



# Production of Al(III)-K(I)-Ti(IV)-sulphate-containing leach liquor from metakaolinite-containing ash derived from South African coal fines

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## Synopsis

South African discard coal fines and  $K_2CO_3$  blends were heated in a laboratory-scale rotary kiln to produce ashes for  $H_2SO_4$  leaching tests. The optimized  $H_2SO_4$  leaching conditions of 6.12 mol.dm<sup>3</sup> (M)  $H_2SO_4$ , solid to liquid ratios 1:5 and 1:10, and 80°C for 8 hours were used.  $K_2CO_3$  was added to increase the dissolution efficiency of K. The objective was to determine if the Al present in metakaolinite ( $Al_2O_3 \cdot 2SiO_2$ ), the Al, K, and Ti in the aluminosilicate glasses, and the Ti in rutile ( $TiO_2$ ) in the ashes could be selectively dissolved in  $H_2SO_4$ . XRF results show that the ashes formed at 700°C dissolved more efficiently (87% Al, 89% K and 23% Ti) compared to the ashes formed at 1050°C. This can be attributed to the presence of  $Al_2O_3 \cdot 2SiO_2$ ,  $K_2CO_3$  melt,  $K_2CO_3$  remnants,  $KAl(SO_4)_2$ , and K-aluminosilicate glass in these ashes. XRD results indicate that the ashes prepared at 1050°C contained anorthite ( $CaAl_2Si_2O_8$ ), microcline ( $KAlSi_3O_8$ ), pseudomullite ( $Al_2O_3 \cdot SiO_2$ ), and silicon spinel ( $2Al_2O_3 \cdot 3SiO_2$ ), which are either insoluble or only sparingly soluble in  $H_2SO_4$ . These minerals resulted in the lower dissolution efficiencies of Al and K. Based on the high dissolution efficiencies of Al and K for the ashes produced at 700°C, coal fines blended with  $K_2CO_3$  could possibly be utilized as feedstocks for the production of aluminium(III), potassium(I), and titanium(IV) and a sulphate-containing leach liquor. Furthermore, the environmental issues and costs associated with the handling and disposal of large volumes of coal fines will also be resolved.

## Keywords

sulphuric acid leaching, aluminium, titanium, potassium, coal ash, XRD, XRF.

## Introduction

Industrial and population growth in developing countries has necessitated the generation of more power to meet increasing energy demands. Coal-based power generation is still one of the most important and effective processes (Izquierdo and Querol, 2012). The increase in power generation results in energy demands being met (Nayak and Panda, 2010), but at the cost of an increase in waste generation (coal fines, coal ash, and gaseous emissions) which give rise to associated environmental and health risks.

South African collieries and gasification and combustion plants dispose of more than 60 Mt of coal fines (>75–1000 µm) per annum that are unavoidable by-products (Reddick, von Blottnitz, and Kothuis, 2007; Matjie *et al.*, 2018). Furthermore, other sources of coal fines (>1 mm < 5 mm coal particles) produced from carbon conversion plants using Highveld coal are pulverized to <75 µm and blown into pulverized fuel boilers to generate electricity and high-pressure steam for the fixed-bed gasification process.

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Current disposal methods for coal fine discards are associated with environmental and health problems, *i.e.* the spontaneous combustion and dust particle emissions to the environment (Moyo *et al.*, 2018; Department of Environmental Affairs, 2012; Muzenda, 2014). Spontaneous combustion is caused by the oxidation of pyrite (FeS<sub>2</sub>) present in the coal, and can result in fires and pyrite oxidation products being released during handling and storage. In addition, high costs are incurred by the disposal of coal fine wastes into slimes dams or disposal areas.

South African commercial power stations produce more than 50 Mt of coal ash per annum, which comprises both bottom ash and coal fly ash (Department of Environmental Affairs, 2018). These ashes contain significant amounts of aluminium (>7.9 Mt), potassium (>0.2 Mt), silicon (>13 Mt), and titanium (>0.5 Mt) (Badenhorst, 2019). According to Ginster and Matjie (2005) and Reynolds-Clause and Singh, (2019) approximately 7.5 Mt of coal ash are re-used in cement applications as extender, wastes treatment, concrete applications, road construction, brickmaking, rubber, paint, geopolymer, soil amelioration, mine backfilling, landfill, and mine drainage treatment. However, more than 43 Mt of coal ash is still being dumped at the disposal sites of South African power stations every year.

Furthermore, coal ash from overseas power stations is utilized in small amounts in industrial applications, *i.e.*, brick manufacturing, building materials, road construction, and ceramics (Nayak and Panda, 2010). The ash by-products, containing significant amounts of Al and smaller amount of Ti (a higher-value inorganic element), also have potential for the recovery of these elements by leaching (Barry *et al.*, 2018; Matjie, Bunt, and van Heerden, 2005; Wu, Yu, and Zang, 2012).

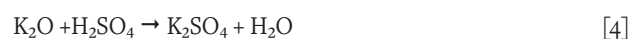
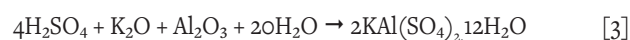
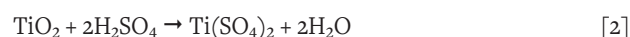
Studies have shown that approximately 80% of the aluminium which is present in South African coal fly ash produced during the pulverized fuel combustion process at approximately 1600°C is associated with mullite (Al<sub>6</sub>O<sub>13</sub>Si<sub>2</sub>), which is not soluble in the sulphuric acid (Matjie, Bunt, and van Heerden, 2005; Freeman, 1993). The balance of the aluminium (20%) is reported to be present in the amorphous aluminosilicate glasses (Freeman, 1993; Matjie, Bunt, and van Heerden, 2005). The leachability of aluminium from the glassy phase will be influenced by the form in which the amorphous materials are present (Seferinoglu, 2003) and surface associated elements which have been found to be more susceptible to leaching (Izquierdo and Querol, 2012).

All inorganic elements that are associated with inactive or non-reactive minerals formed at elevated temperatures are sparingly soluble or insoluble in all mineral acid solutions apart from hydrofluoric acid solution (Paul *et al.*, 2006). These minerals are formed in coal ashes through partial or complete mineral transformation during the coarse coal gasification (1400°C) process and high-temperature (1600°C) combustion (Matjie, Bunt, and van Heerden, 2005; Torma, 1983; Neupane and Donahoe, 2013). All of South Africa's bottom ash and coal fly ash, as well as gasification coal ash containing mullite and anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>), formed at elevated temperatures during the pulverized fuel combustion and gasification processes respectively, are unsuitable leaching using sulphuric acid solution (Matjie, Bunt, and van Heerden, 2005; Torma, 1983). However, it has been shown that the leaching of a heated blend of South African fly ash and quicklime (CaO) with 6.12 M H<sub>2</sub>SO<sub>4</sub> at 80°C and 1:3½ or 1:5 solid to liquid ratios for 4 hours results in high aluminium and titanium extractions of 80-85% and 50% respectively in (Matjie, Bunt, and van Heerden, 2005). Moreover

Sangita, Nayak, and Panda, (2017) and Torma (1983) leached a blend of fly ash from an overseas power station and CaO which was heated to between 1000°C and 1200°C with sulphuric acid solution and achieved an aluminium extraction of 80-99%. This implies that CaO reacted with the alumina that is associated with mullite in the coal ash to form calcium aluminate (CaAl<sub>2</sub>O<sub>4</sub>), which is soluble in sulphuric acid solution (Torma, 1983; Matjie, Bunt, and van Heerden, 2005).

In addition, Sangita, Nayak, and Panda (2017) used sulphuric acid solution to solubilize aluminium from coal fly ash from Chinese power stations, which contained 62% reactive amorphous aluminosilicate glasses, to form pure aluminium sulphate crystals. Furthermore, van der Merwe *et al.* (2017) heated a blend of South African ultrafine fly ash containing cenospheres and either ammonium sulphate or ammonium bisulphide to 400°C and 600°C to produce a solid sample. A conventional hydrometallurgical water method was subsequently applied to selectively solubilize aluminium (47% Al solubilized) from the heated cenosphere blends. These cenospheres are ultrafine particles and roughly 8-1000 µm in diameter with a density lower than 1 g/cm<sup>3</sup> (Kolay, 2001; Vassilev, 2004). Cenospheres, which comprise approximately 1-2% of the fly ash produced during pulverized fuel combustion, comprise a mixture of aluminosilicate glasses with mullite and quartz (SiO<sub>2</sub>) (Kolay, 2001; Vassilev, 2004). Sulphuric acid is mostly used for recovering high-value metals due to its effectiveness, availability, and affordability as a leaching solution (Seidel, 1999). However, the high energy input required to break the bonds between alumina and silica in mullite and K-feldspar crystals, the gas and alkali emissions, as well as the cost of the chemicals, make the proposed H<sub>2</sub>SO<sub>4</sub> leaching process economically unviable as well as environmentally.

Since aluminium, titanium, and potassium species in coal ashes produced from the combustion and gasification processes cannot directly react with sulphuric acid, coal fine waste and a blend of coal fine waste and potassium carbonate were heated at either 700°C or 1050°C in air to produce lower temperature combustion coal ash samples. These temperatures are more typical of what can be expected in a fluidized-bed combustion unit. The low-temperature ashes contain metakaolinite, and amorphous glasses of illite (K, H<sub>3</sub>O)(Al,Mg,Fe)<sub>2</sub>(Si,Al) and microcline. Soluble potassium melt and K<sub>2</sub>CO<sub>3</sub> remnants were produced at either 700°C or 1050°C via combustion of the coal fines, and blends of coal fines and K<sub>2</sub>CO<sub>3</sub>. The Al<sub>2</sub>O<sub>3</sub> from metakaolinite and aluminosilicate glasses, and titanium, and potassium compounds contained in the low-temperature combustion ash samples were dissolved during the sulphuric acid leaching experiments. The possible chemical reactions of Al<sub>2</sub>O<sub>3</sub> from metakaolinite, TiO<sub>2</sub>, K<sub>2</sub>O, and H<sub>2</sub>SO<sub>4</sub> to form the aluminium(III), titanium(IV), potassium(I), and sulphate-containing leach liquor are as follows:



Ash samples derived from kaolinite-containing coal fines, blends of coal fines and K<sub>2</sub>CO<sub>3</sub> have not previously been utilized as an alternative feedstock to heated kaolinite-bearing clays in the production of technical-grade aluminium sulphate salts using sulphuric acid solution (Altiokka *et al.*, 2010; Alquacil, Amer, and

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Luis, 1987; Numluk and Chaisena, 2012). In addition, Phillips and Wills (1982) used the nitric acid leaching route to dissolve alumina from the micaceous residues from smelter grade China clay.

The commercial leaching methods and conditions used during this investigation are applied in the recovery of aluminium from deactivated clay minerals (non-bauxite ores) with Al dissolution efficiencies reaching up to 90% (Ibrahim, Moumani, and Mohammad, 2018; Mark *et al.*, 2019; Numluk and Chaisena, 2012). High-temperature pulverized fuel combustion conditions (approximately 1600°C) (van Alphen, 2005) are used in the commercial power stations to produce fly ash and bottom ash samples. These conditions were not followed in this study as they are not suitable for the production of low-temperature combustion ashes (containing soluble Al, K, and Ti species) of coal fines and blends of coal fines and K<sub>2</sub>CO<sub>3</sub>, which can be leaching using H<sub>2</sub>SO<sub>4</sub> leaching experiments.

## Potential uses of the liquid products

The aluminium(III), potassium(I), titanium(IV), and sulphate-containing leach liquor produced during the acid leaching tests of these coal ashes can possibly be utilized in other chemical industries, *i.e.* technical aluminium sulphate or potassium aluminium sulphate in the form of either liquid or solid can be used as coagulants in water treatment plants. Furthermore, the aluminium(III), potassium(I), titanium(IV), and sulphate-containing leach liquor could be purified through solvent extraction for the production of pure aluminium chemicals, including iron-free aluminium sulphate or iron-free potassium aluminium sulphate. The potassium sulphate solution could be used in potassium chemicals, or in the fertilizer industry, whereas a pure titanium dioxide could be used in the paint/paper industry. The ash residues obtained after leaching could possibly be used as an aggregate in brick manufacturing and masonry concrete.

X-ray fluorescence (XRF) and X-ray diffraction (XRD) techniques were used to characterize the coal fines and blends of coal fines and K<sub>2</sub>CO<sub>3</sub>, the ash samples, and leached ash residues produced from the experiments. The XRF results and the masses of ash samples before and after the H<sub>2</sub>SO<sub>4</sub> leaching tests were utilized in calculating the dissolution efficiencies of inorganic elements after acid leaching of the ash samples prepared at either 700°C or 1050°C.

## Materials and methods

### Coal sampling, preparation, and composition of coals

The sampling of coals from the collieries as well as the preparation methods are reported in Collins *et al.* (2018). Due to the similarities in the chemical and mineralogical properties of coal samples SA1 and SA2, sample SA2 was blended with K<sub>2</sub>CO<sub>3</sub>. SA1, SA2 blend, and SA3 were subjected to low-temperature combustion tests to produce samples for the leaching experiments, XRD and XRF analyses. In addition, SA2, SA1, SA2 blend, and SA3 were submitted for XRD analyses. The characterization analytical methods including proximate, ultimate, and XRF analyses used to determine the chemical composition of coals and the results obtained are also published in Collins *et al.* (2018). The reagents (H<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>CO<sub>3</sub>) used in this investigation are also described in Collins *et al.* (2018).

### Ash samples

The coal samples used in this investigation have similar properties to those of discarded coal fines produced during coal mining and

beneficiation at the South African coal preparation plants. The prepared coal samples were subjected to oxidation in air, using specific conditions to produce the desired ash samples. These ashes have not been used for the commercial production of aluminium sulphate salts although, as stated in the introduction they are thought to be suitable for utilization in the commercial process to produce aluminium sulphate leach liquor from heated kaolinite-bearing clay.

According to Collins (2019), the ash samples prepared at 700°C contain a higher proportion of metakaolinite (alumina associated with metakaolinite is soluble in either H<sub>2</sub>SO<sub>4</sub>, or HCl or HNO<sub>3</sub>) and a small proportion of amorphous glasses of illite and microcline. These ashes are also characterized by a small proportion or zero per cent of Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> pseudomullite, silicon spinel 2Al<sub>2</sub>O<sub>3</sub>.3SiO<sub>2</sub>, and <1% organic carbon, which are only sparingly soluble or insoluble in these mineral acids. A temperature of 700°C was therefore used in this study to produce ashes which can possibly contain a higher proportion of metakaolinite, which may be associated with a higher dissolution efficiency of alumina during sulphuric acid leaching. The ash samples produced at 1050°C are characterized by higher proportions of pseudomullite and silicon spinel, a small proportion (or zero per cent) of metakaolinite, and zero organic carbon. Higher proportions of pseudomullite and silicon spinel, which are sparingly soluble in H<sub>2</sub>SO<sub>4</sub>, could be formed at this temperature. Lower dissolution efficiencies of Al, K, and Ti during sulphuric acid leaching could be expected from these ashes. In addition, Bryers (1986) and Yanti and Pratiwi (2018) found that metakaolinite transformed to silicon spinel at 925°C, which further formed pseudomullite at 1100°C. At 1200-1400°C, pseudomullite transformed to mullite, which is insoluble in mineral acid solutions apart from hydrofluoric acid (Teklay *et al.*, 2014; Bryers, 1986). According to Osawa and Bertan, (2005) pseudomullite and silicon spinel prepared at pH 4 and pH 8 are formed from mixtures of alumina and silica sols at 1050°C and transform to mullite at 1200°C.

The commercial plants that produce aluminium sulphate by H<sub>2</sub>SO<sub>4</sub> leaching of clay-containing kaolinite is employing temperatures of 600-800°C. Heller-Kallai (1978) and Heller-Kallai and Lapedes (2003) heated a mixture of clay containing kaolinite and potassium compounds at 600-700°C to produce synthetic potassium feldspars via the solid state reaction of metakaolinite and potassium cations. Therefore, the temperatures of either 700°C or 1050°C were finally selected for this study, based on the contents of metakaolinite, silicon spinel, and pseudomullite in the coal ashes.

Coal samples of approximately 5 kg were placed to clay fired sample trays and loaded into the hot zone of a rotary kiln. The temperature of the kiln was increased to 700°C at a heating rate of 10°C/min. All sub-samples were heated to 700°C for a residence time of 3 hours under air flow of 80 ml/min to facilitate coal combustion and transformation of the mineral matter and the evolution of volatiles. The furnace was then switched off and allowed to cool for 8 hours and the ash samples were removed once the samples reached ambient temperature. Four representative ash samples were blended to form one homogenous sample. The sample preparation methods set out in ISO 18283 and ISO 13909-4 (Rautenbach *et al.*, 2019) were followed to take representative samples from the bulk ashes prepared at 700°C for the H<sub>2</sub>SO<sub>4</sub> leaching tests and for further heating in a muffle furnace. After placing the representative sample of ash produced at 700°C in the muffle furnace, the



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temperature was increased to 1050°C at a heating rate of 10°C/min. This experimental procedure to produce low temperature combustion ashes at either 700°C or 1050°C was repeated for all the coal samples used in this study.

## Analytical methods

### XRF analysis

XRF analysis of coal ash samples (SA1, SA2 blend, and SA3) prepared at either 700°C or 1050°C to determine the proportions of inorganic elements in these samples was conducted according to the methods proposed by other researchers (Norrish and Hutton, 1969; Matjie *et al.*, 2018).

### XRD analysis

XRD analysis of coal (SA1, SA2, SA2 blend and SA3) and ash (SA1, SA2 blend and SA3) samples was carried out to qualify and quantify the proportions of crystalline and amorphous phases in these samples using the methods suggested by other researchers (Rietveld, 1969; Speukman, 2012; Matjie *et al.*, 2018). The percentage XRD error is 0.2-0.3 and the detection limit is between 0.5 and 5 weight per cent. This implies that XRD results for the trace minerals with smaller crystallite sizes (<1 nm crystallites) in the solid samples which are above this detection limit may not be accurate (Chinchón *et al.*, 1993).

## Experimental procedure

A schematic diagram of the process and analytical methods used in this study for dissolving Al, K, and Ti from coal ash and blend ash samples, is presented in Figure 1.

### Acid leaching

Technical grade sulphuric acid (10 M H<sub>2</sub>SO<sub>4</sub> or 98% H<sub>2</sub>SO<sub>4</sub>, a stable or less reactive and viscous mineral acid) with small proportions of ions (H<sub>3</sub>O<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>) was used to prepare a 6.12 M H<sub>2</sub>SO<sub>4</sub> or 60% H<sub>2</sub>SO<sub>4</sub>, which is very reactive with significant amounts of ions (H<sub>3</sub>O<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>), using deionized water, for the

leaching experiments. A 500 cm<sup>3</sup> round-bottomed container, with sealing lid and cooler, was used as the leaching vessel. An automatic overhead stirrer with base plate (model 720), coupled with a temperature controller with a sensor probe, was used as the heat source. The leaching conditions used in the experiments are stated below.

### 6.12 M H<sub>2</sub>SO<sub>4</sub> leaching

The influence of solid to liquid ratio on the dissolution of the inorganic elements contained in the ash samples was investigated during the acid leaching experiments. The solid to liquid ratios used were 1:5 and 1:10. A 10 g ash sample was accurately weighed out and added into the leaching vessel. The optimized H<sub>2</sub>SO<sub>4</sub> leaching conditions for sintered pellets of a mixture of South African fly ash, coal, and CaO – a solid to liquid ratio of 1:5, temperature of 80°C, time of 8 hours and (6.12 M) H<sub>2</sub>SO<sub>4</sub> (Matjie, Bunt, and van Heerden, 2005) – which achieved the highest leaching efficiency of Al and Ti, were used in this study. A known 6.12 M H<sub>2</sub>SO<sub>4</sub> was transferred into the vessel containing value of coal ash to maintain the solid to liquid ratio of the specific experiment. The slurry was stirred at 200 r/min with an automatic overhead stirrer at 80°C for 8 hours. The hot slurry sample was filtered to produce the leached wet ash residue and leach liquor (filtrate). The ash residue was washed with deionized water to ensure that all dissolved inorganic species were recovered. The leached ash residue was placed in a vacuum furnace and dried at 60°C for 24 hours. The wash solution was combined with the original leach liquor to form the final leach liquor sample. In this investigation, only coal ash and leached ash residue samples were submitted for XRD and XRF analyses. Due to the cost constraints associated with the inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis of the liquid samples, all the leach liquor samples were not submitted for this analysis but were kept for the other purification steps.

### Calculation of dissolution efficiencies

Equation [5] was used to calculate the percentage dissolution

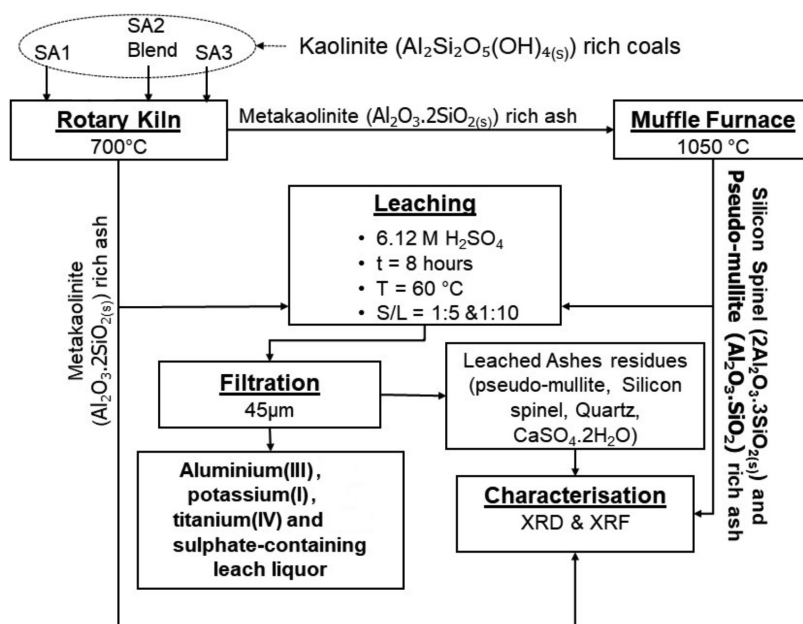


Figure 1—Schematic diagram of the experimental procedure and analytical methods

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efficiency for Al, K, and Ti using the XRF results for the ash samples and the leached ash residues as well as the masses of ashes. In this study the aluminium in the form of the alumina is expected to be selectively dissolved from metakaolinite during sulphuric acid leaching of the coal ash. Al, Ti, and K contained in the aluminosilicate glasses of illite and microcline and Ti in either rutile or anatase, as well as the K in the potassium melt and  $K_2CO_3$  remnants, are also expected to be solubilized. The dissolution efficiency was calculated using Equation [5]:

$$\eta(MO) = \frac{m_{CA} - m_{RES}}{m_{CA}} \times 100\% \quad [5]$$

where

$\eta(MO)$  is the dissolution efficiency of the specific inorganic element (Al, K, or Ti)

$m_{CA}$  is the mass of the specific inorganic element in the coal ash and leached ash residues samples

$m_{RES}$  is the mass of ash residue (after leaching).

The mass of the specific inorganic element in the coal ash and leached ash residue samples can be calculated by using Equation [6].

$$m_{CA} = \left(\frac{\%E}{100}\right) \times m_{sample} \quad [6]$$

where

$m_{CA}$  is the mass (g) of inorganic element (Al, K, or Ti) in the coal ash or leached ash residues

$\%E$  is the percentage of the inorganic element in the coal ash or leached ash residue, as calculated by Equation [7]

$m_{sample}$  is the mass of the ash sample or leached ash residue sample.

The percentage ( $\%E$ ) of inorganic element present in each of the ash and leached ash residue samples was calculated using Equation [7].

$$\%E = \%EO \times \frac{M_{element}}{M_{EO}} \quad [7]$$

where

$\%E$  is the percentage of the element in the coal ash or ash residue sample

$\%EO$  is the percentage elemental oxide in the sample (provided through XRF analysis)

$M_{element}$  is the molecular weight of the element in the oxide

$M_{EO}$  is the molecular weight of the elemental oxide.

## Results and discussion

### Coal mineralogy

The XRD results of the coal samples are presented in Table I. The results indicate that all the coal samples consist mainly of amorphous (non-crystalline) organic carbon. The SA1 sample contains a higher proportion of kaolinite than the other coals tested, while the SA2 coal and SA2 blend samples contain less quartz than SA1 and SA3. Minor proportions of other minerals (microcline, illite, calcite ( $CaCO_3$ ), pyrite ( $FeS_2$ ), and anatase ( $TiO_2$ )) and a high proportion of dolomite ( $CaMgCO_3$ ), were found in all the coal samples evaluated in this study. Other minerals are present in trace quantities. As expected, the SA2 blend also contained a low proportion of  $K_2CO_3$  compared to the percentage of potash added to this coal. This can be attributed to the hydration of  $K_2CO_3$  by the 4% moisture contained in this coal. Also, these XRD results, excluding the SA2 blend, match previous XRD data for other South African coals (van Dyk *et al.*, 2009; van Dyk, Waanders, and Hack, and 2008).

The occurrence of extraneous calcite and extraneous dolomite discrete particles indicates that these minerals could transform at temperatures of 700°C and 1000°C to CaO (quicklime) and a mixture of MgO (periclase) and CaO respectively (Matjie *et al.*, 2018; van Dyk, Waanders, and Hack, 2008). The inherent calcite or dolomite associated with clays (kaolinite, illite, muscovite) and microcline and carbon matrix in the coals can transform at 1200-1400°C to form a molten solution or partial melt (Rautenbach *et al.*, 2021). Furthermore, either the extraneous calcite and dolomite react with each other at 1200-1400°C to form melts during heat treatment. The high-temperature minerals (mullite, anorthite, K-feldspar) formed, which are insoluble in sulphuric acid solution, crystallized at low temperatures from the molten solutions. These minerals can also be formed at elevated temperatures *via* solid-state reactions.

The high-temperature products (CaO and MgO) derived from transformation of either extraneous calcite or dolomite have been found to be responsible for the *in-situ* capturing of sulphur dioxide to form calcium sulphate (Rautenbach *et al.*, 2021). These oxides account for the reduction of gas emissions during coal combustion. In addition, the carbonation reaction will form either calcite or dolomite in the ashes, resulting in the minimization of  $CO_2$  emissions.

Table I

XRD results for the coal samples (wt.%)

Sample	SA1	SA2	SA2 blend	SA3
Kaolinite	18.0	13.4	12.3	13.7
Quartz	10.6	4.0	3.6	7.3
Calcite	-	2.1	1.9	0.7
Dolomite	1.3	6.4	5.3	4.4
Graphite	1.9	0.8	0.4	0.5
Illite	0.8	1.4	0.7	-
$K_2CO_3$	0.0	0.0	6.2	0.0
Microcline	0.7	0.1	-	-
Pyrite	0.1	0.2	-	-
Amorphous (organic carbon)	66.2	71.6	69.6	73.2
Total	100.0	100.0	100.0	100.0

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## XRF analysis

The XRF results of the ash samples prepared from coals at elevated temperatures are presented in Table II. The dominant constituents in the SA1, SA2 blend, and SA3 ashes prepared at either 700°C or 1050°C under air are SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>, with lesser but still significant proportions of CaO, Fe<sub>2</sub>O<sub>3</sub>, MgO, TiO<sub>2</sub>, MgO, and in some cases K<sub>2</sub>O (>18%) and SO<sub>3</sub> (>4%) (Table II). Other oxides, including Cr<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>, P<sub>2</sub>O<sub>5</sub>, BaO, Na<sub>2</sub>O, and SrO, each make up less than 1% of the ashes. These XRF results, with the exception of the ash of the coal sample spiked with K<sub>2</sub>CO<sub>3</sub>, are in good agreement with those of the ash samples prepared from other South African coals using thermochemical processes (Hattingh *et al.*, 2011; van Alphen 2005; van Dyk *et al.*, 2009).

## Coal ash mineralogy

XRD results of the selected ashes of SA1, SA2 blend, and SA3 samples prepared at 700°C and 1050°C are presented in Figures 2-4 and Tables III and IV. These results indicate that the SA2 blend and SA3 ash samples prepared at 700°C, consisted of higher proportions of total amorphous phases (metakaolinite and amorphous glasses of illite and microcline) than the SA1 ash. Higher proportions of total amorphous materials formed at elevated temperatures in the ashes are associated with the mode of occurrence of the fluxing minerals (calcite, dolomite, and pyrite), clays (kaolinite, illite etc.) - and microcline in the coals (Rautenbach *et al.* 2021). The fluxing minerals lower the ash fusion temperature (AFT) values of clays, promoting the formation of melts during heat treatment of coals. The SA1 ash contains a higher concentration of quartz than the other ash samples. Based on the kaolinite and illite/microcline contents in the coals (Table I), metakaolinite could contribute to 95% of the total amorphous content in the coal ashes produced at 700°C.

The XRD results show a lower proportion of total amorphous phases in the ashes after heating either SA1 coal, SA2 blend, or SA3 coal at 1050°C compared the ashes prepared at 700°C (Tables III and IV). The XRD results of the ash samples reveal that kaolinite in the selected coals transformed at 700°C to form metakaolinite in the ashes (Tables III and IV). The total amorphous material contents of these ashes decrease with increasing temperature. Pseudomullite (transformation product of metakaolinite and

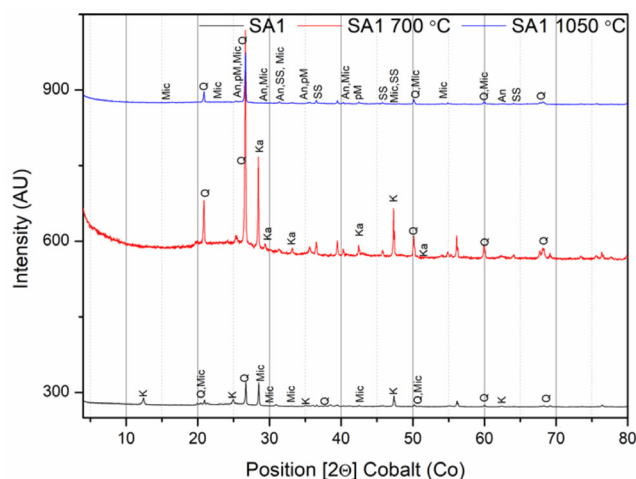


Figure 2—Stacked diffractograms of SA1 (kaolinite-rich) and ashes obtained at 700°C (SA1 700°C (metakaolinite-rich)) and 1050°C (SA1 1050°C (pseudomullite-rich))  
Note: K-kaolinite, Q-quartz, Ka-kalsilite, Mic-microcline, An-anorthite, SS-silicon spinel, An-anorthite, pM-pseudomullite. Intensity - intensity of diffracted radiation and  $\theta$  - diffraction angle

silicon spinel at elevated temperatures) increase with increasing temperature during heat treatment (Tables III and IV). The presence of metakaolinite in the ashes of South African coals can be attributed to the transformation of kaolinite at elevated temperatures (600 - 850°C) (Matjie, van Alphen, and Pistorius, 2006; Matjie *et al.*, 2018, Uwaoma *et al.*, 2020).

The SA1 ash sample prepared at 1050°C contains a lower or zero percent of metakaolinite, and a higher percentage of silicon spinel and pseudomullite (sparingly soluble in mineral acid solution, apart from HF) compared to the SA1 ash samples prepared at 700°C (Tables III and IV). Rautenbach *et al.* (2021) found that mullite crystallizes from the molten aluminosilicate solution formed at 1200-1400°C during the combustion of coals in a laboratory and gasification study of other South African coals. Furthermore, mullite, which is associated with the transformation of the extraneous kaolinite, can also be formed at elevated temperatures of 1200-1400°C *via* the solid-state reaction (Rautenbach *et al.*, 2021).

Table II

Chemical composition of ash samples prepared at 700°C and 1050°C from SA1, SA2 blend and SA3 (wt. %)

Sample	SA1		SA2 Blend		SA3	
	700°C	1050°C	700°C	1050°C	700°C	1050°C
SiO <sub>2</sub>	62.1	62.6	36.3	36.1	57.7	56.9
Al <sub>2</sub> O <sub>3</sub>	28.3	28.3	22.6	22.2	27.5	27.1
CaO	2.7	2.3	8.9	8.6	5.4	5.2
Fe <sub>2</sub> O <sub>3</sub>	2.7	2.7	4.1	4.2	3.8	3.8
TiO <sub>2</sub>	2.1	1.7	1.7	1.6	1.5	1.5
MgO	0.9	0.8	2.3	2.3	2.0	1.8
K <sub>2</sub> O	0.8	0.8	18.4	18.6	0.4	0.7
SO <sub>3</sub>	0.2	0.2	4.4	4.9	0.8	2.1
Cr <sub>2</sub> O <sub>3</sub>	0.1	-	0.1	0.1	0.1	0.1
Mn <sub>3</sub> O <sub>4</sub>	0.1	-	0.1	0.1	0.1	-
P <sub>2</sub> O <sub>5</sub>	0.1	-	0.2	0.2	0.1	0.1
BaO	-	0.2	0.4	0.4	0.3	0.4
Na <sub>2</sub> O	-	-	0.1	-	-	-
SrO	-	0.0	0.3	0.3	0.1	SrO = 0.1
<b>Total</b>	<b>100.0</b>	<b>100.0</b>	<b>100.0</b>	<b>100.0</b>	<b>100.0</b>	<b>100.0</b>

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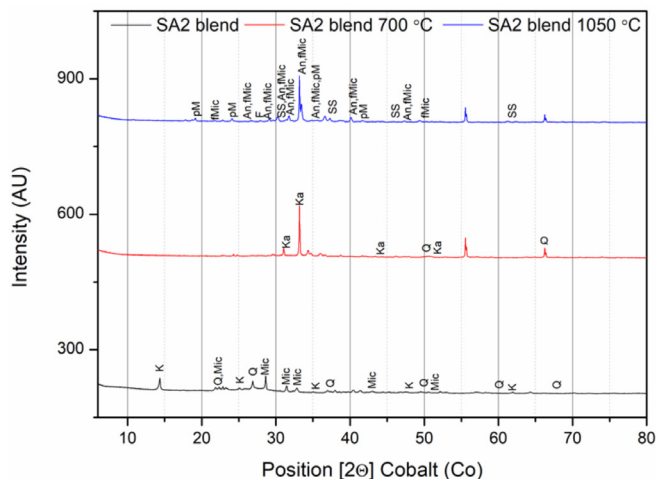


Figure 3—Stacked diffractograms of SA2 (kaolinite-rich) and ashes obtained at 700°C (SA2 700°C, metakaolinite-rich and 1050°C SA2 1050°C pseudomullite) K-kaolinite, Q-quartz, Ka- kalsilite, Mic-microcline, An-anorthite, SS-silicon spinel, An-anorthite, pM- pseudomullite. Intensity - intensity of diffracted radiation,  $\theta$  - diffraction angle

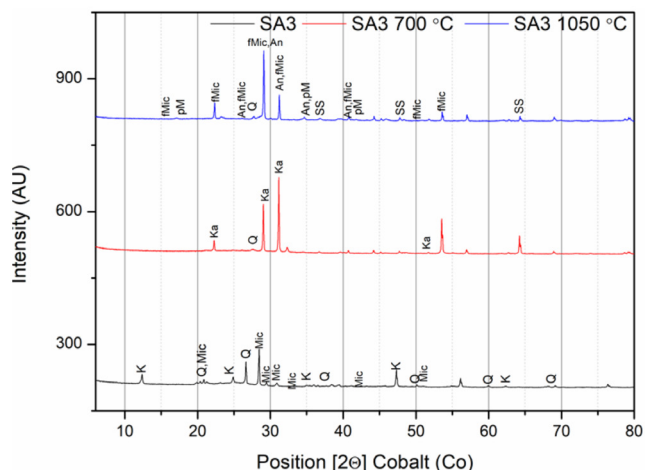


Figure 4—Stacked diffractograms of SA3 (kaolinite-rich) and ashes obtained at 700°C (SA3 700°C, Metakaolinite-rich) and 1050°C (SA3 1050°C (pseudomullite) K-kaolinite, Q-quartz, Ka- kalsilite, Mic-microcline, An-anorthite, SS-silicon spinel, An-anorthite, pM- pseudomullite). Intensity - intensity of diffracted radiation,  $\theta$  - diffraction angle

Khan *et al.* (2017) and Heller-Kallai (1978) studied the transformation of kaolinite in pure kaolinite-containing clay to form metakaolinite at elevated temperatures using XRD analysis, thermogravimetric analysis (TGA), and Fourier transform infrared (FTIR) techniques under oxidizing and inert conditions. They found that almost all of the kaolinite particles in the kaolinite-containing clay samples transformed to metakaolinite at 600–850°C.

The presence of trace periclase in some of the SA1, and SA2 blend ash samples (Table IV) is due to the transformation of the extraneous dolomite at 700°C to form a mixture of CaO and MgO. Hlatshwayo *et al.* (2009) and Matjie, van Alphen, and Pistorius, (2006) used XRD analysis to detect periclase in ash samples from South African carbon conversion plants that utilize thermochemical processes. The surface temperature and the peak temperature in the combustion zone and ash bed of South African carbon conversion gasifiers are 1200°C and 1400°C respectively (Glover *et al.*, 1995; Bunt, 2006). CaO (the transformation product

Table III

Mineralogical composition of the ash samples prepared at 700°C (wt.%)

Sample	SA1	SA2 Blend	SA3
Quartz	45.1	4.0	20.4
Anhydrite	1.6	1.3	1.0
Haematite	1.4	1.3	1.0
Kalsilite	1.2	8.4	-
Portlandite	0.4	0.2	0.1
Magnetite	0.2	-	0.3
Cristobalite	0.1	0.1	0.1
Muscovite	-	-	0.3
Dolomite	-	-	0.1
Calcite	-	-	4.2
Gypsum	-	0.6	0.2
Graphite	-	2.0	3.2
Diopside	-	4.6	-
K <sub>2</sub> CO <sub>3</sub>	-	0.9	-
Kaolinite	-	0.6	-
Periclase	-	-	0.2
Pyrrhotite	-	0.3	0.1
Total amorphous content*	50.0	75.7	68.8
Total	100.0	100.0	100.0

\*Total amorphous content: metakaolinite plus aluminosilicate glasses of illite and microcline plus amorphous K<sub>2</sub>CO<sub>3</sub>

Table IV

Mineralogical composition of the ash samples prepared at 1050°C (wt.%)

Sample	SA1	SA2 blend	SA3
Quartz	43.9	-	37.1
Anhydrite	1.5	0.9	2.7
Pseudomullite	14.2	13.3	3.3
Haematite	-	0.4	2.2
Anorthite	1.2	9.0	1.4
Portlandite	0.2	-	0.2
Magnetite	0.3	-	0.7
Cristobalite	0.4	-	0.5
Muscovite	-	-	0.7
Anatase	-	-	0.1
Microcline	-	9.0	-
Dolomite	-	-	1.2
Calcite	-	-	0.1
Gypsum	-	7.6	0.4
Graphite	-	-	6.4
Diopside	-	0.5	0.3
K <sub>2</sub> CO <sub>3</sub>	-	14.1	-
Kaolinite	-	-	0.2
Periclase	0.8	0.2	-
Pyrrhotite	0.3	-	-
Rutile	-	-	0.8
Silicon spinel	1.4	0.7	2.0
Total amorphous	35.8	44.3	39.6
Total	100.0	100.0	100.0

of either calcite or dolomite associated with kaolinite) can react with metakaolinite at 1400°C to form anorthite either *via* a solid-state reaction or crystallization from the molten aluminosilicate phase containing Ca, Mg, K, Fe, Ti, and Na impurities (Hlatshwayo *et al.*, 2009). Anorthite is insoluble in sulphuric acid solution.

The low content of haematite (Fe<sub>2</sub>O<sub>3</sub>) (Tables III and IV) in the ashes of SA1, SA2 blend, and SA3 prepared at either 700°C or 1050°C was formed by the transformation of pyrite. Anhydrite (CaSO<sub>4</sub>) (Tables III and IV) was formed via the interaction of organic sulphur and organic calcium. Also, free CaO from the



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transformation of extraneous calcite at elevated temperatures can capture sulphur dioxide from the reaction of pyrite in the presence of oxygen or air. Furthermore, CaO in these ashes reacts with water to form portlandite ( $\text{Ca}(\text{OH})_2$ ). A lower cristobalite ( $\text{SiO}_2$ ) content (product of a reaction between silica and alumina) (Tables III and IV) in SA1, SA2 blend, and SA3 ashes prepared at either 700°C or 1050°C, was formed during the transformation of the extraneous kaolinite and illite to metakaolinite, reactive silica, and amorphous glasses of illite. Diopside ( $\text{CaMgSi}_2\text{O}_6$ ) in these ashes (Tables III and IV) was formed by silica reacting with CaO and MgO derived from the transformation of dolomite at elevated temperatures. These XRD results are consistent with those obtained during characterization studies of South African coal ashes produced from thermochemical processes (Hlatshwayo *et al.*, 2009; Rautenbach *et al.*, 2021; Uwaoma *et al.*, 2020).

As expected, the total amorphous content of the ash samples decreases with increasing ashing temperature due to the transformation of metakaolinite in the amorphous phases to silicon spinel during combustion. Silicon spinel subsequently transforms at 1100°C to pseudomullite (Bryers, 1986; Yanti and Pratiwi, 2018). This is supported by the observed decrease in the total amorphous content, which is accompanied by an increase in the content of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ),  $\text{K}_2\text{CO}_3$ , microcline originally detected in the coals, and synthetic microcline and pseudomullite in the ashes (Tables III and IV). An increase in the proportion of insoluble microcline in the SA2 blend ash samples prepared at 1050°C can be attributed to the reaction between potassium ions from the  $\text{K}_2\text{CO}_3$  melt or  $\text{K}_2\text{O}$  reacting with metakaolinite, at elevated temperatures (Tables III and IV) (Rautenbach *et al.*, 2021, Matjie *et al.*, 2018).

Matjie *et al.* (2021) studied the reaction between metakaolinite and potassium cations to form synthetic K-feldspars by heating a blend of 10%  $\text{K}_2\text{CO}_3$  and coal at 700°C and 1050°C in air. In addition, Collins *et al.* (2018) used FACTSAGE™ modelling to predict microcline and kalsilite crystallization at temperatures between 1050°C and 1250°C from the melt of the SA2 blend. Furthermore, potassium cations from  $\text{K}_2\text{CO}_3$  react with metakaolinite derived from kaolinite-containing clay at 600–700°C to form synthetic potassium feldspars (kalsilite ( $\text{KAlSiO}_4$ ), kaliophilite ( $\text{KAlSiO}_4$ ), nepheline ( $(\text{Na}, \text{K})\text{AlSiO}_4$ ), and microcline

*via* solid-state reactions (Heller-Kallai and Lapides, 2003; Heller-Kallai, 1978).

It can be concluded that all selected ash samples from SA1, SA2 blend, and SA3 coal samples produced at elevated temperatures of 1050°C contain a lower proportion of total amorphous material and higher proportions of silicon spinel, pseudomullite, and anorthite than those produced at 700°C. The mineralogical composition of the coal ash samples thus changed as the ashing temperature increased.

### XRF analysis of the leached ash samples

The XRF results for the ash samples prepared at 700°C and 1050°C which were leached with the 6.12 M  $\text{H}_2\text{SO}_4$  at 80°C and solid to liquid ratios of 1:5 and 1:10 for 8 hours are presented in Tables V and VI. The leached SA1 and SA3 ash samples prepared at 1050°C contain a lower proportion of  $\text{SiO}_2$  and a higher proportion of  $\text{Al}_2\text{O}_3$  (Table VI) than the leached SA1 and SA3 ash samples prepared at 700°C (Table V). On the other hand, the leached SA2 blend ash contain a lower proportion of  $\text{Al}_2\text{O}_3$  and a higher proportion of  $\text{SiO}_2$  than the other ash samples (Tables V and VI). Furthermore, the leached SA2 blend ash is characterized by a higher content of CaO in relation to the other leached ash samples prepared at either 700°C or 1050°C. The presence of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and CaO in the leached ash samples prepared at both 700°C and 1050°C is consistent with those of the original SA1, SA2 blend, and SA3 ash samples (Table II) before  $\text{H}_2\text{SO}_4$  leaching at 80°C for 8 hours.

The SA2 blend and SA3 ash samples leached with 6.12 M  $\text{H}_2\text{SO}_4$  contained less  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{TiO}_2$  compared to the original ashes prepared at either 700°C or 1050°C (Tables V and VI). The proportions of these inorganic elements decreased significantly after  $\text{H}_2\text{SO}_4$  leaching. This can be attributed to the reaction between alumina in the metakaolinite and sulphuric acid (Altiokka *et al.*, 2010; Kyriakogona, Giannopoulou, and Pnias, 2017; Equations [1] and [3]). This sulphuric acid solution selectively dissolved alumina from metakaolinite to form aluminium sulphate in the leach liquor.

Silica associated with metakaolinite is insoluble in the sulphuric acid solution and remained in the leached ash residues (Matjie, Bunt, and van Heerden, 2005; Altiokka *et al.*, 2010).

Table V

Chemical composition of the leached coal and blend ash samples produced at 700°C with 6.12 M  $\text{H}_2\text{SO}_4$ , using 1:5 and 1:10 S/L ratios (normalized inorganic oxides – based on the loss on ignition and trace elements (LOI)) (wt.%)

Sample S/L Ratio	SA1		SA2 blend		SA3	
	1:5	1:10	1:5	1:10	1:5	1:10
$\text{SiO}_2$	77.2	79.9	66.8	70.5	77.7	77.0
$\text{Al}_2\text{O}_3$	12.5	13.7	4.2	5.4	13.5	12.6
CaO	5.3	2.1	14.9	14.5	5.3	6.4
$\text{TiO}_2$	2.0	1.8	1.8	1.9	1.9	1.7
$\text{Fe}_2\text{O}_3$	1.1	1.3	2.6	3.7	0.8	1.1
$\text{K}_2\text{O}$	0.4	0.5	2.8	2.2	0.4	0.4
$\text{Cr}_2\text{O}_3$	0.2	0.1	–	–	0.1	0.1
MgO	0.2	0.3	0.2	0.2	0.1	0.2
$\text{P}_2\text{O}_5$	0.1	0.2	–	–	–	–
BaO	–	–	0.3	0.2	–	0.1
$\text{Na}_2\text{O}$	–	–	–	0.1	–	–
$\text{SO}_3$	0.9	0.1	6.0	0.9	0.1	0.3
SrO	–	–	0.4	0.3	0.1	0.1
<b>Total</b>	<b>100.0</b>	<b>100.0</b>	<b>100.0</b>	<b>100.0</b>	<b>100.0</b>	<b>100.0</b>



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Table VI

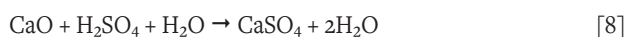
Chemical composition of the leached coal and blend ash samples prepared at 1050°C with 6.12 M H<sub>2</sub>SO<sub>4</sub>, using 1:5 and 1:10 S/L ratios (normalized inorganic oxides – based on the LO.I) (wt.%)

Sample S/L ratio	SA1		SA2 Blend		SA3	
	1:5	1:10	1:5	1:10	1:5	1:10
SiO <sub>2</sub>	66.3	65.9	46.2	56.4	57.7	61.0
Al <sub>2</sub> O <sub>3</sub>	27.2	27.8	5.3	8.0	24.9	26.3
CaO	2.0	1.6	11.1	11.5	5.9	5.0
TiO <sub>2</sub>	1.5	1.5	1.1	1.0	1.5	1.4
Fe <sub>2</sub> O <sub>3</sub>	1.4	1.2	3.0	4.8	1.3	1.4
K <sub>2</sub> O	0.7	0.7	5.4	5.8	0.8	0.6
Cr <sub>2</sub> O <sub>3</sub>	0.1	0.1	–	–	0.1	0.1
MgO	0.2	0.2	0.4	0.6	0.3	0.2
BaO	0.1	0.3	0.3	0.3	0.1	0.2
Na <sub>2</sub> O	–	–	–	0.1	–	–
SO <sub>3</sub>	0.4	0.6	26.9	11.2	7.3	3.8
SrO	–	–	0.3	0.3	0.1	–
<b>Total</b>	<b>100.0</b>	<b>100.0</b>	<b>100.0</b>	<b>100.0</b>	<b>100.0</b>	<b>100.0</b>

Soluble potassium, iron, and titanium species from the ash reacted with sulphuric acid to form potassium sulphate, iron sulphate, and titanium sulphate respectively. In addition, the dissolution of Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O from the ash samples contributed to the SiO<sub>2</sub> content in the leached ash samples (Equations [1], [3], and [4]).

The proportion of Al<sub>2</sub>O<sub>3</sub> in the leached SA1 ash produced at 1050°C and leached SA3 ash samples prepared at 1050°C is consistent with that of SA1 and SA3 ash samples prepared at 1050°C (Table VI). This can be ascribed to the significant amounts of the sparingly soluble silicon spinel, and pseudomullite that were formed in these materials. The XRF results of the coal ash samples and leached ash samples are consistent with those for other coal ash samples and their corresponding leached ash samples (Torma, 1983; Nayak and Panda, 2010; Matjie, Bunt, and van Heerden, 2005; Sangita, Nayak, and Panda, 2017; van der Merwe *et al.*, 2017; Burnet, Murtha, and Dunker, 1984).

The leached SA1 ash prepared at 1050°C contains a lower proportion of CaO (Table VI) than that of the original SA1 ash produced at 1050°C. However, the proportion of CaO (Table V) increased in the leached SA1 ash produced at 700°C, leached SA2 blend ash, and leached SA3 ash samples prepared at 1050°C. This can be attributed to the insolubility of CaO in the sulphuric acid solution. However, other researchers found that Ca<sup>2+</sup> reacts with SO<sub>4</sub><sup>2-</sup> to form gelatinous calcium sulphate, which precipitates during the leaching of the coal ash samples (Nayak and Panda, 2010; Matjie, Bunt, and van Heerden, 2005; Sangita, Nayak, and Panda, 2017; Freeman, 1993; Torma, 1983 (Equation [5])). The chemical reaction between CaO and H<sub>2</sub>SO<sub>4</sub> to form gelatinous calcium sulphate (gypsum) which occurred during the sulphuric acid leaching of coal ash samples is as follows:



The decrease in the proportions of aluminium, potassium, titanium, and iron in the original ash samples can be attributed to the selective dissolution of alumina from metakaolinite and aluminosilicate glasses, and K from either amorphous K<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> remnants, or potassium aluminosilicate glass (Tables V and VI) in the sulphuric acid solution. Fe can be dissolved from haematite, magnetite, and aluminosilicate glasses, while Ti as TiO<sub>2</sub> can be dissolved from rutile/anatase (Equation [2]) and aluminosilicate glasses.

Finally, the XRF results of the leached ash samples are in good agreement with the XRD results (Tables III – VI). The chemical properties of the ash samples and their corresponding leached ash samples varied substantially after H<sub>2</sub>SO<sub>4</sub> leaching.

### Mineralogy leached ash samples mineralogy

XRD results of the ash samples leached with 6.12 M H<sub>2</sub>SO<sub>4</sub> using 1:5 and 1:10 S/L ratios are shown in Table VII. These samples, apart from the leached SA2 blend ash prepared at 1050°C, contain major quartz, anhydrite, and amorphous materials which are insoluble in sulphuric acid. Minor minerals (dolomite, calcite, gypsum, portlandite, and pseudomullite) along with trace minerals (kaolinite, graphite, illite, muscovite, cristobalite) are insoluble in sulphuric acid. In addition, other minor minerals (pyrrhotite, haematite, K<sub>2</sub>CO<sub>3</sub>, rutile, periclase, and anatase) are soluble in the sulphuric acid solution. Furthermore, microcline and muscovite are only sparingly soluble or insoluble soluble in H<sub>2</sub>SO<sub>4</sub> (Table VII).

The presence of dolomite, calcite, kaolinite, and graphite in the other leached ash samples could be associated with the small proportion of unburnt coal particles. In addition, the presence of coal char could be due to the encapsulation of coal particles by the molten ash formed during combustion of the coals. Dolomite and calcite in the other leached ash samples are associated with the reactions of CaO/MgO and CO<sub>2</sub> during sulphuric acid leaching.

The leached SA2 blend ash produced at 1050°C using 1:10 S/L ratio is characterized by high concentrations of the microcline and anhydrite, and low proportions of quartz and amorphous materials (Table VIII) compared to other samples. Anhydrite crystallizes out from the gelatinous calcium sulphate precipitate and gypsum during drying of leached ashes at 80°C (Freeman, 1993; Matjie, Bunt, and van Heerden, 2005). Furthermore, the XRD results of the leached ash samples (SA1 ash, SA3 ash, and SA2 blend ash) show that the proportion of quartz (Table VIII) in the SA1 ash sample produced at 700°C decreased after leaching, due to the formation of the gelatinous calcium sulphate precipitate.

The microcline in the unburnt coal char is insoluble in sulphuric acid. The synthetic potassium feldspar minerals, including microcline, form when potassium species react with metakaolinite at 600–700°C (Heller-Kallai, 1978; Heller-Kallai and Lapidés, 2003; Matjie, *et al.*, 2021). Other potassium feldspars present in the coals begin to transform at temperatures of >1050°C (Matjie *et al.*, 2021).

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Table VII

Mineralogical composition of the leached coal and blend ash samples prepared at 700°C with 6.12 M H<sub>2</sub>SO<sub>4</sub> solution, using 1:5 and 1:10 S/L ratios (wt.%)

Sample temp S/L ratio	SA1		SA2 blend		SA3	
	1:5	1:10	1:5	1:10	1:5	1:10
Quartz	26.8	26.7	7.9	7.4	16.1	23.9
Anhydrite	4.1	3.3	23.1	25.0	7.6	9.9
Gypsum	1.0	1.5	1.9	1.1	0.8	1.0
K <sub>2</sub> CO <sub>3</sub>	0.8	1.2	0.8	1.0	0.5	0.7
Calcite	0.4	0.3	-	0.4	0.1	0.3
Dolomite	0.3	-	0.3	0.2	0.8	0.1
Portlandite	0.1	-	0.1	-	-	-
Muscovite	0.1	0.1	0.5	0.1	0.3	0.2
Microcline	-	-	-	0.3	-	-
Anatase	-	-	-	0.3	-	-
Illite	-	0.1	-	0.5	-	0.4
Graphite	-	-	0.7	-	0.2	-
Kaolinite	-	0.1	-	-	-	-
Pyrrhotite	-	-	0.1	-	-	-
Rutile	-	-	0.1	0.2	-	-
Amorphous	66.4	66.7	64.5	63.5	73.6	63.5
Total	100.0	100.0	100.0	100.0	100.0	100.0

Table VIII

Mineralogical composition of the coal and blend ash samples produced at 1050°C leached with 6.12 M H<sub>2</sub>SO<sub>4</sub> solution, using 1:5 and 1:10 S/L ratios (wt.%)

Sample S/L ratio	SA1		SA2 blend		SA3	
	1:5	1:10	1:5	1:10	1:5	1:10
Quartz	40.0	40.1	0.5	0.6	25.4	32.0
Anhydrite	7.1	6.0	34.0	29.4	15.5	16.9
Gypsum	0.7	0.6	0.8	0.1	-	0.8
K <sub>2</sub> CO <sub>3</sub>	-	0.5	1.3	-	-	0.5
Calcite	0.5	0.8	-	-	-	0.7
Dolomite	0.4	0.5	5.8	0.6	1.2	0.7
Portlandite	0.2	0.3	0.1	-	-	0.4
Muscovite	-	-	0.1	0.1	-	0.1
Microcline	0.8	0.9	-	17.0	-	0.9
Pseudomullite	0.9	1.3	0.5	1.8	7.4	2.2
Periclase	0.2	0.1	-	-	-	0.2
Kaolinite	0.1	0.2	-	-	-	0.1
Hematite	-	-	0.1	-	-	-
Anorthite	-	-	1.8	-	-	-
Illite	-	-	-	0.7	-	0.3
Cristobalite	-	-	0.1	-	0.4	-
Anatase	-	-	1.3	-	-	-
Graphite	-	-	0.9	-	-	-
Pyrrhotite	-	-	-	0.1	-	-
Rutile	-	-	-	0.8	0.4	0.1
Silicon spinel	1.0	0.5	1.5	0.8	1.7	1.0
Amorphous	48.1	48.1	51.0	48.0	48.0	43.1
Total	100.0	100.0	100.0	100.0	100.0	100.0

In addition, quartz and metakaolinite could dissolve in the potassium carbonate melt during heating of the SA2 blend at 1050°C, and microcline/anorthite could crystallize during the cooling of the ash melt (Table VIII). As expected, the mineralogical properties of the leached ash samples differ significantly from those of the original ash samples (Tables III, IV, VII, and VIII). This can be ascribed to the dissolution of soluble minerals in the H<sub>2</sub>SO<sub>4</sub> solution and alumina associated with metakaolinite and Al, Ti, K, Mg and Fe from other aluminosilicate glasses of illite, muscovite and microcline. Furthermore, the significant difference in the mineralogical properties could be

linked to the carbonation of calcium and magnesium oxides, as well as the *in-situ* capturing of sulphur dioxide to form calcium sulphates during leaching.

### Dissolution efficiencies of Al, K, and Ti as calculated from XRF results

The dissolution efficiencies for Al, K, and Ti as calculated from the XRF results after H<sub>2</sub>SO<sub>4</sub> leaching of the coal ash samples are presented in Figure 5. Sulphuric acid leaching of the SA1 ash, produced at 700°C with the 6.12 M H<sub>2</sub>SO<sub>4</sub> using a 1:5 S/L ratio, achieved higher dissolution efficiencies of Al, K, and Ti compared

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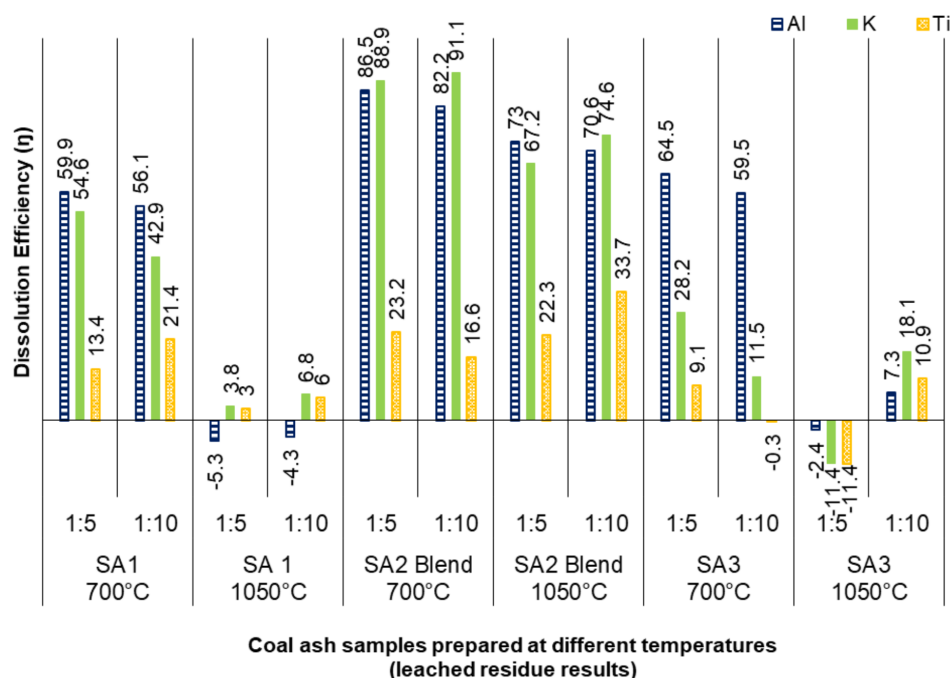


Figure 5—Dissolution efficiencies ( $\eta$ ) for Al, K, and Ti as determined from XRF analysis of leached and original ash samples (leaching conditions 6.12 M  $\text{H}_2\text{SO}_4$ , 80°C, 8 hours, S/L ratio 1:5 and 1:10) Note: Negative dissolution efficiencies of Al and K imply that either Al or K in potassium feldspar, pseudomullite, silicon spinel and microcline, formed at 1050°C which are insoluble in the sulphuric acid solution, resulted in extrapolation errors. Also, a negative dissolution efficiency of Ti implies Ti in Ti-containing minerals formed at 1050°C during the combustion of coal samples polymerized to form insoluble agglomerates in the sulphuric acid solution

to the SA1 ash prepared at 1050°C (Figure 5). The 1:10 S/L ratio attained higher dissolution efficiencies of Al, K, and Ti compared to the SA1 ashes prepared at 1050°C (Figure 5). Also, as the volume/concentration of sulphuric acid solution is increased, precipitation of gelatinous calcium sulphate increases. This can subsequently result in lower dissolution efficiencies of Al and K species during  $\text{H}_2\text{SO}_4$  leaching of the ash samples with higher proportions of CaO. This gelatinous calcium sulphate lost water when heated at 80°C to form anhydrite (Tables VII and VIII).

The low dissolution efficiencies of Al and K for the SA1 ash samples produced at 1050°C are due to the presence of sparingly soluble and insoluble minerals (pseudomullite, silicon spinel, and Ca-anorthite/K-microcline in the ash samples. The interactions of association minerals (calcite/dolomite/ $\text{K}_2\text{CO}_3$  associated with kaolinite) at temperatures of >1000°C resulted in the formation of aluminosilicate melts with K, Fe, and Ca impurities (Klopper, Strydom, and Bunt, 2012). Pseudomullite, anorthite, and synthetic potassium feldspars can subsequently crystallize from this molten solution or partially melted particles. These minerals, which are sparingly soluble or insoluble in the sulphuric acid solution, can also be formed at 600–700°C via solid-state reactions (Heller-Kallai, 1978; Heller-Kallai and Lapides, 2003; Matjie *et al.*, 2021).

The low Ti dissolution efficiencies could be due to Ti being captured in the insoluble crystalline phases in ashes formed during combustion. Also, insufficient free sulphuric acid in the leach liquor could contribute to the lower dissolution efficiency of Ti from rutile and anatase.

The SA2 blend ash samples prepared at 700°C achieved the highest dissolution efficiency of Al, and K (Figure 5) when leached with the 6.12 M  $\text{H}_2\text{SO}_4$  using S/L ratios of either 1:5 or 1:10 compared to those of SA2 blend ashes produced at 1050°C. A similar dissolution efficiency of Ti was attained after leaching SA2 blend ashes produced at either 700°C or 1050°C with 6.12 M  $\text{H}_2\text{SO}_4$  using S/L ratios of 1:5 and 1:10. The leaching of SA1

ash prepared at 1050°C with a S/L ratio of 1:10 achieved higher dissolution efficiencies of Al and K than those of SA3 ashes samples prepared at 1050°C. The high dissolution efficiencies for Al and K (Figure 5) from the SA2 blend ash samples prepared at 700°C are due to the dissolution of Al and K from metakaolinite, the aluminosilicates of illite and microcline,  $\text{K}_2\text{CO}_3$  remnants, and soluble K melt present in these ash samples. These soluble potassium-containing species in the ash could react with sulphuric acid to form potassium sulphate, which in turn could prevent the formation of gelatinous calcium sulphate precipitate (Klopper, Strydom, and Bunt, 2012).

Leaching experiments of the SA3 ash sample prepared at 700°C, with 6.12 M  $\text{H}_2\text{SO}_4$  using a 1:5 S/L ratio, yielded higher dissolution efficiencies of Al and K (Figure 5) compared to those of the SA3 ash produced at 700°C using a solid to liquid ratio of 1:10. Lower or zero dissolution efficiency of Ti was achieved by  $\text{H}_2\text{SO}_4$  leaching of SA3 ashes using solid to liquid ratios of either 1:5 or 1:10. The lower dissolution efficiency of Ti from the SA3 ash, could be due to either a lower Ti content in the original coal sample or the association of Ti with minerals and glassy phases in these ashes which are insoluble in sulphuric acid. The SA3 ash sample prepared at 1050°C achieved the lowest dissolution efficiency of Al, K, and Ti (Figure 5) when leached with the 6.12 M  $\text{H}_2\text{SO}_4$  at either 1:5 S/L or 1:10 S/L.

Low dissolution efficiencies of these elements are attributed to the formation of significant amounts of gelatinous calcium sulphate precipitate and the presence of pseudomullite, silicon spinel, microcline, and anorthite in the ash samples. An Al dissolution efficiency of 85% was obtained by Matjie, Bunt, and van Heerden (2005) when sintered pellets of another South African fly ash, and quicklime (CaO) were leached with 6.12 M  $\text{H}_2\text{SO}_4$  at a temperature of 80°C for 8 hours. Torma (1983) obtained a maximum Al dissolution efficiency of 99% after the  $\text{H}_2\text{SO}_4$  leaching of calcined pellets, which comprise fly ash from

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an overseas power station and calcium carbonate. Van der Merwe *et al.* (2017) showed a low dissolution efficiency of 47% for Al using conventional hydrometallurgical methods to selectively solubilize Al from an ultrafine South African coal fly ash using ammonium sulphate/sulphite solution. All ash samples containing metakaolinite (alumina soluble in  $H_2SO_4$  and silica insoluble in  $H_2SO_4$ ), amorphous glasses of illite and microcline, and potassium carbonate remnants prepared at  $700^\circ C$  achieved the highest dissolution efficiencies of aluminium and potassium compared to the  $1050^\circ C$  ash samples containing pseudomullite, silicon spinel, microcline, and anorthite. Microcline and potassium feldspar, which are insoluble in  $H_2SO_4$ , are associated with the calculated negative dissolution efficiencies of Al and K and resulted in the extrapolation errors. Furthermore, the calculated negative dissolution efficiency of titanium could be attributed to the polymerization or hydrolysis of titanium species to produce agglomerates that are insoluble in sulphuric acid. According to Han, Rubcumintara, and Fuerstenau (1987) and Lasheen (2009) titanium polymerizes to produce hydrolysed titanium agglomerates which are insoluble in sulphuric acid.

## Conclusions

In this study, the Al as alumina from metakaolinite, K from potassium carbonate melt and potassium carbonate/sulphate, and Ti from rutile/anatase contained in the coal ash samples were selectively dissolved in concentrated sulphuric acid solution.

Based on the results the following conclusions can be drawn:

Ashes of kaolinite-rich coals (SA1 and SA3) have comparable chemical and mineralogical properties. The corresponding metakaolinite-rich ash samples from kaolinite-rich coals that were produced at either  $700^\circ C$  or  $1050^\circ C$  have similar chemical properties but different mineralogical properties, apart from the ash of coal SA2 blend with 10%  $K_2CO_3$  additive.

All ash samples produced at  $1050^\circ C$  contain lower proportions of amorphous phase (metakaolinite and aluminosilicate glasses of illite, muscovite, and microcline), higher proportions of pseudomullite, silicon spinel, K-feldspar, and anorthite than all ash samples prepared at  $700^\circ C$ , except for the SA2 blend ash. The metakaolinite in coal ash samples transformed at  $1050^\circ C$  to silicon spinel and pseudomullite as the ashing temperatures increased during combustion of the coals.

As expected, the mineralogical and chemical properties of the ashes leached with sulphuric acid are significantly different to those of the original ash samples (Tables II-IV). This can be attributed to the dissolution of  $K_2CO_3$  remnants and K ions contained in the potassium melt, Al associated with metakaolinite, and soluble Al, K, and Ti species contained in the aluminosilicate glasses in sulphuric acid. Low carbonation of calcium oxide and magnesium oxide to form calcite and dolomite (estimated to be <20%  $CO_2$  *in-situ* captured) respectively, as well as the *in-situ* capturing of sulphur dioxide with free CaO to form calcium sulphates (estimated to be >90%  $SO_2$  *in-situ* captured) in the leaching tests and are associated with the significant differences in mineralogical and chemical properties of the leached ashes. Also, the gelatinous calcium sulphate precipitation that forms during the sulphuric acid leaching of coal ashes can contribute to different mineralogical properties of the leached ashes.

All ash samples containing  $H_2SO_4$ -soluble species of Al associated with metakaolinite, soluble K associated with the

potassium melt, and the added  $K_2CO_3$  remnants formed at  $700^\circ C$  achieved higher dissolution efficiencies of aluminium and potassium compared to the ash samples containing pseudomullite, silicon spinel, microcline and anorthite prepared at  $1050^\circ C$ . The SA2 blend ash prepared at  $700^\circ C$  achieve the highest Al dissolution efficiencies of 87% and 82%, and highest K dissolution efficiencies of 89% and 91% during leaching with 6.12 M  $H_2SO_4$  using 1:5 ratios of and 1:10, respectively. The higher dissolution efficiencies can be attributed to the presence of metakaolinite containing acid-soluble  $Al_2O_3$  and aluminosilicate glasses with soluble species of Al, K, Ti and potassium carbonate remnants in these ash samples, which are soluble in the sulphuric acid solution.

The results indicate that the leaching efficiency of certain metallic and non metallic species from metakaolinite-rich coal ash containing soluble K, Al, and Ti species in the aluminosilicate glasses produced at 'lower' temperatures can be improved by the addition of  $K_2CO_3$ . This is particularly applicable to fluidized-bed combustion ashes.

## Recommendations

The recovery of soluble aluminium and potassium species from coal ash and ash with a potassium additive prepared under conditions used in this study may be possible with 6.12 M  $H_2SO_4$  leaching step. The aluminium(III), potassium(I), titanium(IV) and sulphate-containing leach liquor could be utilized as coagulant in water treatment. The leach liquor could also be subjected to solvent extraction produce pure iron-free aluminium sulphate solution for utilization in paper mills and dye manufacturing. Titanium sulphate solution is used as a mordant in dyeing, and  $TiO_2$  in paint, coatings, paper, pigments, and chemical industries and water treatment; and potassium sulphate liquid as fertilizer. In addition, the leached residues, neutralized with quicklime, could be utilized as aggregate in the road and building industries, brick manufacturing, and masonry concrete applications. Furthermore, the ashes derived from the existing low-temperature combustion of coal via fluidized-bed combustion or gasification technologies could be an excellent feedstock for mineral recovery.

The proposed process for recovery of Al, Ti, and K from metakaolinite-rich coal ashes and ashes of coal fines blended with 10%  $K_2CO_3$  additive using the  $H_2SO_4$  leaching should be subjected to an economic evaluation.

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