In Situ Capturing and Absorption of Sulfur Gases Formed during Thermal Treatment of South African Coals

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ABSTRACT: The objective of this study, the first of its kind on these specific South African low-sulfur coals, was to capture H₂S and SO₂ produced under inert and oxidizing conditions from sulfur compounds present in the coals. The capturing agents were calcium and magnesium oxides formed during the transformation of calcite and dolomite. The effectiveness of two different scrubbing solutions (0.15 M cadmium acetate and 1.1 M potassium hydroxide) for absorption of volatilized H₂S and SO₂ was also investigated. The bituminous coal (coal A) contained dolomite, calcite, pyrite, and organic sulfur. Lignite (coal B) had a high organic sulfur content and contained gypsum, no or low dolomite and pyrite contents, and no calcite. A third sample (coal C) was prepared by adding 5 wt % potassium carbonate to coal A. Under oxidizing conditions and at elevated temperatures, FeS₂ produced Fe₂O₃, FeO, and SO₂. It transformed to FeS and released H₂S under inert conditions. Organic sulfur interacted with organically bound calcium and magnesium at 400 °C in an inert atmosphere to form calcium sulfate and oldhamite ((Ca,Mg)S). CaO, produced from calcite or dolomite, reacted with SO₂ and O₂ at 950 °C to form calcium sulfate. Treatment of lignite at 400–950 °C resulted in 96–98% evolution of sulfur as gases. Hydrogen sulfide formation increased with the increasing thermal treatment temperature under inert conditions for the three coals. Under oxidizing conditions, sulfur dioxide formation decreased with the increasing temperature when heating coals B and C. The lowest ratio (0.01) of H₂S to SO₂ was achieved during thermal treatment of the blend of coal and potassium carbonate (coal C), implying that almost all of sulfur was retained in the coal C ash/char samples. In situ capturing of sulfur gases by CaO and MgO and by the added K₂CO₃ in coal C to form calcium/magnesium/potassium sulfates and potassium/calcium/magnesium aluminosilicate glasses during utilization of these and similar coals could reduce the percentage of sulfur volatilized from the coals by 54–100%, thereby potentially decreasing their impact on the environment.

INTRODUCTION

The inorganic portion of coals consists effectively of two fractions: (1) a range of discrete crystalline mineral particles (i.e., mineral matter) occurring in the coal in different ways and, especially, in low-rank coals and (2) a range of nonmineral inorganic elements dissolved in water in pores or intimately associated with the organic matter. All coals contain sulfur in different forms (pyrite, sulfate, and organic sulfur) varying between 0.2 and 11%. During heating, as in combustion or gasification processes, the minerals originally present in the coal undergo various transformations. Examples of such transformations include, among others, conversion of carbonates to oxides and formation of gaseous sulfur species. Transformations of organic sulfur and sulfur-bearing minerals have been investigated under both reducing/inert and oxidizing conditions and have been reported extensively. While various commercially available coal-cleaning operations can effectively reduce the amount of pyritic sulfur in coals, these operations do not remove organic sulfur. The organic sulfur present in coal is likely to be an issue with regard to potential air pollution and material corrosion during coal utilization.

Pyrite can decompose in different ways depending on the atmosphere, with the transformation processes and products dependent on the temperature, oxygen concentration, flow rates, and particle size. Pyrite undergoes oxidation reactions to form iron oxides such as hematite, maghemite, and magnetite; ferric and ferrous sulfate; and sulfur dioxide during coal combustion. Depending on the concentration of oxygen, the transformation of pyrite can occur in two ways:

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through either the direct oxidation of pyrite or a two-step process, which first involves thermal decomposition in an inert atmosphere to form pyrrhotite, followed by oxidation of the pyrrhotite.\textsuperscript{24} Reactions that occur during the oxidation of pyrite and decomposition of iron sulfate when using different concentrations of oxygen can be described by the following equations.\textsuperscript{3}

\[ 2\text{FeS}_2 + 5.5\text{SO}_2 \rightarrow \text{Fe}_2\text{O}_3 + 4\text{SO}_2 \]  
\[ 2\text{FeS}_2 + 7\text{O}_2 \rightarrow \text{Fe}_2\text{(SO}_4\text{)}_3 + \text{SO}_2 \]  
\[ \text{FeS}_2 + 3\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2 \]  
\[ \text{Fe}_2\text{(SO}_4\text{)}_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{SO}_3 \]  
\[ 2\text{FeSO}_4 \rightarrow \text{Fe}_2\text{O}_3 + \text{SO}_3 + \text{SO}_2 \]  
\[ 2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3 \]  

Lime, which is derived from thermal decomposition of calcite and dolomite, and also from nonmineral Ca associated with organic matter, can interact with or capture \text{SO}_2 and \text{SO}_3 released from the transformations of the organic sulfur and sulfur-bearing minerals to form anhydrite (\text{CaSO}_4).\textsuperscript{25,26} Under an inert atmosphere (e.g., during pyrolysis) or under reducing conditions, pyrite can react at temperatures between 300 and 600 °C to form pyrrhotite (\text{Fe}^{1+} \text{S}) and reactive sulfur.\textsuperscript{3,27,28} This reactive sulfur can react with hydrogen from coal to form hydrogen sulfide.

Sulfur-containing gases pollute the environment and may also deactivate catalysts used in reactions of gases derived from coal, such as the Fischer–Tropsch synthesis.\textsuperscript{29} It is thus important to understand the transformation of sulfur compounds during heat treatment of coal and lignite. Such studies can provide insight to reduce sulfur emission during combustion, gasification, and pyrolysis.

The preponderance of chemical studies on bituminous coals have been carried out with bituminous coals of the northern hemisphere, which were deposited during the Carboniferous era. South African bituminous coals are of Permian age. The kinds of plants that dominated the palaeoflora of the Permian are different from those of the Carboniferous. In addition, the environments of accumulation of plant matter and its initial transformations to coal were likely different. Therefore, one aspect of this study sheds insight into the sulfur chemistry of South African bituminous coals, which are geologically younger than the far more extensively studied northern hemisphere coals. In addition, when studying a particular kind of coal, such as bituminous, it can be insightful to compare a coal of different rank, as was done in this study by including a South African lignite.

Several relatively recent papers in the literature have also reported the use of \text{K}_2\text{CO}_3 and/or \text{Ca(OH)}_2 additives in reactions of coal.\textsuperscript{33,46,49,50} However, those papers concentrate on the use of these added compounds as catalysts for gasification and pyrolysis and discuss recovering and reusing these materials. This article is much different from these other recent studies in that the authors used added potassium carbonate as a sorbent for in situ sulfur capture, not as a catalyst, and that the authors neither address nor contemplate recovery and recycling of the additives.

Sulfur analyses of other South African coals from Highveld mines show that the total sulfur content varies between 0.2 and 11%.\textsuperscript{3,8–10} The present work was the first study of its kind on these specific low-sulfur South African coals. The primary objective of this study was to investigate the transformations of sulfur-bearing minerals and organic sulfur in the two selected coals at elevated temperatures under inert and oxidizing conditions. The two coals were a bituminous coal of 1.13–1.26% sulfur (air-dried basis) and lignite of 0.98% sulfur, in which the majority of the sulfur is present as organic sulfur. In addition, the lignite ash has a higher concentration of alkali elements than does the bituminous coal ash, as discussed below in the Results and Discussion section. To probe the possibility that any significant differences in situ capturing could be due to the alkali elements, a third sample was prepared by doping the bituminous coal with 5% of potassium carbonate.

The secondary objective was to test the effectiveness of two different scrubbing solutions (0.15 \text{M} cadmium acetate dihydrate and 1.1 \text{M} potassium hydroxide solutions) for absorption of volatilized \text{H}_2\text{S} and \text{SO}_2. The absorption of hydrogen sulfide and sulfur dioxide gases using cadmium acetate solutions has not previously been studied in detail during reactions of these South African coals. Cadmium acetate is well known to be useful in the analysis of \text{H}_2\text{S} in the offgases released from conversion and combustion processes of other kinds of coals.\textsuperscript{7,33–35}

Evaluation of mineral matter by quantitative X-ray diffraction and chemical analyses of the coal samples were used to determine sulfur contents, as well as the proportions of sulfur-bearing mineral matter and minerals that are responsible for the in situ capturing of potentially polluting sulfur gases. The study also includes comparisons with data from other analytical techniques, partly to check and confirm the accuracy of the results obtained in this study. The use of such information in understanding the transformation of sulfur-bearing mineral matter in the South African coals and a subsequent sulfur in situ capturing during thermochemical processes are also included in the discussion. The industrial implementation of the results obtained in this study could reduce emission of environmentally harmful sulfur gases (Table 1).

| Table 1. Forms of Sulfur in South African Feed Coal and South African Lignite Samples (wt % Air-Dried Basis) |
|---|---|---|---|
| sulfur forms | feed coal (A) | lignite (B) | feed coal + K\textsubscript{2}CO\textsubscript{3} (C) |
| mineral sulfur (%) | 0.32 | 0.02 | 0.30 |
| sulfate sulfur (%) | 0.08 | 0.05 | 0.02 |
| organic sulfur (%) | 0.48 | 0.9 | 0.45 |
| pyritic sulfur (%) | 0.39 | 0.03 | 0.37 |

## RESULTS AND DISCUSSION

### Coal Composition.

Proximate analysis results are presented in Table 2. The values are consistent with the ranks of the two samples and with other South African coals.\textsuperscript{30} Ultimate analysis results, given in Table 3, indicate relatively low concentrations of total sulfur (1.6 and 1.9% daf) for coals A, B, and C.

Table 1 shows the concentrations of the different forms of sulfur in the three samples. Pyritic sulfur and mineral sulfur are dominant in coals A and C. The pyritic sulfur content in coal B is negligible (0.03%), but coal B is richer in organic sulfur than the other samples.
Coal A and coal B contained the same percentage of sulfatic sulfur lower than that in coal C. This is consistent with the fact that sulfates are minor constituents of the mineral matter of most coals likely arising from oxidation of sulfides. Although we did not determine the sulfur functional groups in these samples, there seems to be a consensus in the literature that sulfates are minor constituents of the mineral matter of most coals likely arising from oxidation of sulfides. Similar forms of sulfur were found to be present in other coals when using sulfur K-edge X-ray absorption near-edge structure (XANES) and X-ray photoelectron spectroscopy (XPS) analyses. In addition, the presence of organic sulfur has been noted in the macerals of South African coals, based on more detailed electron microprobe studies using quantitative element mapping (Table 1).

Table 2. Proximate Analysis Results (Air-Dried Basis) of the Feed Coal and Lignite Samples (wt % Air-Dried Basis)

| samples                | feed coal (A) | lignite (B) | feed coal + K2CO3 (C) |
|------------------------|--------------|-------------|-----------------------|
| moisture (%)           | 3.70         | 18.00       | 5.00                  |
| ash (%)                | 28.50        | 20.40       | 31.78                 |
| volatile matter (%)    | 21.50        | 30.50       | 20.00                 |
| fixed carbon (%)       | 46.50        | 31.00       | 45.11                 |
| total sulfur (%)       | 1.26         | 0.98        | 1.13                  |
| volatile matter (daf)  | 22.00        | 37.20       | 20.46                 |

Table 3. Ultimate Analysis Results of the Coal and Lignite Samples (Dry, Ash-Free Basis) (wt %)

| samples                | feed coal (A) | lignite (B) | feed coal + K2CO3 (C) |
|------------------------|--------------|-------------|-----------------------|
| carbon (%)             | 79.8         | 70.38       | 75.2                  |
| hydrogen (%)           | 3.83         | 5.25        | 3.6                   |
| nitrogen (%)           | 1.87         | 1.17        | 1.76                  |
| total sulfur (%)       | 1.87         | 1.59        | 1.81                  |
| oxygen (% by difference)| 12.62      | 21.6        | 17.63                 |

Table 4. Inorganic Oxide Percentages (wt %) from XRF Analysis of Coal Ash Samples

|                       | feed coal (A) | lignite (B) | feed coal + K2CO3 (C) |
|-----------------------|--------------|-------------|-----------------------|
| SiO2                  | 41.64        | 52.09       | 43.2                  |
| Al2O3                 | 25.2         | 15.05       | 29.56                 |
| Fe2O3                 | 5.65         | 5.15        | 4.02                  |
| TiO2                  | 1.79         | 0.8         | 1.84                  |
| P2O5                  | 0.26         | 0.1         | 0.22                  |
| CaO                   | 13.03        | 9.12        | 11.13                 |
| MgO                   | 3.16         | 3.52        | 2.76                  |
| MnO                   | 0.07         | 0.05        | 0.04                  |
| Cr2O3                 | 0.03         | 0.03        | 0.0                   |
| V2O5                  | 0.02         | 0.02        | 0.0                   |
| Na2O                  | 0.9          | 2.94        | 0.0                   |
| K2O                   | 1.11         | 2.06        | 3.69                  |
| BaO                   | 0.15         | 0.56        | 0.0                   |
| ZrO2                  | 0.08         | 0.03        | 0.0                   |
| SrO                   | 0.27         | 0.25        | 0.0                   |
| ZnO                   | 0.0          | 0.01        | 0.0                   |
| SO3                   | 7.63         | 8.09        | 3.54                  |
| Total                 | 100.09       | 99.87       | 100                   |

Char and Ash Chemistry. Tables 5 and 6 show the differences in the XRF results for char and ash samples produced from the heat treatment of different coal samples under an inert atmosphere (Table 5) and air (Table 6). The concentrations of phosphorus present in the char samples slightly differed. This, and the slight differences in potassium and iron concentrations in other char and ash samples, could be due to the uncertainty of XRF analysis (±1% for both K and Fe with this instrument) and also to the mass loss of coal and lignite during thermal treatment. The XRF results for the char and ash samples are shown in Table 4. The XRF results of the ash derived from coal A are slightly different from the XRF results for the ash sample prepared from the blend of coal A and potassium carbonate (i.e., coal C). The three ashes displayed similar base-to-acid ratios of ≈0.3. These XRF results for the coals evaluated in this study are in good agreement with previous XRF results for other South African coals.

Silicon and aluminum are the dominant elements in the ashes, with lesser but still significant proportions of calcium, produced from the heat treatment of different coal samples under an inert atmosphere (Table 5) and air (Table 6). The concentrations of phosphorus present in the char samples slightly differed. This, and the slight differences in potassium and iron concentrations in other char and ash samples, could be due to the uncertainty of XRF analysis (±1% for both K and Fe with this instrument) and also to the mass loss of coal and lignite during thermal treatment. The XRF results for the char and ash samples are shown in Table 4. The XRF results of the ash derived from coal A are slightly different from the XRF results for the ash sample prepared from the blend of coal A and potassium carbonate (i.e., coal C). The three ashes displayed similar base-to-acid ratios of ≈0.3. These XRF results for the coals evaluated in this study are in good agreement with previous XRF results for other South African coals.
iron, magnesium, potassium, sulfur, and titanium. Lignite ash contains higher concentrations of Na₂O relative to the ashes of coals A and C, which contained no detectable sodium. (The detection limit for sodium with this XRF instrument is 0.03%, and the uncertainty when determining the concentration of sodium in solid samples is 1%). The minor elements Mn, Cr, V, Ba, Zr, Sr, and Zn, reported as oxides, made up ≤0.95% of the ash samples. On the basis of the SO₃ contents in Table 4, the ash of coal A contained 7.63% sulfur reported as SO₃ and coal B ash contained 8.09% SO₃.

The extent of sulfur retention in the ash samples depends partly on the ashing conditions (e.g., heating rate) and partly on the proportion of elements such as Ca, Mg, Na, and K that are available to combine with the gaseous sulfur species released during ash preparation. Because the heating rates used for ashing were the same for all three samples, ashing conditions can be eliminated as a variable that would affect sulfur retention so that ash chemistry is the main consideration affecting the observed results. The ashes from coals A and B contain a large molar excess of CaO and MgO relative to the amount of SO₃ reported in the ash. If CaO and MgO do not react with metakaolinite from dehydration of kaolinite at elevated temperatures (≤950 °C), there is more than enough Ca and Mg in these ashes to account for capturing all of the sulfur. The presence of feldspars (Table 9) such as anorthite and of amorphous material (calcium aluminosilicates) in the chars and ash samples produced at 950 °C implies that some CaO from the transformations of dolomite and calcite and organic Ca reacted with metakaolinite.¹³,¹⁴

The char and ash samples contained low concentrations of sulfur when compared with the parent coal samples, (Tables 4−6). Clearly, most of the sulfur has been released, presumably as SO₂ and/or H₂S (Tables 4−6). More sulfur gases were released under both atmospheric conditions at the higher temperatures. Even coals that would be very attractive for utilization based ondaf sulfur contents <2% can still release much of that sulfur as gaseous compounds. Low concentrations of sulfur in char and ash samples show that most of the sulfur originally present in the coal can be released under conditions used in our experiments. Depending on prevailing environmental regulations, this potential sulfur emission would still need to be addressed (Figure 1).

Mineralogy for Coals (A−C) and Char and Ash Samples. The X-ray diffraction (XRD) results (Table 7, Figure 4) revealed that lignite contained no calcite and pyrite, in comparison with the bituminous coal samples (Table 7, Figure 2, and Figure 3). XRD detected low concentrations of gypsum in lignite but not in the other samples.¹³ The presence of gypsum could account for the sulfate sulfur in lignite. Minor amounts of pyrite, calcite, and dolomite were found in the bituminous coal and bituminous coal + K₂CO₃ blend samples (Table 7 and Figures 2 and 3). Other minerals that are present in the coals (Figures 2−4) are not discussed in detail.

Traces of hematite (Fe₂O₃) and wuestite (FeO) are found in some of the ash samples produced at 400 and 950 °C under oxidizing conditions, most likely produced by the oxidation of pyrite (Table 9). Trace amounts of pyrite are still present in char and ash samples produced under both inert and oxidizing conditions, due to organic carbon matrix inhibiting the transformations of minerals.¹³,¹⁵ Pyrite present in the coal undergoes extensive oxidation at elevated temperatures to form iron oxide (hematite) and sulfur dioxide during heat treatment.¹¹−¹³,¹⁶,¹⁷,⁲⁴,⁴¹,⁵²

Oldhamite (Ca, MgS) also appears to be present in the char and ash samples (Tables 8 and 9). This mineral was not found to be present in any of the samples A−C (Table 7 and Figures 2−4). Lime (CaO), which was formed during the interaction of organically associated calcium, can react with sulfur dioxide and carbon monoxide at 400 °C to form oldhamite under inert conditions. Oldhamite can survive at temperatures >950 °C.³³,³⁴ Carbon or carbon monoxide reduces calcium sulfate formed during the interactions of organic sulfur and organically associated calcium to form oldhamite at temperatures between 950 and 1500 °C during pyrolysis of coal under inert atmospheres.⁴³ The chemical reactions of oldhamite under an inert atmosphere are as follows

\[
\text{CaSO}_4 + 2\text{C} \rightarrow \text{CaS} + 2\text{CO}_2 \quad (7)
\]

\[
\text{CaSO}_4 + 3\text{C} \rightarrow \text{CaS} + \text{CO}_2 + 2\text{CO} \quad (8)
\]

\[
\text{CaSO}_4 + 4\text{CO} \rightarrow \text{CaS} + 4\text{CO}_2 \quad (9)
\]

Formation of oldhamite is responsible for high sulfur retention in the char and ash samples.

The concentration of anhydrite in the char and ash samples varied between 0.6 and 6%. Anhydrite likely formed by interaction of SO₂ gas, derived from the organic sulfur and pyrite, with a combination of CaO released from carbonate minerals in the coal and nonmineral Ca released from the organic matter during heat treatment under oxidizing conditions.³² Formation of anhydrite is primarily responsible for the retention of sulfur in the char and ash samples. In addition, other researchers found that potassium carbonate melt and potassium ions from the decomposition of K₂CO₃ at 891 °C react with organic sulfur and sulfur species from transformation of pyrite at 900 °C to form potassium sulfate.³³ Other potassium species react with metakaolinite from transformation of kaolinite to form either potassium aluminosilicate glass or potassium feldspar. This accounts for the high percentage of sulfur retained in the ash of coal C produced in both inert and oxidizing conditions. In a similar

Table 7. Percentage of Calcium- and Iron-Bearing Minerals in the Coal and Lignite Samples (wt % in Air-Dried Coal)

| samples          | feed coal (A) | lignite (B) | feed coal + K₂CO₃ (C) |
|------------------|---------------|-------------|-----------------------|
| gypsum           | 0.0           | 0.9         | 0.0                   |
| calcite          | 2.5           | 0.0         | 0.7                   |
| dolomite         | 6.2           | 0.5         | 0.9                   |
| pyrite           | 0.2           | 0.0         | 0.1                   |

Figure 1. Tube Furnace connected to scrubber bottles. Photograph courtesy of Romanus Uwaoma, Copyright 2018.
study, both calcium hydroxide and potassium carbonate were added to coal to capture sulfur-bearing compounds during pyrolysis and gasification. Sulfur XANES analysis results indicated that sulfur was retained in the char and ash samples as K₂SO₄ and not as CaSO₄ and CaS. H₂S and COS formed during the transformation of pyrite and organic sulfur were released during pyrolysis and gasification. Ca(OH)₂ added to coal could possibly have reacted with the sulfur species differently than would calcium-bearing minerals inherent in the coal during pyrolysis and gasification. Other researchers found that the excluded minerals, i.e., discrete particles of minerals in the coal, and included minerals, inherent minerals associated within the carbonaceous matrix, react differently during thermochemical processes.11,47

Figure 2. Diffractogram of feed coal (coal A sample).

Figure 3. Diffractogram of feed coal + K₂CO₃ (coal C sample).

Figure 4. Diffractogram of lignite (coal B sample).
Table 8. Concentrations of Calcium-, Magnesium-, and Iron-Bearing Minerals Present in Char Samples Prepared at 400 and 950 °C under a Nitrogen Atmosphere (wt % Air-Dried Solid Samples)\textsuperscript{a,b}

| Minerals         | NB1 | NB4 | NA1 | NA4 | NC1 | NC4 |
|------------------|-----|-----|-----|-----|-----|-----|
| anhydrite        | 1.6 | 0.7 | 0.0 | 1.8 | 3.2 | 0.6 |
| gypsum           | 1.3 | 1.4 | 1.6 | 0.0 | 1.4 | 0.0 |
| microcline       | 2.8 | 3.2 | 2.6 | 0.0 | 2.0 | 2.1 |
| pyrite           | 0.6 | 0.0 | 10.2| 0.0 | 0.0 | 0.0 |
| calcite          | 0.0 | 3.0 | 5.7 | 4.2 | 4.5 | 2.5 |
| dolomite         | 0.0 | 0.0 | 4.6 | 0.7 | 7.4 | 0.0 |
| periclase        | 1.1 | 1.8 | 2.3 | 0.7 | 2.1 | 0.0 |
| oldhamite        | 0.0 | 0.0 | 0.0 | 0.7 | 0.9 | 0.0 |

\textsuperscript{a}NB1 = lignite B @ 400 °C in nitrogen; NB4 = lignite B @ 950 °C in nitrogen. \textsuperscript{b}NA1 = feed coal A @ 400 °C in nitrogen, NA4 = feed coal A @ 950 °C in nitrogen. \textsuperscript{c}NC1 = feed coal A + K\textsubscript{2}CO\textsubscript{3} C @ 400 °C in nitrogen, NC4 = feed coal A + K\textsubscript{2}CO\textsubscript{3} C @ 950 °C in nitrogen.

Table 9. Concentrations of Calcium-, Magnesium-, and Iron-Bearing Minerals Present in Char Samples Prepared at 400 and 950 °C under an Air Atmosphere (wt %)\textsuperscript{a,b,c,d}

| Minerals         | AB1 | AB4 | AA1 | AA4 | AC1 | AC4 |
|------------------|-----|-----|-----|-----|-----|-----|
| anhydrite        | 1.0 | 6.0 | 0.0 | 5.2 | 1.8 | 2.7 |
| gypsum           | 0.0 | 1.6 | 1.6 | 0.0 | 1.5 | 0.0 |
| anorthite        | 0.0 | 0.6 | 2.3 | 0.0 | 0.0 | 4.5 |
| pyrite           | 0.0 | 0.0 | 0.0 | 0.0 | 1.4 | 0.0 |
| calcite          | 0.0 | 0.0 | 0.0 | 0.0 | 1.0 | 4.7 |
| hemaitte         | 0.0 | 0.0 | 5.6 | 11.2| 0.0 | 0.0 |
| wuestite         | 1.7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.7 |
| periclase        | 0.0 | 1.8 | 0.0 | 1.8 | 1.6 | 2.3 |
| oldhamite        | 4.4 | 0.9 | 4.6 | 4.2 | 5.8 | 1.5 |
| portlandite      | 0.0 | 0.0 | 0.0 | 0.0 | 4.9 | 1.4 |

\textsuperscript{a}AB1 = lignite B @ 400 °C in air; AB4 = lignite B @ 950 °C in air. \textsuperscript{b}AA1 = feed coal A @ 400 °C in air, AA4 = feed coal A @ 950 °C in air. \textsuperscript{c}AC1 = feed coal A + K\textsubscript{2}CO\textsubscript{3} C @ 400 °C in air, AC4 = feed coal A + K\textsubscript{2}CO\textsubscript{3} C @ 950 °C in air.

Gypsum was observed to contribute up to 1.6% of the minerals to these samples. Gypsum would not be expected to be present in the char and ash treated at elevated temperatures under either atmosphere because it loses water of hydration completely at about 165 °C. We attribute its presence to the reaction of anhydrite with moisture at ambient temperature during sample preparation. (In fact, anhydrite is sold commercially under various trade names, such as Drierite, for use as a dehydrating agent.)

The absence of lime from the analyses shown in Tables 8 and 9 is attributed to several factors. There is a low concentration of calcite in these samples to begin with. Lime, formed during the decomposition of calcite, dolomite, and organically associated Ca, could have reacted with water vapor to form portlandite (Table 9) and also could have reacted with metakaolinite during transformation of kaolinite at temperatures >900 °C to form anorthite.\textsuperscript{14,25} The small amount of periclase (Tables 8 and 9) noted in the char and ash samples likely formed by decomposition of dolomite or from nonmineral Mg in the organic matter.

Absorption of H\textsubscript{2}S. All cadmium acetate scrubbers formed a yellow precipitate of cadmium sulfide during both the pyrolysis and combustion experiments. The precipitate was separated from the aqueous phase via filtration after a few hours of storage at room temperature. The total masses of the CdS precipitate that was formed during heat treatment under both inert atmosphere and oxidizing conditions were 10 and 540 mg, respectively (Table 10). The amorphous precipitates

Table 10. IC Analysis Results for SO\textsubscript{2}\textsuperscript{2−} on Liquid Samples and Masses of CdS Precipitate at 400 and 950 °C under Inert and Oxidizing Conditions (mol/L mg)\textsuperscript{a,b,c,d}

| Sample Name | SO\textsubscript{2}\textsuperscript{2−} Absorbed by Scrubbers (mol/L) | Masses of CdS Precipitate (mg) |
|-------------|-------------------------------------------------|---------------------------------|
| NB1         | 0.003                                           | 10                              |
| AB1         | 0.005                                           | 120                             |
| NB4         | 0.003                                           | 30                              |
| AB4         | 0.005                                           | 50                              |
| NA1         | 0.006                                           | 40                              |
| AA1         | 0.16                                            | 540                             |
| NA4         | 0.002                                           | 290                             |
| AA4         | 0.015                                           | 20                              |
| NC1         | 0.002                                           | 10                              |
| AC1         | 0.011                                           | 10                              |
| NC4         | 0.005                                           | 210                             |
| AC4         | 0.003                                           | 20                              |

\textsuperscript{a}NB1 = lignite B @ 400 °C in nitrogen; NB4 = lignite B @ 950 °C in nitrogen. \textsuperscript{b}NA1 = feed coal A @ 400 °C in nitrogen, NA4 = feed coal A @ 950 °C in nitrogen. \textsuperscript{c}NC1 = feed coal A + K\textsubscript{2}CO\textsubscript{3} C @ 400 °C in nitrogen, NC4 = feed coal A + K\textsubscript{2}CO\textsubscript{3} C @ 950 °C in nitrogen. \textsuperscript{d}AC1 = feed coal A + K\textsubscript{2}CO\textsubscript{3} C @ 400 °C in air, AC4 = feed coal A + K\textsubscript{2}CO\textsubscript{3} C @ 950 °C in air.

(Figure 8) were dried before weighing and corrected for the mass of the filter paper. Hydrogen sulfide evolved during the transformation of pyritic and organic sulfur\textsuperscript{9,10,19,36–39} at elevated temperatures, under both atmospheres, reacted with cadmium acetate present in the scrubber solution samples to precipitate amorphous yellow cadmium sulfide, Cd\textsubscript{S}.\textsuperscript{7,53–55} These results obtained in this study are consistent with other work on sulfur transformation at elevated temperatures to form H\textsubscript{2}S, COS, and SO\textsubscript{2} during pyrolysis and gasification.\textsuperscript{44,45} The following possible reaction between pyrite and hydrogen from the organic matter can take place at elevated temperatures (400–950 °C) to form hydrogen sulfide and pyrrhotite under inert conditions.\textsuperscript{5,10}

\[
\text{FeS}_2(s) + \text{H}_2(g) \rightarrow \text{H}_2\text{S}(g) + \text{FeS}(s) \tag{10}
\]

The reaction that then takes place is

\[
\text{H}_2\text{S}(g) + (\text{CH}_3\text{COO})_2\text{Cd}(aq) \rightarrow 2\text{CH}_3\text{COOH}(aq) + \text{CdS}(s) \tag{11}
\]

The XRD and inductively coupled plasma mass spectrometry (ICP-MS) results for the yellow precipitate samples clearly confirmed that the purity of the amorphous samples (Figure 8) is 95% containing mainly Cd (77%) and S (18%).

Hydrogen sulfide that was not absorbed by cadmium acetate can react with potassium ions and water present in the second scrubber solution (potassium hydroxide solution) to form water-soluble potassium hydrogen sulfide (KHS).\textsuperscript{40}

IC Analyses. The concentrations of SO\textsubscript{2} gas captured as SO\textsubscript{2}\textsuperscript{2−} by the scrubber solutions (cadmium acetate and potassium hydroxide solutions) during pyrolysis and combustion at 400 and 950 °C are presented in Table 10. Other cadmium and potassium ions in the scrubbers could react with...
sulfate to form water-soluble cadmium sulfate and potassium sulfate. Under both inert and oxidizing conditions, the concentration of $\text{SO}_4^{2-}$ in the scrubber solution samples decreased with increasing temperature for all three coal samples. The low concentrations of $\text{SO}_4^{2-}$ shown in Table 10 may correspond to the available free CaO from the decomposition of calcite or dolomite during heat treatment. CaO can react with sulfur oxide gases to form calcium sulfate. The in situ capturing of the sulfur oxide gases during combustion resulted in significant retention of sulfur in the ash and char.

The concentration of sulfide anions in the scrubber solution samples from the experiments was not determined during the IC analysis. As discussed above, cadmium acetate solution captured hydrogen sulfide as a yellow precipitate of cadmium sulfi de. At ambient temperature, the solubility product constant of cadmium sulfide is $3.6 \times 10^{-29}$, indicating that the sulfide ion concentration in these cadmium solutions is negligible.

\section*{SO$_3$ Volatilized as SO$_2$ during Thermal Treatment of Coals.} From the XRF analysis results (% ash composition), the %SO$_3$ was calculated using the formula

$$\text{%SO}_3 \text{volatilized} = \frac{\text{SO}_3 \text{A} \times \text{initial mass of raw coal/lignite} - [\text{SO}_3 \text{B or C} \times D]}{\text{SO}_3 \text{C} \times \text{initial mass of raw/lignite coal}} \times 100$$

where A indicates values from Table 4, B indicates values from Table 5, C indicates values from Table 13, and [ ] indicates the concentration of SO$_3$.

The calculated results for %SO$_3$ volatilized at 400 and 950 °C during thermal treatment experiments are given in Tables 11 and 12. From these two tables, the trend of increasing %

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
sample name & %S volatilized \\
\hline
NB1 & 95.68 \\
NB4 & 96.30 \\
NA1 & 42.48 \\
NA4 & 66.67 \\
NC1 & 0.00 \\
NC4 & 39.58 \\
\hline
\end{tabular}
\caption{Table 11. %S (Reported as SO$_3$ wt %) Volatilized as H$_2$S/ SO$_2$ during Heating of Coals under Inert Conditions$^{a,b,c}$}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
sample name & %S volatilized \\
\hline
AB4 & 98.0 \\
AA1 & 72.55 \\
AA4 & 85.62 \\
AC1 & 28.17 \\
AC4 & 53.52 \\
\hline
\end{tabular}
\caption{Table 12. %S (Reported as SO$_3$ wt %) Volatilized as SO$_2$ during Heating of Coals under Oxidizing Conditions$^{a,b,c}$}
\end{table}

The results for lignite are consistent with organic sulfur being the dominant sulfur form and with the findings in the literature that much of this sulfur would be in the form of thiols and disulfides. The C–S and S–S bonds are very weak and should readily cleave during thermal treatment. This has been observed for pyrolysis and liquefaction of Spanish Mequinensa lignite,$^{31}$ which has unusually high organic sulfur content (Table 13).
solutions. NB1 = lignite B @ 400 °C under nitrogen, NB4 = lignite (coal B sample) @ 950 °C under nitrogen, NA1 = feed coal A @ 400 °C, NA4 = feed coal (coal A sample) @ 950 °C under nitrogen, NC1 = feed coal + K2CO3 C @ 400 °C, NC4 = feed coal + K2CO3 (coal C sample) @ 950 °C under nitrogen, AB1 = lignite B @ 400 °C under nitrogen, AB4 = lignite (coal B sample) @ 950 °C under air, AA1 = feed coal A @ 400 °C, AA4 = feed coal (coal A sample) @ 950 °C under air, AC1 = feed coal + K2CO3 C @ 400 °C, AC4 = feed coal + K2CO3 (coal C sample) @ 950 °C under air.

Figure 5. Masses of some H2S volatilized at 400 and 950 °C under inert and oxidizing conditions and absorbed by scrubber solutions. NB1 = lignite B @ 400 °C under nitrogen, NB4 = lignite (coal B sample) @ 950 °C under nitrogen, NA1 = feed coal A @ 400 °C, NA4 = feed coal (coal A sample) @ 950 °C under nitrogen, NC1 = feed coal + K2CO3 C @ 400 °C, NC4 = feed coal + K2CO3 (coal C sample) @ 950 °C under nitrogen, AB1 = lignite B @ 400 °C under nitrogen, AB4 = lignite (coal B sample) @ 950 °C under air, AA1 = feed coal A @ 400 °C, AA4 = feed coal (coal A sample) @ 950 °C under air, AC1 = feed coal + K2CO3 C @ 400 °C, AC4 = feed coal + K2CO3 (coal C sample) @ 950 °C under air.

Figure 6. Masses of some SO2 volatilized at 400 (blue) and 950 °C (red) under inert and oxidizing conditions and absorbed by scrubber solutions. NB1 = lignite B @ 400 °C under nitrogen, NB4 = lignite (coal B sample) @ 950 °C under nitrogen, NA1 = feed coal A @ 400 °C, NA4 = feed coal (coal A sample) @ 950 °C under nitrogen, NC1 = feed coal + K2CO3 C @ 400 °C, NC4 = feed coal + K2CO3 (coal C sample) @ 950 °C under nitrogen, AB1 = lignite B @ 400 °C under nitrogen, AB4 = lignite (coal B sample) @ 950 °C under air, AA1 = feed coal A @ 400 °C, AA4 = feed coal (coal A sample) @ 950 °C under air, AC1 = feed coal + K2CO3 C @ 400 °C, AC4 = feed coal + K2CO3 (coal C sample) @ 950 °C under air.

Figure 7. Ratios of some H2S and SO2 volatilized at 400 and 950 °C and absorbed by scrubber solutions under inert and oxidizing conditions. NB1 = lignite B @ 400 °C under nitrogen, AB1 = lignite B @ 400 °C under air; NB4 = lignite B @ 950 °C under nitrogen, AB4 = lignite B @ 950 °C under air; NA1 = feed coal A @ 400 °C under nitrogen, AA1 = feed coal A @ 400 °C under air; NA4 = feed coal A @ 950 °C under nitrogen, AA4 = feed coal A @ 950 °C under air.

Capturing of sulfur-containing gases by calcium species to form calcium sulfates.25,38 The masses of hydrogen sulfide absorbed in the cadmium acetate solution increases with an increase in temperature during the thermal treatment of the calcite-free lignite in air.

Due to the reaction between CaO and sulfur dioxide to form calcium sulfates,13–15 the masses of sulfur dioxide absorbed in the scrubber solutions decreased with an increase in the temperature for experiments in air (Figure 6). The low masses of sulfur dioxide absorbed in the scrubber solutions did not change significantly during thermal treatment under nitrogen. The XRD analysis results indicated that low concentrations of calcite (0.7–2.5%) and pyrite (0.1–0.2%) were present in these coals. The coals also contained organic sulfur (0.5–1%) and mineral sulfur (0.02–0.03%). Lignite (coal B) contained 0.03% pyritic sulfur and 1% organic sulfur. XRD results for the char and ash samples indicated the presence of periclase (MgO), derived from the decomposition of dolomite. In some instances, pyrite transformed to wustite and hematite at elevated temperatures. Calcium sulfate and oldhamite were formed by reaction of organically associated calcium or CaO released from calcite or dolomite, with sulfur-bearing gases formed from decomposition of organic sulfur compounds and pyrite. The formation of anhydrite (at 950 °C under air) and oldhamite (at 400 °C under nitrogen) in the char and ash samples is responsible for significant sulfur retention concentrations in the char and ash samples (Tables 8 and 9).

Coals with relatively high concentrations of CaO from calcite achieved 42–86% reductions of sulfur gas evolution. A 96–98% sulfur volatilization was obtained from heat treatment of lignite (coal B), which contained no calcite, at 400–950 °C in air. Addition of potassium carbonate to the bituminous coal (coal C) containing calcite and dolomite significantly atmospheres. The lowest ratio of H2S to SO2 was achieved after heating the blend of coal and potassium carbonate (coal C) under oxidizing conditions. This suggests that almost >90% of sulfur was retained in the ash and char samples containing anhydrite and in potassium carbonate melt or potash aluminosilicate glasses produced from coal C. Low masses of hydrogen sulfide and sulfur dioxide and low H2S to SO2 ratios can be attributed to reactions among hydrogen sulfide, potassium ions, and water to form potassium hydrogen sulfide. Also, hydrogen sulfide can react with carbon monoxide from decomposition of organic oxygen functional groups to form COS.41,42,45

Excluding samples NA4 and AA4, low ratios of H2S to SO2 (Figure 7) were obtained after thermal treatment under both.
enhanced the retention of sulfur (72–100%) in the ash and char samples under both inert and oxidizing conditions. These high percentages of sulfur retention in the char and ash derived from coal C are attributed to the formation of calcium sulfates, potassium sulfate, oldhamite, and potassium/calcium aluminosilicate glasses (amorphous materials).

The masses of hydrogen sulfide absorbed in the cadmium acetate solutions to form an amorphous CdS precipitate (Figure 8) increased with the increasing temperature during thermal treatment under nitrogen. However, hydrogen sulfide formation decreased with an increase in temperature during heating of samples B and C under oxidizing conditions, entirely consistent with the expected oxidation of sulfur to its oxide. The mass of hydrogen sulfide increases with an increase in temperature during thermal treatment of the calcite-free lignite sample under oxidizing conditions.

The amount of sulfur dioxide decreased with an increase in the temperature when heating samples B and C under the oxidizing condition. The amount of sulfur dioxide absorbed, however, did not change significantly during the thermal treatment of any of the coal samples under the inert conditions.

The lowest ratio of H$_2$S to SO$_2$ was achieved after heating the blend of coal and potassium carbonate (coal C) under oxidizing conditions. Almost 100% of sulfur was retained in the ash/char samples produced from coal C.

#### CONCLUSIONS

Integration of XRD, XRF, proximate and ultimate analyses, IC, and ICP-MS, forms of sulfur and gravimetric analyses, has provided a better understanding the sulfur transformations and in situ capturing of the released sulfur gases during the pyrolysis and combustion of a selected South African low-sulfur bituminous coal and lignite. Most of the sulfur originally in the coal can be released under conditions used in our experiments.

Ashes produced in this study all had similar base-to-acid ratios. Therefore, the basicity or acidity of the ash and the effects of ashing conditions can be eliminated as factors involved in sulfur retention. Sulfur retention must depend upon interactions of sulfur species with specific coal or ash components.

Coals that contained calcite and dolomite (A and C) had a lower degree of sulfur volatilization than that for lignite (coal B), which contained no calcite. Reactive CaO can capture sulfur oxides to form inert calcium sulfates. The coal containing calcite, dolomite, and added potassium carbonate (coal C) produced the lowest volatilization of sulfur in both inert and oxidizing conditions. This indicates an additional benefit of relatively high potassium contents in ash.

Oldhamite, not found in any of the coals, appears in the chars and ashes. Lime can react with sulfur dioxide and carbon monoxide at 400 °C to form oldhamite, which persists to temperatures of >950 °C. This reaction contributes to high sulfur retention.

Under oxidizing conditions, formation of anhydrite is primarily responsible for the retention of sulfur in the char and ash samples. Almost 90% of sulfur was retained in the ash and char samples containing anhydrite. For coal C, sulfur capture was augmented by the presence of potassium carbonate melt or by potash aluminosilicate glasses.

The amount of sulfur dioxide evolved decreased with an increase in temperature for coals B and C under oxidizing conditions. CaO captured SO$_2$ to form anhydrite in the ash or char.

Treatment of lignite, which contained no calcite and no pyrite, at 400–950 °C under inert and oxidizing conditions resulted in 96–98% volatilization of sulfur gases, providing further evidence for the importance of calcium as the primary sulfur-capturing agent in these coals. Under inert conditions, almost all of the sulfur in lignite volatilizes without being captured in the ash, even at 400 °C. This is consistent with organic sulfur being by far the dominant sulfur form.

The amount of hydrogen sulfide released increased with an increase in temperature during the thermal treatment of all coals under inert conditions. Hydrogen sulfide that may have dissolved in the potassium hydroxide solution would form water-soluble potassium hydrosulfide. The masses of sulfur dioxide absorbed in the scrubber solutions decreased with an increase in the temperature when heating coals B and C under oxidizing conditions. This is attributed to the significant amount of CaO from the complete decomposition of calcite or dolomite at elevated temperatures. The free CaO captured SO$_2$ to form anhydrite in the ash or char.

Addition of K$_2$CO$_3$ to bituminous coal eliminated release of sulfur gases during pyrolysis at 400 °C. Even at 950 °C, the reduction in sulfur volatilization achieved by K$_2$CO$_3$ addition is still significant. K$_2$CO$_3$ can also affect the caking behavior of bituminous coals. 49,50 There may be some process advantages.
of adding relatively inexpensive K₂CO₃ to bituminous coal pyrolysis to reduce sulfur gas volatilization.

Thus, the primary agent for in situ capturing of sulfur gases is calcium oxide (transformed product of either calcite or dolomite). Anhydrite or oldhamite (depending on temperature and atmosphere conditions) is responsible for significant sulfur retention. This in situ capturing of sulfur gases by CaO can be augmented by the addition of K₂CO₃ and possibly by MgO from dolomite. Collectively, these factors can significantly reduce the release of sulfur gases during pyrolysis, by 54–100%.

**EXPERIMENTAL SECTION**

**Coal and Lignite Samples.** Coarse (<38 mm)-sized bituminous coal (coal A) and lignite (coal B) samples were taken from the North-West University (NWU) from a South African Highveld coalfield and Karoo sequence, respectively. A representative subsample of coal A was mixed with 5 wt % analytically pure K₂CO₃ to increase the concentration of potassium in the sample (referred to as coal C).

The samples were first crushed to less than 3 mm using a jaw crusher (Samuel Osborne (SA) Ltd, model 66YROLL) and a grinding mill (Usborn Coal Equipment). The crushed sample was screened using a standard sieve to a particle size of <1 mm. Further reduction of the >1 mm fraction was conducted using a 600 rpm Fritsch P-14 rotary mill for an hour and a 280 mm² macrocrusher (model number 46-126) containing 10 mm steel balls. Finally, a laboratory ball mill with stainless steel balls was used to mill the samples to ~212 μm.

**Scrubber Solutions for Absorption of Sulfur Gases from the Thermal Treatments.** Two solutions were used as scrubber solutions. One liter of 1.1 M potassium hydroxide (KOH) solution was prepared by dissolving 64.34 g of KOH in deionized water and then diluting this solution with deionized water to the graduation mark of a 1000 mL volumetric flask. One liter of 1.1 M potassium hydroxide (KOH) solution was prepared by dissolving 64.34 g of KOH as scrubber solutions. One liter of 1.1 M potassium hydroxide (KOH) solution was prepared by dissolving 64.34 g of KOH as scrubber solutions. One liter of 1.1 M potassium hydroxide (KOH) solution was prepared by dissolving 64.34 g of KOH as scrubber solutions. One liter of 1.1 M potassium hydroxide (KOH) solution was prepared by dissolving 64.34 g of KOH as scrubber solutions. One liter of 1.1 M potassium hydroxide (KOH) solution was prepared by dissolving 64.34 g of KOH as scrubber solutions. One liter of 1.1 M potassium hydroxide (KOH) solution was prepared by dissolving 64.34 g of KOH as scrubber solutions. One liter of 1.1 M potassium hydroxide (KOH) solution was prepared by dissolving 64.34 g of KOH as scrubber solutions. One liter of 1.1 M potassium hydroxide (KOH) solution was prepared by dissolving 64.34 g of KOH as scrubber solutions. One liter of 1.1 M potassium hydroxide (KOH) solution was prepared by dissolving 64.34 g of KOH as scrubber solutions. One liter of 1.1 M potassium hydroxide (KOH) solution was prepared by dissolving 64.34 g of KOH as scrubber solutions. One liter of 1.1 M potassium hydroxide (KOH) solution was prepared by dissolving 64.34 g of KOH as scrubber solutions. One liter of 1.1 M potassium hydroxide (KOH) solution was prepared by dissolving 64.34 g of KOH as scrubber solutions. One liter of 1.1 M potassium hydroxide (KOH) solution was prepared by dissolving 64.34 g of KOH as scrubber solutions. One liter of 1.1 M potassium hydroxide (KOH) solution was prepared by dissolving 64.34 g of KOH as scrubber solutions. One liter of 1.1 M potassium hydroxide (KOH) solution was prepared by dissolving 64.34 g of KOH as scrubber solutions. One liter of 1.1 M potassium hydroxide (KOH) solution was prepared by dissolving 64.34 g of KOH as scrubber solutions.

The samples were added to the scrubber bottles connected as shown in Figure 1. Heating at 950 °C makes it likely that the samples have experienced secondary degasification but have not gone beyond the region of active thermal decomposition but not gone beyond this region. Second, coals undergo an additional set of reactions in a temperature region of 550–900 °C, known as the region of secondary degasification. By similar reasoning, heating at 950 °C makes it likely that the samples have experienced secondary degasification but have not gone beyond. The scrubber solutions were connected to the furnace as soon as the sample was introduced at room temperature, the air or N₂ flow was started at a rate of approximately 80 mL/min, and the gas flow bubbled through the scrubbers all through heat-up, the reaction, and cool-down. After the experiment, the residue of each sample was left in the furnace to cool to room temperature before removal. The heat-up rate of the furnace was 10 °C/min, whereas the cooling rate was 3 °C/min. All solid and liquid samples that were generated from the thermal treatment experiments were prepared and submitted for the analyses as mentioned in the Analytical Methods section.

**ANALYTICAL METHODS**

Samples A–C were submitted to the South African Bureau of Standards (SABS), Coal and Mineral Technologies laboratories for the analyses of the forms of sulfur. The ISO 157 method, Standard Part 11, 1959, was used to determine the concentrations of the different sulfur forms (pyrite sulfur, sulfate sulfur, and organic sulfur) as well as mineral sulfur (the sum of pyrite and sulfate sulfur). The percentages of the total sulfur in the different samples were determined through an A632 sulfur determinator using the ASTM D4239 method, ASTM Standards, D2492, Philadelphia, 1988.

The following test methods were used to determine the moisture content (ISO 11722:1999), ash (ISO 1171:2010), volatile matter content (ISO 562:2010 and ISO 1170), and ultimate analysis (ISO 12902-CHN instrumental method). The percentage of the dried basis volatile matter and the percentage of volatile matter(ar) are calculated by the following formulas: %volatile matter (db) = volatile matter(ad) × 100/100 − M(ad) and %volatile matter(ar) = volatile matter(ad) × 100 − M(ar)/100 − M(ad), where ar is as received, db is dried basis, ad is air-dried, and M is the moisture content, which are included in the standard methods, ISO 562:2010 and ISO 1170, respectively.

The original coal samples, along with residual char or ash samples and yellow precipitate samples from the scrubber solutions, were subjected to mineralogical analysis using a PANalytical Inc. X-ray diffraction (XRD) instrument with Rietveld-based X'Pert HighScore Plus Software. Each solid sample was spiked with 20% Si (Aldrich, 99.9% purity) and was subsequently micronized in a McCrone micronizing mill. The prepared solid samples were submitted for determination of the concentrations of amorphous compounds and crystalline phases. Residual char and ash samples were also subjected to X-ray fluorescence (XRF) analysis using the fusion method, where the solids were fused into a borosilicate disk and analyzed by ARL 9800XP Thermo-Scientific XRF spectrometry techniques.

The postreaction cadmium acetate and potassium hydroxide scrubber filtrates from the experiments were mixed (acetic acid was added to prevent the precipitation of cadmium hydroxide) and submitted to the NWU Eco-analytical Laboratory (Centre for Water Science) for ion chromatography (IC) analysis to determine the concentration of sulfate. About 20 μL of the liquid sample was injected into a Metrosep A Supp 4-250/4
anion-exchange column (stationary phase), which was held at 25 °C, with a pressure of 5.83 MPa and a flow rate of 1.00 mL/min. IC analyses of samples were done under isocratic conditions using disodium carbonate (Na₂CO₃) (1.8 mmol/L) and sodium hydrogen carbonate (NaHCO₃) (1.7 mmol/L) as mobile phase with a pH 10.30. The standards used during the IC analysis included fluoride 2.0 mg/L, chloride 2.0 mg/L, nitrite 5.0 mg/L, bromide 10.0 mg/L, and nitrate 10.0 mg/L. CdS precipitate samples were also submitted for inductively coupled plasma mass spectrometry (ICP-MS) analysis (at NWU) for determination of the concentrations of Cd, S, Fe, C, Pb, Al, and Mg.

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**Notes**
Any opinion, finding, conclusions, or recommendations expressed in this material are that of the author(s) and the NRF does not accept any liability in this regard. The authors declare no competing financial interest.

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