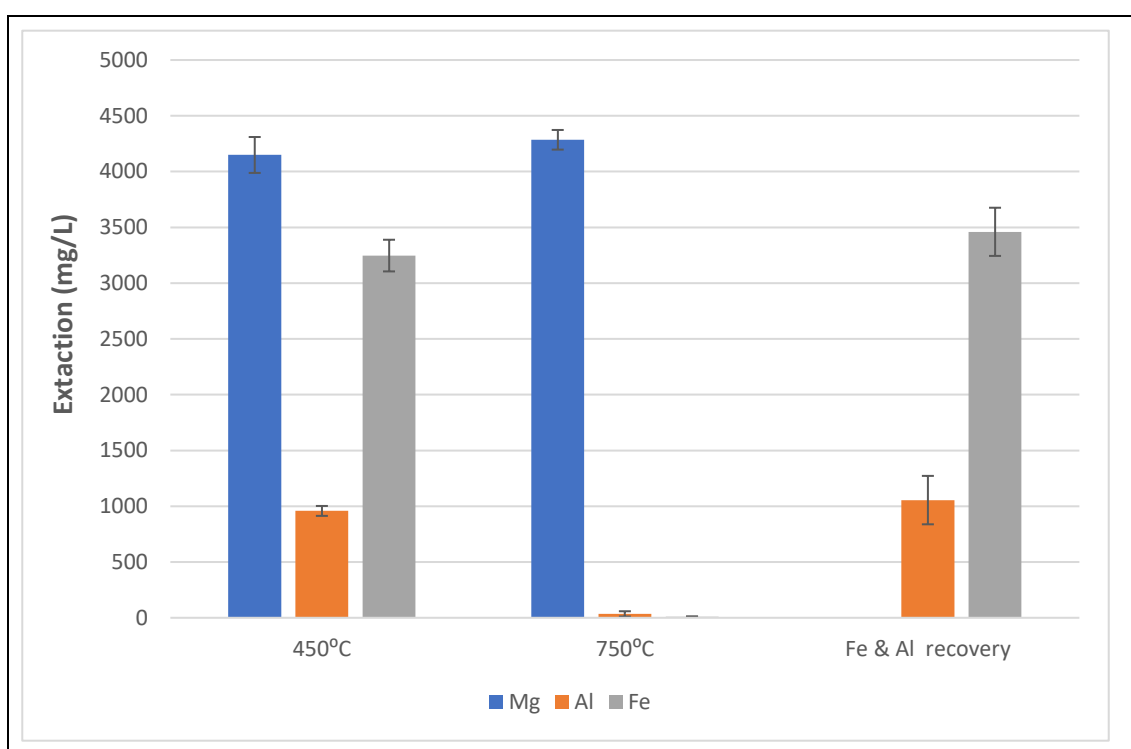


Figure 8.6: Extraction of Mg, Fe and Al after roasting at 450°C , 750°C and re-roasting the 750°C leach residue at 450°C with additional AS (Fe and Al recovery).

8.3 Application to the mine residues

The roasting program used for the mixture of pure metal sulphates was adapted and applied to samples of CS (Table 8.3). Samples were initially roasted at 450°C at a mass/mass ratio of 2:4 CS:AS, to convert the minerals in CS to soluble metal sulphates (Process 1). Additional roasting at 680°C was conducted to retain Fe as insoluble Fe oxide in the leach residue, i.e. decrease the Fe content of the leachate, and retain Mg and Al as soluble sulphates (Process 2). Roasting at 750°C was conducted with the intention to keep only the Mg in soluble sulphate form (Process 3). An additional experiment, using roasting at 680°C with AS, without the initial 450°C roast, was also undertaken (Process 4). This was to reduce furnace time and to ascertain whether a single step process would adequately separate the Fe phase from the Mg and Al phases.

Table 8.3: Roasting programs used for selective separation of Fe, Al and Mg from CS

Sample	Process	Roasting program	Purpose
CS	1	450°C with AS	Thermochemical treatment with AS to convert insoluble minerals to soluble Fe, Al and Mg sulphates
	2	450°C with AS + 680°C	Separate Fe (insoluble oxide, leach residue) from Al and Mg (soluble sulphates, leachate)
	3	450°C with AS + 750°C	Separate Fe and Al (insoluble oxides, leach residue) from Mg (soluble sulphate, leachate)
	4	680°C with AS	Thermochemical treatment with AS to convert insoluble minerals to soluble Al and Mg sulphates; Fe remains in leach residue
Leach residue obtained from 450°C with AS + 680°C roasting program	5	450°C with AS	Recovery of Fe from the leach residue

The mass losses for the different roasting programs are reported in Table 8.4. Mass loss for the roasting product refers to the decrease in mass after thermochemical treatment of CS with AS in the furnace. The roasting product mass losses increased with the additional higher temperature roast after the 450°C roast, as well as when roasting at 680°C without the 450°C roast, although the differences between the programs at higher temperatures were relatively small. This was expected as the mass of Fe-sulphate minerals in the roast residue at 450°C would be higher than the corresponding Fe-oxide minerals in the roast residues at higher temperatures.

Table 8.4: Comparison of % mass loss for roasting products and leach residues after the various roasting programs ($n \geq 2$).

	Roasting program % mass loss			
	Process 1 450°C	Process 2 450°C + 680°C	Process 3 450°C + 750°C	Process 4 680°C
Roasting product	46.0 ± 0.2	57.9 ± 0.05	59.9 ± 0.01	60.8 ± 0.3
Leach residue	56.0 ± 0.5	40.8 ± 0.4	37.1 ± 0.1	34.8 ± 0.4

The leach residue mass losses decreased with the additional higher temperature roast, with the loss for the 450°C roast being substantially higher than the other roast programs. This can be explained by the 450°C roast residue including a larger number of water-soluble ammonium metal sulphates and hydrated metal sulphates than the residues obtained from higher temperature roasts. After the higher roasting temperatures, the leach residues would retain Fe₂O₃ and Al₂O₃, which would reduce the mass loss as only the Mg remains as soluble sulphate at higher temperatures. This was supported by the XRD results (Table 8.6).

Figure 8.7 illustrates the TGA results obtained for the roasting products after the roasting programs using a CS:AS ratio of 2:4 m/m.

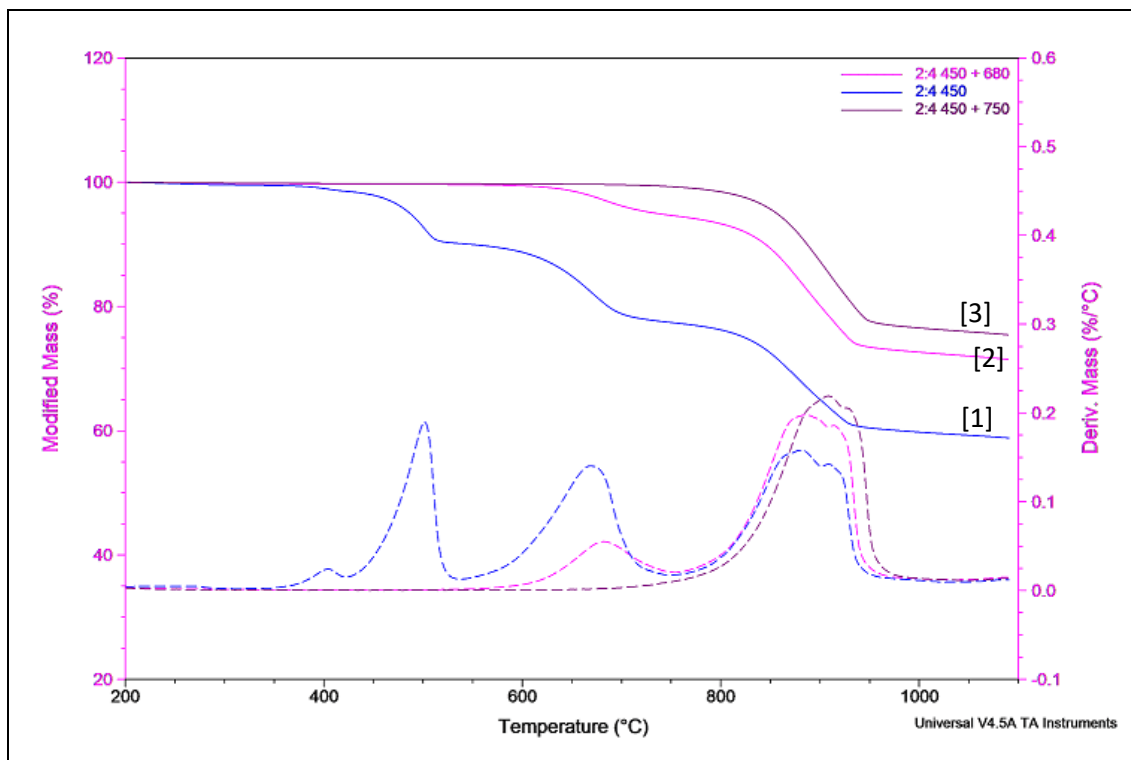


Figure 8.7: Comparison of roasting programs for the CS samples, [1] roasted with AS at 450°C only, [2] roasted with AS at 450°C followed by 680°C and [3] roasted with AS at 450°C followed by 750°C.

For the initial roasting with AS at 450°C (process 1, thermogram 1), the decomposition of $\text{Fe}_2(\text{SO}_4)_3$ to Fe_2O_3 occurred between 425 – 550°C, $\text{Al}_2(\text{SO}_4)_3$ to Al_2O_3 between 550 – 750°C and MgSO_4 to MgO between 800 – 980°C, all of which were considerably lower than for the mixture of pure chemicals (Figure 8.4). This could be as a result of the presence of other phases, e.g. talc and hornblende, that are present in the mine residues.

The thermogram of the roast with AS at 450°C followed by 680°C (process 2, thermogram 2) indicated that $\text{Fe}_2(\text{SO}_4)_3$ phase has been removed, but the $\text{Al}_2(\text{SO}_4)_3$ phase has also been reduced substantially (from ~13% to ~5%). This temperature (680°C) was higher than the temperature indicated as the cut-off for decomposition of $\text{Fe}_2(\text{SO}_4)_3$ formed from roasting CS with AS at 450°C (thermogram 1), for which $\text{Fe}_2(\text{SO}_4)_3$ was completely decomposed just below 600°C. However, the ICP results (Fig 8.8) indicated that some Fe remained as soluble sulphate, even at 680°C, although not visible on thermogram 2. Soluble Fe was decreased by 75 – 79% (Fig 8.8). The thermogram of the roast with AS at 450°C followed by the additional roasting at 750°C indicated that only MgSO_4 was retained as roasting product (process 3, thermogram 3).

The extent of the extraction of Mg, Al and Fe from CS subjected to the various roasting programs and subsequent leaching in water was followed by ICP analysis (Fig 8.8). Table 8.5 compares the % extraction of Mg, Fe and Al for the different roasting programs. The values for maximum possible extraction were determined from original XRF data (Table 4.3), and in the case of the extractable Mg, omitting the Mg content from the talc phase, as reported in Chapter 7 (Fig 7.2).

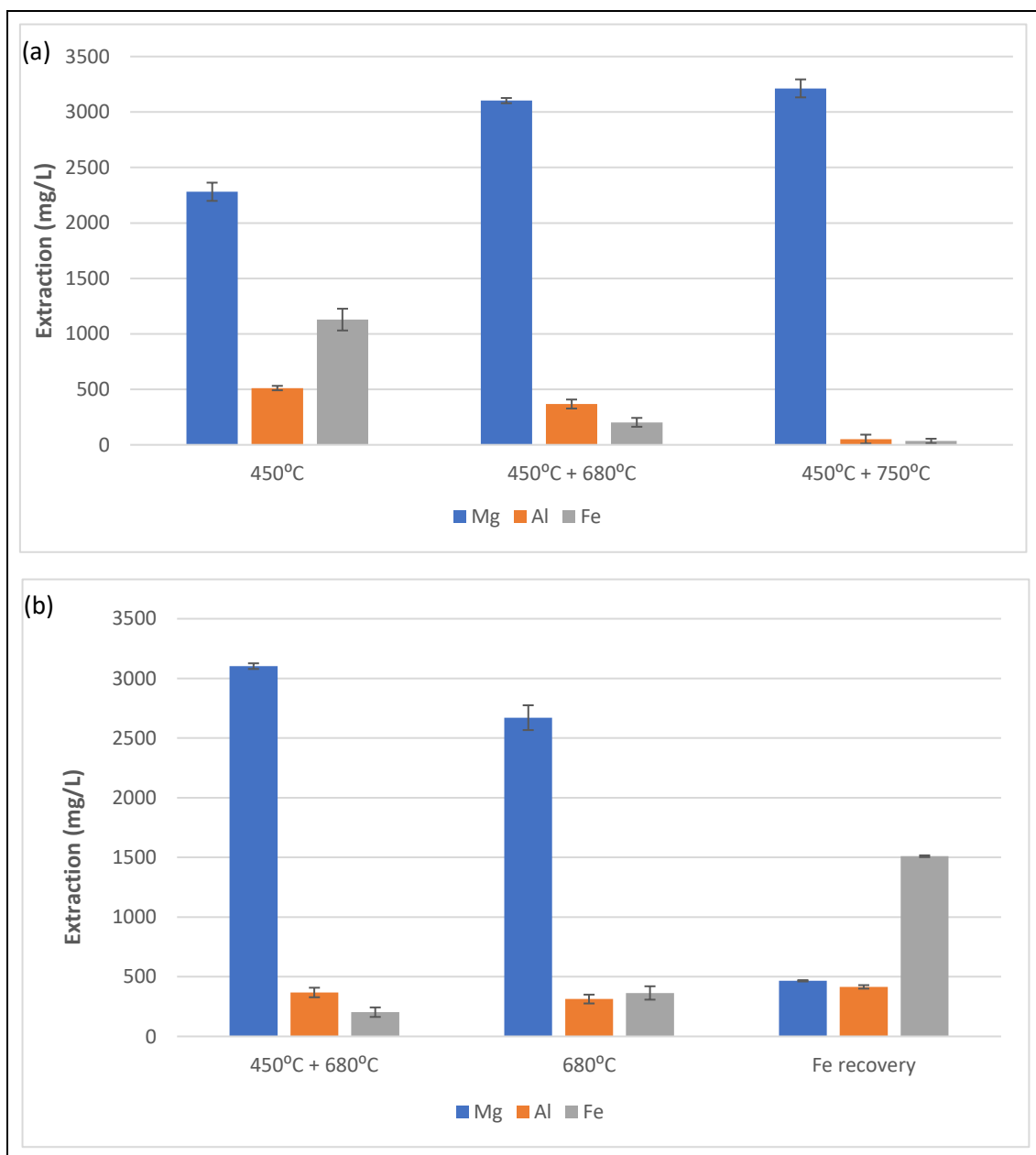


Figure 8.8: Comparison of the extraction of Mg, Fe and Al after following the roasting programs for (a) process 1, process 2 and process 3, and (b) process 2, process 4 and process 5.

Table 8.5: Comparison of the % m/m elemental extraction after the various roasting programs

Roasting Program	Process	%Mg	%Fe	%Al
450°C	1	92.4	64.3	64.9
450 °C + 680°C	2	97.3	12.6	36.4
450°C + 750°C	3	96.6	3.3	4.8
680°C	4	78.4	15.0	28.7
Fe recovery	5	19.4	88.2	53.9

Figure 8.8(a) compares the extraction of Mg, Fe and Al after roasting with AS at 450°C with and without an additional roasting step at higher temperatures. The results supported the reduction in the Al content in the leachate after roasting at 450°C with AS followed by the additional roast at 680°C, as indicated by TGA (Fig 8.7) and also showed that a small amount of Fe was still extracted. The soluble Fe content was, however, decreased by 75 – 79% in the leachate after Process 2 roast (450°C vs 450°C + 680°C; Fig 8.8(a)). The product obtained from the Process 3 roasting program also indicated that a very small percentage of both Fe and Al were still extracted, but there was a 90 – 92% decrease in the soluble Fe content of the leachate.

Figure 8.8(b) compares the extraction of Mg, Fe and Al after the Process 2 roasting program with the Process 4 roasting program, and re-roasted leach residue for Fe recovery (Process 5).

Mg and Al extracted from process 4 was lower (78.4% and 28.7%) than when using Process 3 (97.3% and 36.4%; Table 8.5), whereas the Fe extraction was slightly higher (15.0% vs 12.6%; Table 8.5), indicating that the initial roast with AS at 450°C to convert the phases in the CS to soluble sulphates should not be omitted. Both Mg and Al were retained in the leach residue after Process 2, indicating that although the additional roasting step is decreasing the iron content, it is also decreasing the Mg extracted (Fig 8.8b and Table 8.5).

The TGA and ICP data for analysis of the roasting products and leach residues were supported by XRD results (Figure 8.9; Table 8.6).

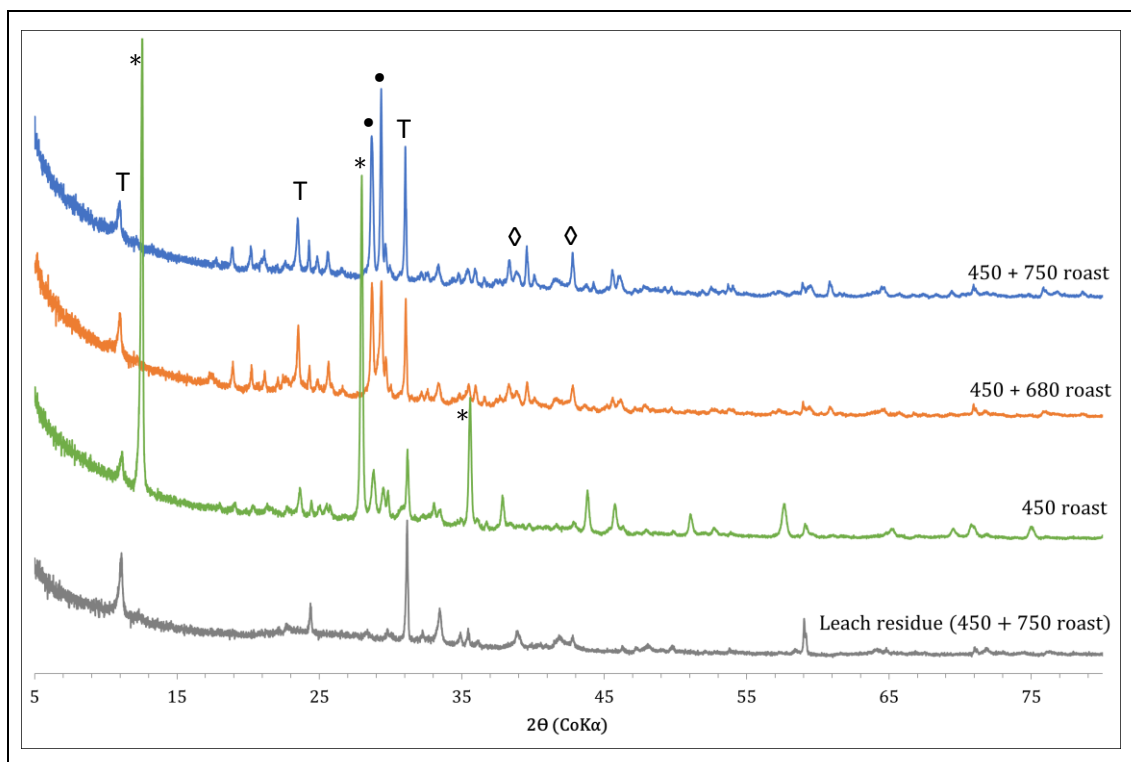


Figure 8.9: Comparison of the XRD reflections for the roast residues after [1] roasting at 450°C with AS, [2] 450°C with AS + 680°C and [3] 450°C with AS + 750°C, as well as the leach residue from the 450°C with AS + 750°C roast. *FeSO₄ minerals; •MgSO₄ minerals; ◇Haematite; T=talc

The reflections from Fe sulphate containing minerals around 2θ of 13°, 28° and 36° decreased once the roasting temperature was increased to 680°C and 750°C from the initial roasting with AS at 450°C. Reflections between 2θ of 29° – 31°, which represent minerals containing Mg sulphate, were not reduced at higher roasting temperatures. Haematite reflections at 2θ of ~39° and 42° were visible for CS treated at 450°C with AS + 680°C and at 450°C with AS + 750°C roasts, as well as for the leach residue. The increase in haematite content was supported by the semi-quantitative XRD results of the leach residues (Table 8.7). The talc reflections at 2θ of 10° and 31° were visible at all roast temperatures as well as in the trace for the leach residue.

Table 8.6 shows that ammonium-metal sulphates were present after the roast at 450°C, but were absent once samples were roasted at 680°C or 750°C, as was seen in Chapter 5. Haematite was the only form of Fe present at the higher roasting temperatures.

Table 8.6: List of newly formed minerals present in the roasting products following thermochemical treatment using different roasting programs

Mineral	Process 1	Process 2	Process 3
	450°C	450°C + 680°C	450°C + 750°C
Efremovite, $(\text{NH}_4)_2\text{Mg}_2(\text{SO}_4)_3$	x		
Hexahydrate, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	x	x	x
Magnesium sulphate, MgSO_4		x	x
Godovikovite, $(\text{NH}_4)\text{Al}(\text{SO}_4)_2$	x		
Millosevichite, $\text{Al}_2(\text{SO}_4)_3$	x	x	x
Sabieite, $\text{NH}_4\text{Fe}(\text{SO}_4)_2$	x		
Anhydrite, CaSO_4			x
Haematite, Fe_2O_3		x	x

The semi-quantitative XRD results for the leach residues of the different roasting programs are presented in Table 8.7. The semi-quantitative XRD results for the original CS raw material were reported in Table 4.2.

Table 8.7: Semi-quantitative mineralogy (mass %) for leach residues after roasting programs.

Mineral	Process 1	Process 2	Process 3
	450°C	450°C + 680°C	450°C + 750°C
Quartz, SiO ₂	21.0	22.2	23.3
Diopside, Ca(Mg,Fe)Si ₂ O ₆	15.3	10.3	10.5
Talc, Mg ₃ Si ₄ O ₁₀ (OH) ₂	55.7	59.1	52.0
Hornblende, Ca ₂ (Mg,Fe,Al) ₅ (Si,Al) ₈ O ₂₂ (OH) ₂	8.0	1.4	
Haematite, Fe ₂ O ₃		7.0	14.2

The quartz (SiO₄) content of the leach residues increased from 4.3% in the CS raw material to 21% as it is liberated by the sulphating reactions of the various silicate phases (Bayer et al, 1982). The increase in hornblende (Ca₂(Mg,Fe,Al)₅(Si,Al)₈O₂₂(OH)₂), from 2.0% in the original CS to 8.0% after the 450°C roast with AS could be due to the amphiboles (an inosilicate) being generally stable at the lower temperatures, and only breaking down at higher temperatures to form chlorite, biotite or other mafic minerals (Nesse, 2000). This temperature is dependent on the type of cation, and increases with increasing Mg content (Földvári, 2011). At the higher roast temperatures (680°C and 750°C), the substantial decrease in hornblende could be due to the phases formed during its decomposition having reacted with AS. Diopside (Ca(Mg,Fe)Si₂O₆), is also an inosilicate with high stability, and has increased from 6.0% in the raw material to above 10% in the leach residues. The slightly lower values at the higher roast temperatures can be explained by the increased presence of haematite.

The occurrence of haematite was also apparent when comparing the colour of the roasting products or leach residues at each roasting program (Fig 8.10), with the residues from the higher roast temperatures having the distinctive brick red colour of haematite (Georgiev et al, 2020).



Figure 8.10: Comparison of (a) the colour of roast products for temperatures (1) 450°C with AS, (2) 450°C with AS + 680°C and (3) 450°C with AS + 750°C, and (b) the corresponding leach residues for (1) 450°C with AS, (2) 450°C with AS + 680°C and (3) 450°C with AS + 750°C.

A comparison of roasting at 450°C with AS + 680°C (process 2) or directly at 680°C with AS (process 4), indicated that there was better extraction of Mg when first using the 450°C with AS roast to convert the minerals in the mine residues to soluble sulphates, before additional roasting at 680°C without AS (Fig 8.6b). There was also improved removal of Fe when using the former program. Re-roasting the 450°C with AS + 680°C leach residue with additional AS (process 5) enabled the recovery of some of the Fe and Al, and also indicated that there had been some Mg lost during the second roasting step of 680°C.

A comparison of the FT-IR spectra of the roasting products for the various roasting programs as well as the 450°C with AS + 750°C leach residue is presented in figure 8.11. The N – H scissoring vibrations at 1420 cm⁻¹ were only visible in the roasts performed at 450°C with AS, supporting the XRD data which reported the presence of ammonium-metal sulphate phases (Table 8.6). The bands in the 1060 – 1070 cm⁻¹ and 590 – 610 cm⁻¹ regions, apparent in all the roasting products, can be ascribed to the sulphate ion

stretching and bending vibrations (Castleman et al, 2021; Rouchon et al, 2012). The increase in the intensity of the bands at $420 - 440 \text{ cm}^{-1}$ for the leach residues obtained from process 5 (450°C with AS + 680°C re-roasted with AS) and process 3 (450°C with AS + 750°C), ascribed to the vibrations of Fe – O bonds (Bumajdad et al, 2011), can be attributed to the increase in haematite content (Table 8.7).

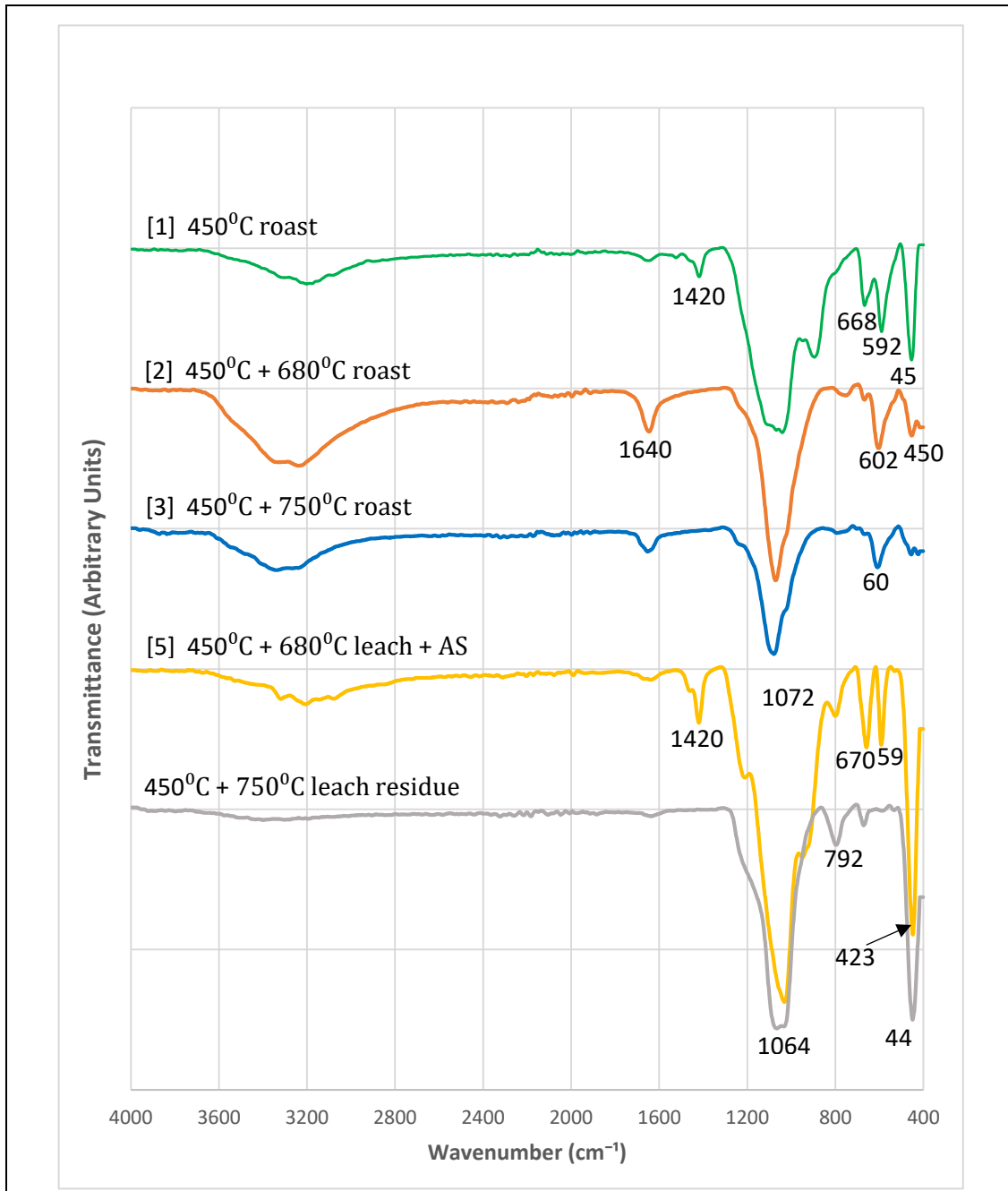


Figure 8.11: Comparison of FT-IR spectra of the roasting products for the various roasting programs and the 450°C + 750°C leach residue. Process numbers are indicated in square brackets.

8.4 Conclusions

Iron can be selectively removed from CS using a sequence of systematic roasting steps, although the temperature ranges used need further testing and refining. Fe can then be recovered from the solid leach residues of the higher temperature roasts by re-roasting the residue with AS at 450°C to form soluble sulphates from the oxide.

The amount of soluble $\text{Al}_2(\text{SO}_4)_3$ was also decreased during the higher temperature roasting, but can be added to the soluble MgSO_4 in the leachate to produce layered double hydroxides (LDHs). This would have been necessary even if all of the Al in the mine residues was retained, as the Mg:Al mol ratio in the leachates was generally higher (5:1 for process 1 to 10:1 for process 2) than the 2:1 or 3:1 mol ratio required for production of LDHs (Fig 8.8).

The leachate from the 450°C with AS + 680°C and 450°C with AS + 750°C roasting programs can be used to synthesise the desired Mg-containing products, as described in Chapter 9.

Chapter 9: Synthesis and Characterisation of Mg containing products

9.1 Introduction

The leachates produced from the dissolution of the soluble metal sulphates in the roast products were used to synthesise a variety of Mg containing products. The leachates from both the 450°C roasts as well as those with reduced iron content (roasted at 680°C or 750°C) were utilised.

These products were characterised using XRD, FTIR, TGA and FE-SEM.

9.2 Precipitation of hydroxides using NH₄OH solution

The leachates obtained from roasting CS with AS at a m/m ratio of 2:4 CS:AS at 450°C (process 1, Table 8.3) and 450°C with AS + 680°C (process 2, Table 8.3) were used to study the precipitation of valuable products via pH control. The leachates were titrated with NH₄OH solution to selectively precipitate the soluble metal ions in solution, i.e. Mg, Fe and Al, in the form of hydroxides. Selective precipitation is a method of separating metal ions in an aqueous mixture using a reagent with anions that form a precipitate which can be separated due to differences in the solubility of the precipitate formed (Zumdahl and DeCosta, 2013).

Figure 9.1 illustrates the stepwise procedure showing the expected pH ranges for the precipitation of metal hydroxides from the leachates. Since the starting pH of the leachate is acidic (pH < 2), the most insoluble of the hydroxide salts, i.e. FeOOH and Fe(OH)₃, will precipitate first (Georgiev et al, 2020; Scholz et al, 2015).

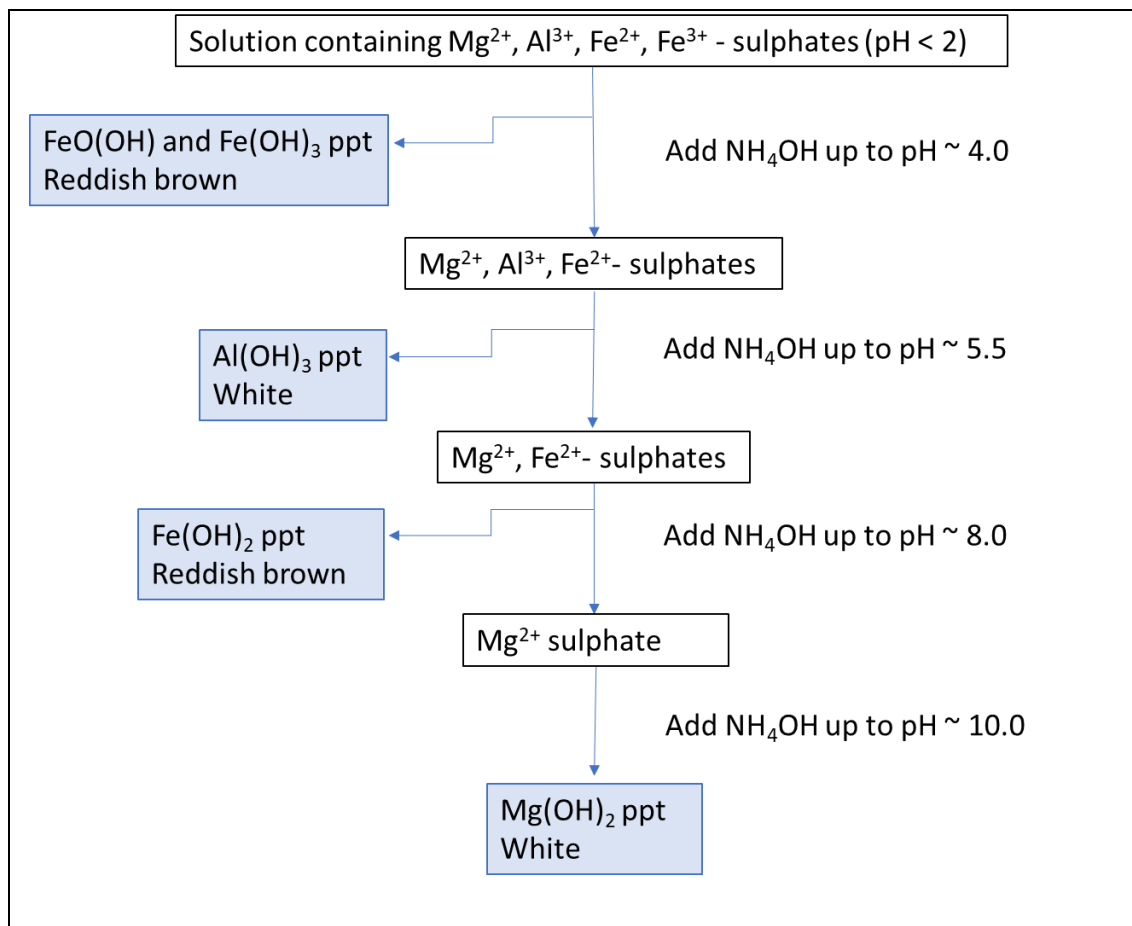


Figure 9.1: Process of selective precipitation for the separation of the metal ions in the leachate as metal hydroxides. Blue blocks indicate expected products.

The published literature indicates that Al(OH)_3 was expected to precipitate around a pH of 6 (Sierra et al, 2017). The Fe component was predicted to precipitate at pH values ranging between 3 to 9, depending on the form of the precipitate, i.e. FeOOH (goethite) from pH ~ 3 (Georgiev et al, 2020; Scholtz and Kahler, 2015), Fe(OH)_3 above a pH of 4 (Romão et al, 2015; Scholtz and Kahler, 2015) and Fe(OH)_2 between a pH of 8 – 9, (Fagerlund, et al. 2012; Nduagu et al, 2013; Romão et al. 2016; Sierra et al., 2017). Mg(OH)_2 was expected to precipitate above a pH of 10 (Nduagu et al, 2012a; Sierra et al., 2017).

A flow diagram illustrating the processes to produce precipitation products from the leachates is given in Fig 9.2.

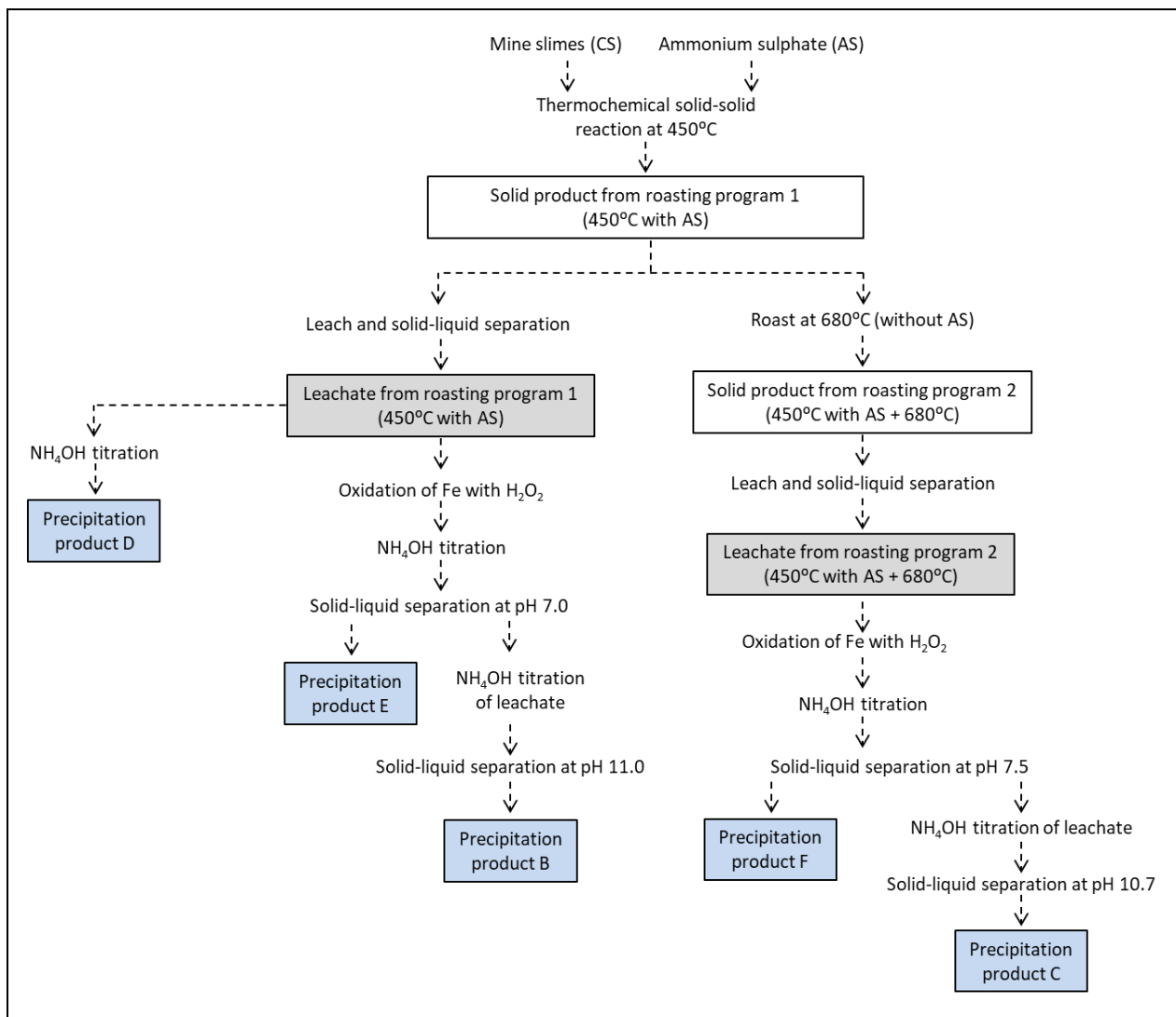


Figure 9.2: Process flow diagram for the extraction of Mg, Fe and Al from CS used as starting solutions (grey blocks) and selective precipitation of products via pH control (blue blocks).

The average concentrations of Mg, Al and Fe in the leachates obtained from Process 1 (roasting CS at 450°C with AS) and Process 2 (450°C with AS and an additional roast at 680°C without AS), initially reported in Figure 8.8, are summarised in Table 9.1. These solutions were used as starting materials during the selective precipitation process.

Table 9.1: Average concentrations (mg/L) of Mg, Al and Fe in the leachates used as starting solutions for selective precipitation of metal hydroxides ($n \geq 2$).

	Process 1 (450°C with AS)	Process 2 (450°C with AS + 680°C)
Mg	2280	3100
Fe	1130	200
Al	510	370

The initial addition of a small amount of the NH_4OH solution to the leachate from process 1 (pH increased to 2.8) caused the leachate solution to change from colourless to yellowish brown with the appearance of some flocculation. The solid product was filtered off at pH ~ 4 , which gave a reddish-brown gel-like product. After drying, it formed hard dark brown granules which XRD analysis reported as being amorphous. The filtrate was murky and after addition of NH_4OH solution the colour became yellowish again and white flocculation was visible. This may indicate the presence of either soluble complexes in solution or colloidal particles in suspension, or both. A technique such as Dynamic Light Scattering (DLS) can be used to confirm whether colloidal particles were present. This however falls outside the scope of this study, and was not investigated further. The remaining solution was filtered at pH ~ 6 as well as pH ~ 7 and pH ~ 9 , which also produced gel-like products. These became red-brown to charcoal coloured granules after drying. These colour changes suggested the presence of Fe in all the precipitates, possibly in different forms and oxidation states, which is supported by observations reported in the literature (Scholtz and Kahler, 2015; Sierra et al., 2017).

In an attempt to improve the separation of the metal ions from the leachate via selective precipitation under controlled pH conditions, the starting leachates (i.e. prior to addition of the alkaline reagent) were also treated with the addition of hydrogen peroxide (H_2O_2) to oxidise divalent Fe^{2+} to Fe^{3+} (Romão et al, 2015). The intention of this step was to reduce the pH at which the Fe would precipitate as $\text{Fe}(\text{OH})_3$ (pH ~ 4.0) and allow $\text{Al}(\text{OH})_3$ (pH ~ 6.0) and $\text{Mg}(\text{OH})_2$ (pH ~ 10) to be separated during the

titration with NH_4OH . The colour of the leachate changed from clear to orange after the addition of H_2O_2 (Fig 9.3).

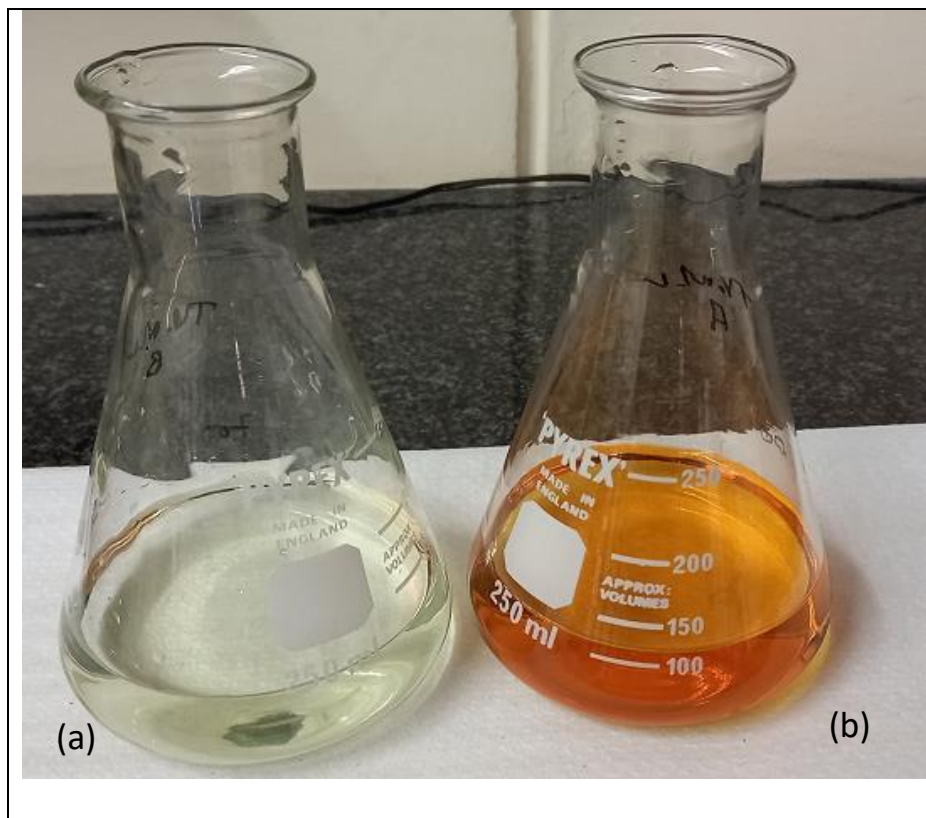


Figure 9.3: Leachate (a) before and (b) after the addition of hydrogen peroxide to the leachate obtained from Process 1.

Table 9.2 summarises the precipitation product numbers (A-F) and the approach used to produce precipitates from the leachates after pH adjustment to different values, including the pH at which filtration of the precipitate was undertaken. The precipitates produced at pH values greater than 10 were compared to precipitates formed from a solution of pure MgSO_4 titrated with NH_4OH solution (Precipitation product A, Table 9.2).

Table 9.2: Summary of the preparation methods followed for some of the precipitates formed after titration of leachates with NH_4OH .

Starting material	pH range for precipitation	H_2O_2	Precipitation product
Pure analytical MgSO_4 solution	4.0 – 11	✗	A
Leachate from 450 ⁰ C roast	1.8 – 4.2	✗	D
	1.8 – 7.0	✓	E
	7.0 – 11.0	✓	B
Leachate from 450 ⁰ C + 680 ⁰ C roast	2.4 – 7.5	✓	F
	7.5 – 10.7	✓	C

Numerous precipitates were collected at various other pH values, but due to having insufficient amounts, these were not characterised fully. Some SEM images of these precipitates are included in Figure 9.8. Products A – F (Figure 9.2 and Table 9.2) were obtained in sufficient quantities for XRD, TGA, FTIR and FE-SEM analyses.

In order to compare the effect of the roasting program followed and the pH at which the products were filtered, products B, C and E were characterised via ICP-OES following complete digestion in HNO_3 . Table 9.3 shows the concentrations of Mg, Fe and Al after dissolving 0.05 g of these precipitates in 20.0 mL of a pH 2 HNO_3 solution. This mass represented approximately 20% m/m of the precipitate formed.

Comparison of the results obtained for product B and product E, both produced from leachate from Process 1 (450⁰C with AS roast) which had been treated with H_2O_2 , showed that relatively high amounts of Fe and Al were present in product E, thus had been removed from the leachate during precipitation up to a pH of 7.0. There was still a small amount of these metals remaining in the leachate which precipitated out at the higher pH level (product B). The occurrence of Mg in the precipitate of product E indicated that some of the Mg was removed from the leachate during precipitation up to at a pH of 7.0. This supports the findings of Sierra et al., (2017) who reported little $\text{Mg}(\text{OH})_2$ precipitation below pH 7, and simultaneous precipitation of Fe and Al hydroxides above a pH of 3.5, when working with serpentine residues.

Table 9.3: Comparison of the concentrations of Mg, Fe and Al (in mg/L) in 0.05 g of some of the precipitates dissolved in 20 mL nitric acid solution.

Precipitate	Product E pH 7 (450°C roast)	Product B pH 11 (450°C roast)	Product C pH 10.7 (450°C + 680°C roast)
Mg	57	790	785
Fe	501	2.0	3.2
Al	189	2.5	2.8

When comparing the compositions of products B and C, i.e. different roasting conditions precipitated at a similar pH, the amounts of Mg, Fe and Al in the precipitates were very similar, indicating that including the additional roasting step at a higher temperature (680°C) had not removed more Fe or Al than using selective precipitation. The Fe remained difficult to separate from the Al and Mg (Table 9.3).

Figure 9.4 illustrates the colour of the Products B and E, obtained from precipitation at different pH values, after aging and drying. The colour of product C was the same as that of product B.



Figure 9.4: The precipitation products from the leachate of the 450°C roast, after filtration at (a) pH of 7.0 (product E) and (b) pH of 11.0 (product B).

The precipitates formed at lower pH values, whether H_2O_2 was added or not, were originally ochre coloured and gel-like in appearance after filtering and then became dark red-brown after aging and drying, as illustrated in Fig 9.4 (a). Mg-rich precipitates formed at a pH > 10 were soft and white (Fig 9.4 (b)). This illustrates that the products formed were not pure (Fig 9.3, products D and E; Table 9.3), which supports the work carried out by Sierra et al (2017), who reported that the Al and Fe concentrations both decreased from a pH of 3.5 and that there was already some decrease in the Mg concentration at pH 7.5. These results are substantiated by the XRD data for the products.

The XRD reflections for Products A - E are illustrated in Fig. 9.5. The strong reflections at 2θ of 21° , 44° , 60° and 69° , as well as the smaller reflections at 2θ of 73.5° , 81° and 86° are characteristic of brucite, i.e $Mg(OH)_2$ (Wang et al, 2011), and featured prominently in the precipitates A, B and C. generated at pH ≥ 10 . Products B and C contained traces of aragonite ($CaCO_3$). The XRD patterns for the precipitates formed at lower pH values (products D and E) revealed that these particles were amorphous in nature, possibly $FeOOH$ or $Fe(OH)_3$ as reported by ul Haq and Haider (2010).

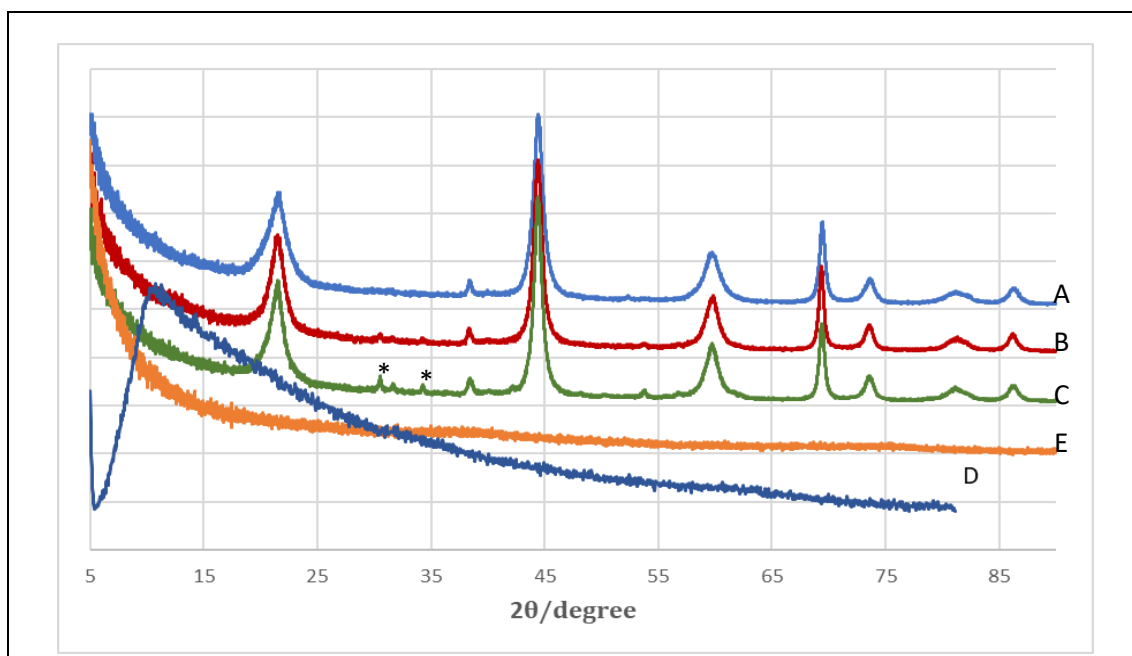


Figure 9.5: Comparison of the XRD reflections for various precipitation products formed at different pH values (Table 9.2). (A) $Mg(OH)_2$ precipitated from pure $MgSO_4$ at pH 11; (B) pH 11; (C) pH 10.7; (D) pH 4.2; (E) pH 7.0. Impurities in the form of aragonite (*) are indicated.

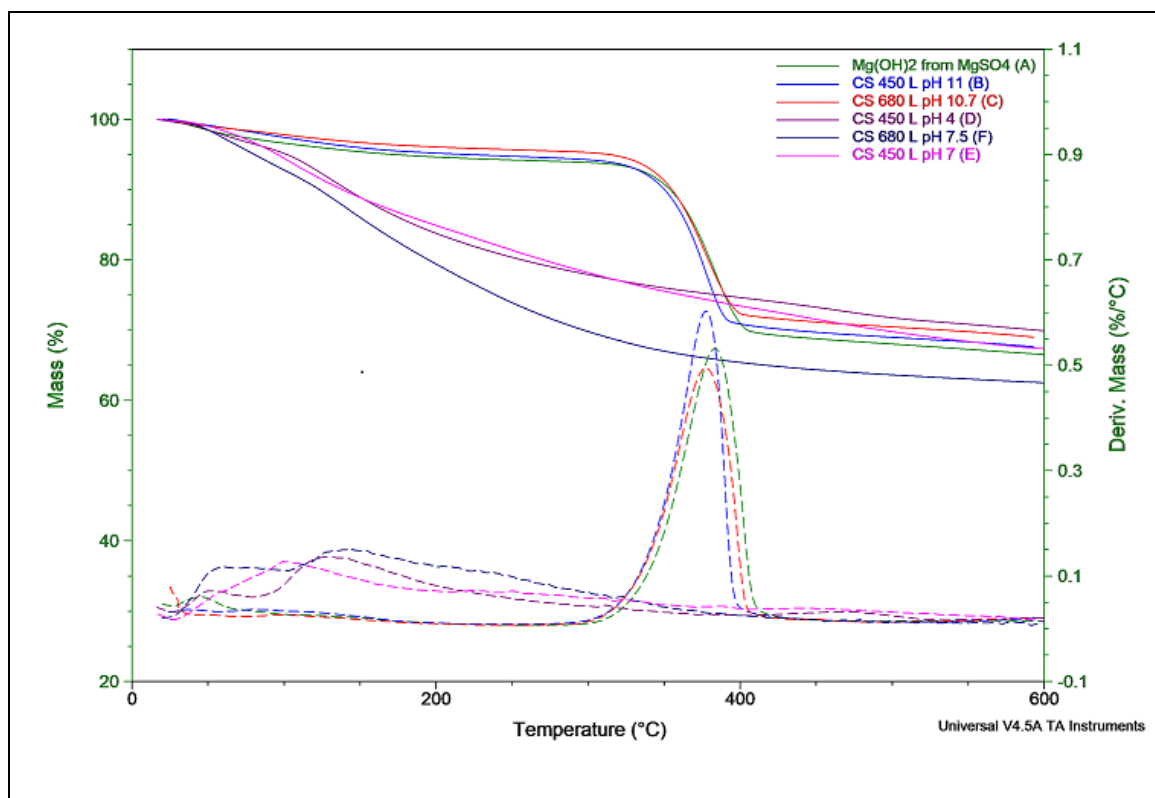


Figure 9.6: TGA thermograms for product A (green), product B (blue), product C (red), product D (purple), product E (pink), product F (navy).

Thermogravimetric analysis of the precipitates is illustrated in Fig 9.6. The TGA thermograms supported the data obtained from XRD analysis, where the precipitates formed at higher pH values (products A to C) were found to consist mainly of brucite. These samples presented a TGA mass loss of ~ 28% between 350°C – 400°C (Alvarado et al, 2000; Földvári, 2011; Hanna et al., 2019), which agrees with the expected dehydroxylation mass loss of 30.9% according to the reaction:



The precipitates formed at lower pH values ($\text{pH} \leq 7.5$) showed a steady mass loss, with two slightly more prominent mass losses, observed in the DTG curve below 200°C, which could be due to the loss of adsorbed water and dehydroxylation of Fe(OH)_3 as this occurs below 200°C (Földvári, 2011), or partial conversion of amorphous Fe(OH)_3 to amorphous FeOOH (Bumajdad et al, 2011) according to the reaction:



In addition, some of the mass loss could be due to the dehydroxylation of $\text{Al}(\text{OH})_3$, which also starts between 180°C - 200°C , depending on particle size and physical form (Földvári, 2011; Hollingbery and Hull, 2010). The presence of both Fe and Al in the precipitate is supported by the ICP-OES data for the redissolution of product E (Table 9.3). The FT-IR spectra for the precipitation products from the leachates are shown in Fig 9.7, and are compared to the $\text{Mg}(\text{OH})_2$ precipitated from pure MgSO_4 (product A).

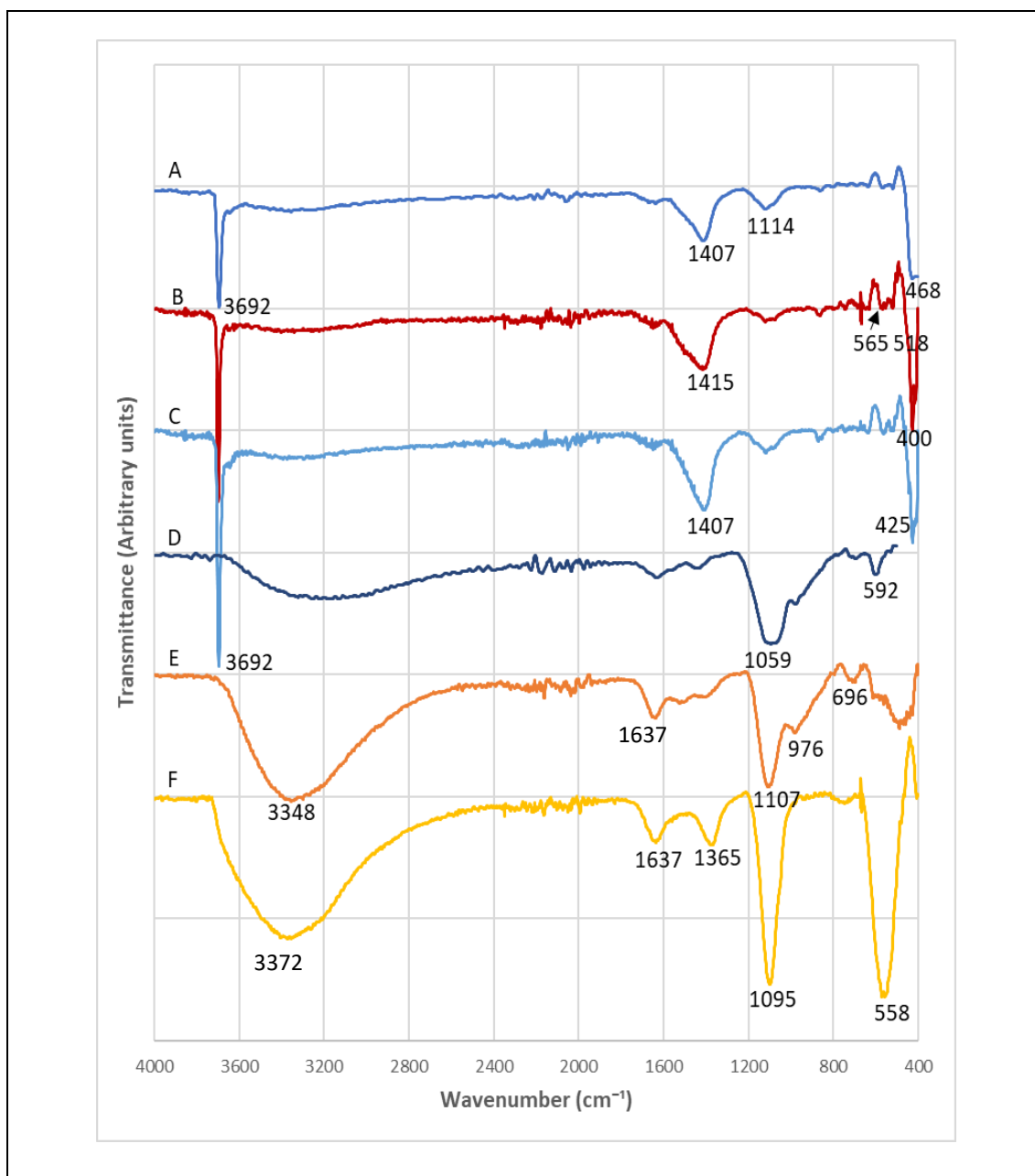


Figure 9.7: FT-IR spectra for various precipitation products compared to $\text{Mg}(\text{OH})_2$ prepared from pure analytical MgSO_4 (product A).

Precipitates formed at the higher pH values (products B and C) have distinctive, sharp Mg–O–H stretch peaks at 3692 cm^{-1} (Hanna et al, 2019; Wang et al., 2011), as well as the Mg–O–H bend vibrations between $1400 - 1420\text{ cm}^{-1}$ which are associated with brucite (Hofmeister and Bowey, 2006; Wang et al, 2011). The peaks between $400 - 460\text{ cm}^{-1}$ are due to Mg – OH stretch vibrations (Hofmeister and Bowey, 2006).

The precipitates prepared at lower pH values (products D, E and F) have a broad band between $2800 - 3700\text{ cm}^{-1}$ which is due to O–H stretching vibrations of adsorbed water. The 1637 cm^{-1} peak is also indicative of water (Bumajdad et al, 2011; Hofmeister and Bowey, 2006). The bands in the region of $558 - 592\text{ cm}^{-1}$ can be ascribed to Fe–O stretching vibrations as well as Al–OH vibrations, and the strong bands between $1059 - 1107$ correspond to Al–O–H vibrations (Bumajdad et al, 2011; Farahmandjou and Soflaee, 2015; González-Gómez et al, 2019; Klopprogge et al, 2004). These precipitates therefore contained both $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$. This is supported by ICP-OES data from the redissolution of precipitates in a nitric acid solution (Table 9.3). The product F spectrum differs slightly from that of products D and E probably due to being synthesised from process 2 leachate ($450^\circ\text{C} + 680^\circ\text{C}$) which contained lower concentrations of both Fe and Al ions (Table 9.1) whereas the latter two were both synthesised from the 450°C leachate. The vibration at 1365 cm^{-1} (smaller in D and E) indicates the presence of carbonate species, possibly due to the absorption of CO_2 from the atmosphere during aging, which was also observed by Han et al (1998).

The morphology of the precipitates was examined using FE–SEM (Fig. 9.8 and Fig. 9.9). Figure 9.8 illustrates precipitates produced from the leachate from roasting program 1 (Fig. 9.1) after the addition of H_2O_2 and precipitation at pH 7.0 (product E) and pH 11.0 (product B), compared to $\text{Mg}(\text{OH})_2$ produced from pure MgSO_4 . The product formed at pH 11 (sample B) shows similar morphology to the $\text{Mg}(\text{OH})_2$ produced from pure MgSO_4 , i.e thin, platelet like particles, which are comparable to the morphology reported for $\text{Mg}(\text{OH})_2$ produced from MgSO_4 using NH_4OH by Alvarado et al (2000) and Henrist et al (2003). This morphology has been described as a result of an intergrowth mechanism where individual platelets have grown simultaneously resulting in particles which are randomly tangled (Henrist et al, 2003).

The particles produced at lower pH (sample E) were globular, pointing to the amorphous nature of the product observed during XRD measurements (Fig 9.5).

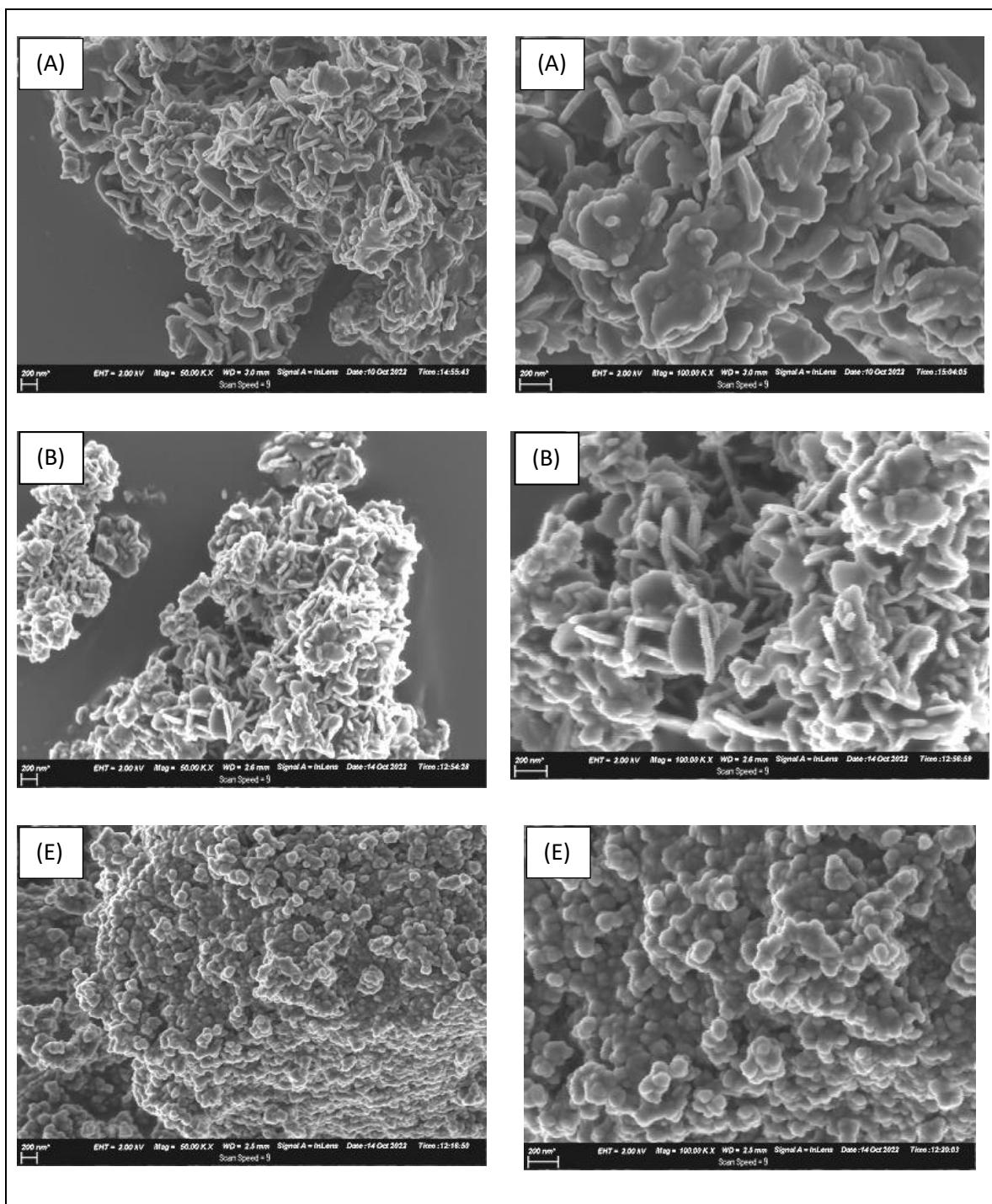


Figure 9.8: FE-SEM images for products (A) $\text{Mg}(\text{OH})_2$ from MgSO_4 ; (E) produced from the leachate from 450°C roast, precipitated at pH 7.0; (B) produced from the leachate from 450°C roast, precipitated at pH 11.0. H_2O_2 was added.

Figure 9.9 illustrates the morphologies of the precipitates produced from the 450°C leachate precipitated between pH 3.8 – 9.0, without the addition of H₂O₂. As illustrated in Figure 9.8, at lower pH values the morphology obtained was globular, with particles being irregular in shape and size, possibly indicating the amorphous nature of the product (Sujana and Anand, 2010).

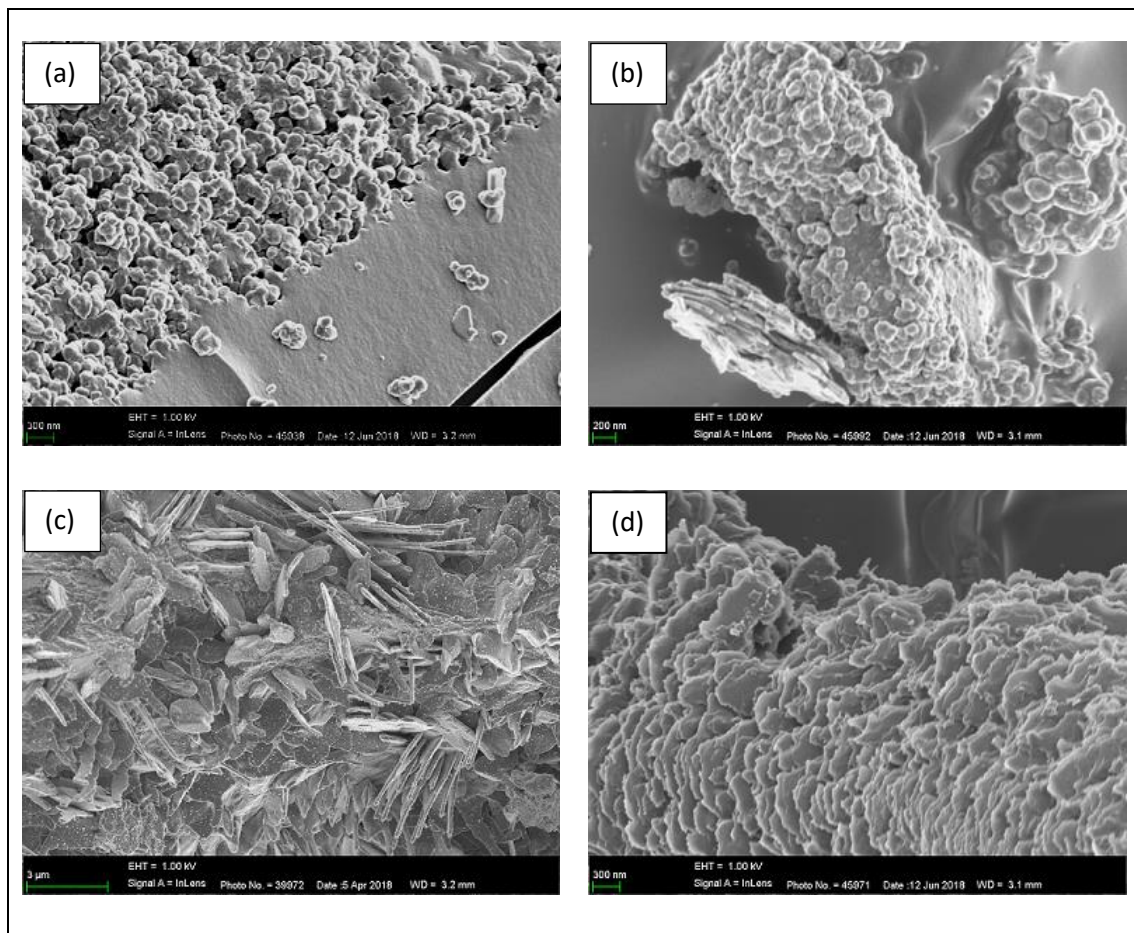


Figure 9.9: FE-SEM images of precipitates produced from 450°C roast leachates at various pH values, without addition of H₂O₂. (a) pH 3.8 (b) pH 4.0 (c) pH 5.2 (d) pH 9.0.

At a pH of 9.0, the precipitates formed thin, platelet like particles, similar in shape to the Mg(OH)₂ formed from pure MgSO₄, but highly agglomerated, which was also observed by Alvarado et al (2000).

It was not possible to perform additional characterisation on these precipitates as insufficient quantities of material were produced.

9.3 Preparation of layered double hydroxides (LDHs)

The composition, properties and applications of LDHs, also referred to as hydrotalcite-like materials, were discussed in Chapter 2.4.2. In general, these are layered anionic clay compounds with a general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O$, where the term in the first bracket, $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}$, describes the composition of the layered double hydroxide layers consisting of divalent (M^{II}) and trivalent (M^{III}) metal cations. The symbol x represents the molar fraction of M^{III} to total metal cations (sum of M^{II} and M^{III}) in the layered structure, and is in the range $0.1 \leq x \leq 0.5$ (Benhiti et al, 2020; Olfs et al, 2009; Theiss et al, 2016). The term $[(A^{n-})_{x/n} \cdot yH_2O]$ represents the composition of the anionic interlayer, with A being the interlayer anion with charge n^- . A can be an inorganic (e.g. CO_3^{2-} , SO_4^{2-} , Cl^- , OH^-) or organic anion (e.g. polymers, amino acids) (Berber et al, 2013; Cavani et al, 1991; Gevers et al, 2019; Olfs et al, 2009).

The leachates obtained from Processes 1 and 2 contained Mg, Fe and Al in soluble form (Table 9.1), with the M^{II} to M^{III} mol ratio being between 2.5 to 3.0 for leachates from process 1, assuming that both the Fe and Al were included as being M^{III} in the LDH structure. Producing Fe-containing LDHs was of interest as these have been used as precursors to produce ferrite spinel materials (Evans et al, 2005; Liu et al, 2003). Fe^{3+} may be substituted for Al^{3+} in the positively charged sheets, as they have the same charge and are similar in size (Mališová et al, 2018). In a study on stabilising flexible PVC with LDHs, Labuschagne et al. (2015) used some Fe (25 mol%) in place of Al. Initially, the leachate from the 450°C roast (Process 1, Table 9.2) was utilised to produce LDHs using two slightly different co-precipitation methods, i.e. slow, pH-controlled addition (method 1) and rapid addition (method 2) of the metal ion solution to a carbonate containing solution (Cavani et al, 1991). Production of LDH's from the leachate through a urea hydrolysis method was tested in comparison (Benhiti et al, 2020; Berber et al, 2013). Pure analytical chemicals ($MgSO_4$ and $Al_2(SO_4)_3$) were used for all methods as a control. Products formed were characterised using XRD, TGA, FTIR and FE-SEM.

9.3.1 Using the co-precipitation methods

Figure 9.10 compares the XRD patterns for LDHs prepared using co-precipitation methods 1 and 2 from the leachates of the 450°C roast (Process 1, Table 9.2) against those prepared from pure analytical chemicals.

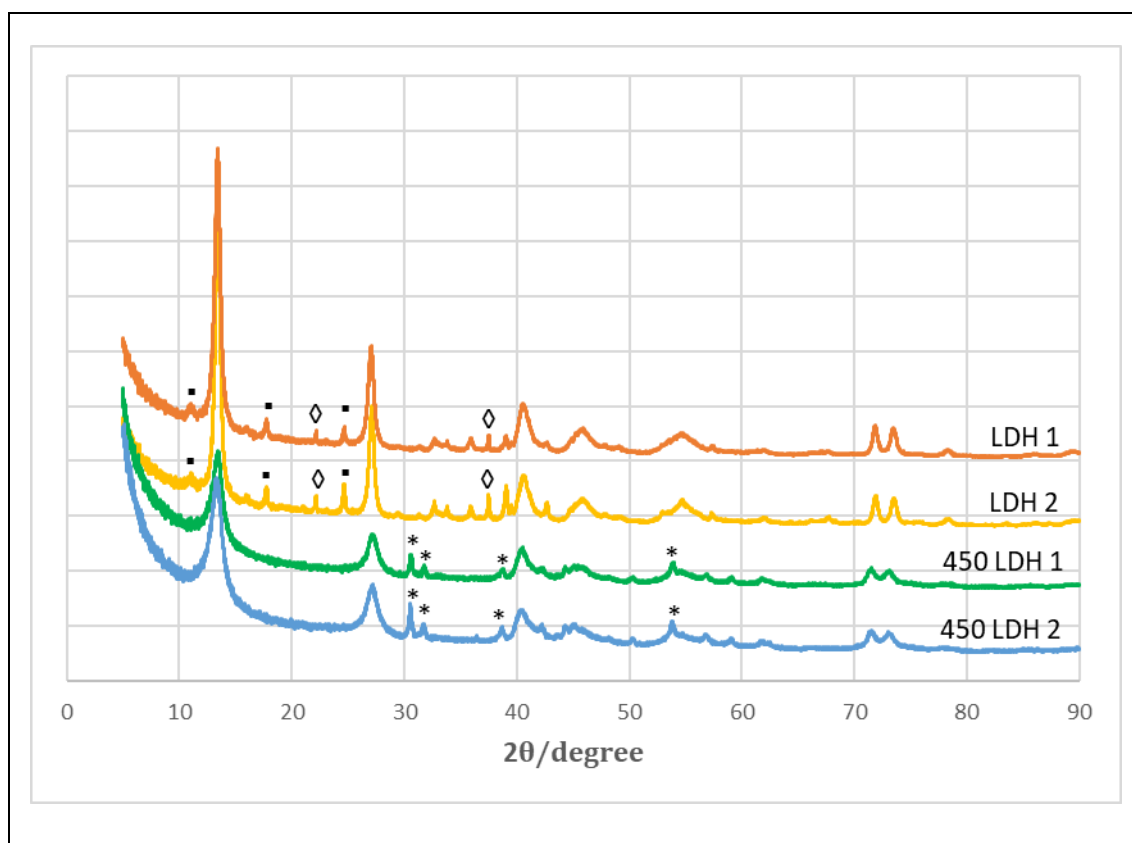


Figure 9.10: XRD reflections comparing LDHs produced by the two co-precipitation methods from pure analytical chemicals (LDH 1 and LDH 2) vs those produced from leachate of a 450°C roast (450 LDH 1 and 450 LDH 2). Impurities in the form of aragonite (*), thenardite (◊) and hydromagnesite (■) are indicated.

The intense reflections at 2θ of 13.6° (primary reflection) and 27.3° (secondary reflection) for all the samples are consistent with the formation of Mg-Al LDHs (Klemkaite et al., 2011; Labuschagne et al., 2015). The reflections of the products from pure chemicals showed higher intensities and were sharper than the reflections of products from the leachates, indicating better crystallinity (Benhiti et al., 2020; Labuschagne et al., 2015; Olfs et al., 2009).

The reflections of the products formed via the two different methods from pure chemicals were almost identical. Those from method 2 were slightly sharper, indicating slightly better crystallinity, but there is very little difference between the two methods used, possibly due to the particle size and distribution of the precipitated LDH being difficult to control with either of these methods (Evans and Duan, 2006). The reflections of the products synthesised from the leachates using the two different methods are also very similar, with the reflections from method 2 also being slightly more intense than those from method 1.

Although a good yield of hydrotalcite was obtained (>85 % m/m), some impurities, in the form of thenardite, aragonite and hydromagnesite were present, as indicated in Table 9.4, which gives the semi-quantitative results of the XRD analysis.

Table 9.4: Semi-quantitative XRD analysis (% m/m) for LDHs produced by co-precipitation.

Mineral	Chemical composition	LDH 1	LDH 2	450 LDH 1	450 LDH 2
Hydrotalcite		86.2	86.1	88.0	88.0
Aragonite	CaCO ₃			12.0	12.0
Thenardite	Na ₂ SO ₄	3.4	4.6		
Hydromagnesite	Mg ₅ (CO ₃) ₄ (OH) ₂ ·4H ₂ O	10.4	9.3		

The presence of thenardite in LDH 1 and LDH 2 can be attributed to the introduction of the Na⁺- counter cation with the carbonate, and the high concentration of sulphate ions from the solution containing pure chemicals. These starting concentrations were higher than the leachate concentrations as the rationale was to ensure the method was feasible. The presence of hydromagnesite can also be explained by the concentrations of the solutions used, specifically excess CO₃²⁻, as it is an impurity that is often encountered when producing LDHs at lower temperatures (Labuschagné et al, 2018).

Aragonite is probably formed due to the presence of Ca^{2+} ions in the leachate, which were extracted during thermochemical treatment of the mine residues (Fig 4.4(c) reports Ca^{2+} content of CS as 2.7% m/m).

The XRD results were supported by thermogravimetric analysis (Fig. 9.11).

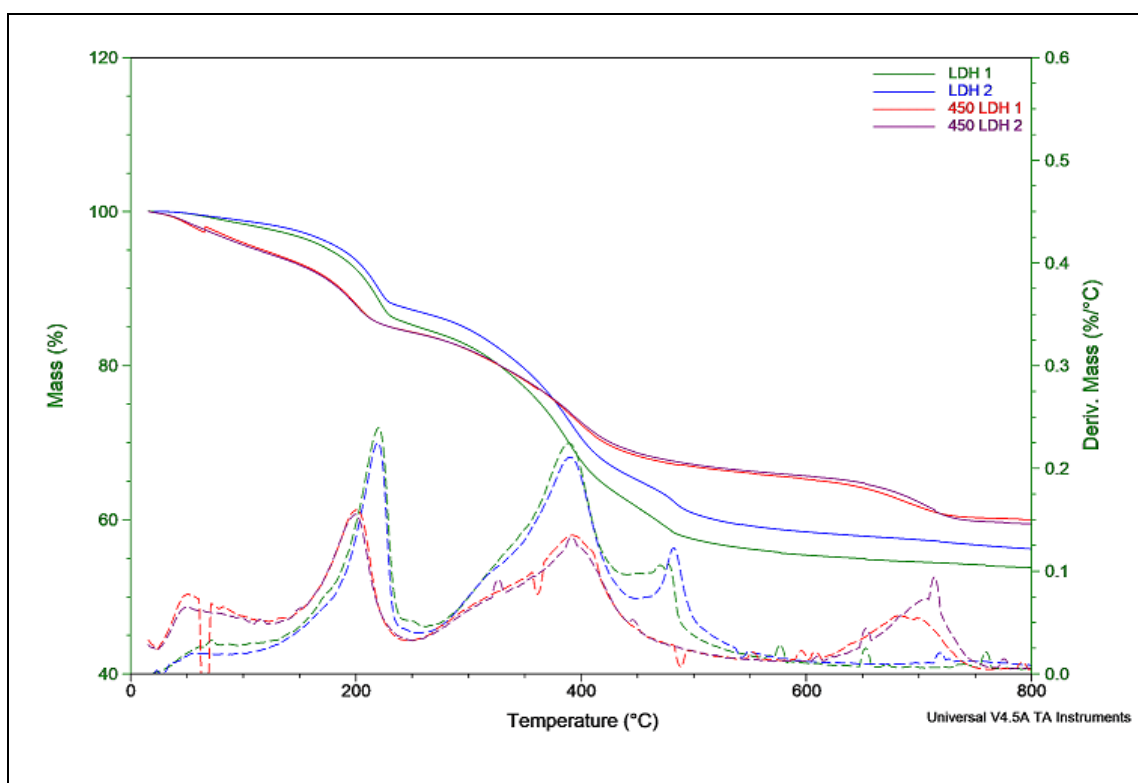


Figure 9.11: TGA thermograms comparing LDHs produced from leachates (450 LDH 1 and 450 LDH 2) to those produced from pure chemicals (LDH 1 and LDH 2), using the two co-precipitation methods.

Each thermogram had three distinctive mass loss steps. The first (up to 250°C) can be described as dehydration as it includes a small loss below 100°C which is due to water physically adsorbed onto the surface of the particles, and a larger mass loss between 150°C and 250°C, that can be attributed to the loss of interlayer water (Benhiti et al, 2020; Gevers et al, 2019; Labuschagne et al, 2015). The loss of interlayer water in the 450 LDH products, which contain Fe, occurred at a slightly lower temperature than in the pure LDH 1 and LDH 2 products, which is similar to what was observed by Gevers et

al (2019) who concluded that the inclusion of Fe reduced the interlayer water retention relative to pure Mg-Al LDHs.

Decomposition of the intralayer hydroxyl and carbonate anions generally takes place in the temperature range of 250°C to 550°C. This may be divided into two mass losses, with a mass loss between 250°C and 400°C that can be ascribed to dehydroxylation of the $\text{Al}(\text{OH})_3$ portion of the LDH layers, and the third (generally between 400 to 550°C) to dehydroxylation of $\text{Mg}(\text{OH})_2$ as well as decarboxylation of the interlayer (Földvári, 2011; Gevers et al, 2019). In some cases, the presence of a single mass loss in this temperature range indicates that there may be coupling of the dehydroxylation and decarbonation processes (Colonna et al., 2018; Klemkaite et al, 2011). This has typically been reported for Mg-Al LDHs with CO_3^{2-} interlayer anions, between 250°C and 450°C (Benhiti et al, 2020; Lalaut et al, 2022; Olfs et al, 2009; Shekoohi et al, 2017).

The products obtained from the pure chemicals were very similar, with a small difference (~15% for LDH 1 vs ~13% for LDH 2) in the first mass loss (dehydration), and a second mass loss of ~20% between 250°C and 450°C which can be assigned to the combination of the dehydroxylation and decarbonation. The final ~8% mass loss between 450°C and 520°C could be associated with the decarboxylation of the hydromagnesite impurity (Földvári, 2011).

The two products made from the 450°C roast leachate had almost identical thermograms. They differed from the pure chemical LDHs in that they had a lower mass loss in the dehydroxylation region (~17%), but with no shift in the temperature range which agrees with the observations of Gevers et al (2019) when Fe is included in the LDH structure. This also suggests that the second mass loss is a combination of the dehydroxylation and decarbonation processes, as was observed for LDH 1 and LDH 2. The third mass loss between 600 - 750°C could be ascribed to the decarbonation of the aragonite impurity (Földvári, 2011).

Figure 9.12 illustrates the FTIR transmission spectra of the LDHs products. The spectra were consistent with spectra of Mg – Al LDHs from the literature which confirmed the precipitation of LDH type materials (Olfs et al, 2009; Labuschagne et al, 2015).

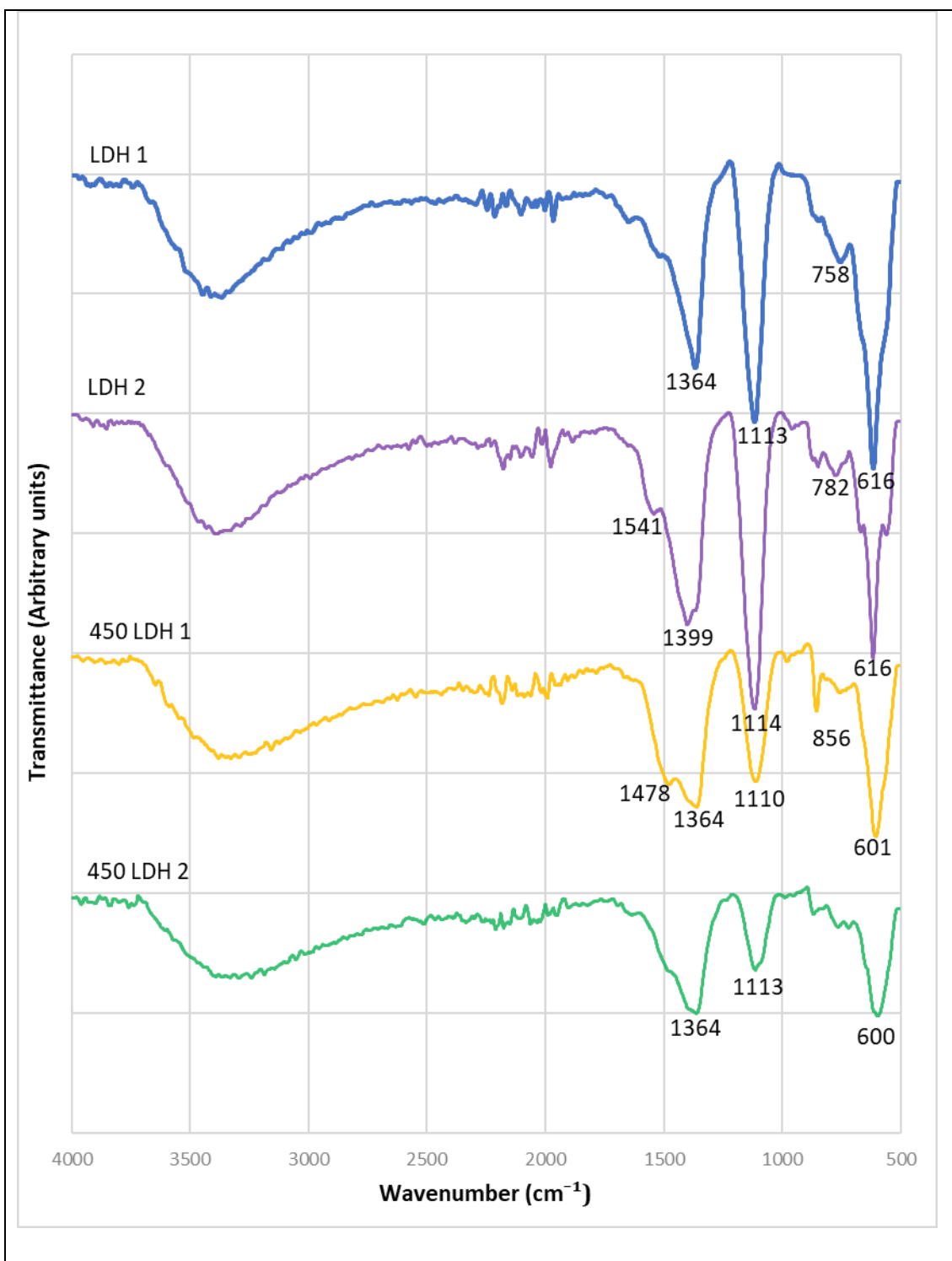


Figure 9.12: Comparison of FTIR spectra for LDHs produced from leachates (450 LDH 1 and 450 LDH 2) to those produced from pure chemicals (LDH 1 and LDH 2), using the two co-precipitation methods.

In general, there are no major differences between the products of the different methods. All products have the broad absorption band between 2700 and 3700 cm^{-1} assigned to O – H stretching vibrations of the interlayer water and hydroxyl groups (Mališová et al, 2018; Olfs et al, 2009; Shekoohi et al, 2017). The peak around 1364 cm^{-1} indicates asymmetric vibrations of the carbonate ion (CO_3^{2-}), particularly the interaction between carbonate and the OH groups of the hydrotalcite layers (Labuschagne, 2015; Mališová et al., 2018). The shoulder at $\sim 1400 \text{ cm}^{-1}$, or double band in the region of 1350 – 1500 cm^{-1} indicates decreasing carbonate symmetry or the disordered nature of the interlayer (Cavani et al, 1991). The absorption bands between 550 and 650 cm^{-1} are due to the stretching vibrations of metals with oxygen (Kloprogge et al, 2004; Mališová et al, 2018; Olfs et al, 2009). The intense peak around 1113 cm^{-1} is attributed to asymmetric stretching of the interlayer CO_3^{2-} ion (Kloprogge et al, 2004; Wang et al, 2018), and in the case of LDH 1 and LDH 2, could include the vibrations of the SO_4^{2-} ion as a result of the thenardite impurity (Cavani et al, 1991; Rouchon et al., 2012).

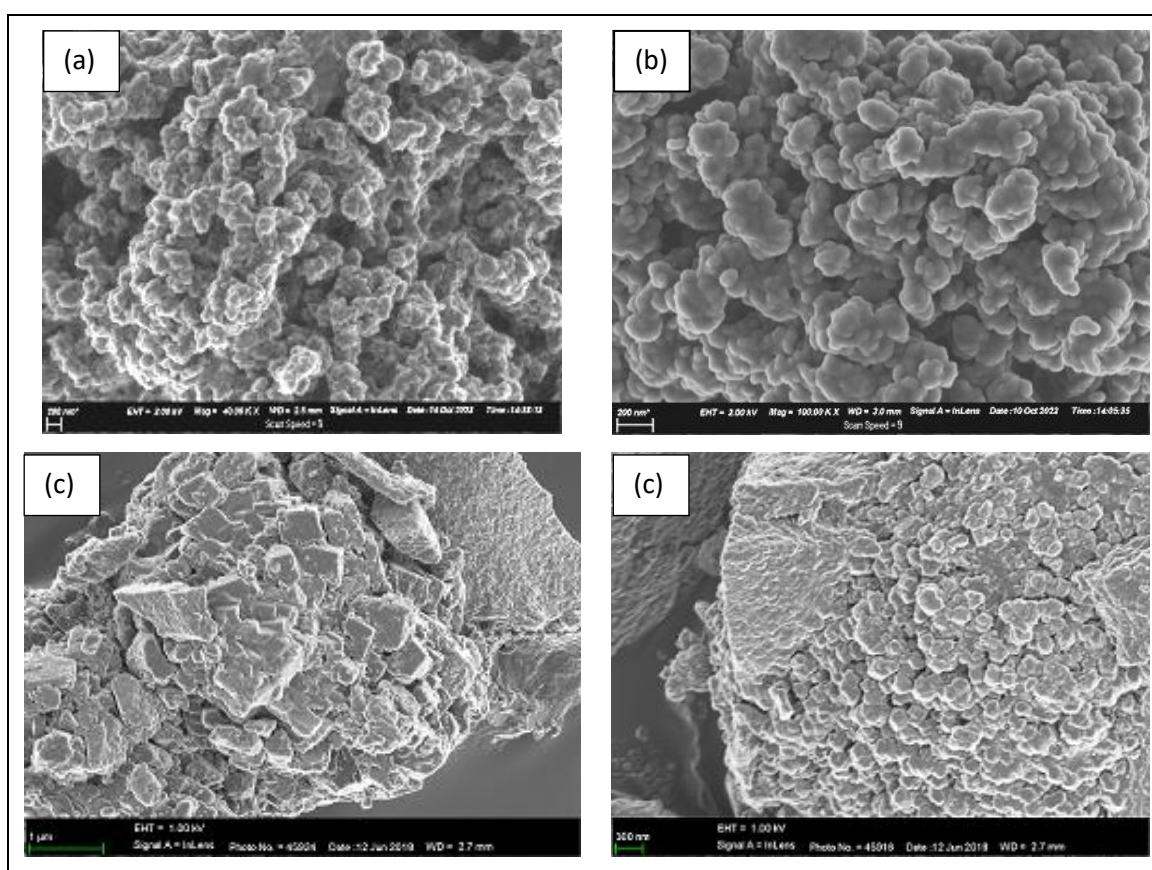


Figure 9.13: SEM images of LDHs obtained from (a) pure MgSO_4 and $\text{Al}_2(\text{SO}_4)_3$ co-ppt method 1 (b) pure MgSO_4 and $\text{Al}_2(\text{SO}_4)_3$ co-ppt method 2 (c) Leachate from 450°C roast co-ppt method 2.

The morphology of selected samples was observed using FE-SEM, as illustrated in Figure 9.13. The micrographs indicated that the particles had an irregular shape with a lateral size of $< 300\text{nm}$, and were highly aggregated with a fairly large distribution of sizes. There were no discernible differences between the particles produced by the different co-precipitation approaches. Particles were not as well formed in the samples prepared from the leachates (Fig 9.13 c), and had additional flaky particles of varying sizes which could be due to impurities.

The products of the two co-precipitation methods were basically no different with regards to all of the characterisation techniques employed. Method 2 was initially less time consuming, but both methods ended with a pH of 10 and were aged and dried for the same amount of time. The products from the leachates differed slightly from the pure chemical products due to the leachates having other cations in solution, notably Fe, as well as being less concentrated. One of the disadvantages of the co-precipitation method is that it introduces counter cation impurities, i.e. Na^+ , which can then manifest in the form of the thenardite that was apparent in LDH 1 and LDH 2 (Table 9.4).

In an attempt to simplify the production of the LDHs, reduce the amount of impurities in the product and minimise the amount of waste produced, a urea hydrothermal method was tested.

9.3.2 Comparison of co-precipitation vs urea hydrothermal methods for production of LDHs from pure chemicals

Figure 9.14 illustrates the comparison of the XRD patterns for the products obtained from the co-precipitation and urea hydrothermal methods using pure MgSO_4 and $\text{Al}_2(\text{SO}_4)_3$.

Although the reflection at 2θ of 23.5° (secondary reflection) for the product of the urea method was broader than that of the co-precipitation methods, indicating poorer crystallinity, the XRD pattern was identical to that of 100% hydrotalcite, with no impurities. By contrast, XRD analysis of the LDHs produced from pure chemicals via the co-precipitation method indicated that the products contained up to 14 % (m/m) impurities (Table 9.4). These results therefore indicate that the urea method can be

used to successfully produce LHDs of high purity from metal sulphate solutions, previously reported using predominantly nitrate- or chloride-salts, albeit with a lower degree of crystallinity at this stage (Table 2.3).

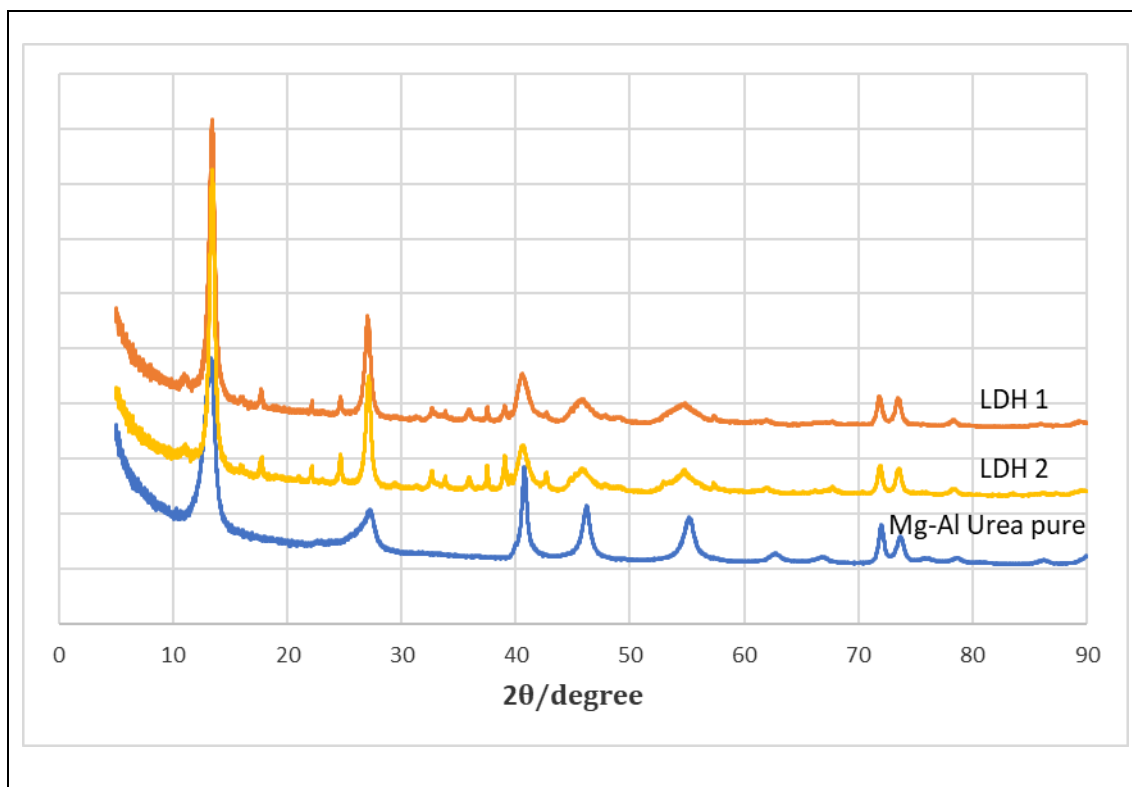


Figure 9.14: Comparison of the XRD reflections for the LDHs produced from pure analytical chemicals using the different co-precipitation (LDH 1 and LDH 2) and urea hydrolysis methods (Mg-Al Urea pure).

In the comparison of the thermogravimetric analysis for the 3 different methods (Fig. 9.15), there was a slightly larger mass loss for the dehydration step between 100 - 240°C for the urea method (~16%), with the peak at 210°C. The dehydroxylation and decarboxylation mass losses between 240 - 470°C are separated into two stages for the urea method. The first of these between 240 - 350°C, which is slightly lower than the onset for the co-precipitation methods, and the second mass loss occurred between 350 - 470°C, both of which are similar to the observations of Naseem et al (2019). The urea method had a very small mass loss (~2%) between 570 - 700°C, possibly a form of carbonate i.e. magnesite, which was not detected by XRD, however the study on urea LDHs by Naseem et al (2019) had a similar observation. The overall cumulative mass

losses for the different methods was similar (LDH 2 and Urea ~43%), with LDH 1 being slightly higher at 45%. These results are supported by the observations of Benhiti et al (2020) with 42% for the co-precipitation method and 37% for the urea method, as well as Naseem et al (2019) with 43% for the urea method.

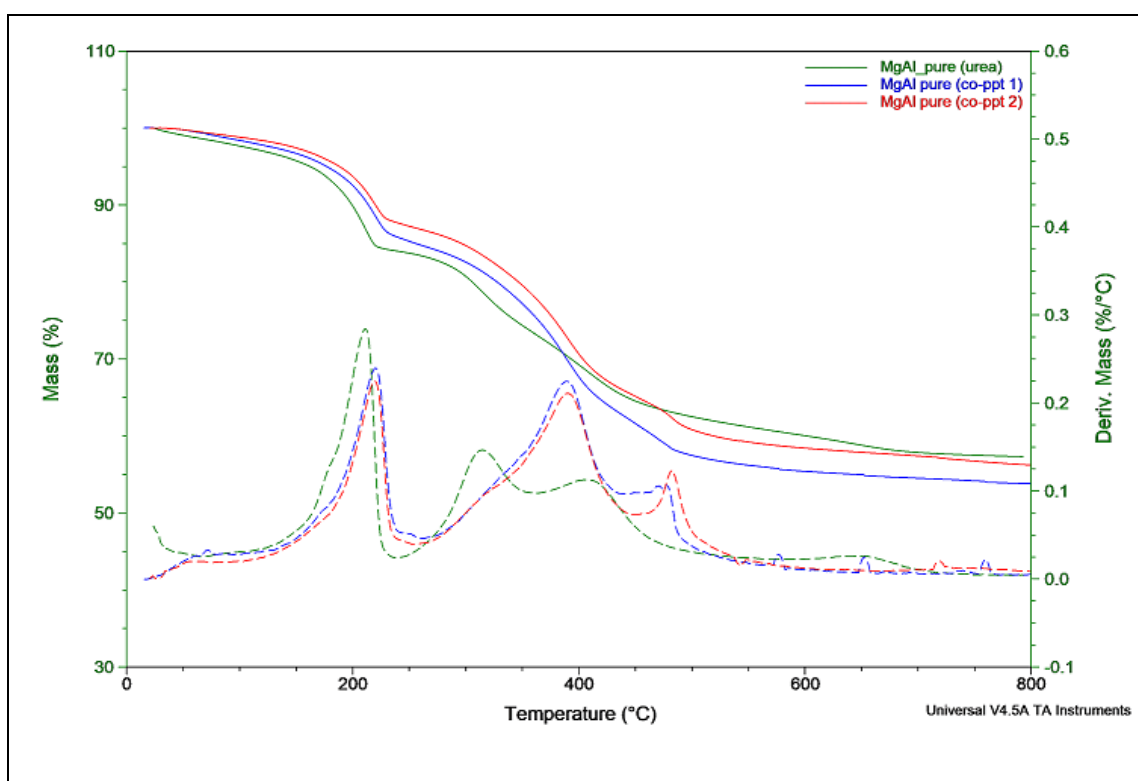


Figure 9.15: TGA comparison of LDHs produced from pure analytical chemicals using different methods.

9.3.3 Using the urea hydrothermal method for production of LDHs from the leachates

The urea method was then utilised to form LDHs from the two leachates, process 1 with the 450°C roast and process 2 with the roasts at 450°C + 680°C (Table 9.2). In the case of the latter, $\text{Al}_2(\text{SO}_4)_3$ was added to the leachate as a seed in some cases, to replace the Al removed by the higher roasting temperature and ensure that the $\text{M}^{\text{II}}:\text{M}^{\text{III}}$ mol ratio was between 2:1 to 3:1.

The XRD reflections for a selection of these products are illustrated in Figure 9.16, e.g., CS Urea A from the process 2 leachate (450°C + 680°C roast) with additional Al added, CS Urea B also from the process 2 leachate (450°C + 680°C roast) with no additional Al added and CS Urea C from the process 1 leachate (450°C roast).

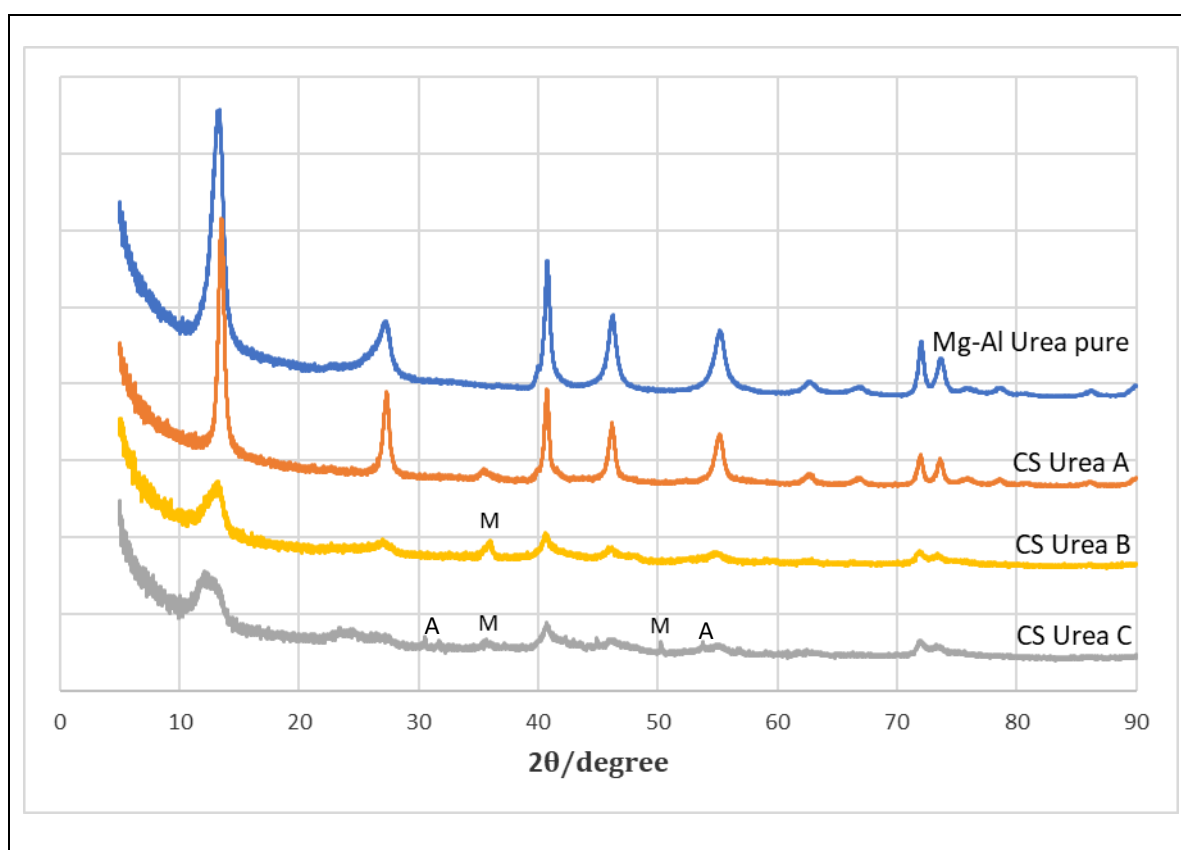


Figure 9.16: XRD reflections comparing a selection of LDHs produced from pure chemicals (Mg-Al Urea pure) and various CS leachates. CS Urea A: process 2 leachate, with additional Al; CS Urea B: process 2 leachate; CS Urea C: process 1 leachate. Impurities in the form of magnesite (M) and aragonite (A) are indicated.

The two other samples illustrated (CS Urea B and CS Urea C), both show the formation of some LDH, however, they were not highly crystalline and had some impurities in the form of magnesite (MgCO_3) and aragonite (CaCO_3). This could possibly be due to the dearth of Al, although in the case of CS Urea C, which was produced from the leachate from process 1 (Table 9.2), the $\text{M}^{\text{II}}:\text{M}^{\text{III}}$ mol ratio was in the accepted range (2.6:1) if the total M^{III} content (i.e. Fe and Al) of this leachate was considered. Further work with a more concentrated leachate from process 1 may improve this result.

The product synthesised from the leachate from process 2 with additional Al added (CS Urea A) formed sharp, intense peaks at 2θ of 13.7° and 27.5° , indicating good crystallinity of the LDH phase, and was reported as 100% hydrotalcite after Rietveld refinement, although there does appear to be a trace of magnesite.

Figure 9.17 illustrates the thermogravimetric analysis for selected products prepared from leachates vs the LDH produced from pure chemicals, using the urea hydrolysis method.

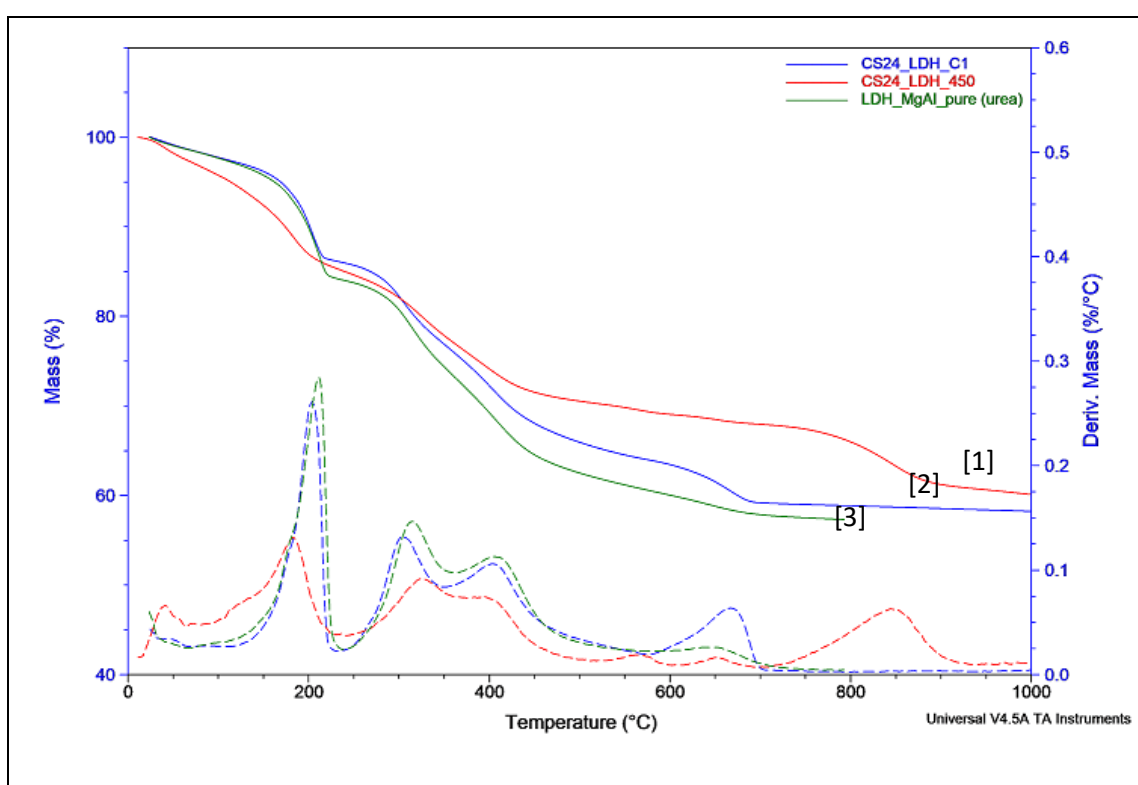


Figure 9.17: Comparison of the TGA thermogram for the LDH produced using the urea hydrothermal method: [1] CS Urea C, produced from the leachate from process 1 (red line), [2] CS Urea A, produced from the leachate from process 2 (blue line) and [3] Mg-Al Urea pure, the LDH produced from pure MgSO_4 and $\text{Al}_2(\text{SO}_4)_3$ (green line).

The product prepared from the leachate after process 2 ($450^\circ\text{C} + 680^\circ\text{C}$ roast) with the addition of Al (CS Urea A, thermogram 2), had a similar thermogram to that of the pure chemicals LDH (Mg-Al Urea pure, thermogram 3), with the exception of a higher mass

loss between 600 to 700°C (~ 6%), which was similar to that observed in the magnesite containing LDHs produced from leachates using the co-precipitation methods (Figure 9.11). This mass loss was also apparent in the studies by Naseem et al (2019) and Hollingbery and Hull (2012) and can be ascribed to the loss of carbon dioxide from decomposition of carbonate species. XRD analysis confirmed the presence of a magnesite impurity for some of the samples prepared from the leachate (Fig. 9.16). The decomposition of magnesite takes place over a wide temperature range with its maximum rate of mass loss occurring between 620 - 650°C (Foldvari, 2011). Although this mass loss was evident in all samples tested, it was more prominent for CS Urea A.

CS Urea C, which was synthesised from the leachate after process 1 (450°C roast), had the mass losses as expected for an LDH, but to a lesser degree, indicating an impure product. There was also an additional mass loss of ~6% between 700 to 900°C, possibly due to decarboxylation of aragonite as a result of the presence of Ca^{2+} -ions in the leachate. This product had poor crystallinity as indicated by the XRD reflections (Fig 9.16).

FTIR spectra are illustrated in Figure 9.18, once again comparing the products manufactured from the leachates against the LDH prepared from pure chemicals using the urea hydrothermal method. The spectra were very similar, with the product of the process 1 leachate (CS Urea C) having slightly less intense absorption between 440 – 770 cm^{-1} , the region in which the stretching vibrations of metals with oxygen would occur. This is particularly noticeable for the sharp, intense peak at 443 cm^{-1} which can be ascribed to Mg – O – Al vibrations (Kloprogge et al, 2004; Wiyantoko et al, 2015), and is possibly due to the lower concentration of Al in the leachate. The sharp peak between 1321 and 1355 cm^{-1} can be allocated to the vibrations of the carbonate ion (CO_3^{2-}), and the broad band between 3000 – 3690 cm^{-1} is due to the OH stretching vibrations of hydroxyl groups and interstitial water.

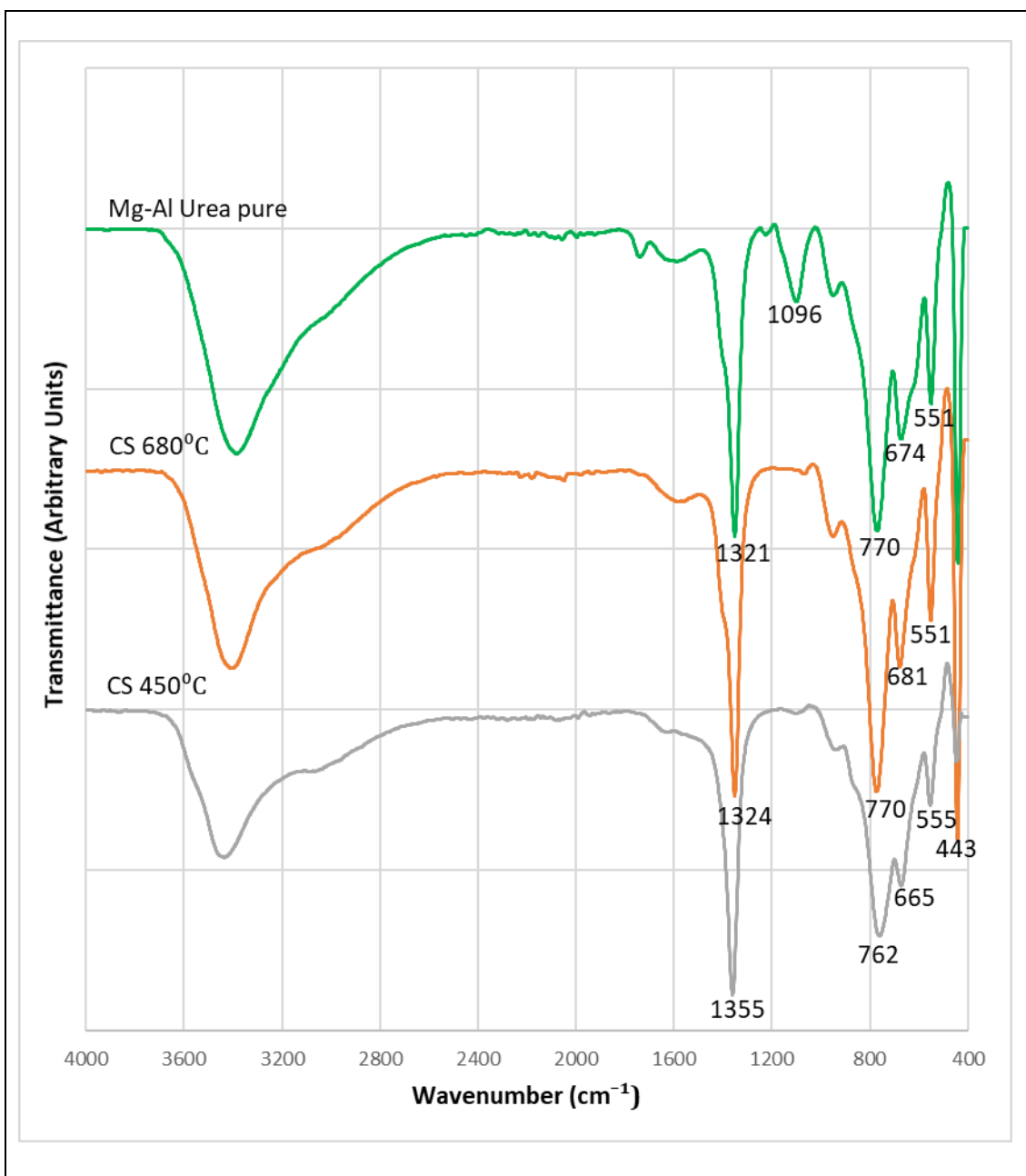


Figure 9.18: LDHs produced using the urea hydrothermal method (a) Mg-Al Urea pure, from pure analytical chemicals, (b) CS Urea A from the leachate of process 2, after roasting CS at 450°C + 680°C and (c) CS Urea C from the leachate of process 1 after roasting CS at 450°C

The morphology of the LDHs were examined using FE-SEM. Figure 9.19 illustrates LDHs produced using the urea hydrolysis method.

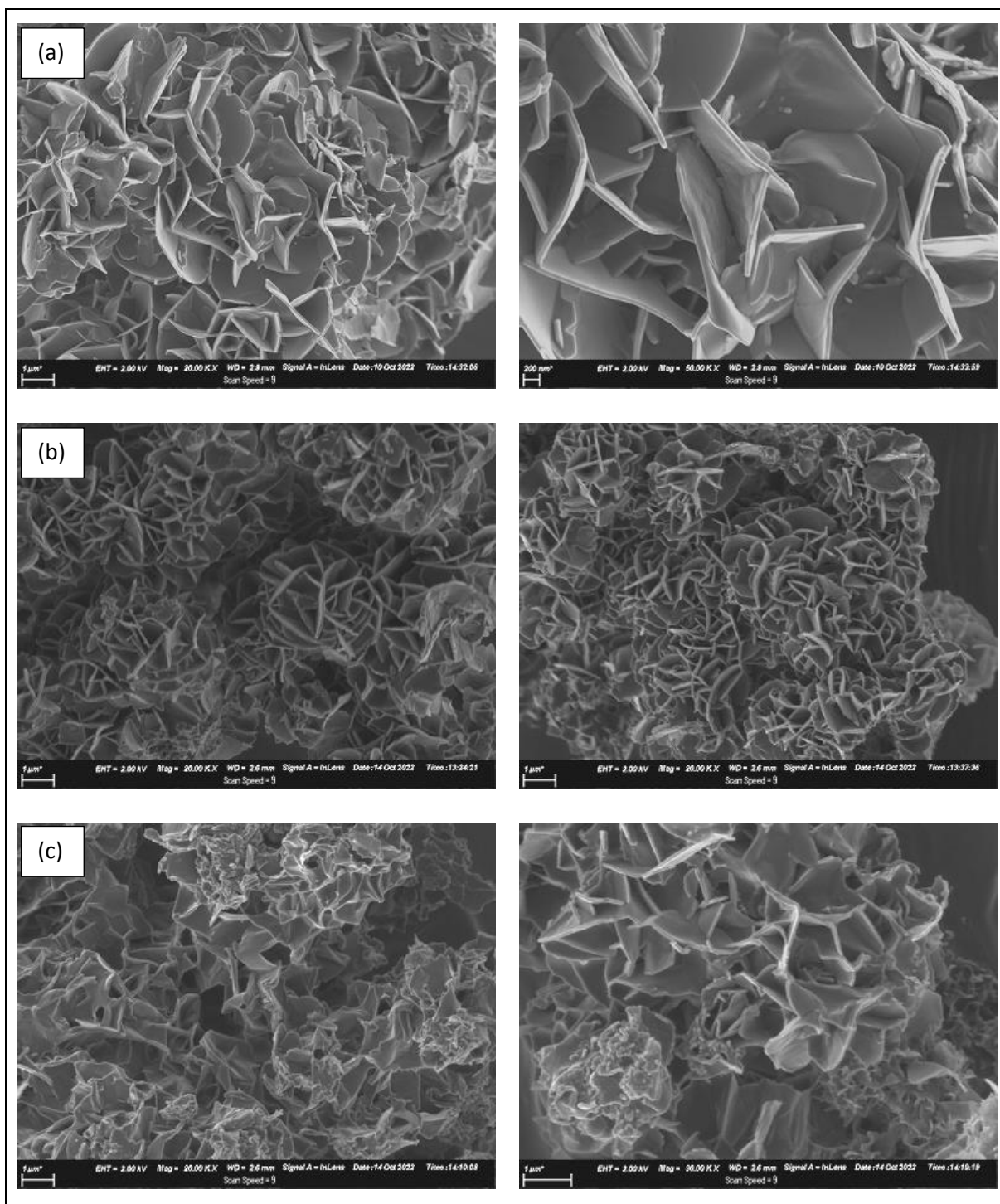


Figure 9.19: LDHs produced from (a) pure MgSO_4 and $\text{Al}_2(\text{SO}_4)_3$, (b) the leachate of process 2, after roasting CS at $450^\circ\text{C} + 680^\circ\text{C}$; (c) the leachate of process 1, after roasting CS at 450°C .

The particles formed using the urea method were thin and flat, resembling a rose. Similar micrographs were reported by Lalaut et al., (2022) and Zeng et al., (2009), where they described the images as having a ‘sand-rose morphology’. These are very different to those formed using the co-precipitation method, which have a much smaller platelet size.

The particle size of the LDHs formed from pure chemicals (Fig 9.19a) were larger ($\sim 2.5 \mu\text{m}$) than those formed from the leachates, but in both cases, they displayed a similar size distribution. The platelet size of products formed from the leachate of process 1 (Fig 9.19c) decreased, possibly due to the presence of Fe as was observed in the study by Naseem et al (2019). Furthermore, it appeared to be less structured, which was also apparent on the SEM micrographs reported by Naseem et al (2019) when Fe was substituted for Al in the LDH.

BET analyses were conducted on selected LDHs produced, for comparison purposes only. The LDHs produced from the urea hydrolysis method had larger specific surface areas than those produced using the co-precipitate method. These results agree with the trend reported by Benhiti et al (2020), although the values are lower. Direct comparisons are difficult as the surface area is affected by the $M^{\text{II}}:M^{\text{III}}$ ratio as well as the cations present in the solution (Theiss et al, 2016; Wang et al, 2018b). The LDHs produced from leachates had a higher specific surface area for both the co-precipitate and urea hydrolysis methods.

Table 9.5: BET Specific surface area (m^2/g) of selected samples.

Sample	LDH 2 (co-ppt)	450 LDH 2 (co-ppt)	LDH urea pure	CS LDH 680 (urea)
BET surface area (m^2/g)	8.6 ± 0.3	34.8 ± 0.2	46.0 ± 0.7	77.0 ± 2.4

9.4 Purification of talc in CS leach residue

It was shown in Chapter 6 that the composition of talc is not altered during the thermochemical reaction with AS or the dissolution process. As the talc content of the slimes does not react with AS, it can be considered a valorisation product, and should remain in the leach residue after the soluble metal sulphates have been extracted.

The leach residue from roasting program 1 (CS + AS at 450°C) was used as the maximum amount of all possible metals in the CS must be removed to ensure that the talc phase is all that remains.

The XRD reflections for the solid leach residue are illustrated in Figure 9.20, and show that there are very few phases other than talc remaining in the residue.

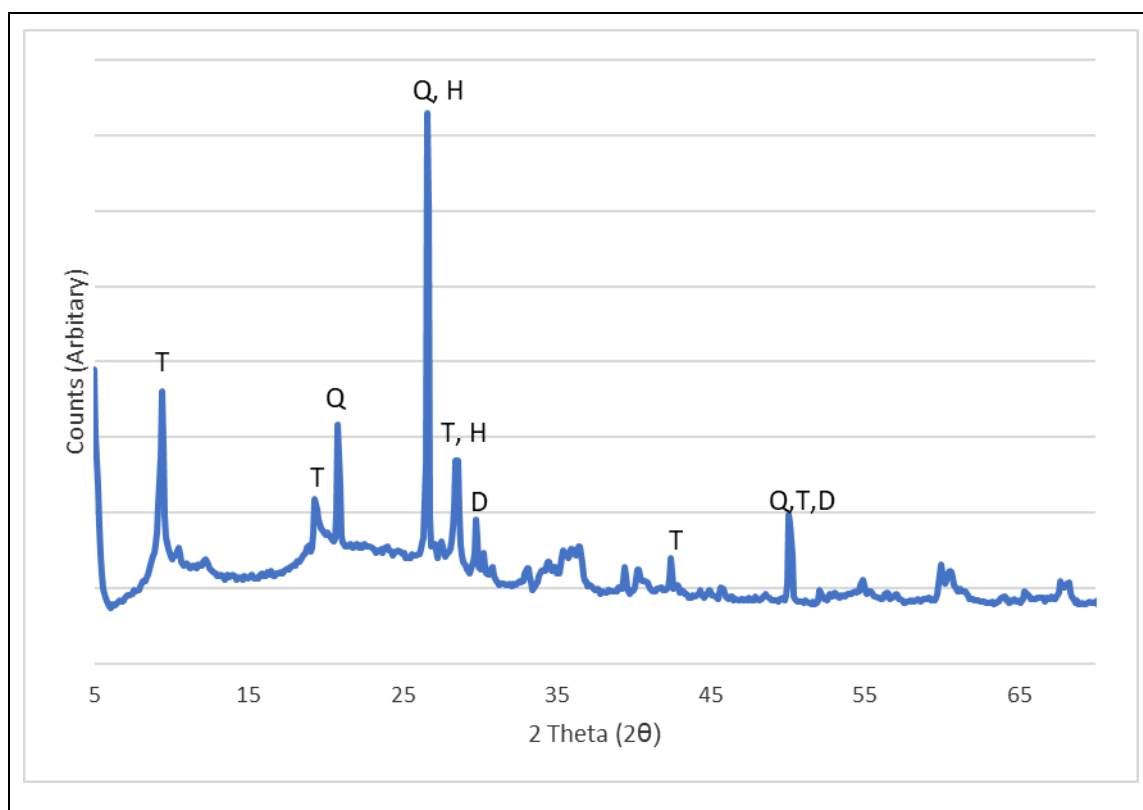


Figure 9.20: XRD pattern for the leach residue, indicating talc (T), quartz (Q), hornblende (H) and diopside (D).

Table 9.6 reports the semi-quantitative mineralogy of the leach residue as determined by XRD. The XRD indicates that talc is the major phase, and the talc content has increased from 30.1% in the slimes (Table 4.2) to 55.7% in the leach residue. The hornblende and diopside phases can be reduced by using the roasting regimen at higher temperatures, which could increase the talc content further (Table 8.7). To maintain the improvement in colour clarity, the higher temperature roast would need to be after the removal of the Fe content by leaching, i.e. re-roast the program 1 (450°C) leach residue at a higher temperature.

Table 9.6: Semi-quantitative mineralogical composition of the leach residue as determined by XRD.

Mineral	Chemical Composition	Mass%
Diopside	$\text{MgCaSi}_2\text{O}_6$	15.3
Hornblende	$\text{Ca}_2(\text{Fe,Mg}_5)(\text{Si}_8\text{O}_{22})(\text{OH})_2$	8.0
Quartz	SiO_2	21.0
Talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	55.7

The XRD results for the leach residue are supported by the TGA analysis which is illustrated in Figure 9.21, compared to the thermogram for the talc that was purified from a commercial sample (Chapter 6).

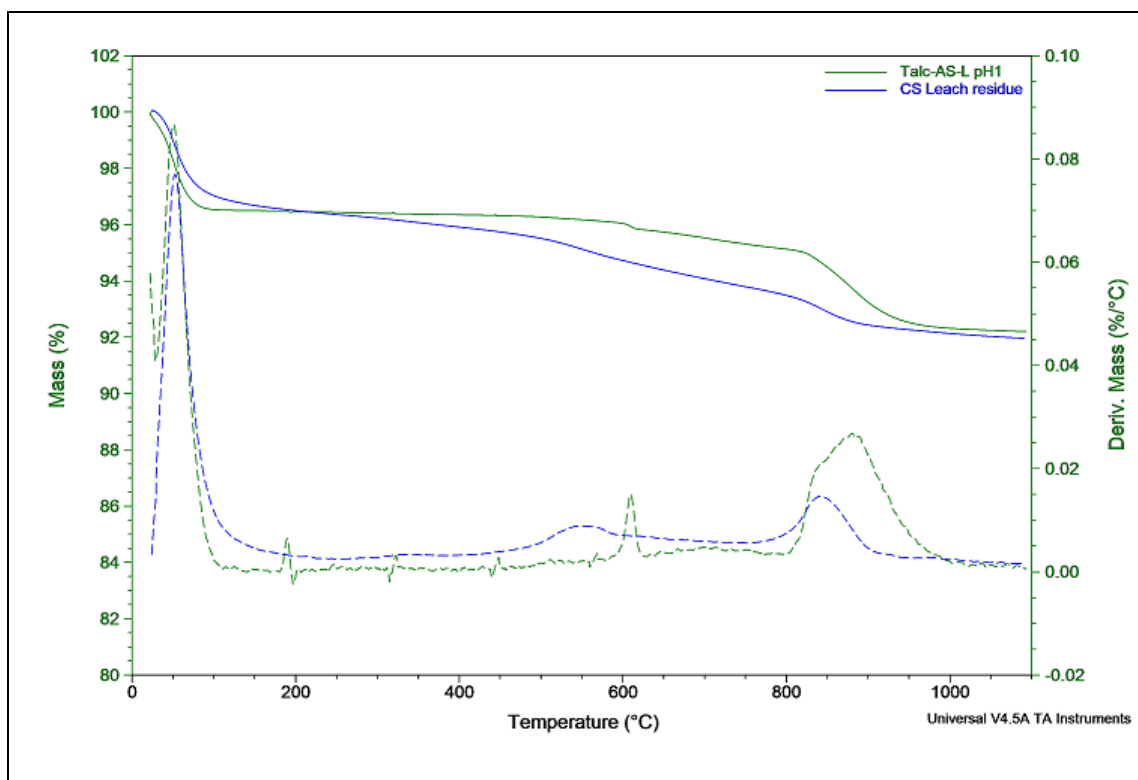


Figure 9.21: Thermograms of the leach residue (blue) after the extraction of soluble metal sulphates vs the commercial talc sample after purification (green).

Both samples have the distinctive mass loss between 800 – 1000°C, indicating the dehydroxylation of talc (Földvári, 2011). The mass loss between 500 – 600°C for the leach residue can be ascribed to the dehydroxylation of the hornblende, as dehydroxylation temperature for amphiboles is dependent on the types of cations present and in particular, the magnesium content of the mineral (Földvári, 2011).

Figure 9.22 illustrates the FTIR spectra of the CS leach residue compared to the original CS as well as the commercial talc sample after purification with AS (Chapter 6). The distinctive talc peaks at 668 cm^{-1} and 1014 cm^{-1} are apparent in the CS leach residue.

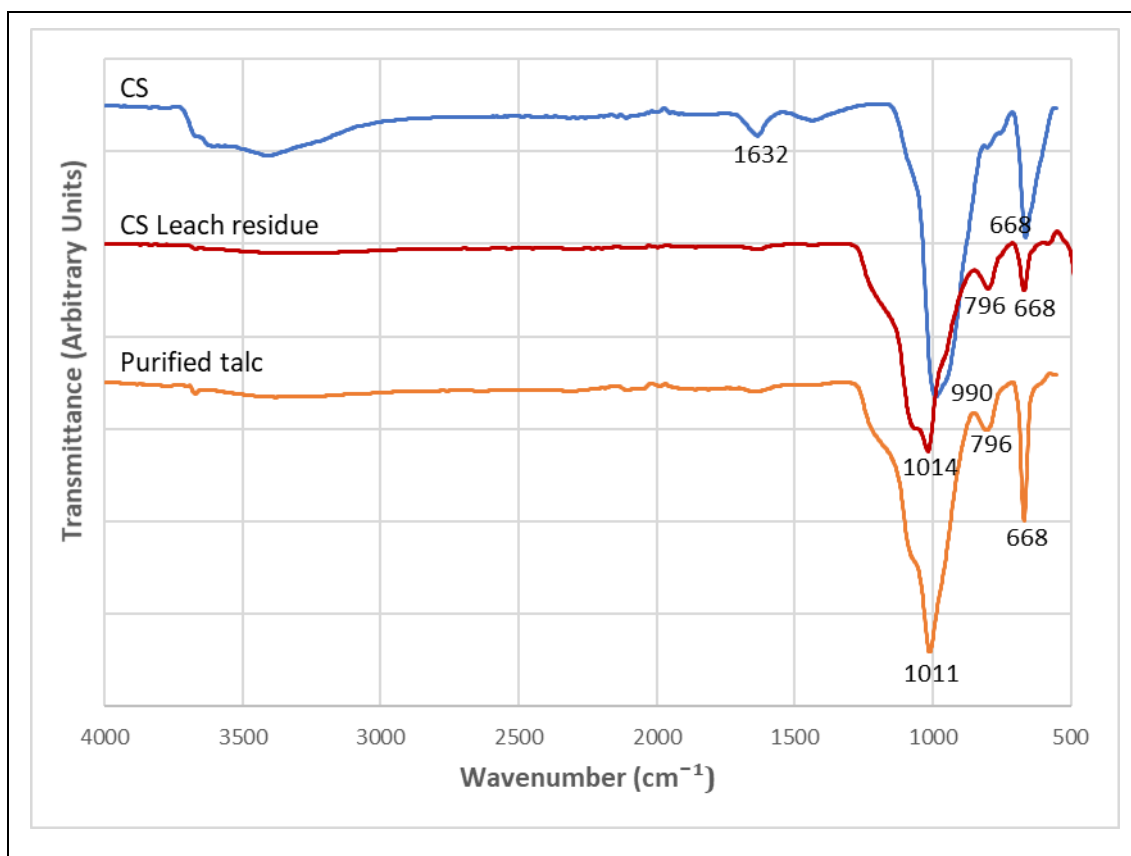


Figure 9.22: Comparison of FTIR spectra for the original CS (blue) vs the CS leach residue (red) and the commercial talc sample purified using AS (orange).

The colour clarity of the leach residue has also improved, from the original grey of the CS to a creamy-white product (Fig 9.23) which may be acceptable in the paint, paper or ceramics industries, as well as a polymer filler.

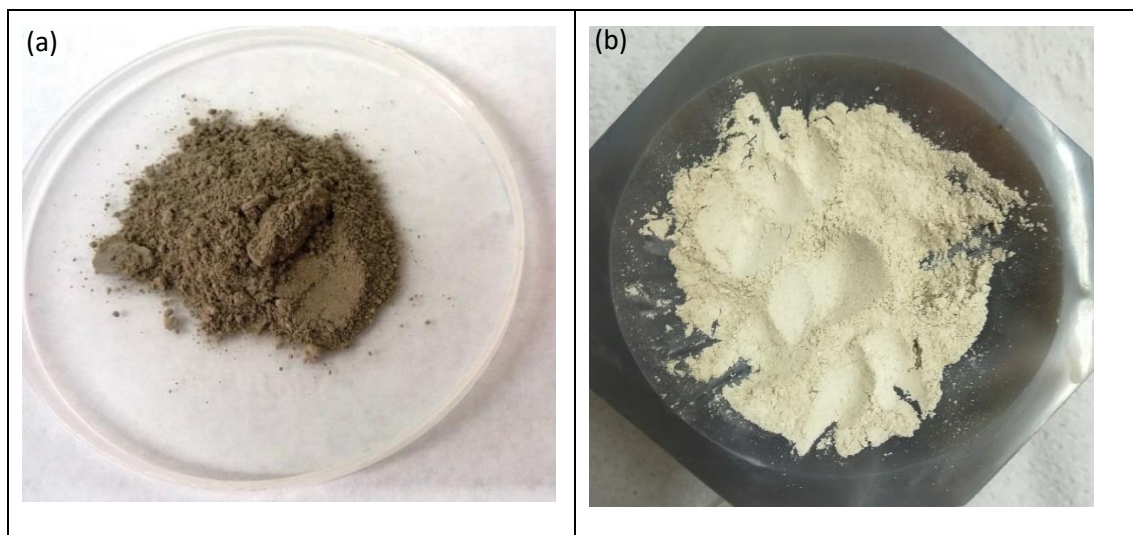


Figure 9.23: Comparison of the colour of (a) the original raw material (CS) and (b) the leach residue.

9.5 Conclusions

$\text{Mg}(\text{OH})_2$ was successfully precipitated from leachates produced after roasting CS and AS at 450°C (process 1) as well as after the roasting at higher temperatures (process 2). The Fe that was precipitated formed an amorphous product that needs to be calcined before characterisation can be carried out. The Al content of the leachate was also not successfully separated using sequential precipitation.

LDHs were successfully synthesised using both the co-precipitation and urea hydrolysis methods. Products formed from the urea hydrolysis method were purer, with fewer impurities. The leachate formed after process 2, with the addition of extra Al, formed the most acceptable product.

The talc content has increased from 30% in the slimes to 56% in the leach residue, after thermochemical treatment of the CS with AS. This could possibly be improved by further processing at a higher roasting temperature or by using a flotation technique. However, due to the improvement in colour clarity, the talc rich residue may find application in the ceramic, paint or paper industry.

Chapter 10: Conclusions and recommendations for future work

10.1 Introduction

Many countries encounter environmental and economic difficulties relating to the handling and management of significant amounts of solid mine waste. One frequently disregarded aspect in the management of mine residues, is that mine waste can serve as unexplored secondary sources for valuable metals and minerals. Although realising the full potential of such waste will require a fundamental shift in the way mine waste is managed, it remains a pivotal aspect of eco-friendly mining. South Africa produced over 188 Mt of diamond mine tailings between 2017 and 2021 (Bullock et al., 2023), which could be regarded as a valuable resource if economically feasible processes can be established to valorise the minerals and metals, i.e. Mg, Fe or Al, contained within the residues.

This thesis contributes to the development of a method to beneficiate some of the vast quantities of mine waste produced annually, and in the process to reduce the environmental problems that result from the piles of tailings.

10.2 Conclusions

Objective 1:

To characterise the mine residues with respect to their physical and chemical properties, with the aim of extracting the maximum amount of metals from the raw materials (Chapter 4).

An understanding of the mineralogical, physical and chemical properties of the mine residues is imperative as they determine the potential for resource recovery. The residues were characterised using XRD, XRF, PSD, FTIR, TGA and FE-SEM.

The mineralogy of the mine residues was a complex matrix dominated by phyllosilicates, especially the clay minerals in the form of smectite (22.7 – 33.0% m/m) and talc (25.2 – 30.1% m/m). The FE-SEM images showed platy, irregularly shaped particles. The chemical composition indicated a large amount of SiO₂ (>45% m/m), explained by the abundance of phyllosilicate materials in both the CS and CT samples. The substantial amount of MgO (>20% m/m) is due to many of the phyllosilicate and other mineral phases being Mg – rich. From these results, Mg (13.1 – 15.7% m/m), Fe (~ 6.6% m/m), Al (2.8 – 3.0% m/m) and Ca (2.7 – 5.4% m/m) were identified as the major elements available for extraction in both CS and CT. The PSD confirmed the fine-grained nature of the residues, with CS having the smaller average particle size which supports the higher reactivity of CS observed.

Objective 2:

To investigate the effectiveness of thermochemical treatment using ammonium sulphate (AS) on the physical and chemical properties of diamond mine residues, as compared to untreated materials. (Chapter 5).

The purpose of thermochemical processing with AS was to facilitate the extraction of metals (Mg, Fe and Al) from CS or CT via the formation of soluble sulphate compounds. The products obtained from thermochemical treatment were characterised using XRD, FTIR, TGA and FE-SEM.

During the thermochemical treatment of CS and CT with AS, the phyllosilicate minerals, with the exception of talc, were transformed into different phases, namely ammonium metal- and metal- sulphates. Other phases that did not react included diopside (pyroxene mineral) and hornblende (amphibole mineral). The newly formed phases, i.e. ammonium metal- and metal -sulphates, were identified by XRD and included Mg, Al, and Fe species, with Mg-species appearing to be the most dominant (Table 5.8). At temperatures $\leq 450^{\circ}\text{C}$, the majority of newly formed minerals were intermediate double salts, i.e., ammonium-metal sulphate compounds.

The physical properties of the thermochemically treated CS and CT were influenced by the roasting temperature. Treatment at lower temperatures produced a hard, dark grey solid, which was difficult to remove from the crucibles, reducing possible yield.

Treatment at higher temperatures produced fewer ammonium-metal sulphates, more metal sulphates and a whiter and softer, free-flowing product, but also indicated a decrease in sulphur content.

The most notable difference in the chemical composition (major oxides measured by XRF) of the reaction products was the presence of sulphur in the form of SO_3 (28.3 – 33.8%), due to the formation of sulphate species. This also varied with roasting temperature. Mass losses obtained during thermal treatment of the untreated raw materials without AS ranged between 6.8 – 7.9% for CS and 2.7 – 3.5% for CT, increasing with increasing furnace temperature. Mass losses during product formation after thermochemical treatment with AS increased with increasing temperature, ranging from 25.3 – 53.1% (Table 5.5). Mass losses after thermochemical treatment at 420°C were significantly lower than the mass losses after thermochemical treatment at 450°C and higher. This was later ascribed to the presence of fewer hydrated and ammonium containing metal sulphates present in the samples thermochemically treated at higher temperatures, i.e., loss of water and ammonia occurred during thermochemical treatment at higher temperatures.

The FE-SEM results displayed that unreacted, smooth irregularly shaped particles were interspersed with numerous well-defined hexagonal structures (Fig. 5.16). Since metal sulphate crystals generally exhibit hexagonal shapes (Doucet et al, 2016), these can be considered to be metal (Mg, Al or Fe) sulphates, formed after thermochemical treatment with AS. These results indicate the potential for extracting major elements from the tailings and slimes.

Objective 3:

To optimise the extraction of the metal sulphates formed from the reaction between the mine residues and AS, using a variety of leaching conditions (Chapter 7).

Extraction of major elements from thermochemically treated CS and CT was accomplished by dissolution of the roast products under different leaching environments, to optimise the extraction of the metals of interest (Mg, Fe and Al). It was also important to ascertain which furnace conditions, i.e. roast temperature and mine

residue to AS roast ratio, provided the maximum extraction efficiency. The extent of the extraction was measured by ICP-OES.

From the range of mass ratios and temperatures tested, the residue:AS ratio of 2:4 was found to provide optimal extraction at a temperature of 450°C. Mg, Fe and Al were successfully extracted from the roast product of the thermochemical treatment at 450°C using both dH₂O and sulphuric acid solutions, with the acidic solutions providing superior extraction. When leaching in dH₂O, the extraction of magnesium was relatively constant with increasing temperature (63.9 – 65.4%), but the iron extraction was adversely affected by the temperature increase, showing a steady decline from 32.7 % when leaching at 20°C to 6.5 % at 95°C (Fig 7.6). Increasing the temperature during acid leaching improved the extraction of the elements of interest. At a pH of 1, both magnesium and iron extraction were improved compared to water leaching, with the most efficient Mg extraction obtained at a temperature of 50°C (64.2% in dH₂O vs 81.7% at pH 1). At ambient temperature, the Fe extraction improved from 32.7% in dH₂O to 39.8% in the pH 1 solution, and at 50°C it had increased to 49.2%. There was some additional improvement in extraction efficiencies with the higher concentration of H₂SO₄ and higher temperatures, but 50°C in the pH 1 solution was selected as the optimum with regard to extraction and energy efficiencies.

When testing various solid to liquid leach ratios, the 1 g solid to 25 mL liquid combination provided an increased concentration of elements in solution with sufficient volume for the synthesis of the desired products.

Objective 4:

To investigate the reactivity of talc during thermochemical treatment with AS. This is to ensure that talc is not contributing to the magnesium being extracted from the mine residues, but can be considered a viable valorisation product. (Chapters 6 & 9).

During the characterisation of the CS and CT, it was noted that there was a relatively high concentration of talc, Mg₃Si₄O₁₀(OH)₂, in the raw material (Table 4.2). As a possible product of the valorisation process of the slimes and tailings, talc could also be a source of magnesium. The reactivity of talc was investigated to exclude it as a potential contributor of magnesium and to ensure that the structure of the talc was not

compromised during the process used. Due to the complexity of the mine tailings and slimes, a talc sample, containing fewer mineral phases than the diamond mine residues, was sourced commercially for this investigation. The process was followed using a variety of complementary analytical techniques, i.e. XRD, TGA, FTIR and FE-SEM.

This study showed that talc exhibits very limited, if any, reactivity with AS to form sulphate minerals when subjected to thermochemical processing under the experimental conditions tested. Mg was not extracted from the talc during the thermochemical processing, which implies that the Mg content in the talc of CS and CT must not be considered when calculating the extraction efficiencies. The composition of talc is not altered during the thermochemical reaction with AS or the dissolution process, therefore the talc content of CS and CT can be considered a valorisation product.

After thermochemical treatment of CS with AS, the talc content increased from 30% in CS to 56% in the leach residue, with quartz, diopside and hornblende being the other phases present. The talc-rich residue obtained after thermochemical processing could find direct application in the ceramics, paint or paper industry due to its improved colour clarity, appearing as a creamy-white product compared to the original grey colour of the CS. Further improvement in the product quality may be achieved by processing it at a higher roasting temperature or by using a flotation technique.

Objective 5:

To synthesise and characterise Mg-, Fe- and Al- hydroxide precipitates from the leachates during sequential precipitation with ammonia solution (Chapter 9).

The leachates produced from the dissolution of the soluble metal sulphates in the roast products were titrated with NH_4OH solution to selectively precipitate the soluble metal ions in solution, i.e. Mg, Fe and Al, in the form of hydroxides. The Fe component was predicted to precipitate at pH values ranging between 3 to 9, depending on the form of the precipitate, i.e. FeOOH (goethite) from pH ~ 3 , $\text{Fe}(\text{OH})_3$ above a pH of 4 and $\text{Fe}(\text{OH})_2$ between a pH of 8 - 9. $\text{Al}(\text{OH})_3$ was expected to precipitate around a pH of 6 and $\text{Mg}(\text{OH})_2$ was expected to precipitate above a pH of 10. These products were characterised using XRD, FTIR, TGA and FE-SEM.

When using leachates from the 450⁰C roast, the residues collected via filtration at pH ~ 4, pH ~ 6 as well as pH ~7 appeared as a reddish-brown gel-like product. After drying, they formed dark brown granules which XRD analysis reported as being amorphous. These colour changes suggested the presence of Fe in all the precipitates, possibly in different forms and oxidation states. Their morphologies were globular, with particles being irregular in shape and size, possibly indicating the amorphous nature of the product. At a pH of 9.0, the precipitates formed thin, platelet-like particles, similar in shape to the Mg(OH)₂ formed from pure MgSO₄, but highly agglomerated. To improve the separation of the Fe from the Al and Mg, H₂O₂ was used to oxidise any Fe²⁺ to Fe³⁺ with the aim of precipitating all Fe as Fe(OH)₃ at a pH of about 4.0. Unfortunately, this was not successful and the precipitates continued to be amorphous up to pH ~ 7.5.

The precipitates produced at pH values greater than 10 were soft and white and were determined by XRD and FTIR to be Mg(OH)₂. Their morphology was also similar to that of the Mg(OH)₂ produced from pure MgSO₄, i.e. thin, platelet like particles.

Mg(OH)₂ was therefore successfully precipitated at pH > 10 from leachates produced after roasting CS and AS at 450⁰C (Process 1) as well as after the roasting at higher temperatures (Process 2). The Fe that was precipitated between pH 4.0 – 7.5 formed an amorphous product that needs to be calcined before further characterisation can be carried out. The Al content of the leachate was also not successfully separated using sequential precipitation.

Objective 6:

To synthesise and characterise layered double hydroxides from the leachates, using a variety of different methods (Chapter 9).

The leachates obtained from Processes 1 and 2 contained Mg, Fe and Al in soluble form (Table 9.1), with the M^{II} to M^{III} mol ratio being between 2.5 to 3.0 for leachates from Process 1, assuming that both the Fe and Al were included as being M^{III} in the LDH structure. LDHs were synthesised from the leachates using two slightly different co-precipitation methods, i.e. slow, pH-controlled addition (method 1) and rapid addition (method 2) of the metal ion solution to a carbonate containing solution, as well as

through a urea hydrolysis method. Products formed were characterised using XRD, TGA, FTIR and FE-SEM.

The products synthesised from the leachates using the two different co-precipitation methods were very similar, with good yield of hydrotalcite obtained (88 % m/m). Some impurity, in the form of aragonite, was present, probably due to the presence of Ca^{2+} ions in the leachate, extracted during thermochemical treatment of the CS. The FE-SEM micrographs indicated that the particles had an irregular shape with a lateral size of < 300nm and were highly aggregated with a fairly large distribution of aggregate sizes.

The urea method was utilised to form LDHs from two different leachates, i.e., Process 1 with the 450⁰C roast and Process 2 with the roasts at 450⁰C + 680⁰C. In the case of the latter, $\text{Al}_2(\text{SO}_4)_3$ was added to the leachate as a seed in some cases, to replace the Al removed by the higher roasting temperature and ensure that the $\text{M}^{\text{II}}:\text{M}^{\text{III}}$ mol ratio was between 2:1 to 3:1. The Process 1 leachate showed the formation of some LDH, however, the products were not highly crystalline and had some impurities in the form of magnesite (MgCO_3) and aragonite (CaCO_3). The product synthesised from the leachate from Process 2 with additional Al added was reported as 100% hydrotalcite using XRD and indicated good crystallinity of the LDH phase. The morphology of the particles formed using the urea method were thin and flat, resembling a rose, and were very different to those formed using the co-precipitation method, which had a much smaller platelet size. The platelet size of products formed from the leachate of Process 1 was decreased relative to that of Process 2, possibly due to the presence of Fe.

LDHs were successfully synthesised using both the co-precipitation and urea hydrolysis methods. Products formed from the urea hydrolysis method had fewer impurities. The leachate formed after Process 2, with the addition of extra Al, formed the most acceptable product in terms of crystallinity and purity.

Objective 7:

To develop a method to separate the iron from the magnesium and aluminium in the thermochemically treated mine residues, prior to leaching, to improve the purity of the magnesium containing precipitates and layered double hydroxides (Chapter 8).

The thermochemical treatment with AS is non-selective at a single temperature, with several metals being co-extracted from the residues. The combination of metals in the leachate made the production of pure Mg-products difficult, as the removal of the Fe-fraction post treatment, via methods such as selective precipitation using pH was challenging, as the Fe appeared to be ubiquitous. Another route to remove the Fe, before leaching, was therefore pursued. This was done by carefully controlling the temperature of the thermal treatment in a subsequent roasting step, thereby thermally decomposing some of the water-soluble ammonium metal- and metal-sulphate species into water-insoluble metal oxides. From the earlier roasting treatments, it was apparent that Fe extraction was decreased at thermochemical treatment temperatures $> 700^{\circ}\text{C}$. The extent of the extraction of Mg, Al and Fe from CS subjected to the various roasting programs and subsequent leaching in water was followed by ICP analysis.

The roast of CS with AS at 450°C followed by 680°C (Process 2) removed most of the $\text{Fe}_2(\text{SO}_4)_3$ phase, with the soluble Fe content of the leachate having decreased by 75 – 79%. Unfortunately, the $\text{Al}_2(\text{SO}_4)_3$ phase was also reduced substantially (from $\sim 13\%$ to $\sim 5\%$). This temperature (680°C) was higher than the temperature indicated as the cut-off for decomposition of $\text{Fe}_2(\text{SO}_4)_3$ formed from roasting CS with AS at 450°C , for which $\text{Fe}_2(\text{SO}_4)_3$ was completely decomposed just below 600°C . The roast of CS with AS at 450°C followed by the additional roasting at 750°C (Process 3) indicated that mainly MgSO_4 was retained as roasting product. A very small percentage of both Fe and Al were still extracted, and there was a 90 – 92% decrease in the soluble Fe content of the leachate.

XRD indicated the presence of haematite for roast products of CS treated at 450°C with AS + 680°C and at 450°C with AS + 750°C , as well as for their leach residues. The increase in haematite content was supported by the semi-quantitative XRD results of the leach residues (Table 8.7). Haematite was the only form of Fe present in the roasting products formed at the higher roasting temperatures. The occurrence of haematite was also apparent when comparing the colour of the roasting products or leach residues at each roasting program (Fig 8.10), with the residues from the higher roast temperatures having the distinctive brick red colour of haematite.

Iron can therefore be selectively removed from CS using a sequence of systematic roasting steps, although the temperature ranges used need further testing and refining.

Fe can then be recovered from the solid leach residues of the higher temperature roasts by re-roasting the residue with AS at 450°C to form soluble Fe sulphates from the oxide.

The amount of soluble Al was also decreased during the higher temperature roasting, but additional $\text{Al}_2(\text{SO}_4)_3$ can be added to the soluble MgSO_4 in the leachate to produce layered double hydroxides (LDHs). This would have been necessary even if all of the Al in the mine residues was retained, as the Mg:Al mol ratio in the leachates was generally higher (5:1 for Process 1 to 10:1 for Process 2) than the 2:1 or 3:1 mol ratio required for production of LDHs (Fig 8.8).

The leachate from the 450°C with AS + 680°C (Process 2) and 450°C with AS + 750°C (Process 3) roasting programs can be used to synthesise the desired Mg-containing products.

10.3 Future considerations

Due to the millions of tons of tailings that are stockpiled in South Africa and the subsequent environmental complications that manifest, additional research on this local resource needs to be conducted.

As the tailings sample (CT) behaved differently to the slimes sample (CS), optimisation of roast ratios and leaching for the CT sample needs to be conducted. The method developed using pure chemicals to optimise the leach volume could be incorporated for the mine residues, to investigate differences in solubility. These findings could then be expanded to include samples from other diamond mines.

To be able to characterise the amorphous gel-like precipitate products, calcination to form the corresponding oxides would be valuable. This could then lead to investigations into possible uses for these products.

As there is no or little research into why the decomposition temperatures for mixtures of minerals relative to individual minerals shift, investigation into the reason(s) would make an interesting study.

Although proof of concept was shown with the formation of both precipitates and LDHs from the leachates, optimisation of conditions to improve the products is required. This

includes investigation of various surfactants to reduce the agglomeration of the product during selective precipitation, as well as the conditions required to produce nanoparticles.

Although Fe was separated from Mg using a roasting program, the temperatures selected were not ideal as the Al content was also reduced considerably. A study to optimise the roasting temperatures used to reduce the soluble Fe content in leachates would be beneficial.

Once high-purity products can be produced from the mine residues, a techno-economic study would be required to assess the feasibility and economic viability of such a process. This would also require mass and energy balance studies as well as exergy investigation.

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