



A study of the volatilisation of coal sulphur during combustion under conditions similar to a blast furnace raceway

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ABSTRACT

Pulverised coal injection (PCI) is used in ironmaking to replace expensive and energy intensive coke with coal, reducing overall costs and greenhouse gas emissions. As the coke making process removes some of the sulphur present in coal, the utilisation of PCI results in the admission of greater levels of sulphur into the blast furnace. The increased sulphur levels could potentially lead to an increase in costs and energy usage related to hot metal sulphur removal processes. In an increasingly volatile market, the ability to make use of higher sulphur coals is also of both financial and logistical relevance.

This work aims to produce a more thorough understanding of the transformation of sulphur introduced through PCI into the blast furnace, leading to changes in coal selection, blending, or mitigation efforts.

The volatilisation of sulphur from four coals used in PCI was investigated using a drop tube furnace (DTF) to produce conditions similar to a blast furnace raceway. Chars and flue gases were analysed using a range of techniques, including X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis, and wet chemistry methods.

The coal's burnout was found to be the biggest factor in coal sulphur volatilisation. It was found that a coal's volatile matter content was a key indicator into the volatility of a coal's sulphur content; it influences the rate of a coal's burnout, the availability of hydrogen for the formation of H₂S, and the reactivity of the produced chars. Coals with higher volatile matter contents are more likely to volatilise their sulphur component at shorter residence times than coals with lower volatile matter contents. The bonding of volatilised sulphur to nascent char was seen in coals with lower volatile matter contents. The sulphur forms present in the initial coal samples were shown to influence the sulphur forms found in the collected chars.

1. Introduction

A 2013 study found that globally, the iron and steel industry contributed to 24% of all greenhouse gas emissions from industrial sources [1]. Blast furnace operation is a highly energy consuming and polluting process accountable for about two thirds of global hot metal production from ore [2,3]. Pulverised coal injection (PCI) is a commonly used method of reducing the reliance on expensive coking coals; improving yield of hot metal per tonne of raw materials; and reducing the greenhouse gas emissions associated with the coking process [4,5]. The exploitation of cheaper, high sulphur coals in PCI could help to alleviate some of the financial pressure that the steel industry currently faces [6]. However, increasing sulphur levels in the blast furnace could lead to an increase in the hot metal sulphur level, adversely affecting the mechanical properties of the produced steel by increasing brittleness in a heated state (red-shortness). [3] Additional hot metal sulphur therefore results in greater expense and energy usage

in the desulphurisation plant further down the steelmaking process and would likely require a change in the blast furnace slag chemistry, which may in turn result in additional energy consumption, decreasing furnace productivity [7]. Increased sulphur levels could also potentially lead to an increase in H₂S emissions from the blast furnace top gas. As a corrosive gas, this could potentially lead to issues in plants where the blast furnace gas is utilised, however due to the presence of scrubbing technologies, this could potentially prove to be the most efficient phase in which sulphur can be removed from the blast furnace and is a key factor in the undertaking of this study.

Sulphur is an undesirable, yet important component of coal. It can be found in varying amounts, from trace quantities to high quantities in excess of 10% of the coal mass [8,9]. Sulphur compounds can be described as either organic or inorganic. These can then be defined further as a range of sulphur forms [6,10–12]. The distribution of sulphur forms is believed to correlate to a range of factors, including

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Table 1
Proximate analyses, distribution of sulphur forms, and 35 ms char reactivity.

Coal	Proximate analysis/wt% (dry basis)			Sulphur forms/wt% (dry basis)				35 ms char reactivity
	Fixed carbon	Volatile matter	Ash	Pyritic sulphur	Sulphatic sulphur	Organic sulphur	Total sulphur	$t_{0.5}/m$
A	71.9	20.9	7.2	0.04	0.00	0.24	0.28	140.6
B	60.9	34.8	4.3	0.01	0.07	0.35	0.43	123.9
C	68.9	21.2	9.9	0.05	0.02	0.32	0.39	178.3
D	58.1	38.5	3.4	0.05	0.08	0.26	0.39	86.4

coal rank, maceral composition, and geological conditions [13–17]. Pyritic and organic sulphur often exist in varying quantities in most coals, whilst sulphates are usually found in more weathered coals and their relative quantity in coal is usually lower than that of pyrite and organic sulphur [14,18–20].

Organic sulphur compounds are a major component in most coals and can often account for over 50% of sulphur in coal [13,21]. Organic sulphur is fixed within the chemical structure of the coal matrix [22]. The distribution of organic sulphur within the coal matrix can be correlated to the rank of coal. As coal rank increases, aromaticity in the coal also increases, leading to increases in the relative proportions of aromatic and heterocyclic organic sulphurs within the coal [6,12,23]. Several authors have shown that organic sulphur species showing aromatic and heterocyclic properties also show an increase in thermal stability [6,12,15,24,25]. It is hypothesised that coals with higher proportions of aromatic and heterocyclic organic sulphur would therefore less readily volatilise their organic sulphur when being injected into the blast furnace during PCI. Discovering whether this influences the amount of sulphur that is transferred to the hot metal or the slag could lead to the introduction of several energy and cost saving measures.

This study aims to explore the transformations of sulphur species in injected coals throughout an environment with conditions similar to the raceway region of a blast furnace, formed where the hot air blast and pulverised coal is injected through the tuyeres at the base of the furnace. Current knowledge of sulphur within the blast furnace is heavily focused upon coke, hot metal, and slag sulphur, with significantly less information available regarding gaseous sulphur or the impact of sulphur from PCI within the furnace. The ever increasing constraints placed upon the steel industry, such as more stringent emissions targets, requirements to reduce costs, and the availability of natural resources, have been an influencing factor in the exploration of this topic. It is hypothesised that by studying the volatilisation of sulphur from pulverised coal injection, a better understanding of the transformation of sulphur throughout the blast furnace can be achieved. The knowledge could potentially then be exploited in coal selection and blending, blast furnace operation, and via changes to steelmaking processes. As there is no established method of studying sulphur volatilisation from PCI, this study also seeks to create a repeatable method of analysing future injected fuel sulphur.

2. Material and methods

2.1. Materials

A selection of four coals used for pulverised coal injection were supplied by TATA Ltd. for use in this study. Two high volatile bituminous coals and two medium volatile bituminous coals were used. The coals were ground to a pulverised size specification ($100\% < 300 \mu\text{m}$, $50\% < 75 \mu\text{m}$) using a TEMA disc mill and classified by dry sieving using BS ISO 1953:2015. The classified samples were oven dried at 105°C prior to proximate analysis as discussed in Section 2.2.1. The analysis results are displayed in Table 1 along with the distribution of sulphur forms discussed in Section 2.2.4 and the 35 ms char reactivity discussed in Section 2.2.5.

2.2. Methods

2.2.1. Proximate analysis

Proximate analysis was conducted using BS ISO 17246:2010. In this standard, coal is analysed for moisture, ash, and volatile matter. In this work, the results are reported on a dry basis and so the moisture content is disregarded. Drying was undertaken prior to testing by heating the samples at 105°C for an hour before being cooled in a desiccator.

Fixed carbon (C_{fix}) is calculated in Eq. (1). Ash (A) was measured using the method described in BS ISO 1171:2010. The ash is what remains after the coal has been incinerated in air and is derived from inorganic complexes present in the original coal and associated mineral matter. In this case, samples were heated at 500°C for an hour before being heated at 815°C for an hour to establish the ash mass. The volatile matter (V) was measured using the method described in BS ISO 562:2010. The volatile matter of a coal is determined as the mass portion that is lost when the coal is heated in the absence of air at 900°C for 7 min.

$$C_{fix} = 100 - (A + V) \quad (1)$$

2.2.2. Drop tube furnace

A drop tube furnace (DTF) was used to replicate conditions similar to the raceway region of a blast furnace coal injection system. The key conditions being high temperatures, high heating rates, and a dynamic, dilute particle phase [26]. In this study, coal samples were passed through the DTF at a temperature of 1100°C with residence times of 35 ms, 100 ms, and 700 ms. 1100°C is a typical hot blast temperature and specific to the application being studied [27]. Residence times were controlled by altering the length of a moveable water cooled collection probe up to a maximum length of 1.2 m from a water cooled inlet feeder. The coal samples were fed into the top of the furnace with a feed rate of 30 g/h, entrained into a laminar air flow of 20 l/min. The partially burnt coal (char) was collected in a cyclone collector at the bottom of the furnace. The exhaust gas was then passed through a cellulose filter, which collects a volatile mixture of tar and fine particulates. The flue gas was sampled post filter for gas analysis. The method expands upon those used by previous users of the furnace [5,28–30].

2.2.3. Gas analysis

Gas analysis of the DTF flue gas was conducted using a Testo 350XL. SO_2 , and H_2S levels were measured in real time and tracked using Testo's easyEmission software. The Testo 350XL sampled the DTF flue gas at a rate of 1 l/min in parallel to the exhaust line. Calibrations were performed by Testo Limited prior to the commencing of the study and checked regularly with calibration gases provided by Rockall Safety Limited.

2.2.4. Analysis of sulphur content

The determination of sulphur forms present in the coal and 35 ms char samples was conducted using the process described in BS 1016-106.5:1996. The method described by the standard allows the identification of pyritic and sulphatic sulphur in a coal sample. This is done by utilising the different solubilities of pyrites and sulphates in dilute hydrochloric and nitric acids under reflux conditions, such that each can be taken into solution successively and determined directly. Organic sulphur (S_o) is calculated from the measured total sulphur

(S_T), sulphatic sulphur (S_S), and pyritic sulphur (S_P) using Eq. (2). The 35 ms char was selected for this additional analysis as it was deemed the most relevant for consideration of the initial volatilisation of sulphur in the blast furnace raceway. As the coals have relatively low sulphur contents, large quantities of coal and char were required for utilisation of this standard. This made analysis of the 100 and 700 ms chars impractical as time restraints prevented the production of the required amounts of char.

$$S_O = S_T - (S_S + S_P) \quad (2)$$

Total sulphur of the coals and chars was measured using a LECO SC144DR carbon and sulphur analyser. The analyser combusts the sample in an excess of oxygen and measures the produced CO_2 and SO_2 , comparing this with the inputted sample mass to calculate the percentage masses of carbon and sulphur in the sample.

The burnout of the coal samples was used in production of a sulphur mass balance. The burnout (%) was calculated using the ash tracer method, as shown in Eq. (3), using the ash content of the coal (A_{coal}) and the ash content of the corresponding char (A_{char}). The ash tracer method is a commonly used method of analysing the mass lost during partial combustion of a sample. The method assumes that the coal ash remains conserved in the char residue under the test conditions and that no ash species are volatilised. This assumption may therefore lead to a small degree of error; however, the ash tracer method is a more reliable way of measuring the combusted portion of the coal in this instance as experimental constraints prevent accurate mass measurements before and after the coal is passed through the DTF. It is used as a normalising value in the production of the sulphur mass balances, an adaptation of its use in previously published work [29].

$$\text{Burnout}(\%) = \frac{10^4(A_{char} - A_{coal})}{A_{char}(100 - A_{coal})} \quad (3)$$

Error values were calculated by propagating the standard deviations of the burnout and total sulphur measurements.

2.2.5. Char reactivity

Char reactivity was analysed using a Mettler-Toledo TGA/DSC. Samples were first devolatilised in nitrogen to remove any remaining volatile matter from the char, allowing the reactivity of the remaining char to be analysed. Samples of 10 mg were held at 900 °C in a CO_2 flow of 100 ml/min for 420 min. Mass loss was measured against time and used to calculate char conversion in Eq. (4) below. 900 °C was selected as the experimental temperature as this temperature can be found in the blast furnace above the cohesive zone where unburnt char may accumulate and interact with gaseous CO_2 [31].

$$x = \frac{m_{initial} - m}{m_{initial} - m_{final}} \quad (4)$$

where x is the char conversion, $m_{initial}$ is the initial sample mass, m is the instantaneous mass, and m_{final} is the mass of the final char ash. The results of this experiment are expressed in the gasification figure $t_{0.5}$, which is the time in minutes taken to reach 50% char conversion. The lower the $t_{0.5}$ number, the more reactive the char [30].

2.2.6. XPS

A Kratos Axis Ultra DLD system was used to collect XPS spectra using monochromatic Al $K\alpha$ X-ray source operating at 144 W (12 mA \times 12 kV). Data was collected with pass energies of 160 eV for survey spectra, and 20 eV for the high-resolution scans with step sizes of 1 eV and 0.1 eV respectively. Samples were mounted by pressing on to doubled sided Scotch tape (type 665) which was attached to a glass slide to ensure the sample was floated from the spectrometer. Analysis was performed using the Hybrid mode, which utilises a magnetic immersion and electrostatic transfer lenses to enhance electron detection. Data was collected over a rectangular analysis area of approximately 300 \times 700 μm^2 . A magnetically confined low energy electron charge compensation system was used to minimise charging of the sample surface, and

all spectra were taken with a 90° take of angle. A base pressure of ca. 1×10^{-9} Torr was maintained during collection of the spectra. Data was analysed using CasaXPS (v2.3.24) after subtraction of a Shirley background and using modified Wagner sensitivity factors as supplied by the manufacturer.

3. Results and discussion

By analysing the volatility of coal sulphur in the DTF, it may be possible to predict the effect that each of the component sulphur forms may have on the sulphur chemistry of a blast furnace. This could prove to be crucial information when considering coal selection or blending as it could minimise the need for costly desulphurisation processes or improve blast furnace efficiency by allowing changes to slag chemistry. By manipulation of coal blends, it may be possible to mitigate against the formation of undesirable sulphur compounds within the blast furnace by removing certain sulphur sources or by exploiting specific coal properties that affect sulphur transformation within the furnace.

3.1. Char burnout, 35 ms char reactivity, and total sulphur volatilisation

The relative burnouts of the coal chars can be seen along with the relative volatilisation of the coal sulphur to H_2S or SO_2 in Fig. 1, whilst Fig. 2 shows the distribution of sulphur between the solid and gaseous phases at each of the studied residence times. The char reactivity of the produced 35 ms chars can be found in Table 1.

Coal A has the lowest total sulphur of the four tested coals. After 35 ms, the majority of the original sulphur remains in the char with only 29.3% of the sulphur being liberated to H_2S . The burnout of Coal A's 35 ms char was quite low, only 11.1%. This was much lower than the burnouts of all the other coals at 35 ms. After 100 ms, 50.2% of sulphur was liberated to H_2S with a burnout of 35.6%. After 700 ms, 98.3% of sulphur was liberated to H_2S with a burnout of 95.0%.

Coal B had the highest total sulphur of the four tested coals. After 35 ms, 66.6% of the sulphur had been liberated to H_2S with a 48.8% burnout. The result after 100 ms is comparable to the 35 ms residence time, with 65.1% of sulphur liberated with a burnout of 55.8%. The similarity between the two residence times is likely explained by the large volatile matter content in the coal (34.8%) being quickly liberated in the first 35 ms. In the same sense, the similarity in the amount of sulphur liberated can likely be attributed in part to the liberation of less thermally stable sulphur compounds, such as aliphatic organic sulphurs or pyrite, and the survival of more thermally stable sulphur compounds in the char, such as thiophenes and sulphates, which has previously been shown to occur by several authors [11,12,24,32–35]. After 700 ms, 99.5% of the sulphur has been liberated with a 98.2% burnout. In this instance, SO_2 is the major gaseous product. This is thought to be primarily produced by the oxidation of H_2S as opposed to being directly released from the coal.

Coal C liberated 61.3% of its sulphur at 35 ms with a burnout of 43.0%. At 100 ms, the sulphur liberated was 54.4% with a burnout of 45.6%. At 700 ms, 98.3% of sulphur was liberated at 95.4% burnout. H_2S remains the major gaseous product at 700 ms with a smaller fraction of SO_2 being produced. Coal C showed a larger initial volatilisation of sulphur than the other medium volatile coal, Coal A, and was more closely following the trend of the high volatile coals, Coals B and D. Coal C's initial rate of burnout is also higher than Coal A's, but not quite as great as the highly volatile coals, Coals B and D. Why Coal C does not continue to behave like Coals B and D may be explained by the reactivity of the produced char. Table 1 shows that Coal C produced the least reactive 35 ms char. Reactivity of a char has been linked to the presence of pores in the char, which would allow for the increased flow of gases into the char particle [30]. This would likely accelerate the decomposition and volatilisation of the remaining, non-volatile char particle.

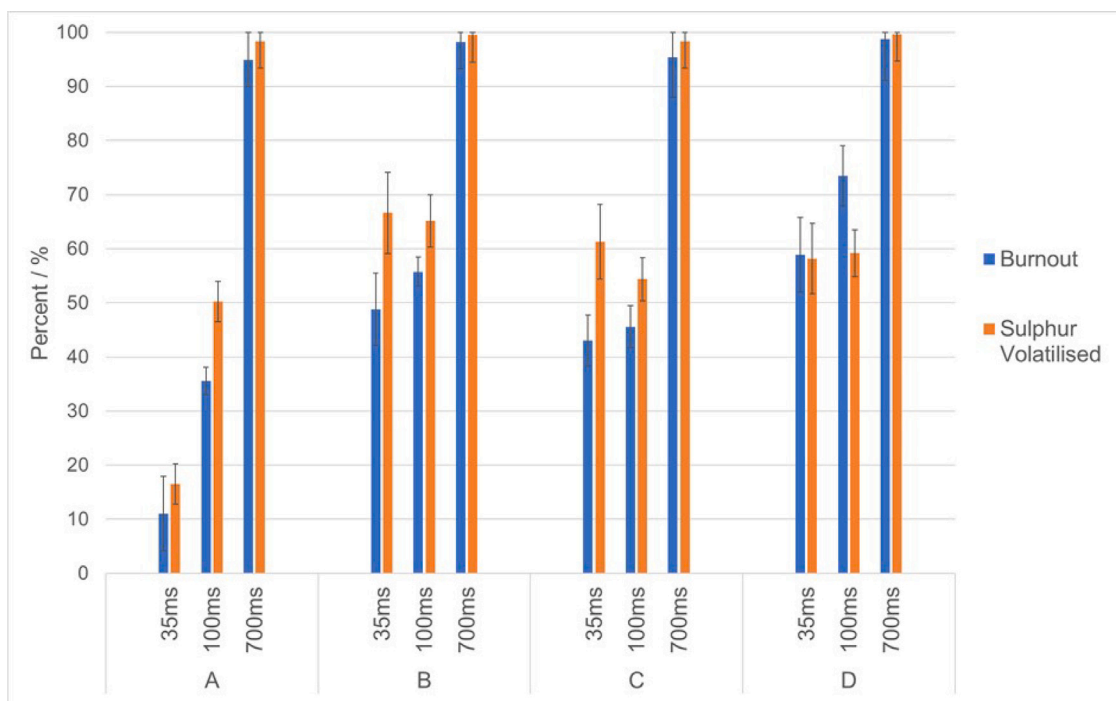


Fig. 1. Relative burnouts and coal sulphur volatilisation to H₂S or SO₂ of DTF 35 ms, 100 ms, and 700 ms chars.

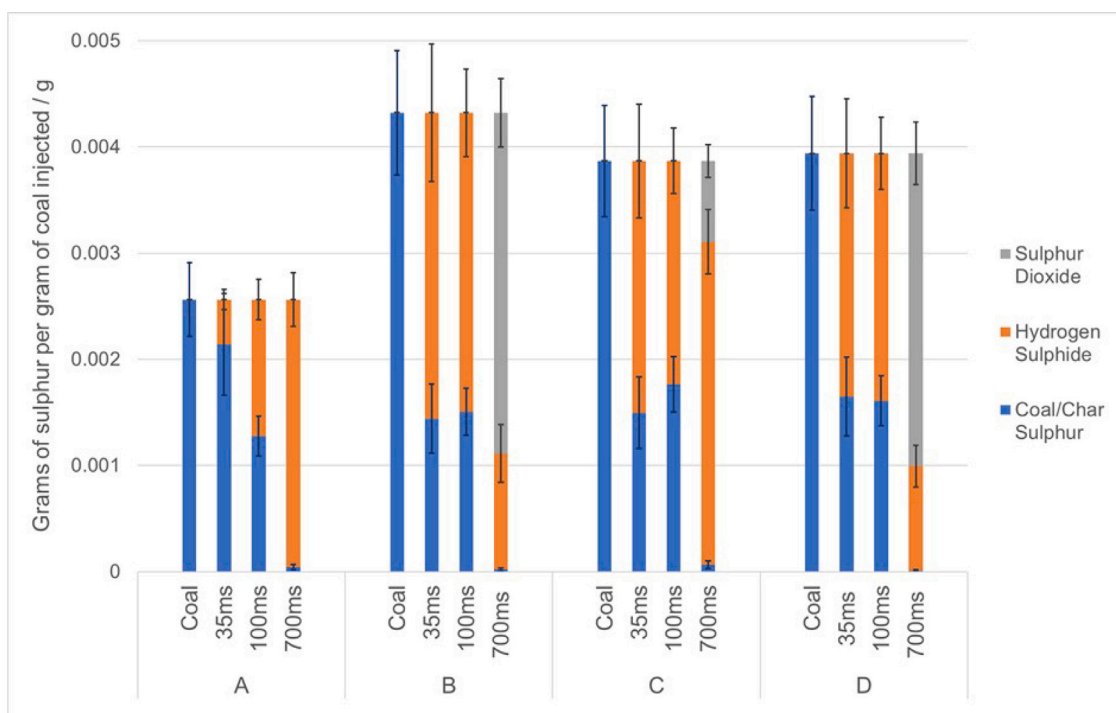


Fig. 2. Distribution of sulphur in sampled coals, DTF exhaust gases, and 35 ms, 100 ms, and 700 ms chars.

Coal D liberated 58.2% of its sulphur at 35 ms with a burnout of 58.9%. At 100 ms, 59.2% of sulphur was liberated with a burnout of 73.5%. This is the largest change in burnout between 35 ms and 100 ms, whilst maintaining only a small change in the amount of sulphur liberated, supporting the idea that most of the less thermally stable sulphur compounds are liberated in the first 35 ms. After 700 ms,

99.7% of sulphur is liberated with a burnout of 98.8%. SO₂ is the major gaseous product.

Comparing the results of each coal, the emission of coal sulphur in the DTF appears to be occurring in a two-step process, with the decomposition of less thermally stable sulphur compound occurring at lower residence times, with the decomposition of more stable sulphur

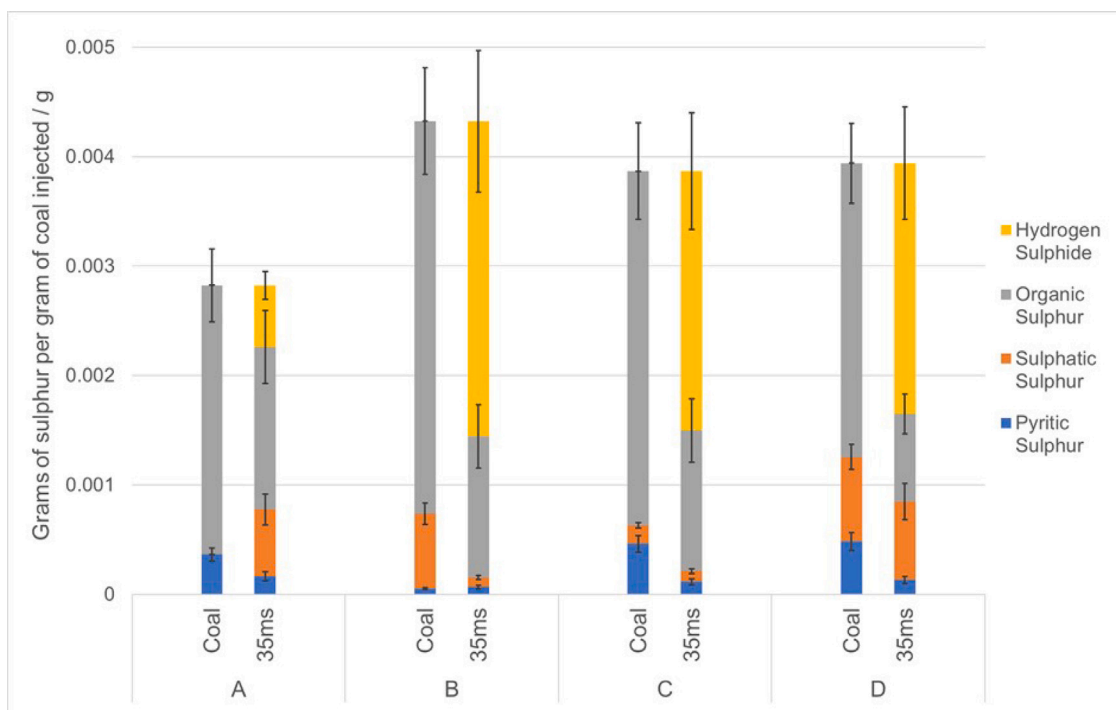


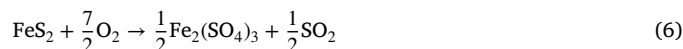
Fig. 3. Distribution of sulphur species in sampled coals, DTF exhaust gases, and 35 ms chars.

compounds occurring at some point between 100 ms and 700 ms upon combustion of the remaining, non-volatile component of the coal molecule.

The heterogeneous nature of coal, along with the dynamic interactions in the DTF are likely responsible for the measured increase in sulphur retained in the chars between the 35 ms and 100 ms residence times of Coals B and C. The differences are within the scope of experimental error and assumed not to be as a result of any one influencing factor. SO_2 is primarily produced by the oxidation of the newly produced H_2S [36]. Whilst the DTF is an environment where oxygen is in excess for the complete combustion of the coal and any intermediary compounds released upon the decomposition of the coal, other factors likely limit the rate at which the combustion of H_2S occurs. The coals with the greater volatile matter content, which volatilise their sulphur more quickly, have produced the greatest quantities of SO_2 at 700 ms, whilst the coal with lowest volatile matter content has not produced any SO_2 at 700 ms. Coals with higher volatile matter contents often produce chars with large pores, which can be identified by their increased char reactivity as shown in Table 1 [30]. This could possibly accelerate the decomposition of the remaining char, volatilising any sulphur within. By volatilising at an earlier residence time, sulphur compounds will have longer to oxidise to SO_2 before leaving the DTF.

3.2. Distribution of solid sulphur forms between coals and 35 ms chars

The determination of sulphur forms experiment allowed the identification of the sulphur forms in the coals and 35 ms chars. From this, it is possible to show which sulphur forms were volatilised to H_2S in the DTF. The results are shown in Fig. 3. The sulphur in Coal A was shown to be primarily organic, with a small portion of pyrite and no detected sulphates. In the 35 ms char, the portions of pyrite and organic sulphur decreased by 54.2% and 39.7% respectively, whilst sulphates were also detected. This could be because of the oxidation of portion of the coal pyrite to iron (III) sulphate by a mechanism such as the one reported by Schwab and Philinis below, or by the reaction of gaseous sulphur forms with calcium or iron oxides [37].



With Eq. (6) possibly being a sum of the equations below.



Schwab and Philinis reported that within the range of 400–500 °C, the oxidation of pyrite proceeds chiefly via Eq. (5). The oxidation of pyrite by Eq. (6) was found to only contribute a minor proportion of sulphate formation with the rate of reaction decreasing with increasing temperature, however that experiment was conducted at a lower temperature, over a much longer duration, and without the presence of combustible coal which could limit the amount of oxygen available for these reactions to occur [37]. The low burnout of Coal A's 35 ms char may produce conditions where the excess oxygen in the DTF is able to react with solid sulphur forms to produce sulphates, as opposed to being consumed by reacting with any volatilised hydrocarbons. No SO_2 was detected by the Testo 350XL, suggesting that any produced SO_2 was either subsequently trapped within the char, or that the amount released was under the limit of detection.

Coal B was shown to contain primarily organic sulphur. A small sulphate content and a very small pyrite content was measured. After 35 ms, the char had a burnout of 48.8% whilst 66.6% of the sulphur had been liberated. 64.1% of the organic sulphur was volatilised, whilst 87.2% of the sulphate content was volatilised. Pyrite content measured a slight increase, however was within range of experimental error.

In contrast to Coal A, Coal B demonstrated a high burnout at 35 ms, likely due to its increased volatile matter content. Not only would this likely raise the temperature of the coal particles whilst passing through the DTF due to the increased amount of combustion, but also consume a greater amount of oxygen, possibly producing an area of localised oxygen deficiency around the coal particles and becoming comparable to flash pyrolysis conditions. The increased volatile matter content of Coal B would also produce a larger amount of H_2 upon thermal decomposition. Gu et al. showed that a H_2 atmosphere would increase the volatilisation of coal sulphur during pyrolysis, encouraging the formation of H_2S [32]. The combination of these conditions may be

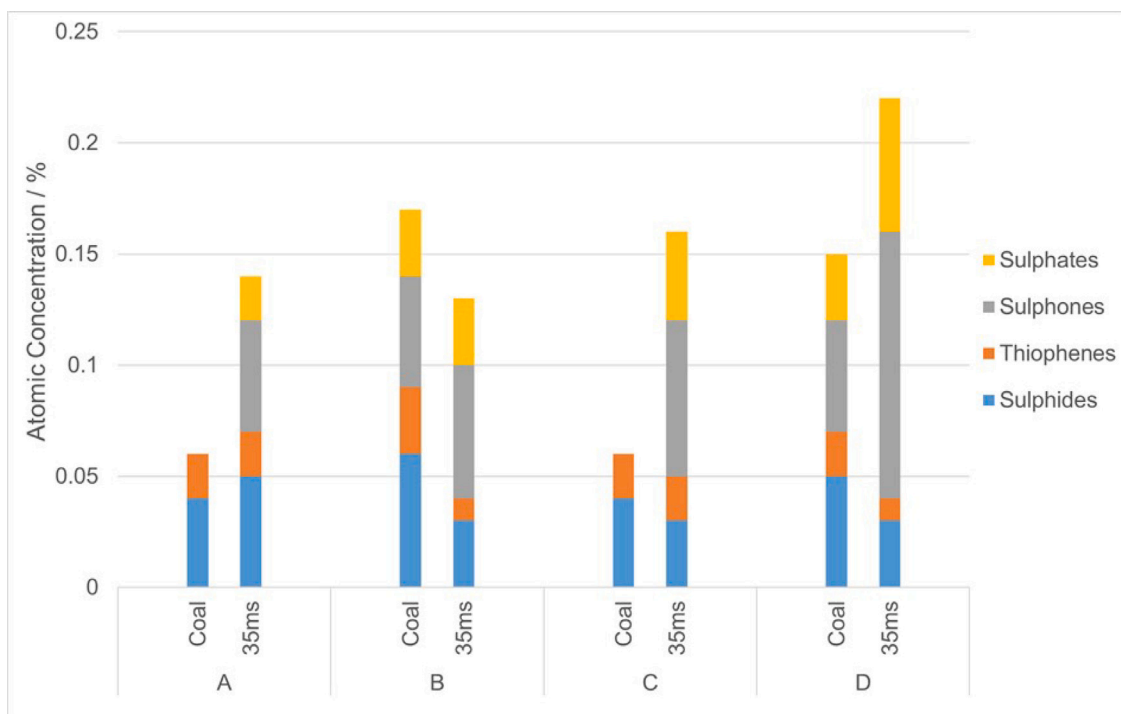


Fig. 4. XPS measurements of surface sulphur species on sampled coals and 35 ms chars.

produce enough of a difference between the two coals to explain why sulphates are formed in Coal A, but removed from Coal B.

Sulphates in coal are primarily calcium or iron sulphates [18–20]. Calcium sulphate is a very thermally stable compound, not readily decomposing at temperatures under 1000 °C. Iron sulphates, however, are known to decompose at much lower temperatures and therefore, this suggests that sulphates in Coal B are primarily iron sulphates [34]. The thermal decomposition of sulphates usually leads to the emission of SO₂, however, none was detected in this case. It is theoretically possible to draw a series of reactions in which H₂S can be produced from iron sulphates without the release of comparable amounts of SO₂. Mullens et al. investigated the reductive pyrolysis behaviour of iron (II) sulphate (FeSO₄) and iron (III) sulphate (Fe₂(SO₄)₃). It was shown that iron (II) sulphate could be reduced to troilite (FeS) in the reaction below [34].



If conditions in the DTF could be compared to flash pyrolysis, then via this reaction pathway, it is possible that iron sulphates could thermally decompose without producing enough SO₂ to be above the limit of detection of the Testo 350XL.

The majority of sulphur in Coal C was found to be organic, with a small pyrite portion and a smaller sulphate portion. After 35 ms, the char had a burnout of 43.0% and had liberated 61.3% of the sulphur present in the coal. The changes in sulphur forms were unsurprising with 75.1% of pyrite, 60.3% of organic sulphur, and 43.0% of sulphates being volatilised. As mentioned in Section 3.1, Coal C has an unexpectedly high burnout and volatilisation of sulphur. With large portions of all sulphur forms being volatilised,

The sulphur in Coal D, like the other three coals, was primarily composed of organic sulphur compounds. It did have the highest proportion of inorganic sulphur, however, with pyrite and sulphates both being measured. After 35 ms, the char had a burnout of 58.9% with 58.2% of the original sulphur being liberated. Of this, 72.9% of the pyrite and 70.1% of the organic sulphur was volatilised. Only 7.5% of the sulphates were lost. This is indicative of the presence of calcium sulphates in Coal D that are not easily thermally decomposed.

It can be seen from the results of the four coals that the volatilisation of most sulphur forms occurs at a greater rate than the burnout of the coals. In terms of which sulphur forms may be exiting the raceway region in a blast furnace environment, considering the burnout of a coal may allow some ability to predict the sulphur containing products. Coals with high burnouts will likely behave predictably in terms of the sulphurous products of their partial combustion, volatilising the majority of the sulphur present, leaving mainly the more thermally stable sulphur compounds in the char. Coals with lower burnouts may behave differently, seeing portions of the sulphur content oxidised in the solid phase as opposed to volatilised. However, this conclusion cannot be made with the current amount of low burnout coals analysed and additional investigation would need to be completed.

By looking at the work of previous authors, it could be hypothesised that pyrite would decompose readily under the conditions in the DTF and likewise therefore be thought to also decompose readily within the blast furnace raceway, however small amounts of pyrite have been detected in all of the 35 ms chars [12,37–39]. This may be explained by Maes et al. who studied the desulphurisation of pyrite. The decomposition of pyrite to H₂S and elemental iron was shown to occur in a two-step process. The conversion of pyrite to troilite is described by the equation below, whilst the conversion of troilite to iron is already described above in Eq. (10) [38].



Maes et al. showed that the presence of a small amount of H₂S in the atmosphere could reverse the reduction of troilite in Eq. (10), therefore inhibiting the desulphurisation process. The reversible nature of pyrite desulphurisation may therefore explain why pyrite is still detected in all of the 35 ms chars, despite being one of the more thermally unstable sulphur forms found in coal. Considering this, it may be possible for small portions of an injected coal's pyrite content to survive the blast furnace raceway region within any unburnt char.

3.3. XPS analysis of coals and 35 ms chars

XPS was used to show the differences in the sulphur chemistry on the surface of the coal before and after passing through the DTF

with a residence time of 35 ms. Where the analysed portion of sample is representative of the whole sample surface, atomic concentration is comparable to an element's percentage concentration [40]. It is assumed in this instance that by having the scanning area being large enough to encompass several coal/char particles that this is achieved, however this is a potential source of error.

Examining Fig. 4, it is interesting to see that none of the coals or chars reach the same sulphur contents as the bulk values obtained from the LECO in Fig. 2. The differences are quite large, with the surface measurements being between 20%–65% of the bulk sulphur measurements. Whilst this could be indicative of systematic error, each instrument was carefully calibrated prior to use and so confidence in the measured values is high. The data could therefore be indicating a variation between the surface and bulk sulphur values. This could be explained somewhat by the presence of inorganic sulphur compounds, which tend to exist as larger inclusions within the coal as opposed to being distributed more evenly within the coal macromolecule.

It can be seen for three of the four coals, that the relative atomic concentrations of sulphur compounds increase on the surface of the chars in comparison to the coals. The reduction in carbon content in the chars after their partial burnouts could possibly be identified as the reason for these changes, however as the rate of bulk sulphur volatilisation was greater than the rate of char burnout for three of the four coals, it would be expected that the relative sulphur content on the char surfaces would decrease as opposed to increase for those chars. This could therefore suggest that sulphur is migrating from the bulk of the coal molecule to the surface, in which sulphur is liberated within the core of coal particle but then bonds to nascent char on the surface of the particle. The phenomenon of released sulphur bonding to nascent char has been identified by several authors [10,23,35,41–43]. It is possible to see increases in the proportion of oxidised sulphur forms on the surfaces of the chars in comparison with the coals. This is not surprising to see in a post combustion sample. Generally, across the samples there is a reduction in less thermally stable sulphides, the maintenance or slight loss of more thermally stable thiophenes, and the maintenance or increase in oxidised sulphones and sulphates. This correlates well with the changes to the bulk sulphur forms shown in Section 3.2. By comparing the results of the XPS with the sulphur distributions discussed in the bulk samples in Section 3.2, the most notable changes are with the organic sulphur forms. Where in some coals, large decreases in bulk organic sulphur are seen, there are also large increases in the quantity of sulphones present on the surface. Sulphone can be produced by the oxidation of a sulphide or by the reaction of SO₂ with a hydrocarbon. The large increase in sulphones seen on the char surfaces and the lack of SO₂ measured by the Testo 350XL could be an indication of the reaction of produced SO₂ with nascent char.

4. Conclusion

Four blast furnace injection coals have been studied via use of a drop tube furnace. The presence of sulphur in iron produced in a blast furnace is costly and time consuming to remove, this work is a necessary part of understanding the fate of the sulphur from injection coals with a view to influencing the selection and blending of injected coals.

- The biggest contributing factor to the volatilisation of coal sulphur appears to be the burnout of the coal particle. The rate of coal burnout is often increased with increased volatile matter content, as was the case with the studied coals.
- Coals with lower volatile matter contents showed the largest increase in the presence of oxidised sulphur forms in the char. The formation of H₂S is known to be dependent on the availability of volatilised hydrogen, which itself is linked to volatile matter content. Where insufficient hydrogen is available, the bonding of volatilised sulphur to nascent char appears to occur.

- Coals with higher volatile matter contents not only produce higher char burnouts and more H₂S, but generally also produce more reactive chars. This could lead to the accelerated decomposition of the remaining, non-volatile component of the char, volatilising any sulphur within.
- The volatile matter content of a coal could therefore be considered a key indicator to the rate of sulphur volatilisation during pulverised coal injection.
- The volatilisation of sulphur from a coal appears to occur in a two stage process. During the combustion of the volatile matter content of a coal, less thermally stable sulphur compounds in the coal decompose, volatilising the sulphur. More thermally stable compounds do not decompose until the combustion of the remaining non-volatile coal macromolecule.
- The sulphur forms existing in the initial coal samples can therefore give an indication of the sulphur forms that could be found in any unburnt char.

CRediT authorship contribution statement

Chay A. Davies-Smith: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Julian M. Steer:** Conceptualization, Methodology, Supervision, Project administration, Funding acquisition. **Richard Marsh:** Supervision, Project administration, Funding acquisition. **David Morgan:** Formal analysis, Investigation.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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