



Thermogravimetry as a research tool for the development of an ammonium sulphate roasting process for selective metal extraction from minerals

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Abstract

The ammonium sulphate roasting process involves reacting mineral-bearing materials with ammonium sulphate via a solid–solid roasting process and subjecting the resulting roast residue to aqueous leaching. This process enables the simultaneous, non-selective co-extraction of strategic metals from the starting materials. However, effective separation of the extracted metals is often mandatory to produce quality products of high purity. In this study, the combined application of thermogravimetric analysis, X-ray powder diffraction and inductively coupled plasma optical emission spectrometry confirmed the non-selectivity of the process when applied to a South African diamond mine residue residue roasted with ammonium sulphate in a 1:2 mass ratio (m/m) at 450 °C for 2 h, with magnesium, iron and aluminium being co-extracted into water-soluble metal sulphates. Thermogravimetry was then applied to develop a multi-step, multi-temperature selective roasting process using mixtures of pure commercial metal sulphate salts. The first step of the modified process successfully separated iron and aluminium sulphates from magnesium-sulphates in the roast residues by thermally decomposing soluble iron and aluminium sulphates into insoluble oxides via calcination at 750 °C for 2 h. This temperature was lower than the one at which magnesium sulphates convert into magnesium oxide. In the second and final step, iron and aluminium were recovered from the oxide minerals via solid–solid re-roasting with ammonium sulphate at 450 °C for 1 h, causing the oxides to revert back to their water-soluble sulphate forms. The effectiveness of the modified process was subsequently verified using a diamond mine residue, showing that the soluble iron and aluminium contents in the magnesium-bearing leachate could be reduced by over 90%.

Keywords Metal extraction · Mine residue · Thermochemical treatment · Selectivity · Thermogravimetric analysis · Ammonium salt

Introduction

The mining sector is integral to the South African economy, yet its operations result in the production of substantial amounts of waste mine residues such as tailings and slimes.

These residues may pose significant environmental issues and occupy extensive land that could be utilised for alternative economic purposes. On the other hand, if processed into valuable products, these same residues may have the potential to be an economic resource that promotes sustainability.

The ammonium sulphate ((NH₄)₂SO₄) roasting process is an emerging technology for the purification of silicate minerals (e.g. talc; [1]) and the extraction of strategic metals from mineral-bearing materials [2]. The latter includes materials such as coal fly ash [3–5], laterite nickel ore [6], platinum group metals (PGMs) tailings [7, 8], slags [2, 9], bauxite residue [10], serpentinite rocks [11–13], and other residues [14–16]. The basic principle of the process relies on the use of the thermochemical reactivity between (NH₄)₂SO₄ (as chemical additive) and reactive oxide or silicate minerals

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to convert the insoluble metal components into their respective water-soluble metal sulphates and/or intermediate double salts (i.e. ammonium-metal sulphate-based compounds $(\text{NH}_4^+-M-\text{SO}_4^{2-})$). This step is followed by aqueous leaching in water or dilute acid to dissolve the sulphate compounds and extract the valuable metals to solution. This process has a number of benefits, such as low corrosion of equipment (in comparison to acid leaching using strong acids), high metal recovery, and the use of a widely available, low-cost, recyclable chemical agent $(\text{NH}_4)_2\text{SO}_4$.

The success of the $(\text{NH}_4)_2\text{SO}_4$ roasting process depends greatly on the silicate lattice structure of minerals contained in the parent material. For instance, minerals such as cordierite (the only Mg-bearing cyclosilicate) [11, 17] and talc (a phyllosilicate) [1, 11] have limited to no reactivity with $(\text{NH}_4)_2\text{SO}_4$ during solid–solid thermal treatment. On the other hand, the magnesium contained in the two phyllosilicate minerals vermiculite and phlogopite is highly reactive with $(\text{NH}_4)_2\text{SO}_4$ during roasting [11]. Serpentine minerals display varying degrees of reactivity with $(\text{NH}_4)_2\text{SO}_4$, with lizardite pairing the favourable features more often than antigorite [12, 17, 18], even though the two minerals lizardite and antigorite are both Mg-rich 1:1 trioctahedral layer minerals with an ideal composition of $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$. This is because minerals' behaviour during the $(\text{NH}_4)_2\text{SO}_4$ roasting process 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 [11].

A challenging aspect associated with the $(\text{NH}_4)_2\text{SO}_4$ roasting process, experienced by the authors when reprocessing coal fly ash [4] and PGM tailings [7], is its lack of metal selectivity during the thermochemical step. This non-selectivity leads to the simultaneous co-extraction of several elements (e.g. Al, Ca, Mg, Fe and Ti) to solution due to the chemical affinity between $(\text{NH}_4)_2\text{SO}_4$ and major elements under thermal conditions. Similar observations were made in other studies. For example, Zhang et al. [19] revealed the simultaneous extraction of Fe and Mn along with the elements of interest (V, Ti) from vanadium slag. Romão et al. [20] observed the co-extraction of Fe, Ni, Cr, Cu along with the element of interest (Mg) from serpentinite.

Effective separation of the extracted dissolved elements can be problematic (e.g. Al and Fe, Ca and Mg), although it is often essential to produce quality products of high purity. Increasing the roasting temperature to selectively convert some water-soluble metal sulphates and/or intermediate double salts into their respective insoluble metal oxides can successfully separate metals, although examples in the literature are limited. An example is that copper and nickel can be separated by decomposing ammonium ferric sulphate to iron oxides by increasing the roasting temperature from 450 to 500 °C following initial roasting

of mixed oxide-sulfide nickel ore [21]. In a study by Saba et al. [22], where $(\text{NH}_4)_2\text{SO}_4$ was used to extract Mn from a low grade ore containing 27.5% Fe, it was observed that the soluble Fe content and therefore its extraction decreased at roasting temperatures above 700 °C. These findings aligned with those of Meng et al. [23] in their study of Sc extraction from bauxite ore, where no Fe was extracted at temperatures above 650 °C. Fekete et al. [24] proposed a process for separation of a mixture of ZnSO_4 and $\text{Fe}_2(\text{SO}_4)_3$, derived from the sulphation of a ZnFe_2O_4 waste material. This involved annealing at 400–450 °C for extended durations or heat shock treatment between 600–650 °C, resulting in the conversion of $\text{Fe}_2(\text{SO}_4)_3$ into Fe_2O_3 . ZnSO_4 , being thermally stable at these temperatures, can be separated from the water-insoluble Fe_2O_3 by dissolving it in water. More recently, Kamberović et al. [25] demonstrated the selective extraction of Cu, Pb and Zn from a sulphate-rich jarosite tailing waste by converting the Fe-sulphate phases to hematite through roasting at 730 °C.

The objective of this paper is three-fold. Firstly, the study confirms the hypothesised non-selectivity of the $(\text{NH}_4)_2\text{SO}_4$ roasting process when applied to a South African diamond mine residue. Secondly, the study uses thermogravimetry to develop a multi-step, multi-temperature selective roasting process using mixtures of pure commercial metal sulphate salts as models of solid residues generated via the $(\text{NH}_4)_2\text{SO}_4$ roasting process. Finally, the effectiveness of the selective process is tested on the diamond mine residue.

Experimental

Starting material and chemicals

Ammonium sulphate $((\text{NH}_4)_2\text{SO}_4)$ and deionised water were AR grade and were sourced from Merck Chemicals (Pty) Ltd. AR-grade metal sulphate salts (aluminium sulphate octadecahydrate $(\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O})$, iron(III) sulphate hydrate $(\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O})$ and magnesium sulphate heptahydrate $(\text{MgSO}_4 \cdot 7\text{H}_2\text{O})$) were supplied by Labchem, South Africa. The three hydrated metal salts were placed in a muffle furnace at 400 °C for 2 h to remove the crystallisation water and produce their anhydrous forms, i.e. $\text{Al}_2(\text{SO}_4)_3$, $\text{Fe}_2(\text{SO}_4)_3$ and MgSO_4 .

A sample of mine slime (SL) was obtained from a mine in South Africa. The particles were finely grained, with the percentile diameters $D(v,0.1)$, $D(v,0.5)$ and $D(v,0.9)$ calculated from laser diffraction volume data being 2.0 µm, 9.6 µm and 161.6 µm, respectively.

Methodology

Non-selective metal co-extraction from mine slime using conventional roasting with $(\text{NH}_4)_2\text{SO}_4$

The control experiment consisted of subjecting 8.0 g of the mine slimes sample (SL) to roasting with 16.0 g of $(\text{NH}_4)_2\text{SO}_4$ in a 1:2 mass ratio (m/m) in a muffle furnace at 450 °C for 2 h, to generate a roast product (SL_{AS}) containing water-soluble metal sulphate compounds formed from the thermochemical reaction between reactive minerals and $(\text{NH}_4)_2\text{SO}_4$. SL_{AS} was then leached in deionised water using a ratio of 1:25 mass to volume (m/v), i.e. g mL^{-1} , under continuous mixing condition at 50 °C for 2 h. After leaching, the suspension was filtered through a Sartorius polycarbonate Track-Etch membrane. The leach residue ($\text{SL}_{\text{AS-L}}$) was washed with deionised water and air-dried. The acidified filtrates were characterised using ICP-OES. This leaching-filtration-washing-drying procedure is hereafter referred to as the “leaching method” and was used on all roast products generated in this study.

Selective metal extraction method development using synthetic metal sulphate salt mixture

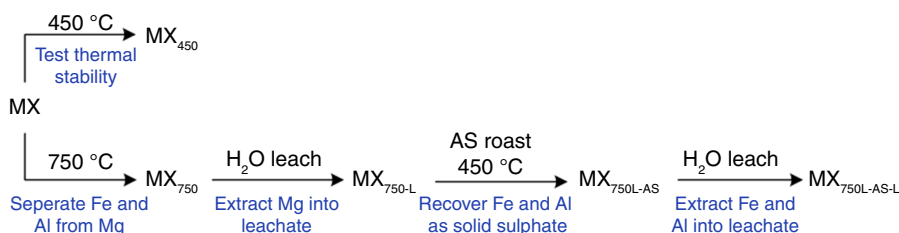
TGA studies The three anhydrous metal sulphate salts MgSO_4 , $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Al}_2(\text{SO}_4)_3$ were finely ground using a mortar and pestle. The individual salts were then combined to produce a salt mixture (hereafter called “mixture” or MX) with a similar mass ratio to that of the mine slime sample (SL) (i.e. Mg:Fe:Al at 3:2:1). The mixture served as an analog to the solid residue SL_{AS} generated following roasting of the mine slime with $(\text{NH}_4)_2\text{SO}_4$. The thermal behaviour and decomposition temperature ranges of each individual sulphate salt were studied using TGA. The mixture was also investigated for direct comparison because the decomposition temperatures of the individual metal sulphates may shift considerably when combined together with other metal sulphate species [26]. The insight gained from the TGA data was then used to develop a multi-stage roasting-leaching regime for the selective extraction of Mg from Fe and Al contained in the mixture.

Selective roasting-leaching regime In order to test the findings derived from the TGA data, the following roasting-leaching regime was developed. MX was first roasted at either 450 °C or 750 °C for 2 h. According to the TGA results obtained for MX, roasting at 750 °C was expected to convert Fe and Al sulphates into insoluble Fe and Al oxides. At completion of the roasting treatments, the roast products MX_{450} and MX_{750} were leached using the leaching method described earlier. The leach residue obtained from roasting the mixture at 750 °C ($\text{MX}_{750\text{-L}}$) was roasted with $(\text{NH}_4)_2\text{SO}_4$ in a 1:2 m/m ratio at 450 °C for 1 h and the new roast residue ($\text{MX}_{750\text{-AS}}$) was leached to yield a new leach residue ($\text{MX}_{750\text{-AS-L}}$). The roasting regime applied to the mixture, and the purpose of each roasting step, is summarised in Fig. 1 and Table S1 (Supplementary material).

Evaluation of the selective roasting-leaching regime using mine slimes

The effectiveness of the selective roasting-leaching regime was evaluated by preparing a new batch of SL_{AS} following the procedure described in section “Non-selective metal co-extraction from mine slime using conventional roasting with $(\text{NH}_4)_2\text{SO}_4$ ”. Once SL_{AS} was formed, it was roasted at 550 °C, 680 °C or 750 °C to form the $\text{SL}_{\text{AS-550}}$, $\text{SL}_{\text{AS-680}}$ and $\text{SL}_{\text{AS-750}}$ roasts, respectively. According to the TGA results, it was anticipated that roasting SL_{AS} at these three temperatures would convert Fe sulphates into insoluble Fe oxides to separate Fe from Al and Mg via selective thermal conversion of water-soluble Fe sulphates into insoluble Fe oxides to yield roast products $\text{SL}_{\text{AS-550}}$ and $\text{SL}_{\text{AS-680}}$, or to convert both soluble Al- and Fe sulphates into the corresponding insoluble oxides while retaining the Mg as soluble MgSO_4 in $\text{SL}_{\text{AS-750}}$. $\text{SL}_{\text{AS-680}}$ was then leached using the leaching method to dissolve Mg and Al and form the leach residue $\text{SL}_{\text{AS-680L}}$. $\text{SL}_{\text{AS-680L}}$ was subsequently roasted with $(\text{NH}_4)_2\text{SO}_4$ at 450 °C to convert insoluble Fe into soluble Fe sulphates, yielding $\text{SL}_{\text{AS-680-AS}}$. Roasting of SL at 680 °C with $(\text{NH}_4)_2\text{SO}_4$ without the initial 450 °C roast was performed to reduce furnace time and to ascertain whether a single-step process would adequately separate the Fe phase from the Mg and Al phases. This roast product was labeled $\text{SL}_{\text{AS high}}$. The roasting regime applied to the mine slimes,

Fig. 1 Roasting programs used for selective separation of Fe, Al and Mg from MX



and the purpose of each roasting step, is summarised in Fig. 2 and Table S2 (Supplementary material).

Characterisation of solid materials and leachates

Solid materials Chemical compositions of solid materials were obtained using XRF fused bead analysis (Thermo Fisher Perform'X Sequential XRF with OXSAS software). The loss on ignition (LOI) was determined by roasting the sample at 1000 °C for at least 3 h until a constant mass was obtained. Mineralogical compositions were obtained using a PANalytical X'Pert Pro Powder Diffractometer (XRD) equipped with an X'Celerator detector and variable divergence- and fixed receiving slits, with Fe filtered Co-K α radiation ($\lambda = 1.789 \text{ \AA}$). Mineral phase concentrations were determined by Rietveld quantitative analysis with Highscore software with accuracy in the region of $\pm 1\%$. The samples were micronised in a McCrone micronising mill and prepared for XRD analysis using a back loading preparation method.

TGA analyses were performed on a TA Instruments SDT Q600 Thermogravimetric Analyzer & Differential Scanning Calorimeter (DSC). Approximately 20 mg of sample was

placed in a 90- μL alumina pan and heated from ambient to 1100 °C at a heating rate of 10 °C min^{-1} . Each test was conducted using a flow rate of 100 mL min^{-1} of nitrogen (N_2).

Leachates All leachates were acidified to a pH below 2 with concentrated nitric acid and analysed for their major element content by inductively coupled plasma optical emission spectrometry (ICP-OES) at an accredited laboratory (Waterlab Pty Ltd, Pretoria, South Africa).

Results and discussion

Characterisation of mine slime (SL)

The bulk chemical composition of SL is shown in Table 1. The sample was predominantly composed of SiO_2 , MgO , Fe_2O_3 , Al_2O_3 , CaO and TiO_2 and exhibited a positive loss on ignition (LOI = 8.3%). The mineralogy of SL was complex (Table 2 and Figure S1 in the Supplementary material). It was dominated by phyllosilicate clay minerals (69% m/m), more specifically 33% smectite (most probably saponite or montmorillonite, or a mixture of both), 30% talc, 5%

Fig. 2 Roasting programs used for selective separation of Fe, Al and Mg from the mine slimes (SL)

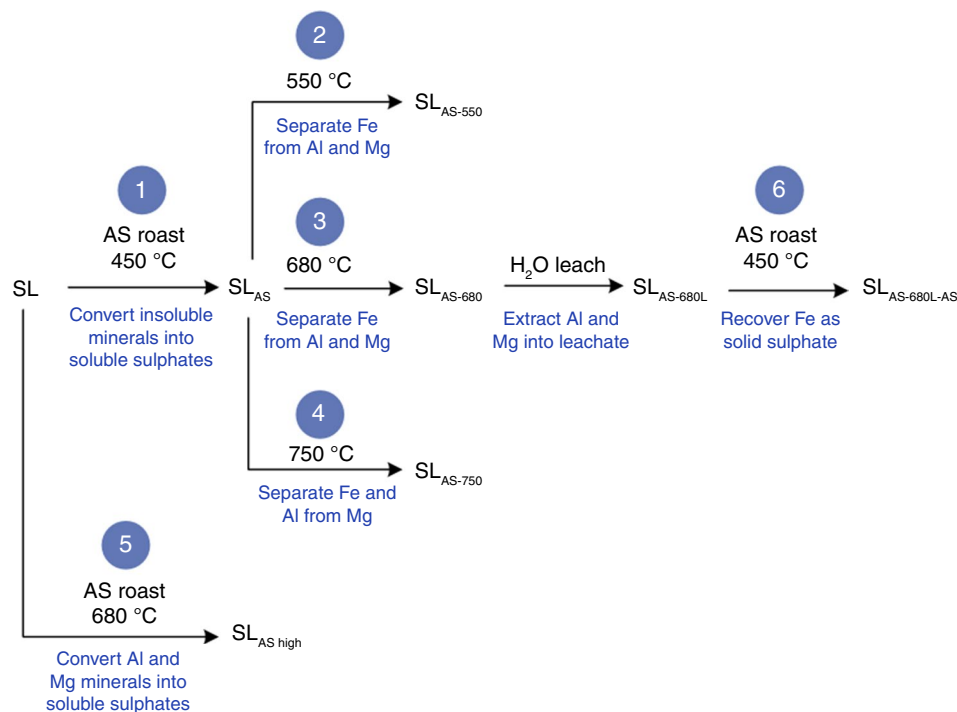


Table 1 Chemical composition of SL (XRF, % m/m)

SiO_2	MgO	Fe_2O_3	Al_2O_3	CaO	TiO_2	K_2O	Na_2O	P_2O_5	LOI ^a	Total ^b
47.0	23.4	9.4	5.4	3.6	1.3	0.6	0.3	0.1	8.3	99.3

^aLoss on ignition

^bOther elements (<0.1% m/m): MnO , NiO , Cr_2O_3 , V_2O_5 , ZnO and SrO

Table 2 Mineralogical composition of SL (XRD, % m/m); clay minerals are indicated above the dotted line

Mineral group	Mineral name	Approximate chemical formula	Abundance (% m/m)
Phyllosilicate clay minerals	Smectite	(Ca,Na,H)(Al,Mg,Fe,Zn) ₂ (Si, Al) ₄ O ₁₀ (OH) ₂ ·xH ₂ O	33
	Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	30
	Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	5
	Lizardite	Mg ₃ Si ₂ O ₅ (OH) ₄	1
Mica	Phlogopite	KMg ₃ Si ₃ AlO ₁₀ (F, OH) ₂	8
Chlorite	Clinochlore	(Fe,Mg,Al) ₆ (Si,Al) ₄ O ₁₀ (OH) ₈	4
Mineral group	Mineral name	Approximate chemical formula	Abundance (% m/m)
Pyroxene	Ferrian Diopside	Ca(Mg,Fe)Si ₂ O ₆	6
Oxides	Quartz	SiO ₂	4
Carbonates	Calcite	CaCO ₃	4
Feldspar	Plagioclase	(Na,Ca)(Si,Al) ₄ O ₈	2
	Microcline	KAlSi ₃ O ₈	1
Amphibole	Hornblende	Ca ₂ (Mg,Fe,Al) ₅ (Si,Al) ₈ O ₂₂ (OH) ₂	2

kaolinite and 1% lizardite. The abundance of these phyllosilicate clay minerals accounted for the large amount of SiO₂ (47%, Table 1), and since many of these minerals contain magnesium, it also explained the substantial MgO content (24%, Table 1). Additionally, SL contained 8% phlogopite, 6% ferrian diopside, and various minor and trace minerals, each present in quantities less than 5% m/m. Based on these findings, Mg, Fe and Al were identified as the major elements available for extraction from SL. Si, even though the most abundant element, was not expected to be extractable using the process of solid-state reaction with (NH₄)₂SO₄ [27]. In the context of this study, the selective extractive behaviour of Mg, Fe and Al was of particular interest.

Non-selective metal co-extraction from slime using conventional roasting with (NH₄)₂SO₄

Conventional roasting of SL with (NH₄)₂SO₄ was used to collect baseline data and demonstrate the non-selective co-extraction of major elements when using this process (Process 1, Fig. 2). Optimising the roasting temperature or the SL to (NH₄)₂SO₄ ratio was outside the scope of this study. The baseline data were then used to assess the effectiveness of the modified process.

The mineralogical characterisation of the roast product obtained from Process 1 (SL_{AS}) by XRD indicated the occurrence of several newly formed metal sulphate phases (MgSO₄·6H₂O, (NH₄)₂Mg₂(SO₄)₃, Al₂(SO₄)₃, (NH₄)Al(SO₄)₂ and NH₄Fe(SO₄)₂) (Table 3 and Figure S1 in the Supplementary material). These results provided the first confirmation of the simultaneous extraction of several major elements (Al, Fe, Mg) from parent minerals present in the slime during the thermochemical step. The identification of

Table 3 List of newly formed minerals present in the roasting products of selected roasting programs

Mineral*	Process 1 SL _{AS}	Process 3 SL _{AS-680}	Process 4 SL _{AS-750}
Efremovite, (NH ₄) ₂ Mg ₂ (SO ₄) ₃	x		
Magnesium sulphate, MgSO ₄	x	x	x
Godovikovite, (NH ₄)Al(SO ₄) ₂	x		
Millosevichite, Al ₂ (SO ₄) ₃	x	x	x
Sabieite, NH ₄ Fe(SO ₄) ₂	x		
Anhydrite, CaSO ₄			x
Hematite, Fe ₂ O ₃		x	x

*The full mineralogical composition of SL is reported in Table 2

Mg (2.3 g L⁻¹), Fe (1.1 g L⁻¹) and Al (0.5 g L⁻¹) in the leachates following aqueous leaching of SL_{AS} presented the second confirmation that elemental co-extraction had occurred.

Selective metal extraction method development using the pure metal sulphate mixture (MX)

TGA study

Table 4 summarises the decomposition reactions and theoretical TGA mass losses expected for the dehydrated pure metal sulphates and MX. Theoretical TGA mass losses were calculated from the stoichiometry of the decomposition reactions presented in the table. Figure 3a compares the decomposition behavior of the individual pure metal sulphates and MX.

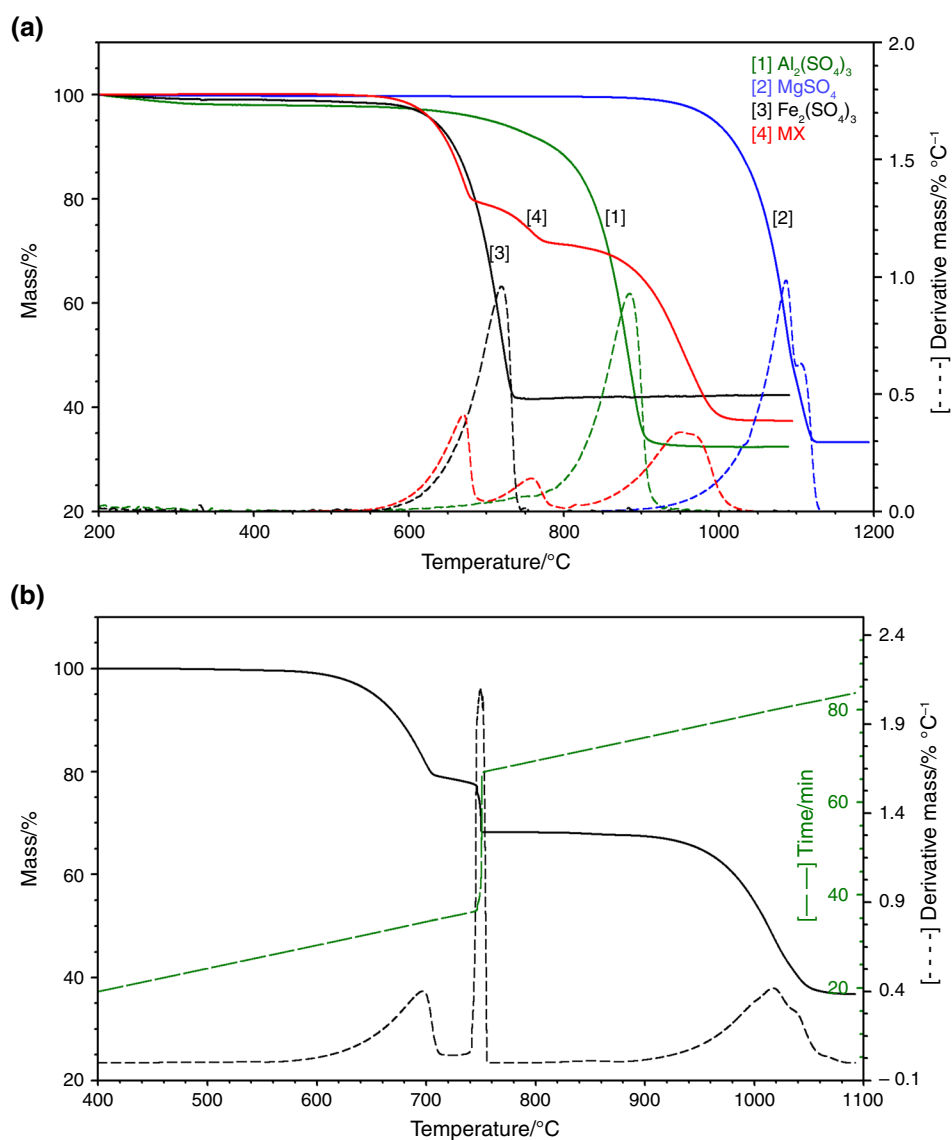
Table 4 Decomposition reactions and calculated theoretical mass losses expected for pure metal sulphates and MX

Decomposition reaction	Composition of MX/% m/m	Theoretical TGA mass loss/%	
		Pure	MX
$\text{MgSO}_4 (\text{s}) \rightarrow \text{MgO} (\text{s}) + \text{SO}_3 (\text{g})$	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

The TGA mass losses obtained for dehydrated pure MgSO_4 (67.0%; 900–1125 °C), $\text{Al}_2(\text{SO}_4)_3$ (70.7%; 600–925 °C) and $\text{Fe}_2(\text{SO}_4)_3$ (57.8%; 550–750 °C) were in agreement with the calculated values reported in Table 4. These mass loss values were calculated on a dry mass basis,

with the temperature at 200 °C taken as the onset. The average of duplicate TGA measurements indicated that the mass losses and decomposition temperature ranges for MX were 19.9% between 550 °C and 680 °C ($\text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{Fe}_2\text{O}_3$), 9.0% between 680–775 °C ($\text{Al}_2(\text{SO}_4)_3 \rightarrow \text{Al}_2\text{O}_3$) and 33.1% between 775 and 1030 °C ($\text{MgSO}_4 \rightarrow \text{MgO}$). The minimum in the DTG curve was used to assign temperature ranges. The mass losses obtained for decomposition of the metal sulphates contained in MX agreed well with the expected values (Table 4). A shift in decomposition temperatures for the metal sulphates in MX in comparison to that of the pure metal sulphates was clearly shown by the TGA results. All metal sulphates in MX had decomposition temperature ranges lower than those of the pure metal sulphates, and their decomposition events were not well separated, especially for the decomposition of $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Al}_2(\text{SO}_4)_3$. The results obtained for the thermal stabilities of $\text{Fe}_2(\text{SO}_4)_3$,

Fig. 3 **a** Comparison of TGA decomposition behaviour of the individual pure metal sulphates vs MX, and **b** TGA analysis of MX with an isotherm at 750 °C for 30 min



$\text{Al}_2(\text{SO}_4)_3$ and MgSO_4 contained in MX are summarised in Fig. 4.

Development of selective roasting-leaching regime for MX

The insight gained from the TGA data was used to develop a multi-stage roasting-leaching regime for the selective extraction of Mg from Fe and Al contained in MX. Figure 4 illustrates that separation of Fe from Al and Mg in a mixture of their sulphate salts may be achieved by thermally treating 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 are kept in the soluble sulphate form, i.e. between 550 and 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 and 775 °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 any of the solid leach residues with $(\text{NH}_4)_2\text{SO}_4$ at 450 °C is anticipated to convert the remaining insoluble metal oxides back into soluble metal sulphates, which can again be recovered by aqueous leaching.

In order to test the findings derived from the TGA data, MX was roasted at either 450 °C or 750 °C. The roasting regime applied to MX, and the purpose of each roasting step, is summarised in Fig. 1 and Table S1 (Supplementary material). Roasting at 450 °C was performed to confirm the thermal stability of the metal sulphates at the temperature used for thermochemical treatment of the mine residues with $(\text{NH}_4)_2\text{SO}_4$. The roasting temperature for separation of Mg from Fe and Al was adjusted from 775 °C to 750 °C, using the temperature at which the rate of decomposition of $\text{Al}_2(\text{SO}_4)_3$ contained in MX is at its maximum, i.e. the peak temperature in the DTG curve (Fig. 3a). This was done to limit the conversion of MgSO_4 into MgO in an effort to

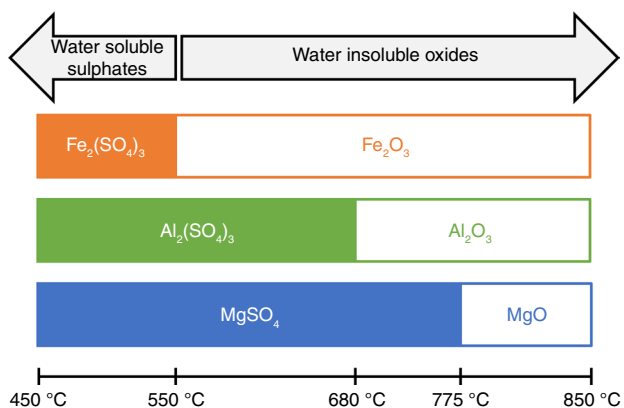


Fig. 4 Thermal stabilities of water-soluble metal sulphates in MX and their conversion into insoluble metal oxides

retain most of the Mg in the leachate and all of the Fe and Al in the solid leach residue. This hypothesis was tested by repeating the TGA analysis of MX using a heating rate of 20 °C min⁻¹ and inclusion of an isotherm at 750 °C for 30 min (Fig. 3b). Mass losses obtained for the decomposition of the pure metal sulphates $\text{Fe}_2(\text{SO}_4)_3$ (21.0%), $\text{Al}_2(\text{SO}_4)_3$ (10.5%) and MgSO_4 (31.3%) were similar to the expected values (Table 4) and those obtained during the normal TGA ramp experiment (Fig. 3a). These results indicated that complete decomposition of $\text{Al}_2(\text{SO}_4)_3$ can be attained when lowering the roasting temperature of MX from 775 to 750 °C, and that MgSO_4 did not decompose during the isothermal step at 750 °C. Finally, the solid leach residue obtained from roasting MX at 750 °C was thermochemically treated with $(\text{NH}_4)_2\text{SO}_4$ at 450 °C and leached in water to recover the Fe and Al.

TGA analysis of roast products MX_{450} , MX_{750} and $\text{MX}_{750\text{-AS}}$ is illustrated in Fig. 5. Curve 1 (MX_{450}) showed that Mg, Fe and Al remained in the soluble sulphate form after oven roasting of MX at 450 °C. All three metals can therefore be extracted from MX_{450} by aqueous leaching. Curve 2 (MX_{750}) was similar to that reported for pure MgSO_4 (Fig. 3a), indicating that only Mg remained in the sulphate form after roasting MX at 750 °C. This was supported by the ICP-OES data (Fig. 6).

$\text{MX}_{750\text{-AS}}$ was the product obtained from thermochemical treatment of the leach residue from the 750 °C roasting program ($\text{MX}_{750\text{-L}}$) with $(\text{NH}_4)_2\text{SO}_4$ (Fig. 1). The purpose of thermochemical treatment of $\text{MX}_{750\text{-L}}$ was to determine whether Fe and Al could be recovered from their respective oxides (Fe_2O_3 and Al_2O_3). The presence of $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Al}_2(\text{SO}_4)_3$ in curve 3 ($\text{MX}_{750\text{-AS}}$) illustrated that both Fe and Al locked in oxide forms can be recovered as water-soluble metal sulphate forms after re-roasting of $\text{MX}_{750\text{-L}}$ with $(\text{NH}_4)_2\text{SO}_4$. This result proves that the conversion of the metal sulphates to metal oxides is reversible when re-treating with AS at 450 °C. Decomposition of the $\text{Fe}_2(\text{SO}_4)_3$ in $\text{MX}_{750\text{-AS}}$ overlapped with that of $\text{Al}_2(\text{SO}_4)_3$ between 580 and 830 °C, as indicated by the shoulder in the DTG curve. Excess $(\text{NH}_4)_2\text{SO}_4$ is also apparent (400–550 °C, curve 3), as was observed previously for thermochemical treatment with $(\text{NH}_4)_2\text{SO}_4$ at 450 °C for 1 h [1, 4, 8]. The rate of decomposition of $\text{Fe}_2(\text{SO}_4)_3$ to Fe_2O_3 , determined from the peak temperature in the DTG curves, was at its maximum at 700 °C for both MX_{450} and $\text{MX}_{750\text{-AS}}$. However, the onset of decomposition of $\text{Al}_2(\text{SO}_4)_3$ occurred below 700 °C, evident by the overlap in DTG curves between 600 and 800 °C (Fig. 5, curves 1 and 3). Efficient thermal separation of Fe_2O_3 from $\text{Al}_2(\text{SO}_4)_3$ may therefore be challenging when applying a subsequent roast of MX at 700 °C. A TGA mass loss of 10.3%, indicating the temperature range over which 50% of $\text{Fe}_2(\text{SO}_4)_3$ has decomposed, was noted for MX_{450} between 580 and 680 °C (Fig. 5, curve 1). This

Fig. 5 Comparison of TGA curves for roasting products [1] MX₄₅₀, [2] MX₇₅₀ and [3] MX_{750L-AS}

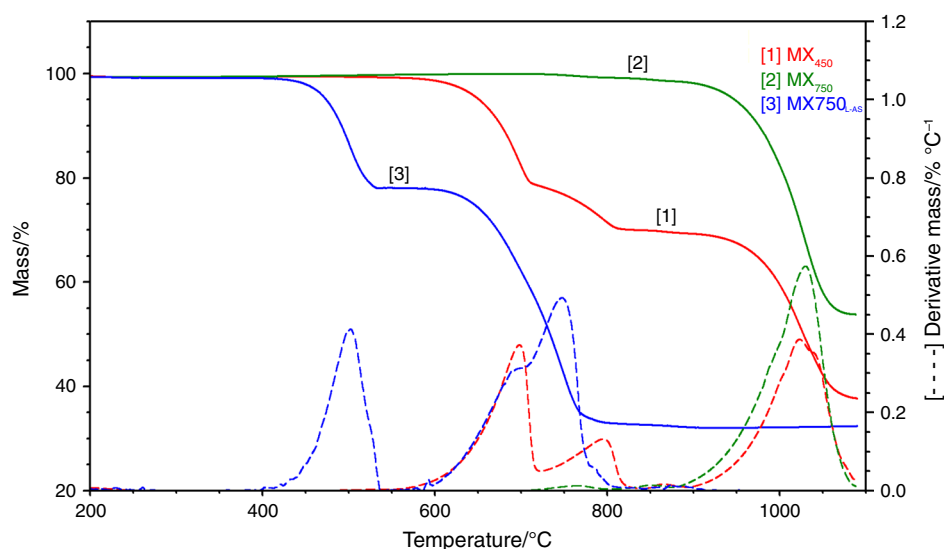
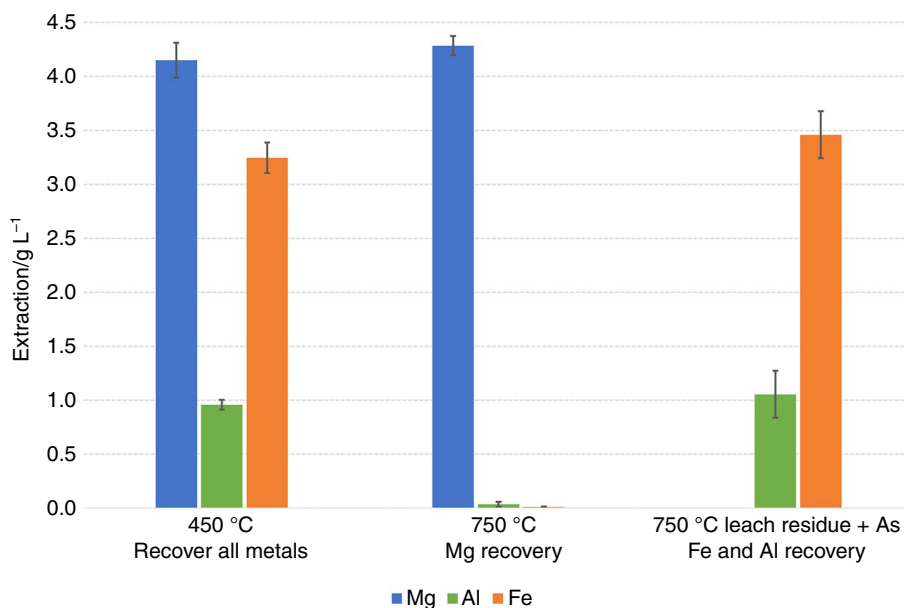


Fig. 6 Extraction of Mg, Fe and Al after roasting MX at 450 °C and 750 °C, and re-roasting the 750 °C leach residue at 450 °C with additional (NH₄)₂SO₄ (AS) (Duplicate samples; *n* = 2)



midway point for decomposition of Fe₂(SO₄)₃ was selected as the roasting temperature to retain Mg and Al as soluble sulphates when applying this program to SL. This temperature was similar to the temperature reported by Meng et al. [23], i.e. ≥ 650 °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 SL.

The proposed separation method was tested by aqueous leaching of MX₄₅₀, MX₇₅₀ and MX_{750L-AS} (Fig. 6). Mg, Al and Fe were all extracted from leaching of MX₄₅₀. A very small amount of dissolved Fe and Al (0.3% and 2.4% of the original amount, respectively) was measured in solution after leaching of MX₇₅₀. The presence of Fe-oxides in the leach residue of MX₇₅₀ (i.e. MX_{750-L}) was evident

by its dark red colour (Fig. 7). Particulate hematite is typically red in nature [28, 29]. This was supported by XRD data, which confirmed that hematite (Fe₂O₃) was the major Fe-containing phase in MX_{750-L}, with strong reflections at 2θ of 28.5°, 38.5°, 41°, 48°, 64°, 74° and 76° (Fig. 7). Fe and Al were also successfully recovered and extracted from MX_{750L-AS}, after re-roasting of MX_{750L} at 450 °C with additional (NH₄)₂SO₄, and no Mg was identified in the leachate (Fig. 6).

Application to the mine residues

The roasting program used for the mixture of pure metal sulphates was adapted and applied to the mine slimes sample. SL was initially roasted at 450 °C with (NH₄)₂SO₄ to

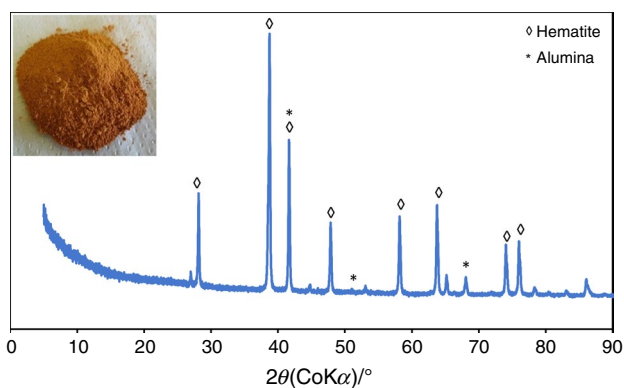
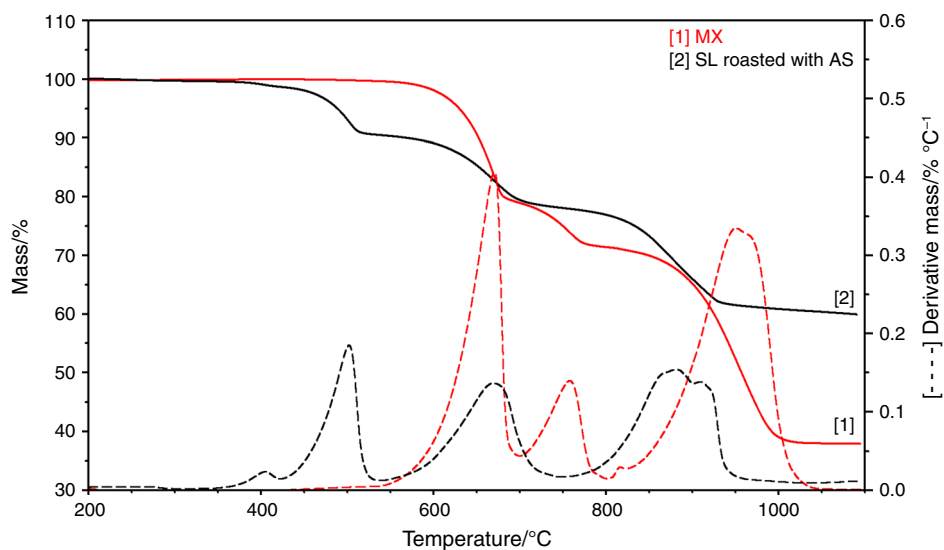


Fig. 7 XRD pattern and colour of $\text{MX}_{750\text{-L}}$, with \diamond indicating the reflections for hematite (Fe_2O_3) and * for alumina (Al_2O_3)

convert the minerals in SL to soluble metal sulphates (Process 1). Additional roasting at either 550 °C or 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 (Processes 2 and 3). The rationale behind the inclusion of an additional roasting step at 550 °C is explained later in the discussion. Roasting at 750 °C was conducted with the intention to keep only Mg in soluble sulphate form (Process 4). An additional experiment, using roasting at 680 °C with $(\text{NH}_4)_2\text{SO}_4$, without the initial 450 °C roast, was also undertaken (Process 5). 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. Finally, recovery of Fe from the leach residue obtained from Process 3 was tested by re-roasting the solid leach residue at 450 °C with $(\text{NH}_4)_2\text{SO}_4$ (Process 6). These roasting programs and the purpose of each roasting step, are summarised in Fig. 2 and Table S2 (Supplementary material).

Fig. 8 Comparison of TGA analyses of [1] the pure sulphate mixture (MX) versus [2] the product of thermochemical treatment of SL with $(\text{NH}_4)_2\text{SO}_4$ (SL_{AS})



XRD analysis of the roasting products from Processes 1, 3 and 4 indicated the presence of ammonium-metal sulphate and metal sulphate phases containing Mg, Al and Fe after roasting of SL at 450 °C with $(\text{NH}_4)_2\text{SO}_4$ (Table 3, Process 1 and Figure S1 in the Supplementary material). The ammonium-metal sulphate phases were absent following roasting at 680 °C or 750 °C (Table 3, Processes 3 and 4). At these higher roasting temperatures, MgSO_4 and $\text{Al}_2(\text{SO}_4)_3$ were observed as the only phases containing Mg and Al, while Fe_2O_3 was the only form of Fe present.

Figure 8 compares the TGA curves obtained from Process 1, i.e. the product of thermochemical treatment of SL with $(\text{NH}_4)_2\text{SO}_4$ (SL_{AS}) to that of the mixture of pure sulphate salts (MX). For SL_{AS} (curve 2), the decomposition of $\text{Fe}_2(\text{SO}_4)_3$ to Fe_2O_3 occurred between 425 and 550 °C, $\text{Al}_2(\text{SO}_4)_3$ to Al_2O_3 between 550 and 750 °C, and MgSO_4 to MgO between 750 and 980 °C, all of which were considerably lower than for the mixture of pure chemicals (curve 1). This shift in decomposition temperatures may be attributed to numerous factors such as differences in particle size [25], variations in structural order, the presence of impurities [25], or even the presence of other phases such as talc and hornblende in the mine residues. Furthermore, this paper reports a shift in the decomposition temperatures of the metal sulphates in MX when compared to that of the pure metal sulphates (Fig. 3a). To account for the shift in the decomposition temperature ranges of the metal sulphates contained in SL, an additional program involving roasting at 550 °C was incorporated to facilitate the separation of Fe from Al and Mg (Fig. 2, Process 2). In comparison, the roasting program applied in the separation of Fe from Al and Mg in MX, which included additional roasting at 680 °C, was also implemented for SL (Fig. 2, Process 3).

Figure 9 illustrates the TGA results obtained for the roasting products after applying the roasting programs to

SL. The absence of a mass loss between 425 and 550 °C in curve 2, obtained for SL_{AS-550} , indicated that the $Fe_2(SO_4)_3$ phase was decomposed during the additional roasting step at 550 °C. Decomposition of $Al_2(SO_4)_3$ (550–750 °C) and $MgSO_4$ (800–980 °C) was still observed. The TGA result obtained for SL_{AS-680} (curve 3) indicated that the $Fe_2(SO_4)_3$ phase was decomposed, but the mass loss due to decomposition of the $Al_2(SO_4)_3$ phase has also been reduced substantially (from ~13 to ~5%) when the temperature of the additional roasting step was increased to 680 °C. This temperature (680 °C) was higher than the temperature indicated as the cut-off for decomposition of $Fe_2(SO_4)_3$ in SL_{AS} (curve 1), for which $Fe_2(SO_4)_3$ was mostly decomposed at about 550 °C, while decomposition of $Al_2(SO_4)_3$ already commenced. It was therefore anticipated that leaching of SL_{AS-550} and SL_{AS-680} will not yield Fe in solution, the extraction of Al from SL_{AS-680} should be lower than from SL_{AS-550} , and the Mg concentrations should be similar. TGA analysis of SL_{AS-750} , the solid product obtained from roasting SL with $(NH_4)_2SO_4$ at 450 °C followed by additional roasting at 750 °C, indicated that only $MgSO_4$ was retained in the roasted product (curve 4). The $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$ phases were fully decomposed following roasting at 750 °C. Aqueous leaching of SL_{AS-750} was therefore expected to yield only Mg in solution.

The extent of Mg, Al and Fe extraction from SL subjected to the various roasting programs and subsequent leaching in water was followed by ICP-OES analysis, reported as elemental concentration (Fig. 10a) and percentage elemental extraction from SL (Fig. 10b). The values for maximum possible extraction were determined from the XRF data (Table 1), excluding the Mg content of the 30% m/m talc phase present in SL (Table 2). A prior study indicated that talc exhibits minimal, if any, reactivity during

thermochemical treatment with $(NH_4)_2SO_4$ under experimental conditions similar to this study [1].

Leaching of the product from Process 1 (SL_{AS}) yielded Mg (2.3 g L⁻¹), Fe (1.1 g L⁻¹) and Fe (0.5 g L⁻¹) in the leachate (Fig. 10a). More than 90% of extractable Mg and approximately 65% of total Al and Fe were leached from SL_{AS} (Fig. 10b, Process 1). The ICP-OES results of the leachates supported the reduction in the Al content predicted by TGA analysis of the solid products obtained from Processes 2 and 3, i.e. after roasting SL at 450 °C with $(NH_4)_2SO_4$ followed by an additional roast at either 550 °C or 680 °C. However, Fe continued to be extracted even when performing the additional roast at 680 °C, despite the absence of visible decomposition of $Fe_2(SO_4)_3$ in curves 2 and 3 (Fig. 9). The soluble Fe content of the leachate for Process 3 was, however, decreased by 75–79% (Process 1 vs. Process 3; Fig. 10). Additional roasting at 550 °C did not negatively impact the extraction of Al, but increasing the roast temperature to 680 °C resulted in a substantial loss of Al. These results indicate that separation of Fe from Al, without substantial loss of Al, remains a challenge. The leachate obtained from Process 4 primarily contained Mg, with minimal Fe and Al still being extracted. The Fe and Al contents in this leachate were reduced by ca. 90% compared to those from Process 1. It suggests that the effective separation of Mg from Al and Fe can be achieved by incorporating an additional roasting step at 750 °C.

Mg and Al extracted from Process 5 (78.4% and 28.7%; Fig. 10b) were lower than when using Process 3 (97.3% and 36.4%; Fig. 10b), whereas the Fe extraction was slightly higher (15.0% vs 12.6%; Fig. 10b), indicating that the initial roast with $(NH_4)_2SO_4$ at 450 °C to convert the Mg- and Al-containing phases in the SL to soluble sulphates should not be omitted.

Fig. 9 Comparison of the TGA curves of [1] SL_{AS} , [2] SL_{AS-550} , [3] SL_{AS-680} and [4] SL_{AS-750}

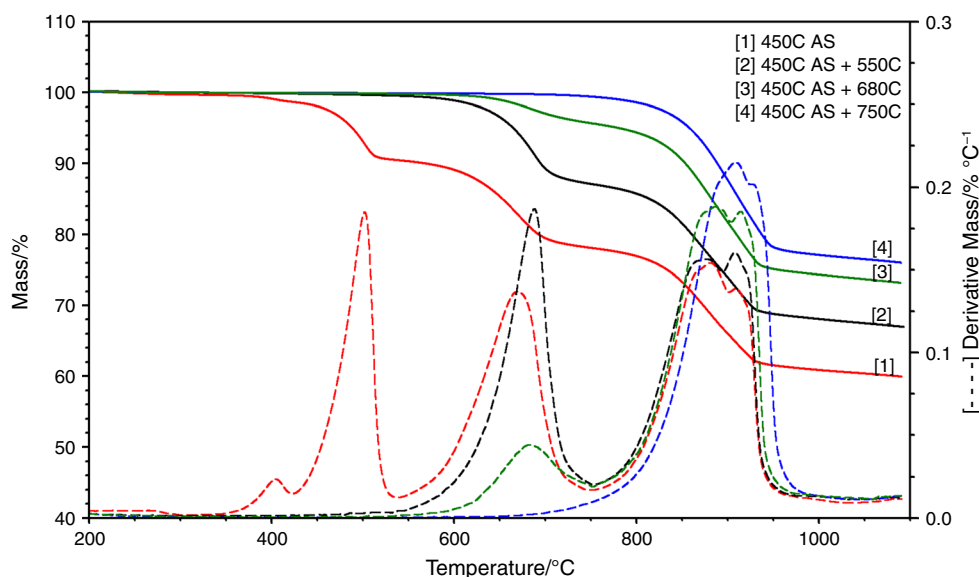
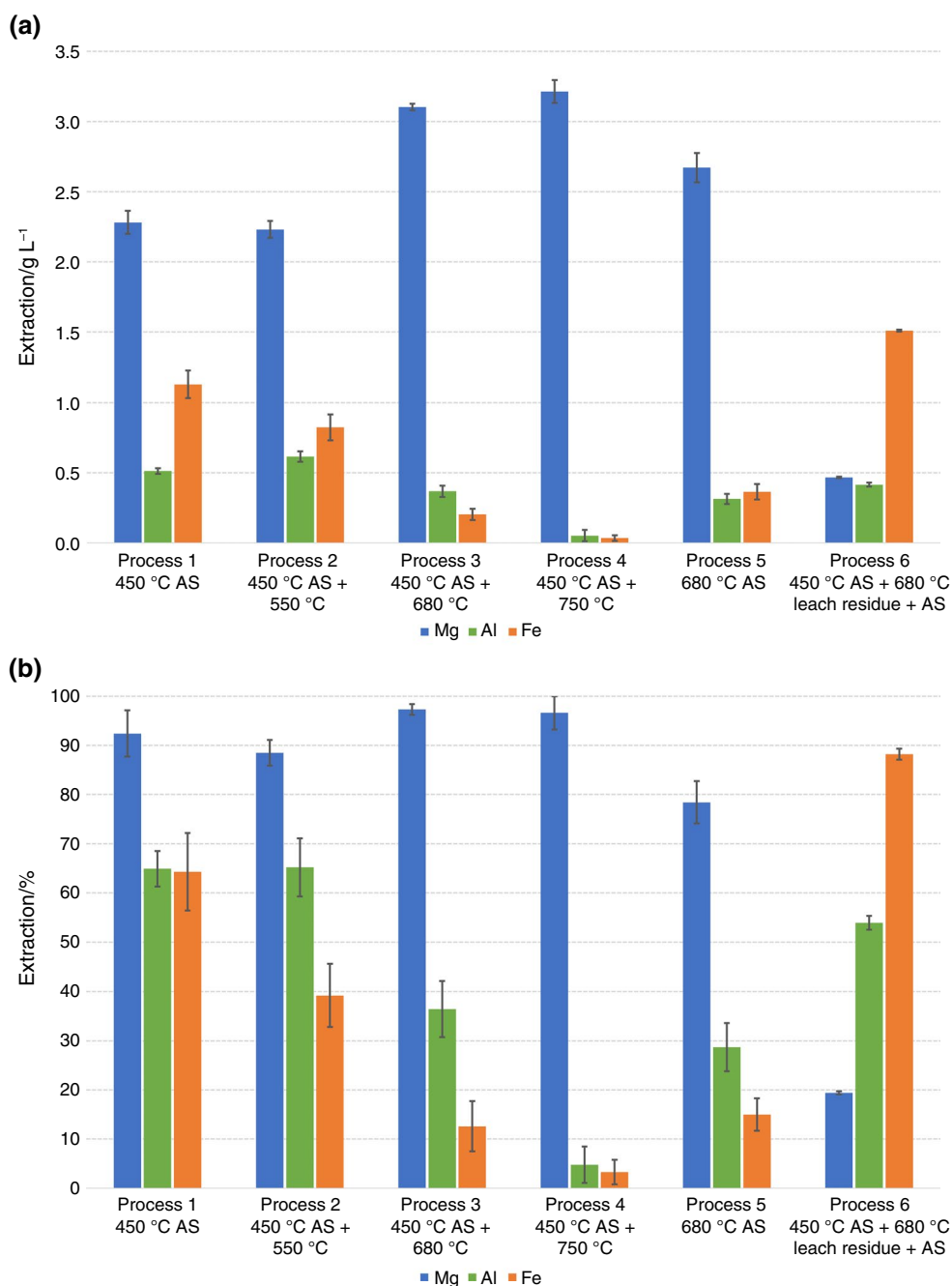


Fig. 10 Comparison of **a** the concentration and **b** percentage elemental extraction (% m/m) of Mg, Al and Fe after treatment of SL by the various roasting programs ($n=2$)



Fe was successfully recovered from Process 6, where the leach residue from Process 3 (SL_{AS-680L}) was re-roasted with (NH₄)₂SO₄. The leachate was enriched in Fe with a concentration of 1.5 g L⁻¹, while Mg and Al occurred in concentrations of approximately 0.5 g L⁻¹ (Fig. 10a). This process led to the recovery of almost 90% of the Fe content from SL (Fig. 10b).

The solid leach residues obtained from Processes 1, 3 and 4 were analysed via semi-quantitative XRD to confirm the efficient dissolution of sulphate minerals during the leaching process and to identify potential application for these

residues (Table 5). Talc was the predominant phase in all these residues, constituting over 52%, a substantial increase from the 30% talc content in SL. The talc residue obtained from Process 1 appeared as a creamy white product, compared to the original grey colour of SL. Given its improved colour clarity, this residue may hold promise for direct application in the ceramics, paint or paper industries. The occurrence of the hornblende and diopside phases can be reduced by using the additional roasting regimen at higher temperatures, which could lead to a residue which is further enriched in talc content (e.g. Process 3, Table 5). The presence of

Table 5 Semi-quantitative mineralogy (% m/m) for the leach residues obtained after roasting

Mineral	SL*	Process 1 450 °C AS	Process 3 450 °C AS + 680 °C	Process 4 450 °C AS + 750 °C
Talc, Mg ₃ Si ₄ O ₁₀ (OH) ₂	30	56	59	52
Quartz, SiO ₂	4	21	22	23
Diopside, Ca(Mg,Fe)Si ₂ O ₆	6	15	10	11
Hornblende, Ca ₂ (Mg,Fe,Al) ₅ (Si,Al) ₈ O ₂₂ (OH) ₂	2	8	2	
Hematite, Fe ₂ O ₃	–		7	14

*The full mineralogical composition of SL is reported in Table 2. Quantities reported for SL in this table are only for the phases which occurred in the leach residues obtained from the roasting programs

hematite (Fe₂O₃) increased at higher roast temperatures, corresponding to the reduction in leached Fe during Processes 3 and 4 (Fig. 10). Although some of these residues had a slightly higher talc content, their brick-red colour (similar to the image displayed for M_{X750-L} in Fig. 7) may limit their suitability for application in the aforementioned industries. The absence of sulphate minerals in the residues confirmed the efficiency of the leaching process.

Conclusions

- Thermochemical treatment of South African diamond mine residues with (NH₄)₂SO₄ followed by aqueous leaching was a non-selective process, which resulted in the simultaneous extraction of Mg, Al and Fe into solution.
- Separation of Mg from Fe and Al was efficiently achieved using a selective roasting program prior to leaching.
- Fe was selectively removed from the leachates using a sequence of systematic roasting steps, although the temperature ranges used require further testing and refinement. The remaining Fe in the leach residue was successfully recovered from the solid leach residues by re-roasting the residue with (NH₄)₂SO₄ to convert the oxide into the soluble sulphate form. The challenge of separating Fe from Al, without substantial loss of Al, remains.
- The Mg-rich leachate from Process 4 may be used to produce pure Mg(OH)₂ by precipitation with ammonia solution. The synthesis of Mg/Al or Mg/Fe layered double hydroxides (LDHs) can be pursued from the leachates obtained from the remaining processes, as a combination of these divalent and trivalent cations are required for its synthesis. The solid leach residue obtained following processes 1 and 6 could be considered for applications in the ceramic, paint or paper industry since it is enriched in talc and benefits from an improved colour clarity.
- Thermogravimetry played a crucial role as research tool during the method development for the separation of

these elements from the mine residue sample. It was used to identify and quantify the soluble sulphates formed during thermochemical treatment and to determine the decomposition temperature ranges of metal sulphates.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10973-024-13151-2>.

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Declarations

Conflict of interest The authors declare that they have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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