

The Behaviour of Mineral Matter from Pulverised Coal Injection in the Blast Furnace Raceway

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<u>Abstract</u>

Coal injection into the blast furnace is used as a means of reducing cost, and improving output and energy efficiency. However, the coals injected all contain mineral matter which converts to ash upon heating and has various effects in the blast furnace.

Ash investigated in this thesis contained quartz, kaolinite, illite, calcite, dolomite, apatite and gypsum. The elements silicon, aluminium, iron, calcium, potassium, sodium, sulphur, titanium and phosphorus were identified in varying proportions. The behaviour of the ash and elements in the blast furnace is dependent on their relative amounts.

It was found that high fusion temperature (FT) occurred due to high levels of silicon and aluminium, found in quartz and clays, whereas low fusion temperatures were related to high calcium and magnesium, found in calcite and dolomite.

A drop-tube furnace (DTF) was used to prepare chars from coals and it was observed that the fusion temperature of the char ash increased with temperature and residence time. This was attributed to mullite formation and amorphous material formation in the DTF. The mullite and amorphous material were linked to increased ash fusion temperature.

In the DTF, alkali volatilisation generally increased with temperature and residence time. However in low FT ash, it was observed that volatilisation decreased at high residence time for two low FT ashes, thus these ashes were able to retain alkalis.

Sulphur release from the ash was found to increase with temperature and residence time in the DTF. Coals containing calcium in the form of carbonate minerals were able to fix sulphur into the ash in the form of anhydrite.

Combustion reactivity of ash added to coal was measured using Thermal Gravimetric Analysis (TGA), and found to act as diluent. The effect of ash on coke gasification reactivity was catalytic. Ashes with higher calcium showed higher catalytic behaviour.

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Table of Abbreviations and Nomenclature

Abbreviation	Name
AFT	Ash Fusion Testing/temperature
AI	Abrasion index
CCS	Carbon capture and storage
CRI	Coke reactivity index
CSR	Coke strength after reaction
DTF	Drop-tube furnace
EDS or EDX	Energy-Dispersive X-Ray Spectroscopy
FC	Fixed carbon
FT	Fusion Temperature
GCI	Granular coal injection
HGI	Hardgrove grindability index
HTA	High temperature ash/ashing
HV	High volatile
ICP-OES	Inductively coupled plasma optical emission spectroscopy
LV	Low volatile
MIF	Mineral Intensity Factor
MTA	Medium temperature ash/ashing
MV	Medium volatile
NBO/T	Non-bridging oxygen to tetrahedral atoms
PCI	Pulverised coal injection
PCR	Pulverised coal rate
PF	Pulverised fuel
RDF	Refuse derived fuel
SEM	Scanning electron microscope
TGA	Thermal Gravimetric Analyser / Analysis
tHM	Tonne of hot metal
VHTA	Very high temperature ash/ashing
VM	Volatile matter
XRD	X-ray diffraction
XRF	X-ray fluorescence
YGP	Yancy, Geer and Price (abrasion index test apparatus)

Chapter 1. Introduction

1.1 The Usage of Coal

Coal is one of the most important energy sources in the world accounting for some 38% of global electricity generation, with countries such as South Africa, China and Australia primarily relying on coal for electricity. Coal is responsible for 71% of the world's steel production and is also the major energy source used for the production of cement, requiring around 200 kg to produce a tonne of cement. Additionally, the waste material from the combustion of coal, namely ashes, slags and flue gas treatment residues, is used to supplement Portland cement. Coal can also be converted into liquid fuels (World Coal Association, 2019).

Figure 1 shows historical energy usage, with a future projection, across all sources of energy in the world. Looking at the mauve projection, it can be seen that coal usage is expected to stabilise over the next few years. This is because the growth of coal in India and China is offset by declining use of coal in North America and Europe.



Figure 1: World energy usage, past and forecast (IEA, 2018).

The energy trilemma is a three way approach to energy supply and it encapsulates cost, sustainability and security. Only when all three can be met, does a particular energy source satisfy the energy trilemma. For example, renewable energy is sustainable, but it may not be available on demand, and the cost may or may not be acceptable. Coal is an affordable and accessible fuel (World Coal Association, 2015) however its high carbon content leads to it emitting a large amount of CO₂

for the amount of energy produced (EIA, 2019), hence the long-term future of coal can be considered unsustainable (IEA, 2014). In light of growing energy demand, where coal is currently and forecasted to be used in greater amounts, a sustainable future for coals lies in the large scale deployment of Carbon Capture and Storage (CCS) and in building high efficiency supercritical coal plants (World Coal Association, 2015).

1.2 Coal Formation

Coal is a combustible carbonaceous sedimentary rock that predominantly formed from dead organic plant matter that was deposited several hundred million years ago. Successive generations of trees and vegetation died and accumulated in swampy areas, likely alongside shallow seas, lakes and rivers. This accumulation of organic material might take hundreds or thousands of years to build up. Sediment, such as mud and sand, was washed in by water and built up on top, sealing the plant accumulation. As the coal is buried under ever greater amounts of sediment, the temperature and pressure increases which causes the carbon content to increase, volatile matter to decrease, and hydrogen and oxygen contents to decrease (Speight, 2005; Speight, 2013). The extent of this process determines the type of coal formed going from lignite, subbituminous, bituminous, through to anthracite which is the highest ranking coal with the most carbon and the highest energy content, and is outlined in Table 1. The volatile matter for specific types of coals falls into set ranges, for example, low-volatile bituminous coal yields between 14 and 22% of volatile matter on a dry, mineral-matter-free-basis. These volatile matter yields helped with naming the coal samples used in this thesis on the basis of their volatile matter- a parameter that is typically used by blast furnace operators and is further discussed in Section 1.4.5 Pulverised Coal Injection. In addition, should the reader wish to compare the coals used in this thesis to a standard classification, they are able to do so using this table.

					Calorific
			Fixed Carbon and		Value on a
			Volatile Matter on a		Moist,
			Dry, Miner	al-Matter-	Mineral-
			Free-l	Basis	Matter-
					Free-Basis
			Fixed Volatile		Calorific
	Class	Group	Carbon	Matter	Value
			(%)	(%)	(MJ/kg)
High Rank		Meta-anthracite	> 98	< 2	
	Anthracite	Anthracite	92 – 98	2 – 8	
		Semi-anthracite	86 – 92	8-14	
	Bituminous	Low-volatile			
		bituminous	78 – 86	14 – 22	
		Medium-volatile			
		bituminous	69 – 78	22 – 31	
		High-volatile			
		bituminous A	< 69	> 31	> 32.6
		High-volatile			
		bituminous B			30.3 - 32.6
		High-volatile			
		bituminous C			26.8 - 30.3
	Subbituminous	Subbituminous A			24.5 - 26.8
		Subbituminous B			22.1 - 24.5
		Subbituminous C			19.3 - 22.1
Low	Lignite	Lignite A			14.7 - 19.3
Rank		Lignite B			< 14.7

 Table 1: Coal classification with carbon content, volatile matter and calorific value.
 (Information reproduced from ASTM D-388. 2004)

The organic material is formed of carbon, hydrogen, oxygen, and nitrogen containing structures which are the coal macerals. The organic coal macerals are analogous to the inorganic minerals (Ward, 2002) and there are three broad groups of maceral, namely, vitrinite, liptinite (also known as exinite) and inertinite, and these further divide into subcategories (Speight, 2013).

1.3 Challenges to the Steel Industry

Climate change poses a great threat to the future of our planet, and while there is rising awareness of the issue, global emissions are still increasing. This trend is set to continue as demand for energy, materials, food and transport rises and the population further increases.

Iron and steel account for 7% of global CO₂ emissions, and steelmaking is inherently carbon intensive. However, looking at the bigger picture, steel has several advantages over other materials. It is infinitely recyclable and widely recycled; and is essential to the building of a low carbon infrastructure thus yielding a net carbon

saving over its initial production (Ciftci, 2017). Since the 1960s, the energy required to make a tonne of steel has dropped by 61%. Nonetheless, ironmakers are starting to reach the limits of efficiency and although incremental increases in efficiency yield a reduction in carbon emissions, Mittal (2019) argues that an energy source other than coal, or else carbon capture, is required to actually tackle the problem. If the steel industry is to respond to the problem of climate change, it needs to act globally.

Reducing energy consumption is important for the environment and costs but Tata Steel IJmuiden describes how, in Europe, they are already reaching the limits with current technology and only through creating new innovative technologies, can they expect to make further significant reductions in CO_2 . With current blast furnace technology, Tata Steel produces 1.7 tonnes of carbon dioxide emissions for every tonne of steel produced, which is around the lowest in the world. However, work is being carried out on an alternative to the blast furnace and it is known as HIsarna, which is currently in its pilot stage. The HIsarna reactor is essentially a turbulent melting pot reactor into which oxygen, coal and iron ore is directly injected, yielding hot metal and slag, that is tapped off from the bottom of the reactor. HIsarna emits around 20% less carbon than the blast furnace because it eliminates the need to create coke, sinter and pellets, all of which are energy intensive processes in themselves. In addition, there is great potential for carbon capture and storage because the off gas is almost 100% CO_2 (Tata Steel, 2017).

Over the last decade the UK steel industry has faced serious pressure for a number of reasons including high energy costs, being undercut by Chinese imports, and a steel market running in overcapacity thus lowering the prices. In the UK, this resulted in the closure of SSI Redcar steelworks in autumn 2015, and job losses in Scunthorpe and Scotland (Williamson, 2018).

China is the largest consumer, producer and exporter of steel and increased its steel production to meet domestic consumption. As a result, China has been producing more steel than it can use, which has created a glut that has been exported at low prices to the rest of the world such as Europe and the United States. It is not a simple case of just producing less steel, because blast furnaces run continuously at predetermined rates with high fixed running costs. Running the furnaces at less than 80% output reduces raw material efficiency, and this is not even taking into account the capital cost of the steelmaking infrastructure itself. The result of this overcapacity is that China has been able to undercut European production costs where companies have described how environmental taxes and high electricity costs hamper their competitiveness. At the point in time when Tata Steel UK became unprofitable, US Steelmaking also experienced job losses (Pooler, 2015). Authorities in the US and EU responded by imposing tariffs on steel that is seen to be dumped (sold for less than it cost to produce) from a number of countries. The problem has lessened and China has since taken steps to reduce overcapacity (Pooler & Feng, 2017).

High value products have a part to play in reducing insecurity in an unpredictable market because, on the other hand, steelmaking in South Korea and Japan was largely unaffected by the reduction in prices, due to a large proportion of high-end steel in their sales. High-end steels include "differentiated" products such as high strength and alloyed steels that are used in the automotive and aerospace sectors. Sales of these are low volume, high value products have helped to protect these countries from the wholesale downturn in the market (Pooler, 2015).

There is likely to be a shift towards high-end steel in the forthcoming years. Changes in the way that steel is used will affect the kind of steel that is produced. It is likely that higher strength steels will be used more efficiently thus requiring less material. Additive manufacturing means that complicated shapes can be manufactured and there is scope for reducing weight. Currently Siemens uses additive manufacturing to make gas turbine blades and GE makes aircraft seat buckles and engine fuel nozzles (Williamson, 2018). Technology is essential to developing ways in which higher value products can be used which offer more to the customer, last longer and use less material. For example, British Steel has developed a new grade of train rail material, HP335, which does not require heat treatment to produce higher wear resistance, and has a better rolling contact fatigue life. Both of these points makes the rail last longer and saves money in the long term for the operators. Additionally, British Steel has developed thermally sprayed zinc alloy coated rail which significantly increases rail life in corrosive environments (Williamson, 2018).

The price of iron ore hit a 5 year high of \$126 per tonne on 2nd July 2019 having risen by more than 70% in one year. This has been due to increased Chinese demand coupled with reduced iron ore supply from Australia and Brazil (Sanderson, 2019). Nonetheless, the most expensive feedstock into the blast furnace is coke, with coking coal costing more than \$200 per tonne in 2018 (FocusEconomics, 2019a) and this does not include the price of converting the coal into coke. It is forecasted that the demand for metallurgical coke will increase by a compound

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annual growth rate of 2.9% until 2027. This is broadly due to an increase in steel demand which will arise from growing building of infrastructure and construction; as of 2017, iron and steel accounted for 87% of metallurgical coke demand. In the future, India and South East Asian countries are likely to increase home production of steel which will drive up coke demand (Roker, 2019).

The use of coal injection in a blast furnace reduces the amount of coke required which has significant cost benefits. It also increases the quality of iron produced; increases furnace throughput; and reduces the harmful emissions associated with coke making (Carpenter, 2006). It also should be taken into account that during the process of coke making, the amount of coke created will always be less than the parent coal (around 70%) because volatile matter is evolved from the parent coal and some is lost as gases (Geerdes, et al., 2009). However, when injecting coal directly into the blast furnace, theoretically, all of the organic material can be put to use. Currently the price of thermal coal is around half of the price of metallurgical coal (FocusEconomics, 2019b), so it is clear that the price of coke is a major driver for coal injection in the blast furnace.

Figure 2 shows the historical and future projection of the availability of scrap steel in the world. It can be seen that there is set to be a large increase that will be brought about mainly from obsolete products. This is going to play a role in the future of steelmaking where the predominant means of processing scrap steel is via the electric arc furnace (EAF). As of 2015, 1.2 Gt of steel was produced via the blast furnace - basic oxygen furnace route, and 405 Mt was from EAFs (Ciftci, 2017). However, it should be noted that a proportion of the feed to an EAF is in the form of pig iron from the blast furnace, and this is in order to dilute undesirable elements, such as copper, that are present in scrap metal. In the future, there will be a large increase in the availability of scrap steel which gives an opportunity for the UK to focus on steel recycling instead of making steel from iron-ore. This is associated with a 50% reduction in greenhouse gas emissions and it also makes sense in the UK where energy prices are high. Global demand of steel is set to increase, but much scrap steel will arise from end of life goods, so it is feasible that future steel demand could be met by recycling alone as the global stock of steel reaches a point where there is enough for the requirements of each person (Allwood, 2016).



Figure 2: Historic and future projection of steel scrap availability (Ciftci, 2017)

It is clear that the steel industry is unpredictable and dominated by market forces that are challenging to control. Steel has an incredibly important role to play in providing the material for the infrastructure of developing countries and for the future of a low-carbon economy. Looking from a UK perspective and from the situation discussed, a site such as Tata Steel in Port Talbot, Wales, cannot expect to compete with China or India in terms of cost and production volume on bulk commodity steel. According to Naito (2006), reduction of pig iron production costs will reach a limit with present technology. In addition the pressure of global coke scarcity and ever more demanding environmental regulations will place pressure on the steel industry.

Tata must incorporate more high-end steels into its business model. Drawing upon research expertise, it can be expected to develop and produce high technology, value added products that require less material to produce, but command much high prices, and are less affected by changes in the price of bulk steel. Currently the sites in IJmuiden and Port Talbot produce slab, hot and cold rolled coil, galvanised coil, with IJmuiden also producing some coated strip products (Tata Steel, 2019).

Regarding steel recycling, changes in the supply chain could mean that scrap created in the UK is reprocessed in the UK, which would reduce imports and exports, leading to lower carbon emissions. The HIsarna process is focussed on providing a 20% reduction on current best practice technologies in IJmuiden with the potential to sequester an almost 100% CO₂ exhaust gas stream (Tata Steel, 2017).

Having been the backbone of global development for over a century, coal has lately received attention for its high carbon dioxide emissions compared to other fossil

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fuels hence it becoming out of favour in Europe, but it still represents one of the few ways in which to extract iron from iron ore. Iron ore (composed primarily of iron oxide) reacts with carbon to yield liquid iron and carbon dioxide, and so long as the demand for steel outstrips the supply of scrap, it will be necessary to perform this task. Alternatively, there is the possibility of using hydrogen or biochar to reduce iron ore (Feliciano-Bruzual, 2014; Åhman, et al., 2018; The Engineer, 2019), and in principal these methods do work, but the reality of being able to create the amount of renewable hydrogen necessary, or being able to plant and process the number of trees required for biochar, should be the subject for another PhD.

1.4 Ironmaking and the Blast Furnace

1.4.1 Blast Furnace Operating Principle

Currently, the two main routes to produce steel are the blast furnace and the EAF. The EAF uses electricity to melt scrap steel, so it does not create iron from mined raw materials, although it should be noted that a proportion of blast furnace pig iron is used as a feedstock for the EAF. However, 70% of the world's steel production occurs via the blast furnace route which converts mined iron ore into hot metal. It is the preferred method in areas of high steel demand and where iron ore and coal are easily obtainable (Osborne, 2013).

The blast furnace is a refractory lined shaft that operates continuously. It is a countercurrent reactor with coke, limestone flux, and iron ore (sinter and pelletised material) being fed into the top of the furnace in alternating layers, meanwhile, pulverised coal entrained in hot 1200°C oxygen-enriched air is injected at equally spaced zones around the lower part of the furnace (Geerdes, et al., 2009). The partial combustion of coal at the lower half of the furnace provides heat to the furnace and creates the reducing gases necessary to convert the iron ore into iron. A schematic is shown in Figure 3.



Figure 3: Blast Furnace Schematic with regions and temperature zones [reproduced from (Geerdes, et al., 2009)]

The body of the furnace is a steel shell that is lined with refractory bricks. The hearth is the area at the base of the furnace where the molten iron and molten slag collect. Above this area is the bosh which is an inverted truncated cone, after which there is a short vertical section called the belly. Above this is a truncated cone that ends in a short verticle section at the top, known as the throat, through which the raw materials of coke and iron ore are fed in layers. In addition to the coke and iron ore, limestone is added. These solid materials are collectively known as the burden. As the material in the furnace moves downwards, it maintains the layered structure as shown in Figure 3. Hot blast air enriched in oxygen is fed into the blast furnace at the junction between the hearth and belly and this is essential for the combustion of coke and any auxilary reductants. The energy for the hot blast comes from the combustible gases leaving the blast furnace that are burned in stoves to heat the blast air to around 1100°C to 1300°C before it enters into the blast furnace. There is a large toroidal pipe (marked 6 in Figure 3) that circumferentially surrounds the blast furnace. This is known as the bustle pipe and is essentially a manifold for a number of tubes, called tuyeres that branch from this pipe and provide the hot blast air into the base of the furnace axially at set intervals, as illustrated in Figure 4. In addition to hot blast, pulverised or granular coal is introduced near the opening of the tuyeres via coal injection lances, hence this enters with the blast air. The injection of this hot blast and coal plume creates a void at each tuyere, known as the raceway, which is discussed in more detail in Section 1.4.3. Hot reducing gases such as CO and H₂, formed from reaction of the air with the coke and coal rise up the furnace and reduce the iron ore to form iron. As coke is consumed in the raceway area, the burden descends. Molten iron flows down to the hearth, and molten slag formed from coke and coal ash, iron ore gangue, and limestone, floats on top of the molten iron (Hill, et al., 2004; Geerdes, et al., 2009). This thesis is particularly concerned with how the mineral matter from pulverised coal injection effects the raceway and surrounding areas.



Figure 4: Axial arrangement of tuyere raceways in a blast furnace (Geerdes, et al., 2009).

Ironmaking in the blast furnace requires carbonaceous material such as coke, coal and other hydrocarbons, in order to reduce the iron ore. The metric "tonne of hot metal" is an industry term used as a relative measure for all reactants and products that enter and leave the blast furnace, with respect to the amount involved in the production of 1 tonne of hot mtal. A typical blast furnace requires around 500 kg/tHM (kilograms per tonne of hot metal) of reductant, such as coke and coal (Babich, et al., 2002), this is also known as the fuel rate. With the aim being to reduce coke input, the coke rate may be 300 kg/tHM with 200 kg/tHM being coal injection (Carpenter, 2006; Geerdes, et al., 2009). All modern blast furnace use coal injection as a result of scarcity of coking coal; environmental concerns about coke making; and cost of coke leading to an increase in the price of hot metal (Sau, et al., 2018).

1.4.2 Chemical Reactions

Reducing Gases

The two reducing gases in the blast furnace are carbon monoxide and hydrogen. In the raceway, oxygen reacts with coal carbon and coke carbon as follows:

 $C + O_2 \rightarrow CO_2$

Equation 1: Char combustion reaction.

Injected coal contains hydrogen and water which leads to the formation of H_2 as a reducing gas. Also, water can react with carbon to create carbon monoxide and hydrogen:

$$H_2O + C \rightarrow CO + H_2$$

Equation 2

As the reducing gases react with the iron ore, they produce carbon dioxide and water. At furnace temperatures exceeding 1000°C, the carbon dioxide reacts with the coke to form CO:

$$CO_2 + C \leftrightarrow 2CO$$

Equation 3: Reverse Boudouard / solution loss reaction

And this CO can be used again for reduction of iron ore.

Reduction in the Blast Furnace

As the CO rises up the blast furnace, it reduces the iron ore. The states of reduction throughout the furnace are shown in Figure 5. Iron oxides can be reduced to iron via direct reduction or indirect reduction. Indirect reduction occurs at the top of the furnace between iron ore and the reducing gases carbon monoxide and hydrogen, with the products being carbon dioxide and water. Direct reduction occurs in the bottom of the furnace between coke carbon and FeO leading to the formation of carbon monoxide (Babich, et al., 2008). The following reactions are reactions between a gas and the iron ore, hence they are termed 'indirect reduction'. The first stage of reduction to occur to the iron ore is from haematite (Fe₂O₃) to magnetite (Fe₃O₄):

> $3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$ Equation 4

Further down as the furnace becomes hotter, the magnetite is converted to wustite (FeO):

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$

Equation 5

In the cohesive zone, the wustite is converted to iron:

 $FeO + CO \rightarrow Fe + CO_2$

Equation 6

Substituting hydrogen for carbon monoxide in the iron reduction reactions above produces water instead of CO₂.

Not all of the reducing gases are fully utilised, so they leave the top of the blast furnace and are used as fuel gas for heating the blast air, and other uses (Hill, et al., 2004).



Figure 5: The successive reduction states of iron ore in the blast furnace (Geerdes, et al., 2009).

Summary of Slag Formation

The purpose of adding the limestone is to help form the slag. Slag forms from all the impurities in the blast furnace such as the coal and coke ash, iron ore gangue and limestone itself. The limestone (calcium carbonate) decomposes upon heating to produce calcium oxide:

$$CaCO_3 \rightarrow CaO + CO_2$$

Equation 7

The calcium oxide reacts with the alumina and silica to produce an aluminosilicate slag as follows:

$$2CaO + Al_2O_3 + SiO_2 \rightarrow Ca_2Al_2SiO_7$$

Equation 8

Moreover, some of the sulphur in the feed materials that converts to iron sulphide can be removed by the slag as calcium sulphide:

$$FeS_2 + 2CaO + C \rightarrow 2CaS + FeO + CO$$

Equation 9

The slag composition is much more complicated than this as there are many other elements that can be contained within it and these include Na, K, Fe, Mg, Ti and other trace metals.

Carburisation of the molten iron occurs as it drops through the active coke zone and deadman to reach 4.5% carbon; this lowers the liquidus temperature of the molten metal (Geerdes, et al., 2009).

Charge materials contain numerous elements beside iron and these have various destinations during the blast furnace process. They can be: dissolved into the hot metal; leave via the slag; be emitted in the top gas, or even absorbed into the blast furnace refractory.

1.4.3 Raceway

The blast furnace raceway is formed when high velocity gas is injected axially into a packed coke bed (Guo, et al., 2013; Wu, et al., 2019). The momentum of the high velocity blast pushes coke away from the tuyere nose to create the raceway (Sau, et al., 2018). A diagram of the raceway is shown in Figure 6. The nozzle through which blast air and injection coal enters is known as a tuyere. Injection coal is fed into the tuyere via an injection lance. The temperature in the blowpipe is the same as the blast air at around 1100°C to 1300°C (Hill, et al., 2004; Naito, 2006; Geerdes, et al., 2009) and this is where coal devolatilisation begins to occur (Zhang, et al., 2010). The bird's nest is the region at the back of the raceway where some of the partially burned char accumulates.



Figure 6: Cross-section of the raceway. Taken from Chen, et al. (2007).

Reaction of coke in the raceway with oxygen modifies the raceway shape and size and helps to maintain stability (Guo, et al., 2013). Raceway dimensions vary based upon a combination of the kinetic energy of the blast and injectant, and on the coke properties (Babich, et al., 2002). The raceway is larger when operating under coke only conditions, and increasing the blast temperature slightly increases the raceway depth, however, according to Babich, et al. (2002), the effect of oyxgen content and moisture content has not been shown to have an effect thus far. The main reactions occurring in the raceway are $C + O_2 \rightarrow CO_2$; $C + H_2O \rightarrow H_2 + CO$; $C + CO_2 \rightarrow 2CO$ and $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ and this is where the bulk of the hot reducing gases are created (Sau, et al., 2018).

Regarding coal injection particle size, Wu et al. (2019) found that small particles follow the gas streamline and recirculate for a long time in the raceway. However, with larger particles exceeding 130 μ m, more than half of them will continue in the direction in which they are travelling and land in the coke bed at the back of the raceway. Similar findings were made by Guo, et al. (2005), who found that large particles of around 200 μ m tend to maintain their axial direction of travel through the raceway, whereas small particles become entrained in the flow fields and remain for longer residence times and are more affected by turbulence. This led to a broad range in particle residence times of 25 ms to 1000 ms.

The raceway depth is about a metre from the lance tip (Guo, et al., 2005; Sau, et al., 2018). According to Bortz and Flamert (1983), with raceway depths of around 1 to 1.5 metres, and blast velocities of 200 m/s, this gives a theoretical raceway residence time of 5 - 7.5 ms which is much lower than reported by Guo et al. (2005), however it should be borne in mind that this was a theoretical approximation. Direct measurement of the raceway in a furnace is highly challenging owing to the high temperature and pressure, and toxic gases (Sau, et al., 2018). According to mathematical modelling by Zhang, et al. (2010) residence time of particles within the raceway may be 30 ms to 50 ms, with peak temperatures of 2150°C. From this literature, it can be seen that there are widely varying estimates of raceway residence time. Given the turbulent nature of the raceway, it is likely that some particles remain in the raceway for quite some time, but one must take into account that coal reactivity, particle size, and raceway conditions have a large part to play in this discussion.

Zhang et al. (2006) performed digital image processing of raceway flame temperatures and found the kernel of the flame is about 2000°C when a mass of coal powder is being blown in, and around 1800° C to 2100° C otherwise. Wu, et al. (2019) state the temperature is higher at the outer surface of the plume where oxygen content is higher, and lower in the centre of the plume. The heating rate in the raceway is in the order of 10^{5} K/s (Ishii, 2000; Chen, et al., 2007) with moisture evaporation, devolatilisation, combustion of volatiles, and combustion of char occurring as the coal particle combustion process (Zhang, et al., 2010).

Devolatilisation occurs very quickly and is complete not long after leaving the tuyere and char burnout occurs in the raceway, not tuyere (Zhang, et al., 2010). Wu et al. (2019) found that most of the coal particles burn out in the raceway with the remainder burning in the coke bed.

1.4.4 Coke

Heat from coke is required to melt the iron and slag, and drive the solution loss reaction. The solution loss reaction is between coke and CO₂ and it produces CO at high temperatures (Geerdes, et al., 2009). Coke is central to the blast furnace process as it acts as an energy source, a reducing agent, and as structural support for the burden (Gornostayev, et al., 2018). The porous nature of coke allows gases to permeate up through the blast furnace stack (Carpenter, 2006). The iron ore is not permeable, and becomes cohesive and molten in the lower part of the furnace. The presence of coke that remains solid at high temperatures allows molten iron and molten slag to drip downwards into the hearth (Geerdes, et al., 2009). Oil, gas, plastics and coal can provide energy and reducing gases, but only coke possesses the strength and porosity to support the weight of burden and allow gases and liquids to permeate. As coal injection has become widedspread, the usage of coke has reduced which means that its layers within the stack have become thinner and residence time within the furnace has increased. In coke production, the amount of moisture, sulphur, ash and alkali metals are tightly controlled, and lower is better. The Coke Reactivty Index (CRI) and Coke Strength after Reaction (CSR) test are both used to determine coke quality. If the coke is too reactive in the furnace, it will break down into finer material and this reduces the permeability. Hence, the coke must maintain a good strength after reaction so as to retain a permeable size having reached the lower part of the furnace (Díez, et al., 2002). Coke degradation and fines generation occur due to mechanical stresses, solution loss reaction, thermo-mechanical impact, and chemical attack from alkalis (Gupta, et al., 2008).

Coke making involves heating coal at 1100° C to 1200° C in an oxygen deficient atmosphere with the aim being to concentrate the carbon (Vasko, et al., 2005; Osborne, 2013). Depending on the volatile matter, it takes roughly 1.4 tonnes of coal to make 1 tonne of coke (Carpenter, 2006). During the coking process, coal ash reports directly to the coke, while the sulphur present in the parent coal is found partially in the resulting coke. Coke in the slag helps to reduce SiO₂ and MnO. Coke should have high carbon, low sulphur, low ash, low alkalis (Osborne, 2013). Coking coals are expensive owing to their unique plastic properties and limited supply (Bennett & Fukushima, 2003). Scarcity and cost of coking coals, and environmental concerns about coke making lead to an increase in the price of hot metal (Sau, et al., 2018). Coke is the most expensive feed material into the blast furnace (Gupta, et al., 2008; Hill, et al., 2004), owing to the stringent environmental regulations surrounding its production, so there has been a lot of attention to reduce its use, and coal injection is one of the alternatives that has been employed (Hill, et al., 2004), and is discussed in detail in the next section.

1.4.5 Pulverised Coal Injection

In the late 1950s and early 1960s oil and gas injection through the tuyeres was common. The oil crisis in the 1970s caused the revival of coal injection and it has been increasing ever since (Bennett & Fukushima, 2003; Mathieson, et al., 2005) to greater than 200 kg/tHM typically used at present, which makes up around 40% of the total reductant supply to a blast furnace (Osborne, 2013). Increasing the amount of coal injection means that less coke needs to be used in the blast furnace (Carpenter, 2006). The endothermic chilling effect of large volumes of fossil fuels limits their injection rate into the blast furnace, and this effect increases with hydrogen content. In addition, at higher injection rates, increasingly limited oxygen available for combustion has the same chilling effect. A significant advantage of coal over oil and gas is that it has a much lower chilling effect on the combustion zone thus it can be injected at higher rates (Babich, et al., 2002).

The use of pulverised coal is advantageous to the ironmaking process for a number of reasons which are as follows (Bennett & Fukushima, 2003; Carpenter, 2006; Osborne, 2013).

- Money is saved due to reduced consumption of expensive coke, and pulverised coal injection (PCI) allows the blast furnace operator to choose cheaper coals than the coking variety. Moreover, one tonne of coke can be replaced by one tonne of PCI which reduces the overall consumption of coal since volatile mass is lost during the coke making process.
- The service life of coke ovens is increased because less coke needs to be produced for blast furnaces. A reduction in coke consumption also delays expensive maintenance of coke ovens, or the building of new ones.
- 3. There is an increase in the productivity of the furnace, i.e. a furnace of a given size can produce more hot metal than with coke only operation.

- 4. PCI enables greater flexibility during operation because the injection parameters can be altered much more quickly than the deposition and location of solids into the top of the furnace; it takes 5.2 hours to travel from the top of the furnace to tuyere level (Geerdes, et al., 2009, p. 17)
- 5. The consistency in the quality of the hot metal is improved due to lower amounts of undesirable elements.
- Carbon emissions are reduced. Life Cycle Analysis by Tata Steel showed a 6.7% reduction in CO₂ emissions when the PCI rate increased from 16 kg/tHM to 116 kg/tHM (Sripriya, et al., 2000).

The objective of PCI is to maximise its rate in order to maximise the benefits described above. In the early period of PCI, the focus was on increasing the combustibility, but once high PCI rates had been achieved, the focus turned to problems with permeability and heat loss in the lower part of the blast furnace. A selection of pulverised coal rates around the world shows that they are almost all in excess of 200 kg/tHM. In Europe, lower fuel rates are preferred with highest possible productivity, for example IJmuiden 7BF running at 216 kg/tHM, but in Japan the fuel rates are higher with the excess converting to a gas that is used in the integrated steelworks, for example Fukuyama 1BF running at 265.5 kg/tHM (Naito, 2006). Baosteel in China has been running at PCI rates of 220 kg/tHM to 260 kg/tHM in 2005 (Baosteel, n.d.). Thus, it is possible for the injectant rate to reach up to and in excess of 250 kg/tHM with a 50:50 ratio of coal to coke but incomplete combustion within the raceway, gas permeability within the shaft, and dirtying of the deadman make this difficult in practice (Babich, et al., 2002).

There are limited parameters used in industry to assess the suitability of a coal as a pulverised injection fuel. Fuel ratio, defined as the ratio of fixed carbon to volatile matter, is a commonly used metric to try and predict the combustion behaviour of different coals (Gupta, et al., 2006) and has been used in several papers as a parameter of interest (Bortz & Flamert, 1983; Du, et al., 2010; Kurose, et al., 2001). Coal combustibility increases with volatile matter (Barranco, et al., 2006; Du, et al., 2010; Suzuki, et al., 1984), but a higher carbon content coal is able to replace more coke (Hill, et al., 2004), which is beneficial to reducing the coke input. According to Ozer et al. (2017) coal reactivity increases with decreasing rank because lower rank coals have higher volatile matter, are more porous and have more oxygen containing functional groups.

The metric for a coal's ability to replace coke is known as replacement ratio, and is based upon the carbon content of the coal / blend being injected (Geerdes, et al., 2009), hence low volatile coals offer a better replacement ratio (Bennett & Fukushima, 2003). In the past, high volatile coals have been the preferred choice, but more recently the use of lower volatile coals has become more widespread (Ishii, 2000) as understanding of PCI has improved (Bennett & Fukushima, 2003).

According to Bennett and Fukushima (2003), at high PCI rates (>160 kg/tHM) the following changes were observed in the blast furnace: changing raceway size; reduced permeability of coke surrounding the raceway; changes in raceway temperature profile; mechanical degradation of raceway coke; decrease in the deadman temperature. In the blast furnace, coal reactivity in the raceway is an important factor to consider since as the amount of coal injected increases, this leads to problems of increased amounts of partially burned char which reduces the permeability in the furnace, leading to sub optimal gas flow resulting in uneven temperature distribution. Coke erosion is also responsible for reducing permeability in the furnace (Ishii, 2000).

Partially burned char that does not undergo solution loss, either becomes trapped in the furnace or exits as a dust (Bennett & Fukushima, 2003); Sau, et al. (2018) state that partially burned char tends to accumulate in the lower part of the furnace. The properties and effectiveness of the diminishing masses of coke compound the situation, since, with increasing coal injection rate, the coke rate is reduced to compensate, resulting in thinner coke slits thus affecting permeability, especially in the cohesive zone. A decrease in central gas flow results in an increase in peripheral gas flow, thus there is greater heat loss from the furnace walls, and an increase in top gas temperatures as a result. Moreover, this diversion of reducing gases results in less interaction with the burden, lessening heat exchange in the centre of the furnace, and leading to insufficient ore reduction. The flow of FeOrich slag resulting from incomplete reduction also serves to lower temperatures (Naito, 2006). Thus, it is clear that stable operation of a blast furnace is dependent on an even flow of gas up the furnace and an unhindered flow of molten iron and slag to the hearth of the furnace (Carpenter, 2006).

Exceeding 200 kg/tHM, the replacement ratio starts to decrease; this is on account of lower combustion efficiency. Thus, when working close to the limit, proportionately more PC needs to be injected to maintain a linear replacement ratio (Bennett & Fukushima, 2003). Hence, there is a case of diminishing returns at

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high coal injection rates, and it is evident that partially burned char may accumulate if it is not consumed. Additionally, as stated by Naito (2006), the coke rate often increases slightly which somewhat negates the benefits of the higher PCI rates.

Further research into the combustion kinetics of coals and blends is required to create optimal blends at high PCI rates (Bennett & Fukushima, 2003). There are some solutions to the above mentioned problems; increasing the blast temperature, oxygen enrichment, and improved injection lance design have helped to alleviate some of the issues posed by increasing PCI rates (Bennett & Fukushima, 2003; Osório, et al., 2006). Burden distribution such as central coke charging is a useful technique to maintain a central gas flow up the furnace (Naito, 2006).

1.4.6 Grinding

Blast furnace injection coals are ground prior to injection in the blast furnace. There are two types of coal grinding specification and these are pulverised and granular. The majority of coal injection systems use PCI (pulverised coal injection) where 70-80% of the coal is ground to less than 75 μ m, with fewer plants opting for GCI (granular coal injection) where the top size of the coal is nominally 2 mm, with around 20-30% being less than 75 μ m (Carpenter, 2006) (Du, et al., 2010). Power station mills are specified to grind coal to 100% < 300 μ m, 75% < 75 μ m (Barranco, et al., 2006). According to (Carpenter, 2006), the coarser specification reduces grinding and drying costs, but at the expense of burnout in the raceway, where the higher burnouts achieved by smaller particle sizes are preferable. PCI is favoured in Germany and Japan, while GCI is used in Britain (Carpenter, 2006), namely Scunthorpe and Port Talbot, and also by Bethlehem Steel's Burn Harbor, Indiana Plant since 1995 (Hill, et al., 2004), where grinding costs of granular coal are around 60% lower than for pulverised coal.

It is generally accepted that pulverised coal burnout is greater than granular, however, the performance difference between the two may be reduced by the effect of fragmentation, (Dacombe, et al., 1999; Steer, et al., 2015a). Increasing fineness of coal increases burnout and coarser grinds resulting from worn pulveriser mills produced lower burnout, but the difference was less than expected (Barranco, et al., 2006). In a trial by Hill, et al. (2001) at Bethlehem Steel in the United States, it was observed that the performance of granular coal was not inferior to pulverised. A study by Du, et al. (2010), showed decreasing the particle size below 75 μ m had little effect in increasing the burnout due to particle

agglomeration taking place, thus negating the benefit of any further reduction in particle size.

1.5 Aims and Objectives of the Thesis

All coals contain mineral matter, which, when combusted, creates ash. Mineral matter is highly variable between different coals, both in terms of mineral and elemental composition.

The aim of this thesis was to use X-ray diffraction mineral analysis to identify differences in the amount of quartz, clays and carbonates in coal ashes and make a connection with the concentration of silicon, aluminium, iron, calcium, magnesium, potassium, sodium and sulphur in the elemental analysis of the ash. A relationship between mineral and chemical information, and the ash fusion temperature, was sought to inform upon effects that might occur in the blast furnace raceway. This involved determining the effect of heating environment on mineralogy, chemistry and fusion temperature using a muffle furnace and a drop-tube furnace in order to draw parallels between laboratory and blast furnace heating environments.

The extent of volatilisation of potassium, sodium and sulphur under these heating conditions was also of interest. Physical properties such as abrasiveness, particle size and bulk density of ashes from chars, were investigated with a view to relating particle behaviour to the blast furnace raceway. Finally, this thesis aimed to identify whether ashes were catalytic or inhibitory on the combustion of coal and gasification of coke, by using a thermogravimetric analyser.

The objectives of this thesis were as follows:

- To relate the ash fusion temperature with the relative amounts of acidic (silicon, aluminium and titanium) oxides, and basic (calcium, iron, magnesium, potassium and sodium oxides).
- 2. To determine the effect of heating environment on ash fusion temperature and relate this to the blast furnace.
- To determine how much of the alkalis potassium and sodium are volatilised, and how much sulphurous gases are released as the mineral matter undergoes high temperature conditions.
- 4. To identify differences in the abrasiveness of coal ashes between different coals and under different heating conditions, and to determine the extent to which abrasiveness is related to physical properties observed under the SEM and mineralogy.

5. To investigate any catalytic or inhibitory effect of ash on the reaction of coal and coke, and what impact this has in the raceway region of the blast furnace? To relate the findings with the ash chemistry, for instance iron, calcium and alkali content.

An improved understanding of ash in the blast furnace process can be used to advise of any problems that may arise from using different coals. This information will be useful to identifying problematic coals and adjusting blends to improve behaviour in the blast furnace.

A drop-tube furnace (DTF) was used to simulate raceway environments as closely as was possible in the scope of this thesis. Chars were prepared under different reactions to relate to different areas and conditions in the raceway. The ashes from these chars were analysed to answer the following questions.

1.6 Thesis Structure

Chapter 1 introduced the reader to the context of coal in the world, in steelmaking, and in this thesis. It summarised the aspects of climate change, and the current and future challenges to the steel industry. The blast furnace process was described. The aims and objectives of the thesis were laid out.

Chapter 2 is the literature review that contains a strong focus on coal mineral matter and how it affects blast furnace coal injection. Areas considered include char combustion, ash melting behaviour, alkali volatilisation, sulphur in the blast furnace and the abrasiveness of ash. The findings of the literature review are used to inform the research hypothesis.

Chapter 3 details the materials and methods. Where appropriate, method background is described. The methods themselves are defined on a step by step basis. Analysis techniques are explained. Experimental error is also discussed.

Chapter 4 displays the results of X-ray diffraction and elemental analysis of the coal minerals. It relates these findings to the ash fusion temperatures (AFT) observed in the different ashes. Particular attention is paid to how the temperature and residence time in the drop-tube furnace (DTF) affects the fusion temperature. AFT is related to blast furnace effects such as slag chemistry, and raceway and deadman permeability.

Chapter 5 is a result chapter focusing on components of ash volatilised or released in the gas phase, namely, potassium, sodium and sulphur. The relationship between drop-tube furnace temperature and residence time, and the degree of devolatilisation /release for the elements is investigated. The results of this chapter are used to inform upon possible effects in the blast furnace.

Chapter 6 is an analysis of physical properties of ash. The results of abrasion testing of ashes are displayed. Ashes from DTF chars were investigated to determine the effect of heating environment on ash physical properties. The abrasiveness of the ash is related to the morphology of the ash, found using SEM. The particle size of the ashes was measured to look for links between abrasion, DTF reaction environment and ash morphology. The findings of the experiments from this chapter are related more specifically to the tuyere region of the blast furnace where abrasion is an issue.

Chapter 7 uses a Thermal Gravimetric Analyser (TGA) to investigate how ashes of varying chemistries and properties affect the reactivity of coal combustion, and coke gasification. The results in the chapter are used to inform how ashes may effect coal combustion in the raceway, and the effect on coke gasification in the bird's nest and deadman.

Chapter 8 is the discussion of the findings of the results from this thesis. Each of the coals tested is evaluated in relation to the findings of the thesis. There is a strong focus on the industrial implications of the work from the thesis. This chapter finishes with the conclusions of the thesis.
Chapter 2. Literature Review

The literature review performs four key purposes in this thesis. It informs the research areas of the thesis; it identifies a knowledge gap where further research is required; it validates the findings of the results chapters; and it provides insight into how these findings might affect the blast furnace.

The study of mineral matter in the blast furnace is multi-facetted, thus requires the exploration of a large body of literature in diverse areas. This chapter is intended as a comprehensive review of the topics discussed in the thesis.

2.1 Coal Particle Combustion

The combustion of coal particles is dependent on the coal properties and reaction conditions. It is a sequential process, but with partial overlap, occurring with: heating of the particles and loss of water; volatile matter release; ignition and combustion of the volatiles; ignition and combustion of the char (Carpenter & Skorupska, 1993). Volatile burnout occurs very quickly, however char combustion occurs much more slowly and its rate is determined by physical and chemical factors therefore it determines the burn-out time of the coal in the furnace (Jayanti, et al., 2007). For example devolatilisation at a heating rate of 10⁴ K/s to 10⁵ K/s might take 10 ms to 100 ms, whilst char combustion could take between 1 and 4 seconds (Lu, et al., 2001). Particle heating rates in the blast furnace are in the order of 10⁵ K/s (Chen, et al., 2007). During the sequence of coal particle combustion, different types of reaction occur. Combustion of gaseous volatiles is a homogeneous gas/gas reaction, while that of liquid volatiles is a heterogeneous liquid/gas reaction. The reaction of char is a heterogeneous solid/gas reaction that is influenced by its pore structure, size, shape, density and reactivity. Given more time, a char will combust more fully. Like all reactions, the rate of char combustion is determined by chemical kinetics and mass transport limitations. Char combustion can be described using an Arrhenius based expression, but given the heterogeneity of coal as a fuel, it can be difficult to accurately predict the combustion process (Carpenter & Skorupska, 1993).

The sequence of combustion in a pulverised fuel (PF) boiler occurs in the same way as in the blast furnace raceway, however the operating conditions are very different. The blast furnace raceway is hotter (~2200 °C vs. ~1500 °C), with shorter residence times (~20 ms vs. ~200 ms) and a pressure in the raceway of some 4-5

bar compared to PF boilers. Moreover, the reaction atmosphere is far higher in CO_2 and CO (Ishii, 2000).

Figure 7 shows the processes occurring during coal devolatilisation. It can be seen that moisture and volatiles are lost in the initial stages. Vaporisation of Na, K, S and Cl occur simultaneously. The fragmentation of coal occurs and included minerals are released during combustion.



Figure 7: Coal combustion and mineral release. Taken from Mann and Ludlow (1997), cited in Benson and Sondreal (2002, p. 13).

There are many points discussed in the literature review which can relate to this diagram. The formation of sodium, potassium and sulphur vapours, and the release of included minerals are important factors whose effect in the blast furnace is investigated in this thesis.

2.1.1 Devolatilisation

Temperature, heating rate and coal rank all influence the amount and composition of volatile matter yielded from a coal (Yang, et al., 2014). Increasing the temperature and residence time increases the amount of volatile release (Kobayashi, et al., 1977). Pyrolysis is the breaking of larger molecules into smaller molecules due to thermal decomposition. If the temperature is high enough and the molecule is small enough, it changes from a solid to liquid to gas phase and pressure build up within the particle causes degassing. The process of chemical bond breaking and volatile movement out of the particle is called devolatilisation (Fletcher, 2017). R-factor is the ratio of volatile release under rapid heating conditions (such as in a DTF) to volatile release following proximate analysis. There can be significant variation between coals so R-factor can be used to better characterise fuels for industry (Gibbins, et al., 1993; Chen, et al., 2007). Decreasing particle size and increasing reaction temperature cause an increase in the R-factor, and an increase in devolatilisation rate. The R factor is lower for large (74-149 μ m) particles than for (44-74 μ m) small ones. The reactivity of unburned material from low volatile coal is lower than that of high volatile coal. Stefan flow, the release of gas from the solid surface, can cause sticky particles to have more difficulty agglomerating which can lead to a bimodal particle distribution of agglomerated and non-agglomerated particles (Chen, et al., 2007). Bituminous coals soften and enter a plastic phase where swelling occurs as coals are heated. Swelling effects are more pronounced under higher heating rates (Yu, et al., 2003) and lead to coal agglomeration (Shampine, et al., 1995).

Small particles are quicker to heat up and devolatilise than large particles. They combust more effectively owing to their higher surface area to volume ratio which increases reaction with oxygen, but moreover, their increased tendency to circulate in the raceway gives them more chance to encounter oxygen-rich zones for reaction as well as increasing their residence time. Calculated and experimented burnouts increase with volatile matter. High volatile coals are less sensitive to particle size. Burnout is rapid at first, due to volatilisation, but increases at a decreasing rate further into the raceway during char oxidation. As coal injection increases, burnout decreases owing to lower oxygen concentration. Higher injection rates of high volatile coal have less of an effect on burnout (Guo, et al., 2005).

It has been found that blending coals can lead to burnout improvements exceeding the sum of their parts, as the volatile matter in high volatile coals can promote the combustion of the lower volatile coals in the blend owing to an increase in particle temperature due to the volatile release (Steer, et al., 2015a).

2.1.2 Kinetics of Char Combustion

There are three regimes of reaction that can occur during coal char combustion. Under Regime I, there is plentiful oxygen to the reacting particle and the oxygen concentration at the particle surface is not much lower than that of the free stream, so the reaction rate is limited by the particle size and temperature, and not by the amount of oxidant present at the particle surface. Regime I is known as chemical control. During Regime III, most oxygen is consumed before even reaching the particle surface, hence the oxygen cannot diffuse fast enough to the particle surface and pores so the concentration at these points is lower than the free stream oxygen. Regime III is known as diffusion controlled reaction; it is more likely to occur at high temperatures, high reactivity coals and small particle sizes. Regime II is a combination of I and III and, is likely to be the case in real world combustion (Osborne, 2013), for instance during char combustion in a DTF (Lu, et al., 2001). However, according to Bai et al. (2017) devolatilisation and char combustion occurs sequentially for large coal particles 150 - 212 μ m in size, and simultaneously for small coal particles in the range of 106-150 μ m when analysed in a DTF with image analysis. The coal tested was bituminous. Moreoever, for the sequentially burning large particles, there were two peaks of luminosity caused by the combustion of volatiles and the combustion of char.

Since char combustion is exothermic, the particle temperature may be higher than the surrounding gas by several hundred degrees. The gas at the surface of the particle may be more reducing than the bulk gas as the particle consumes oxygen (Senior & Flagan, 1982). For a bituminous coal tested in a DTF, it was found that char surface area was greatest at around 40-50% burnout due to the formation of numerous mesopores and micropores, however the reactivity of the char was reducing by this point because the reactive amorphous carbon had been preferentially consumed leaving more ordered carbon as combustion progressed. Surface area reduces after this point as pores merge. Preferential consumption of amorphous char was found to be responsible for diminished reactivity as burnout increased (Lu, et al., 2001).

2.1.3 Particle Fragmentation

Fragmentation is an effect that can occur to coal particles depending on their rank, size, volatile matter yield, and the conditions in which they are heated. Following DTF testing in nitrogen at 1400°C by Friedemann et al. (2016), it was found that anthracite particles disintegrated upon heating while brown coal gave a bright tail due to devolatilisation and did not fragment under any of the investigated particle sizes, temperatures, and residence times. HV bituminous coal showed fragmentation behaviour but less than anthracite. Anthracite fragmentation occurs due to its properties. In the case of high vitrinite content, this makes the coal brittle therefore not resistance to thermal stresses. Brown coals have a higher porosity which leads to a higher resistance against thermally induced stresses. Increasing temperature promoted internal thermal and mechanical stresses giving rise to greater fragmentation (Friedemann, et al., 2016). In other work, particle fragmentation increased with increasing particle size and DTF temperature. It also

was noted that the outer shell of a particle fragments into many pieces whilst the core remains more stable and fragments into comparatively fewer pieces (Dacombe, et al., 1999).

2.2 Mineral Matter

Mineral matter is an integral part of the coal that needs to be accounted for. The mineral matter in coal has a range of effects in the blast furnace which are investigated and discussed in this thesis. The majority of processes that use coal have defined limits to the amounts of particular minerals or elements in the inorganic matter. Better understanding of the mineral matter allows for more complete utilisation of available coal reserves (Renton, 1982). Mineral matter is a complex system owing to the various physical and chemical conditions under which the coal formed (Gluskoter, 1975).

2.2.1 Terminology and Coal Mineral Composition

There is some misunderstanding, in the literature, of the terms "ash", "mineral matter" and "inorganic matter" (Vassilev & Tascón, 2003). "Ash" is the remaining residue formed from the mineral matter in coal after it has been fully combusted. Ash is different from mineral matter owing to the chemical and physical changes that have occurred during combustion (Raask, 1985; Ishii, 2000; Speight, 2005).

According to Vassilev and Vassileva (1996), the term mineral matter only applies to materials that can be defined as minerals in a geological sense. That is, they are naturally and inorganically formed solid structures with long-range geometrical order, i.e. crystallinity, and can be represented by a chemical formula. Amorphous structures such as glasses are termed mineraloids (Hefferan & O'Brien, 2010). The minerals found in coal are categorised as: silicates, carbonates, sulphides, sulphates, phosphates, metal oxides / hydrated oxides, and chlorites (Renton, 1986; Ward, 2002; Vassilev & Tascón, 2003; Speight, 2005), as shown in Table 2. Gluskoter (1975) and Ward (2016) give a broader definition to include the above geological definition of mineral matter, plus all the additional inorganic components that are composed solely of elements from an inorganic source; that is, they do not contain organically derived carbon, hydrogen, oxygen, nitrogen and sulphur. So although, the mineral matter contains the above elements, for example, carbonates contain carbon and oxygen, sulphides contain sulphur, and sulphates contain sulphur and oxygen, these elements form part of the inorganic material, therefore they are regarded as mineral matter or inorganic material, depending on the definition that one chooses. In this thesis, the broader definition of mineral matter that includes other inorganic matter will be used for two reasons, firstly, the elemental analyses carried out on a bulk sample of ash are unable to determine the precise source of the inorganic element, and secondly, the focus of this thesis is on the effects of the mineral matter in the blast furnace, so it is less concerned with the precise origin of any particular component, and more so with how it affects the blast furnace.

Another distinction that needs to be made is between *inherent* and *extraneous* minerals as this effects how minerals behave within the coal matrix. The minerals that are intimately associated with the organic matter are termed inherent mineral matter. These minerals can possibly only be removed chemically. Mineral matter that comes from within or between the coal seams is known as extraneous mineral matter. It is possible to wash this type out to remove it (Ward, 2002). Included and excluded minerals follow the same definition as above (Gupta, et al., 1996), and excluded minerals may be formed from included minerals that are released from the coal during crushing processes (Taylor, et al., 1998). The average diameter of most mineral grains in coal is 20 μ m, with few exceeding 100 μ m, except in the case of localised massive occurrences of pyrite or marcasite (Renton, 1982), but this illustrates that intensive grinding of a coal would be able to break up and release inherent mineral matter. Whether minerals are included and excluded may effect how they interact within the coal and with the blast furnace. For example, catalytic interactions are more pronounced when the catalyst is intimately associated with the organic material (Levendis, 1989), and excluded minerals are far more likely to cause wear to grinding and coal injection equipment (Raask, 1985).

Table 2 shows the more common minerals that are found in coal, and how they are categorised. The melting temperatures of individual minerals are useful for future work in this thesis where ash fusion temperatures are investigated. There are many additional uncommon minerals that are found in coal and these are detailed in the literature (Rao & Gluskoter, 1973; Gluskoter, 1975; Raask, 1985; Renton, 1986; Ishii, 2000; Ward, 2002), along with the following information. The majority component of coal mineral matter is clay at 50-60%, with quartz being the next greatest contributor at around 1 to 20%. The clays found most commonly and in greatest abundance are kaolinite, illite, and mixed layer illite-montmorillonite. Sulphur is an essential element required for plant life where it is found in proteins, hence why it is found in coal deposits. On average bituminous coals have a sulphur content of

1% to 4.5%, with pyrite being a more significant source of sulphur than organically bound sulphur, in a ratio of roughly 3:2 (Raask, 1985). There is usually some form of carbonate such as calcite and siderite, although depending on the region, ankerite and dolomite may be more common. Sulphates are rare in fresh coals, and generally occur in weathered coals where the pyrite decomposes to a form of hydrated iron sulphate, of which there are a number of forms, with varying degrees of hydration. Phosphates are sometimes found in coals, the most common being fluorapatite (calcium phosphate). Rutile (titanium dioxide) is often found, but the presence of iron oxides is less common. Usually, iron oxides form in high temperature ash from the decomposition products of minerals such as pyrite. The number of different minerals that can be present in coals is on account of the fact that they can be found anywhere in the world. Table 2: Common coal minerals with melting or decomposition temperatures (Rao & Gluskoter, 1973; Gluskoter, 1975; Raask, 1985; Renton, 1986; Ishii, 2000; Ward, 2002).

			Mineral	Formula	Melting / Decomposition Temperature (°C)
Major	Silicates	Clay Minerals	Kaolinite	Al₂Si₂O₅(OH)₄	1810 (Mullite)
			Illite	K _{1.5} Al ₄ (Si _{6.5} Al _{1.5})O ₂₀ (OH) ₄	1000-1300
			Smectite	Na _{0.33} (Al _{1.67} Mg _{0.33})Si ₄ O ₁₀ (OH) ₂	
			Muscovite	KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂	1000-1300
			Montmorillonite	$(Na,Ca)_{0.33}(Al,Mg)_{2}(Si_{4}O_{10})(OH)_{2}.nH_{2}O$	
			Chlorite	(MgFeAl)₅(SiAl)₄O10(OH)8	
			Mixed Layer / Interstratified	Usually random layers of illite and montmorillonite or chlorite.	
		Silica	Quartz	SiO2	1710
Minor	Silicates	Feldspars	Orthoclase	KAlSi₃O ₈	
			Plagioclase (Albite)	NaAlSi₃O ₈	
			Plagioclase (Anorthite)	CaAl ₂ Si ₂ O ₈	
	Carbonates		Calcite	CaCO₃	927*
			Dolomite	(CaMg)(CO₃)₂	777*
			Ankerite	Ca(Fe,Mg)CO₃	727*
			Siderite	FeCO₃	527*
	Sulphides		Pyrite	FeS₂ (cubic)	802*
			Marcasite	FeS₂ (orthorhombic)	802*
			Pyrrhotite	FeS _x	1027
	Sulfate		Gypsum	CaSO ₄ .H ₂ O	1452
			Barite	BaSO₄	1582
			Bassanite	CaSO ₄ .½H ₂ O	
	Phosphates		Apatite	Ca₅F(PO₄)₃	>1227
	Metal Oxides		Anatase	TiO ₂	
			Rutile	TiO ₂	1827
			Hematite	Fe ₂ O ₃	1567
			Magnetite	Fe₃O₄	1592
	Chlorides		Halite	NaCl	801
			Sylvite	KCl	770

Decomposition temperature
Debudration temperature

Dehydration temperature

There are several terms used to describe the way in which the coal minerals, found in coal today, came into being in the first place. Coal minerals can be classified as biogenic, detrital or authigenic. Authigenic is further split into syngenetic and epigenetic. Biogenic minerals comprise less than 1% and account for the phases formed from animal and plant remains. Detrital minerals were transported by wind and water into the peat swamp. Authigenic minerals formed in the peat swamp or coal seam. Syngenetic minerals formed at the same time as the coal was formed, and epigenetic minerals formed after the coal had reached its final rank (Ward, 2016). To summarise, coal mineral matter can be composed of many different minerals as shown in Table 2. In general testing, the most common minerals are clays, quartz, carbonates, sulphides and some form of metal oxide. In terms of specific mineral names, these are represented by kaolinite, illite, montmorillonite, quartz, calcite, pyrite and possibly rutile (Gupta, et al., 2008).

Clays

Clays form more than 50% of coal mineral matter. The classification of clays is discussed in this section. There are five main groups of clay that are made up in two different structures as shown in Figure 8. These structures are 1:1 clays and 2:1 clays. There is only one clay group with the 1:1 structure and this is kaolinite. The remaining four groups are 2:1 clays and these are mica, chlorite, vermiculite and smectite. Mica and illite are used interchangeably, but illite is a blanket term to name the clay minerals that make up the mica group (Renton, 1986). The term illite will be used in this thesis to avoid confusion as this is the most common term in the literature. Kaolinite, illite and chlorite clays do not expand in water, whereas vermiculite and smectite do expand. The clays are made up of alternating layers of tetrahedral SiO₂ and octahedral alumina Al_2O_3 . In coal mineral matter, the two commonest clays are kaolinite and illite, and they serve as a significant source of aluminium to the ash (Filippidis, et al., 1996; Tian, et al., 2011).



Figure 8: Clay Structure Classification. Taken from Ghadiri et al. (2015).

Clay is predominantly formed from phyllosilicate minerals however there can be associated phases found in clays. Individual clay minerals are less than 4 μ m but typically less than 2 μ m in size. (Guggenheim & Martin, 1995; McReynolds, et al.,

2008). Raask (1985) states that clay minerals are typically less than 20 μ m across, but this is in the context of a coal where there is agglomeration of minerals.

The clays contain bound water within their lattices with kaolinite containing the most at 14%. Illite contains 4.5% and montmorillonite contains 4%. Mixed layer clays also have interlayer adsorbed water (Gluskoter, 1975).

2.2.2 Ash Yield vs Coal Particle Size

Raask (1985) describes how more mineral matter is found in different amounts according to coal particle size. In the coals tested, 20 to 76 µm coal contains a similar mass of ash to ungraded coal. Whereas, ash content at particle sizes of 76 to 200 µm is around 50% to 80% of that of ungraded coal. As the particle size decreases to lower than 20 µm the mass of ash yielded rises to 1.3 times that of ungraded coal, and a further drop in particle size to less than 10 µm may contain between 1.5 and 2.5 times as much ash. Therefore it can be seen that the minerals are concentrated in the smallest particle size material. This is on account of aluminosilicate clay minerals which form the bulk of the mineral matter in coal and are dispersed sediments of 0.1 to 10 μ m thus concentrate in coal particles below 20 µm. Silica and carbonates are more likely to be found in mid-range pulverised particles at 20 to 76 µm. Pyrite is found as large nodules in coal. Moreover, Littlejohn (1966) cited in (Raask, 1985, p. 33) has suggested that coal that floats at 1300 kg/m³ can be considered as pure coal, and anything that sinks at 2000 kg/m³ can be considered as pure ash. Ash particle agglomeration was observed at 800°C and 1000°C with melting occurring thereafter (Vassileva & Vassilev, 2005).

2.2.3 The Effect of Heat on Mineral Matter

When performing ashing, combustion, gasification or coking on coal, the mineral matter is subjected to high temperatures which change the form of the mineral matter. Most of the mineral matter is affected and the changes that occur depend on the temperature and conditions. This section deals with each mineral type in turn and goes through the possible changes that can occur. The last two minerals in this section: anhydrite and haematite, are formed from the decomposition products of some of the former minerals.

Quartz

Quartz is the only mineral to be not affected by high temperature ashing (Rao & Gluskoter, 1973; Speight, 2005; Ribeiro, et al., 2015) although quartz and silicates may react with metal silicates or metal oxides such as iron oxides from decomposed

pyrite, thus fixing the metals (Rao & Gluskoter, 1973; Speight, 2005). At temperatures exceeding the ash test such as in a combustor, the amount of quartz is lower than in low temperature ash (LTA) as some of it converts to cristobalite (Matjie, et al., 2012). Cristobalite is a polymorph of quartz and would be expected to form at 1470°C and above (Smykatz-Kloss & Klinke, 1997). According to Creelman, et al. (2013), quartz is a thermally inactive mineral, with little change occurring in pulverised fuel systems. Quartz inversion does occur at 573°C and is associated with an expansion of 0.45%, and this is the point at which α -quartz converts to β - quartz (Smykatz-Kloss & Klinke, 1997), but as far as the mineral matter is concerned, the properties change little.

Clays

Upon heating, the clays break down in a number of stages starting with the release of water and followed by the loss of structural OH groups which causes the aluminosilicates to rearrange their structure (Vassilev, et al., 1995). According to Grim and Bradley (1940), dehydration and breakdown of clays such as kaolinite, muscovite and montmorillonite starts at 250°C. In work by Garg and Skibsted (2015), thermal decomposition for montmorillonites occured in the order of dehydration up to 200°C, with dehydroxylation beginning at 500°C, and being complete at 800°C, followed by amorphization and crystallisation. Ribeiro et al. (2015) observed that there was an increase in amorphous material due to illite decomposition at 500°C however illite, muscovite and montmorillonite are still present in high temperature ash (HTA) and up to 900°C (Vassileva & Vassilev, 2005). These clays are still present in HTA because illite and smectite group minerals lose structural water at 850°C – 950°C (Gupta, et al., 2008). Once structural water has been lost, clays become amorphous and cannot be detected by XRD. Under HTA conditions, it is possible to see illite, muscovite and montmorillonite, but kaolinite has become amorphous meta-kaolinite at these temperatures, and cannot be identified with XRD. The structure of the clays is no longer crystalline and can be regarded as multi oxide glasses in structure (Garg & Skibsted, 2015) with the formation of amorphous oxides / glasses at temperatures in excess of 1000°C (Grim & Bradley, 1940).

The effect of heat on kaolinite is as follows: kaolinite > metakaolin > mullite + cristobalite (Creelman, et al., 2013) and this is shown in Figure 9. According to (Chakraborty, et al., 2003), above 600°C, kaolinite breaks down into metakaolin also known as amorphous kaolinite. Amorphous mullite begins to be formed from

kaolinite at 980°C, with crystalline material being produced at 1050°C and increasing up to 1350°C. In the process of mullite formation, silica is released. Figure 9 shows that illite begins to dehydrate at 350°C but remains in a dehydrated form until 850°C, hence it can be observed in HTA. Moreover, conversion to spinel and mullite does not complete until around 1100°C, so illite can still be observed up to these temperatures.



Figure 9: Kaolinite and Illite Reaction Schemes. Kaolinite scheme (Lee, et al., 1999). Illite scheme (McConville & Lee, 2005).

According to Qiu et al. (2016), under coking conditions the amount of quartz in the ash increases due to decomposition products of kaolinite. It would appear that the conversion of kaolinite to quartz occurs more readily when given enough time, which decreases the amount of mullite and cristobalite produced. Hence, there is a relationship between the amounts of mullite and cristobalite, and quartz. It can be expected that high proportions of kaolinite in coal mineral matter can give rise to elevated proportions of mullite in the ash (Vassilev, et al., 1995; Spears, 2000) and illite contributes towards glasses (Spears, 2000).

Carbonates

Calcite $[CaCO_3]$ and dolomite $[CaMg(CO_3)_2]$ decomposition occurs around 680-915°C releasing CO₂ and leaving metal oxides behind (Vassilev, et al., 1995). Qiu et al. (2016) observed partial decomposition of calcite in coking conditions at 650°C, and full decomposition by 850°C. DTF work at 1300°C by (Wen, et al., 2016) showed that pyrite (FeS₂), siderite (FeCO₃) and ankerite $[Ca(Fe,Mg)CO_3]$ decompose. Siderite decomposes to haematite (Fe₂O₃) and ankerite decomposes to lime (CaO) (Reifenstein, et al., 1999).

Apatite

Apatite $[Ca_5F(PO_4)_3]$ is a stable mineral under ashing conditions and at 1350°C. At temperatures as high as 1600°C, 80% still remains as the remainder of the apatite is dehydrated (Reifenstein, et al., 1999).

Pyrite

Pyrite can decompose under LTA conditions (Vassilev & Tascón, 2003) and due to weathering (Speight, 2005). The first step of pyrite decomposition is to pyrrhotite (FeS_x) (Hong & Fegley Jr., 1997). Under heating conditions, pyrite decomposes mostly by 300°C and fully by 400°C (Filippidis, et al., 1996) to give haematite and sulphur dioxide.

Anhydrite

Anhydrite (CaSO₄) is a sulphate that is unlikely to be found in fresh coals. Gypsum (hydrated calcium sulphate) is most likely to be found in weathered coals. Anhydrite is a dehydrated calcium sulphate that is formed from the dehydration of gypsum and also the reaction of CaO with SO₂ from calcite and pyrite decomposition, respectively (Matjie, et al., 2012). It typically increases with temperature up to a maximum at around 1000°C (Raask, 1985; Vassileva & Vassilev, 2005). Work by Filippidis et al. (1996) showed that anhydrite started to become present at 300°C and was well established by 450°C. Decomposition of anhydrite did not start to occur until 1200°C.

Haematite

Haematite is unlikely to be found in great quantity in the mineral matter, but increases with temperature up to 1100-1200°C (Vassileva & Vassilev, 2005). Haematite is a typical decomposition product of pyrite, ankerite and siderite that is commonly found in HTA. Filippidis et al. (1996) detected hematite at 300°C onwards in a pyrite-rich coal and 600°C onwards in another coal. According to Ribeiro et al. (2015), haematite was not detected by XRD in unburned coal, but iron can be detected by magnetic means. However, in burned samples haematite was identified by XRD.

2.2.4 Mineral Interactions at High Temperature

In the previous section, the effect of heat on the individual minerals was discussed. In a real ash system, these minerals comprise a mixture and interactions can occur between them. The mineral content of coal indicates the properties of the ash that will be formed following combustion (Speight, 2013). These include physical properties such as ash fusion temperature and hardness, as well as chemical properties. This section briefly details the minerals present in ash, and then discusses the interactions that occur.

Composition of Very High Temperature Ashes

In terms of the minerals in ash, Matjie et al. (2011) found that gasifier ash contained quartz, mullite, anorthite, cristobalite (formed from kaolinite and illite), diopside (CaMgSi₂O₆) and magnetite. Tian et al. (2011) reported similar plus haematite at 1050-1250°C. Gupta et al. (2008) performed mineral analysis following coking conditions and described ash with mullite, quartz, a small amount of cristobalite and significant amounts of amorphous material. Illite persisted in a small number of the cokes tested, as did apatite (calcium phosphate), anatase and rutile (titanium oxides). Iron was present, but not in the form of haematite owing to the absence of oxygen in the coking process. Progressive heating of coal mineral matter to 1500°C in an oxidising atmosphere showed formation of maghemite, mullite and cristobalite at 900°C to 1000°C accompanied by a decrease in the amorphous material resulting from kaolinite decomposition at 550°C. This is because the amorphous kaolinite material is converted into mullite and cristobalite. At 1500°C, the amount of quartz, cristobalite and maghemite start to decrease to create a second generation of amorphous material which increases sharply. Mullite also increases at this temperature. The main proportion of fly ash is amorphous material (glass) with mullite, quartz, cristobalite and traces of clay minerals and iron oxides (Ward & French, 2006; Ribeiro, et al., 2015). Coals with high proportions of kaolinite lead to elevated proportions of mullite (Vassilev, et al., 1995; Li, et al., 2016) and upon heating clay converts to mullite and amorphous aluminosilicates (Matjie, et al., 2012), as shown in Figure 9. According to Qiu et al. (1999), mullite and anorthite are formed by the reaction of quartz with Al₂O₃ and CaO respectively, at around 1000°C and this is accompanied by a reduction in the quartz peak.

Fixing of Metals and Alkalis into Aluminosilicates

Alkali metals, such as sodium and potassium, that volatilise easily are released, and are captured by the Si-Al system in kaolinite to produce albite (NaAlSi₃O₈), and muscovite (KAl₃Si₃O₁₁) in a temperature range of 1000-1200°C (Li, et al., 2016). Decomposition products of clays are a disordered (glass/amorphous) mixture of silica and alumina (aluminosilicates) which are able to react with fluxing elements such Na, Ca and K, and refractory elements such as Mg. The first phase to be formed from a pure aluminosilicate melt is mullite, and when alumina is exhausted, silica in the form of cristobalite is formed. Iron in the system can form spinels or it can produce iron aluminosilicate glasses. If there is calcium in the system, then a calcium aluminosilicate called anorthite (CaAl₂Si₂O₈) will form, and the presence of sodium leads to Ca-Na aluminosilicates (Creelman, et al., 2013). Matjie et al. (2012) also observed the formation of anorthite from the incorporation of calcium with aluminosilicates. In addition, there was an increase in the amount of amorphous material. Wen et al. (2016) performed high temperature combustion in a DTF at 1300°C and found significant integration of elements such as calcium and iron into aluminosilicates. Furthermore, quartz reacted with other minerals to form aluminosilicates. Mullite changes little, but in some cases can absorb iron and calcium to form aluminosilicates. When the coal was run through the DTF, there was a shift from discreet minerals, to a number of newly formed aluminosilicates. The proximity of the minerals to each other has a large effect on the aluminosilicate forming reactions. Extraneous minerals do not react very effectively with inherent minerals until they have been released from the carbonaceous matrix during char combustion (Wen, et al., 2016).

Volatilisation and fixing of metal and alkali species has a practical application that can reduce the amount of alkali in the gas phase. In gasification, aluminosilicates additives that react with K and Na and are useful for K₂O and Na₂O capture; kaolin is added to reduce ash-related problems (Ozer, et al., 2017). Li et al. (2016) determined that kaolin fixed alkalis in the mineral phase which prevented them from evaporating into the flue gas, however beyond 1100°C the kaolin was too molten to capture alkali metals. Vapours released from a flame include sodium, potassium, sulphur and chlorine. Solid and liquid particles generated during combustion include silicates, aluminosilicates, iron-rich compounds, calcium oxide and magnesium oxide. Sodium in high temperature deposits (>1038°C) was found to be concentrated in the amorphous melt phase and not the crystalline phase. The sodium was derived from aluminosilicates. In addition, temperatures below 1038°C are said to favour the formation of sulphate phases such as calcium sulphate (Benson & Sondreal, 2002). Thus, if combustion temperatures exceed ~1100°C, the ability for undesirable vapours to be fixed into aluminosilicates, is reduced. Regarding sulphur fixing, the introduction of calcium into coal ash can capture sulphur thus reducing pollutant gases (Levendis, 1989).

Summarising the Effect of Heat on Mineral Matter

It can be seen that the mineral matter in coal undergoes a number of changes as it is exposed to heat. As the temperature increases beyond high temperature ashing conditions, changes from decomposition and thermal breakdown to amorphisation occur. In summary, carbonates and pyrite decompose to form oxides, typically calcium, iron and sulphur, giving rise to haematite and anyhydrite. Clays dehydrate, dehydroxylate and break down in structure to form amorphous aluminosilicates and can release metals such as potassium, sodium and calcium. Depending on the conditions, all the aforementioned metals can potentially be absorbed by the aluminosilicates to form a number of different compounds. Additionally, the aluminosilicates resulting from clay breakdown give rise to mullite formation. Quartz can become integrated into aluminosilicates, and it can change phase to cristobalite. Thus the resultant composition of fly ash and slag is typically aluminosilicate glass, mullite, and cristobalite or quartz.

2.2.5 Catalytic Effect of Ash

In coal ash many of the elements are catalytic, for instance iron, calcium and potassium oxides are effective catalysts for gasification (Gupta, et al., 2008). It has been reported that alkali metals, alkaline earth metals and transition metals are highly effective as catalysts for gasifying carbon into carbon dioxide (Nomura, et al., 2006), however while alkaline earth metals such as Be, Ba, Mg and Sr can catalyse gasification, they do so to a lesser extent than Ca and K (Kapteijn, et al., 1986). Miuraa et al. (1989) reviewed a large body of literature pertaining to the reactivity of coal char gasification and established that for low rank coals, mineral components containing Ca, K, Na, Fe and Mg act as the gasification catalysts and that for higher rank coals, gasification was controlled by their intrinsic reactivity; this being related to bonding and active sites. This is in contrast to Zou et al. (2014) who found that the catalytic effect of MnO_2 , CaO and Fe_2O_3 was greater on anthracitic than bituminous coals when tested at 1% concentration in a TGA in air. Nonetheless, the effectiveness of a catalyst is more prominent in lower temperatures processes such as gasification, when compared to high temperature combustion (Tomita, 2001), for example, alkalis potassium and sodium were ionexchanged into acid-demineralised coals but this did not improve combustion. The same process was applied to calcium, which was found to increase char particle temperatures at concentrations less than 5000 ppm (McCollor, et al., 1989). Ca and Fe in mineral matter are known to be especially effective catalysts for gasification.

There is great variation in the reactivity of different coals and this can be attributed to mineral matter (Tomita, 2001). During the formation of coke, the catalyst is deactivated. The catalyst can be restored by combusting or gasifying the coke, where the catalyst will provide a positive effect during this process (Tomita, 2001). A key factor controlling reactivity is the extent to which the catalyst is dispersed in the carbon. Physical mixing is the least effective method, with impregnation being better, and ion exchange metal cations leading to the best dispersion upon heating (Levendis, 1989; Tomita, 2001). Nonetheless, it is important to consider the impact of mineral matter in the coal as it was found that the use of a potassium carbonate catalyst in coal gasification was hampered by deactivation due to reaction with the coal mineral matter (Tomita, 2001). Referring to the Section 2.2.4, this is likely on account of the potassium carbonate thermally decomposing into potassium oxide and becoming fixed into the aluminosilicates formed from clay breakdown.

Levendis et al. (1989) investigated the effect of calcium on synthetically produced chars using calcium carbonate precipitation, impregnation with calcium acetate, and calcium ion exchange. Highly porous chars had uniform levels of calcium throughout their structures whereas the low-porosity chars had high levels of surface calcium but low levels internally. The high porosity chars typically showed a tenfold increase in gas evolution above the uncatalysed control but decreased from 400°C to 500°C. The heightened rates of reaction only occurred for the proportion of char that was successfully impregnated. So if the material was 60% calcium loaded, the rate of gas evolution dropped off after 60% conversion and assumed the uncatalysed rate. At temperatures exceeding 900°C, the catalytic effect is less pronounced than the low temperature combustion, but still significant. In spite of the calcium catalyst blocking some of the pores, there was still a positive effect on combustion. Ion exchange was the most effective method of introducing catalyst. It should be emphasised that in the above work, the use of synthetic chars provides a different substrate to coal, which means that the effect of calcium additives on real coal chars may be different.

Coal mineral matter has been shown to have an intrinsic catalytic effect. When comparing the steam gasification reactivity of the demineralised brown coal chars versus the parent coal chars, the parent coal chars gave off greater volumes of CO_2 and H_2 gases than their demineralised counterparts. CaO was a more potent catalyst than CaCO₃ with good dispersion of both being important (Kuznetsov, et al., 2013). This work is in agreement with Kyotani et al. (1986) who used Temperature Programmed Desorption (TPD) and observed that successful steam gasification was attributed to the presence of mineral matter because when the coal char was demineralised, there was almost no gas evolution. It was also found that calcium caused H₂O to be evolved; calcium and magnesium were responsible for evolution of CO₂, while the CO evolved was on account of sodium and iron. In addition, exchanged metal species Ca and Na significantly catalysed the gasification reaction. Ohtsuka and Tomita (1986) found that the use of 5% calcium catalyst on brown coal during steam gasification occurred at around 700°C which was around 150°C lower than the uncatalysed reaction.

Diego (1992) cited in Spears (2000) confirmed the catalytic effect of pyrite and illite, and the inhibitory effect of quartz and kaolinite. These findings are corroborated by (Manzanares et al. 1988) who used density separation to separate macerals, and found that pyrite reduces ignition temperatures and inertinite which contains quartz and kaolinite increases ignition temperatures. Clay mineral type can be linked to maceral type, for example vitrinite plays a role in increasing reactivity compared to inertinite as it contains more catalytic mineral matter for gasification (Ozer, et al., 2017). Lee and Whaley (1983) state that vitrinite and liptinite are more reactive than inertinite.

Catalytic Mechanisms

The ashes of different coals have different levels of catalytic behaviour and this is related to their mineral matter and elemental composition. It has been discussed that alkalis, alkali earth metals, and transition metals are able to catalyse the gasification of char. These include potassium, calcium, and iron, respectively. A study of the literature discusses different catalytic mechanisms but the science is not fully understood. Catalytic mechanisms include changes to surface chemistry, increasing the number of active sites, carbonate-oxide cycles, and redox cycles. According to Freund (1986), calcium is a highly effective catalyst that works by increasing the number of active sites.

Ban, et al. (2018) describe how the addition of Ca and K catalysts resulted in significant weakening of the C=O bond, where carboxylate groups were replaced with metal-carboxylate species. When the metal ions combine with the carboxyl groups on the polycyclic aromatic hydrocarbons, this decreases their stability and reduces the extent of graphitisation. K interacts via ionic forces substituting H from COOH; Ca also does this but additionally interacts in the form of polycarboxylic coordination, and it was suggested that these dual effects led to the increased

effectiveness of the calcium catalyst as observed by Ban et al. (2018). Addition of calcium and potassium significantly reduced the activation energy for the CO_2 gasification reaction.

It has been observed (Ohtsuka & Tomita, 1986) that interconversion between calcium carbonate and calcium oxide occurs in the gasification region. This mechanism is thus described. CaO is effective at chemisorption with CO_2 to form $CaCO_3$ as shown in Equation 10. This undergoes a solid state reaction with carbon to from CO as shown in Equation 11 (Cai, et al., 2017).

 $CaO + CO_2 \rightarrow CaCO_3$ Equation 10 $CaCO_3 + C \rightarrow CaO + 2CO$ Equation 11

For iron catalysed gasification, firstly the CO_2 adsorbs and dissociates onto a metal catalyst to form a catalyst- CO_2 complex, as shown in Equation 12. Secondly, this complex migrates to a carbon structure to react and produce two CO molecules, and release catalytically active iron, as shown in Equation 13.

 $Fe_nO_m + CO_2 \rightarrow Fe_nO_{m+1} + CO$ Equation 12 $Fe_nO_{m+1} + C \rightarrow Fe_nO_m + CO$ Equation 13

The subscripts *n* and *m* take account that the iron catalyst could be in different forms: Fe metal, FeO, Fe₂O₃, and Fe₃O₄ (Cai, et al., 2017). This is affected by the operating conditions of gasification, such as temperature and ratio of CO₂ to CO (Ohtsuka, et al., 1986). A temperature of at least 700°C is required for iron to have a clear catalytic effect. The ability for the catalyst to wet and spread on the carbon substrate is an important factor to ensuring sustained catalytic activity. The multiple oxidation states of iron suggest that intermediate forms may take part in the catalytic process (Furimsky, et al., 1988).

The most effective catalysts are generally the carbonates, oxides and hydroxides (Mckee, 1983). Deactivation of potassium catalyst occurs due to interaction with inherent aluminosilicates (Radovic, et al., 1984). Poisoning of an iron catalyst can occur due to sulphur (Hüttinger, 1983).

2.2.6 Physical Effect of Ash on Combustion

Jayanti et al. (2007) performed CFD analysis on coals and found that the increased char reactivity due to ash was negligible, and that ash had the effect of reducing the char reactivity as it blocked pores resulting in lower oxygen diffusing into and out of the char leading to lower furnace temperatures. This work is corroborated by Kurose et al. (2001) who combusted three (40% – 50%) high ash coals and found that as ash content increased, the oxygen consumption and gas temperature decreased. The reasons given for this were that as the char is covered with ash, the oxygen diffusion is reduced, and also ash has a high specific heat capacity that reduces flame temperatures. Additionally, the lower combustion temperature meant that oxygen was used up more slowly. Moreover, as char combustion proceeded, the effect of pore blockage worsened as the ratio of ash to carbon increased, resulting in a thicker layer of ash developing on the chars.

2.2.7 Ash Melting Behaviour

Ash melting behaviour is dependent on the elemental composition, mineral composition, and interactions between the minerals. It is not possible to accurately predict the ash fusion temperature (AFT) based on any one of these pieces of information, thus it is important to measure the AFT using testing. In a coal fired furnace, if the fusion tempearure is low, the molten ash will make its way to the bottom of the furnace, and if it is high, it will make its way out the top as fly ash (Speight, 2013). In the blast furnace, high fusion temperature causes ash to stick in the coke bed, whereas lower FT allows the ash to melt and flow through the coke (Khairil, et al., 2002). Thus a high FT ash could reduce blast furnace permeability. The AFT and viscosity of coal ash is greater than slag (Song, et al., 2009).

Element Effects

The element oxides found in ash may be divided into three groups: acids (SiO₂, TiO₂, P_2O_5); amphoteric oxides (Al₂O3 and Fe₂O₃); and bases (Na₂O, K₂O, CaO, MgO, MnO, NiO (Lolja, et al., 2002). If they are to be divided into two groups, then Al₂O₃ would be among the acids and Fe₂O₃ among the bases (Vorres, 1977; Lolja, et al., 2002). Ash from lower rank coals typically have lower melting temperatures due to having more alkaline components (Pisupati & Krishnamoorthy, 2017). This is in agreement with (Vassilev, et al., 1995) who cites the higher concentrations of sulphur, calcium, magnesium, iron and sodium as being responsible. Higher rank coals with greater proportions of silicon, aluminium and titanium typically have higher ash fusion temperatures (Vassilev, et al., 1995; Vassileva & Vassilev, 2002). According to

Creelman et al. (2013), fluxing elements such as Na, Ca and K reduce the solidus temperature of aluminosilicates, mullite and magnesium may increase it, but does not reduce it. The variable composition of glasses and disequilibrium present in slags makes it difficult to perform thermodynamic modelling (Creelman, et al., 2013). High sulphur content can lead to reaction with calcium and magnesium sulphates in the HTA with a fluxing effect (Vassilev, et al., 1995). Liu et al. (2013) observed that in a synthetic five component system of $(SiO_2-Al_2O_3-CaO-Fe_2O_3-K_2O)$, increasing Fe₂O₃ causes AFT to decrease while potassium does not appear to have any effect, however it was observed by Huffman et al. (1981) that potassium has an effect in lowering AFT, but not so much as calcium and iron. It was noted that aluminium increases ash fusion temperatures. Mishra et al. (2016) describes how Factsage thermochemical software was used to predict the deformation temperatures and determined that deformation and fusion temperatures increase with increasing SiO₂, Al₂O₃, and K₂O, and that they decrease with increasing Fe₂O₃ and MgO. 815°C lignite ash was rich in basic calcium compounds such as anhydrite and calcium silicate which gave rise to a lower melting temperature (Li, et al., 2017). According to a review by Tian et al. (2016), high fusion temperatures are related to the amount of calcium, iron, aluminium and sulphur (in that order). Van Dyk et al. (2009), state that calcium and iron content, especially, is thought to give a reasonable estimation of the ash fusion behaviour. Dai et al. (2018) agree upon the fluxing effect of calcium and magnesium.

Ash fusion temperature is lower under reducing conditions, compared to oxidising conditions (Huffman, et al., 1981; Nel, et al., 2014; Chen, et al., 2017). Acid oxides that combine with oxygen easily can form a polymer structure and increase the AFT. Basic oxides can terminate polymer structures and decrease the AFT (Chen, et al., 2017). The difference in ash fusion temperature in oxidising and reducing conditions has been related to the oxidation state of iron. Under oxidising ash fusion temperatures. Under reducing conditions most iron occurs as Fe²⁺ state, which acts as a basic oxide that lowers AFT (Vorres, 1977; Chen, et al., 2017). Under oxidising conditions, it was shown that sodium can react with sulphur to form Na₂SO₄ which had the effect of lowering the amount of sodium in the aluminosilicates, giving a high AFT. Meanwhile, under reducing conditions, the sodium remains in the aluminosilicates which gives a lower AFT compared to oxidising conditions. However, in coals with high Al₂O₃ and SiO₂, sodium-aluminosilicates would form preferentially (Chen, et al., 2017).

Ash Fusion Mineral Effects

Coals that were high in acidic oxides and refractory minerals such as quartz and kaolinite, led to higher sintering and fusion temperatures. It was found that adding kaolin clay increases fusion temperatures up to a point of diminishing returns (Li, et al., 2016; Li, et al., 2017). Speight (2013) states that iron bearing minerals such as pyrite tend to reduce the FT whereas aluminium containing minerals such as kaolinite and illite raise it. Ashes with a high FT have increased concentrations of metakaolinite and mullite (melting point (MP) 1810°C), quartz (MP 1713°C), titanium oxides (MP 1827°C), and aluminium oxides (MP 2050°C) (Vassilev, et al., 1995). Li et al. (2016) determined that high melting temperature minerals produced in ash, such as mullite, drive up the melting temperature of the ash.

Calcium oxide or calcium carbonate is commonly added to entrained-flow gasifiers to reduce the ash fusion temperatures. Calcium causes the formation of anorthite which decreases the AFT, and it also causes the formation of gehelenite which increases the AFT. Using Factsage and MD simulations, it was shown that the melting temperature of an amorphous SiO₂, Al₂O₃, CaO system was reduced by 200°C with the addition of 15% of CaO. There was a further drop in temperature up to 40% but this was less pronounced at the higher concentrations. At less than 15%, the most stable structure in that ternary system is mullite. This changes to anorthite over 15%, and may be the point affecting the liquidus structure. The calcium atom interacts with the tricluster AI-O which are part of mullite and this lowers the melting temperature (Dai, et al., 2018). Vassileva and Vassilev (2002) posit that during coal combustion Fe, Ca, S, Mg, Na, P, and Mn become oxides that react with silicates to form fluxing type minerals that make up a low temperature eutectic of Fe-Ca-Mg-Na-Mn silicates. Findings by Liang et al. (2019) showed that increasing the calcium oxide content in coal ash reduced the melting temperature up to 35% addition rate, but beyond this, the ash fusion temperature increased again.

Regarding blending, adding acidic ashes to basic ashes, did not immediately increase the fusion temperatures. Up to 30% mass addition of acidic ash caused a reduction in AFT, whereafter, it started to increase. Blending the coals in various proportions gave an AFT of less than the original coals- 100°C to 200°C less in some cases. The effect of mixing ashes, therefore, did not have an additive effect on AFT (Li, et al., 2017). The interaction of minerals can form a low melting point eutectic causing the softening temperature of blended ashes to decrease (Qiu, et al., 1999). A eutectic is a mixture of two or more components that, at certain ratios, can inhibit

the crystallisation of one another leading to a mixture with a melting point that is lower than each of its constituent parts (Gala, et al., 2013).

Acid/Base components and other elemental ratios

The effect of acidic and basic components have been discussed. Several authors have used a base to acid (B/A) ratio to give some indication of melting behaviour.

Akar et al. (2009), Matjie et al. (2012), and Li et al. (2017) used a base to acid ratio of ($Fe_2O_3 + CaO + MgO + Na_2O + K_2O$) to ($SiO_2 + Al_2O_3 + TiO_2$). It was determined that with increasing ratio there was lower FT.

Vassileva and Vassilev (2002) described a detrital to authigenic index of $(SiO_2 + Al_2O_3 + K_2O + Na_2O + TiO_2) / (Fe_2O_3 + MgO + CaO + SO_3)$, which when high, coincided with a high fusion temperature. Authigenic and detrital minerals were discussed in Section 2.2.1 Terminology and Coal Mineral Composition.

The oxide content and ratios cannot be reliably used to predict the ash melting behaviour, because ash melting behaviour is a complex interplay of physical and chemical processes with gas, liquid and solid phases. However it was noted that an increase in basic oxides decreased the AFT. There was greater correlation of the AFT with the oxide content than the initial deformation behaviour, which is determined more by the mineral behaviour (Lolja, et al., 2002).

The SiO_2/Al_2O_3 (S/A) ratio does not appear to have a big effect on ash fusion temperatures. It is more related to the viscosity of the liquid phase where a higher S/A ratio gives higher viscosity (Yan, et al., 2017).

Vincent's formula (Gray, 1987) was used to calculate a predicted ash fusion temperature and is shown as follows:

 $AFT = 1934 - 13B - SiO_2 + 30F_A + 2.9CaO + 40K_2O - (0.51Al_2O_3 x MgO)$ Where $B = CaO + MgO + FeO + Na_2O + K_2O$ And $F_A = (SiO_2 + TiO_2 + P_2O_5) / Al_2O_3$

Equation 14: Vincent's formula for predicting the ash fusion temperature (Gray, 1987)

It was investigated in this thesis but found to be an inaccurate predictor of ash fusion temperature.

Slag

The formation of slag has been briefly presented in the introduction. Slag forms from the impurities in the blast furnace feed materials, namely, coal and coke ash, iron ore gangue, and limestone. The melting temperature and viscosity are important parameters that are determined by the slag chemistry and need to be controlled to ensure that the slag flows through the furnace without affecting permeability. The ability for the slag to perform desulphurisation is also very important. Slag basicity is dependent on the proportions of basic CaO and MgO, and acidic SiO₂ and Al₂O₃ (Babich, et al., 2008). The basicity is given by Equation 15:

 $B = \frac{CaO + MgO}{SiO_2 + Al_2O_3}$

Equation 15: Slag Basicity Chemical Equation

These four oxides make up 95% of the slag. Chemical analysis of some German ground granulated blast furnace slags (GGBFS) found that the percentage proportions of SiO₂, Al₂O₃, CaO, and MgO were (30-40%), (12-22%), (35-45%) and (~8%), respectively. In Germany, slag is the main ingredient for regular cements (Tänzer, et al., 2015). The majority of the slag is non-crystalline amorphous material (Song, et al., 2009; Tänzer, et al., 2015). Decreasing the content of Al₂O₃ and MgO contained within iron ore sinter is beneficial as this influences the reducibility and melting property of the sinter and results in lower slag volumes (Ishii, 2000). High aluminium slag has low fluidity (Naito, 2006).

Slags form from coal minerals that undergo thermal decomposition to make glasses. Metal oxides tend to flux the melt and these include iron oxide, alkali metals oxides (sodium and potassium), and alkali earth metal oxide (calcium). When looking at a ternary phase diagram, the presence of K₂O significantly lowers the liquidus temperature of an aluminosilicate based system (Osborne, 2013, p. 347). When a liquid slag or ash is cooled quickly, it will form a glass (Osborne, 2013).

Sodium oxide, calcium oxide, and iron oxide, in this order of effectiveness, reduce the viscosity of slag by weakening tricluster oxygen bonds. Moreover, some high melting temperature minerals are converted to lower melting temperature minerals which helps to reduce slag viscosity (Dai, et al., 2019). In work by Song et al. (2009), the addition of calcium in the form of limestone decreases the AFT of the ash and slag up to 35% content after which point there is a rapid increase because the sub-liquidus phase transforms from anorthite to gehlenite if further calcium is added.

Summarising the effect of elements on ash fusion temperature

In summary, it is well documented that silicon, aluminium and titanium raise ash fusion temperatures, while calcium, iron and sulphur lower them. However, there is some discrepancy with magnesium and, in particular, potassium. Thus, the proportions of refractory and fluxing elements influence the melting temperature, however simply taking the chemical analysis as a predictor of AFT is not reliable because mineral interactions also play a role (Vassilev, et al., 1995).

2.3 Effect of Mineral Matter in the Blast Furnace

Mineral matter has a range of effects during coal combustion. Ward (2016) describes mineral matter in a negative sense, stating that it offers "little if anything" to the use of coal. It has been termed a diluent which displaces combustible matter leaving ash when the coal is burned. This ash contributes to the slag formation in the blast furnace and needs to be removed. Mineral matter may also cause abrasion, corrosion, clogging or pollution during coal processing and use. Indeed, the majority of issues seen during coal utilisation are caused by the inorganic mineral matter and not the organic maceral constituents (Ward, 2016). This position is echoed by Speight (2005) who says that mineral matter, regardless of its makeup, is considered both undesirable and detrimental during mining, preparation, transportation and combustion. The aim of coal preparation is to reduce the quantity of mineral matter present. Clinker formation, fly ash, slagging and boiler tube corrosion are all problems that occur because of mineral matter.

Spears (2000) and Akhavan (2014) share an unfavourable view of clay minerals stating a twofold effect on combustion efficiency: they reduce the calorific value of coal by dilution and the reactions of the clay at high temperatures are endothermic. Bennett and Fukushima (2003) state that ash takes energy to melt, can impede oxidation during coal injection, and is the principle source of alkalis.

On the other hand, Tomita (2001) describes the mineral matter in coal as an unintentional catalyst, with components in the mineral matter being catalytic to varying extents. According to (Hill, et al., 2004), an increase in ash content did not adversely affect furnace permeability and productivity. The blast pressure and volume could be kept at the same levels as for a lower ash coal and furnace heat loss was much the same. Hot metal silicon and sulphur content were similar to the low ash coal. The only noticeable affect was an increase in slag volume, and more coke needed to be used to compensate for the lower carbon content of the coal.

2.3.1 Alkalis and Circulating Elements in the Blast Furnace

Common circulating elements in the blast furnace include sulphur, alkalis such as Na and K, zinc and silicon (Iljana, et al., 2013). Alkalis enter the blast furnace through the feed of raw materials. Alkali silicates can be found in the iron ore gangue, and coke contains alkali aluminosilicates (El-Geassy, et al., 1986). Coal injected into the tuyeres contains alkalis bound in clays such as illite and montmorillonite. The two main alkalis of interest are potassium and sodium, which are found in the respective clays. Illite is the main source of potassium (Gupta, et al., 2008).

The recirculation of alkali causes an increase in alkali concentration at the lower part of the furnace.

Alkalis that enter via the coal minerals are vaporised in the raceway. Alkali silicates from the iron-ore descend through the blast furnace until the temperature is high enough for them to be reduced releasing potassium vapour at around 1500 – 1700 °C. The process can happen with coke carbon (El-Geassy, et al., 1986; Yang, et al., 2000), freshly reduced iron (El-Geassy, et al., 1986) or carbon monoxide (Iljana, et al., 2013). The reactions shown below represent potassium K, but this can be substituted with sodium Na in all of the following reactions.

a. $K_2SiO_3 + C(s) \leftrightarrow 2K(g) + SiO_2(s) + CO(g)$ Equation 16

b.
$$K_2SiO_3 + Fe(s) \leftrightarrow 2K(g) + SiO_2(s) + FeO(g)$$

Equation 17

c.
$$K_2SiO_3(s,l) + CO(g) \leftrightarrow 2K(g) + CO_2(g) + SiO_2(s)$$

Equation 18

Alkali oxides can be reduced to alkali vapour in the presence of carbon or carbon monoxide as follows:

d.
$$K_2O + C(s) \leftrightarrow 2K(g) + CO(g)$$

Equation 19

e.
$$K_2O + CO(g) \leftrightarrow 2K(g) + CO_2(g)$$

Equation 20

 Some, but not all, of the newly formed alkali vapours react with carbon and nitrogen to form KCN and NaCN cyanide vapours as follows at around 1300 to 1600°C: a. $K(g) + C(s) + \frac{1}{2}N_2(g) \iff KCN(g,I)$

Equation 21

- 3. The boiling points of potassium cyanide and sodium cyanide are 1625°C and 1530°C, respectively. As these vapours ascend the blast furnace they reach areas of lower temperature where they condense on the burden and some penetrates the blast furnace walls.
- The condensed alkali cyanides react with carbon dioxide at less than 1100°C to produce alkali carbonates.

a. $2K(g) + 2CO_2(g) = K_2CO_3(s) + CO(g)$ Equation 22

b. $2KCN(g) + 4CO_2(g) = K_2CO_3(s) + 5CO(g) + N_2(g)$ Equation 23

- 5. A certain amount of these alkali cyanides and carbonates pass out in the top gas, but the majority attaches to the burden or condenses on the walls.
- 6. As the alkali species descend the furnace again, the carbonates which are unstable at more than 1300°C are released into the vapour phase again and the cycle continues. Thus, alkalis circulate within the furnace as cyanide and alkali vapours on the way up and carbonates and liquid cyanides attached to the burden on the way down. The addition of new alkali material from ore and coal in addition to the existing cycle concentrates alkali in the furnace.
- Scaffolds form when oxidised alkali vapours adhere to cooler regions of the blast furnace refractory, whereupon the deposition of liquid alkali cyanides at 562 – 1625 °C encourage the sticking of fine particles from coke and iron ore and which helps to build up the scaffold.

Alkali input is detrimental to blast furnace operation for a number of reasons (Slizovskiy & Tangstad, 2010; Dastidar, et al., 2018). They cause erosion wear to the blast furnace lining, especially in the high temperature region. They are responsible for swelling and break up of iron ore lump, pellets and sinter, thus generating fines. They form extensive scabs known as scaffolds by condensing on the refractory at the higher areas of the blast furnace; these scaffolds affect the burden decent and reduce the life of the lining (El-Geassy, et al., 1986; Pichler, et al., 2014). They catalyse the gasification of coke (in the reverse-Boudouard or solution loss reaction) leading to coke degradation, higher coke consumption and generation of coke fines in the lower part of the furnace (Abraham & Staffansson, 1975; Dastidar,

et al., 2018). The reaction between coke and CO_2 occurs at it fastest in the melting zone of the blast furnace. This can be partly attributed to there being a high concentration of alkali of around 10 times that found in the coke itself, at this region (Tomita, 2001).

Alkali and alkali cyanide vapours are found towards the bottom of the furnace where the temperatures are greater. Alkali and alkali oxide vapours are responsible for attacking the refractory. Alkali wear at the top of the furnace is minimal and the extent of damage is greatest around and just above tuyere level, and affects the whole of the bosh. An undamaged refractory brick is made up, predominantly, of SiO₂ and Al₂O₃ at a proportion of around 50% : 40%, creating mullite and α cristobalite, with around 1.5% of Fe₂O₃ and some other materials. Potassium penetrates into the brick to a great extent causing wear and cracking to the brick. Sodium also penetrates, but to a lesser extent, of about 20% of that of potassium. This is likely because potassium exists in vapour form at a lower temperature of 766°C compared to sodium of 890°C (El-Geassy, et al., 1986), and so is more available to enter the pores of the refractory bricks. Moreover, the reduction of potassium oxide to potassium vapour occurs 200°C lower than sodium oxide to sodium vapour. Hence, sodium oxide is a more stable compound. According to Dastidar, et al. (2018) potassium mainly affects the refractories since sodium gets removed with the slag.

In addition, carbon is found as a foreign element in the fireclay bricks. The wear of the bricks occurs when the potassium reacts with mullite and cristobalite in a reducing atmosphere to form kalsilite (a potassium aluminosilicate) plus carbon. This reaction is accompanied by a volume expansion of 6% which exacerbates the effect. Additionally, the reaction of alkali vapours with glass and cristobalite forms a liquid phase which may accelerate the wear. Zinc can penetrate through the whole brick, but in small quantities, leading to the formation of zincite (ZnO) and willemite (2ZnO.SiO₂). Deashed coke reacted with potassium vapour showed cracking when the vapour concentration exceeded 4% (Narita , et al., 1981).

The mechanism whereby alkalis cause damage to the iron ore pellets is that they catalyse the formation of sharp iron whiskers and protrusions from the ore pellets, which induce stresses and cause the pellets to crack more easily (Pichler, et al., 2014). In other work, a combination of potassium and sulphur was shown to have a highly swelling effect on haematite pellets. During reduction at 800-1000°C, potassium carbonate was added at a concentration of 0.5 mol% and the sulphur

was introduced as a gas. The presence of calcium oxide with sulphur also promotes swelling. Calcium oxide on its own does not cause swelling (Hayaski & Iguchi, 1989).

Some solutions have been proposed to combat the effect of alkalis. Utilisation of small 25 mm diameter coke mixed with the iron ore has been used to improve permeability in the lower part of the blast furnace. This is achieved because the smaller coke reacts preferentially to the charged lump coke (45 mm diameter) thus preserving the size of the lump coke for lower down in the furnace. The proximity of the small coke to the ore and its higher surface area makes it more reactive than the lump coke. However, it is important to not add too much small coke since unreacted fragments will reduce voidage and thus decrease permeability in the lower part of the furnace (Kashihara, et al., 2015).

The majority of alkalis enter the slag, where it is tapped off, but some of it leaves in the off-gas. Alkali leaving in the slag is preferable as this removes the problem from the other parts of the furnace (Dastidar, et al., 2018). According to El-Geassy et al. (1986), potassium predominantly exits with the top gas, while sodium is removed in the slag. Decreasing the basicity [(CaO + MgO) / (SiO₂ + Al₂O₃)] of the slag by reducing the limestone input helps in the removal of alkalis, however, an acidic slag also increases hot metal silicon and sulphur, which is undesirable (Dastidar, et al., 2018), additionally, the slag viscosity and iron oxide content increases, and the temperature of the hot metal reduces. Other methods to reduce alkali vaporisation include increasing the oxygen in the blast which reduces the ability for alkali silicates to be reduced, and also reducing the temperature of the furnace which reduces the extent of alkali devolatilisation (Yang, et al., 2000).

2.3.2 Interaction between PCI Ash and the Raceway/Deadman Coke

Part of the mineral matter from PCI melts and/or vaporises and can be deposited onto the coke in the deadman. This can cause the reactivity of the coke to increase in much the same way as alkali deposition, which leads an increase in coke reactivity and the generation of fines. Surface deposits of coal ash can cause the coke to agglomerate as the sticky ash acts as a binder between individual coke lumps. This has the potential to increase the pressure drop due to reduced permeability in the furnace (Khairil, et al., 2002). Figure 10 is a representation of how pulverised coal ash particles travel out the raceway and interact with dripping slag and the deadman. The majority of ash generated from PC combustion travels upwards in the direction of furnace flow, while a lesser amount travels circumferentially further into the furnace and deadman coke. The upward moving ash reacts and is captured by the dripping slag falling from the cohesive zone. Ash that travels into the deadman can cause 1-3mm fines that reduce the permeability at the deadman surface. This has the effect of reducing the temperature in the deadman with a resultant increase in slag viscosity (Ichida, et al., 2001). On the other hand, according to Iwanaga (1993), partially burned char gasifies quicker than lump coke which helps to reduce coke degradation.



Figure 10: Ash behaviour and interaction with dripping slag in and around the raceway (Ichida, et al., 2001).

According to Khairil et al. (2002), high melting temperature ash tends to deposit on the surface of coke and is likely to adhere to the coke and not drip down compared to low melting temperature ash which has a lower viscosity and will run off the coke more easily. In an investigation by Zou et al. (2017), the fluidity of high melting temperature ashes was increased by the introduction of Fe_2O_3 and CaO, which had the effect of enabling the lower viscosity ash to enter deeper into the coke pore structure, while catalysing the reaction between the ash and the coke.

Pertaining to the effect of the intrinsic ash in coke, it has been reported (Gornostayev & Härkki, 2006) that the mineral matter in coke can block pores reducing reactivity, and low AFT can cause this to happen further up the furnace. Additionally, chemical rearrangement of melting of mineral matter may create weak spots in coke and reduce its strength.

2.3.3 Hot Metal Silicon

Silica is a refractory oxide with low volatility at less than 1727°C. Calcium and magnesium fall into this category. Silica present in coal ash and will vaporise, nucleate and condense depending on the surrounding conditions. Higher temperatures and a more reducing atmosphere (CO-rich) increase the effect. Silica will not strongly vaporise directly, but requires these other conditions. Typically temperatures approaching 1727°C allow the following equilibrium vaporisation reaction to occur: $SiO_2(l) + CO \leftrightarrow SiO(g) + CO_2$ (Senior & Flagan, 1982). An issue with increased PCI rates is that the amount of silicon in molten metal tends to increase. The reaction between char carbon and SiO₂ present in the char ash also causes SiO gas to be generated under reducing conditions. SiC is also generated between the same two reactants. Coke silicon is responsible for a large amount of silicon oxide generation, and this increases with temperature as the melting coal ash is better able to permeate the coke pores and thus increasing reactivity. However, the production of SiO from pulverised coal happens at 3x the rate owing to a high surface area for reaction. The production of SiO happens in the furnace where the temperature exceeds 1700°C and silicon absorbed into the hot metal is proportional to the amount SiO generated (Matsui, et al., 2003). Typically, hot metal silicon content should be between 0.3 and 0.7% (Geerdes, et al., 2009).

2.3.4 Sulphur

Sulfur has a negative environmental impact and is an undesirable element in steels, therefore it is important to understand sources of sulfur in the blast furnace raw materials (Gornostayev, et al., 2018). Sulphur is present in all fossil fuels to varying degrees, in inorganic (pyrite) and organic form (Vernon & Jones, 1993). High sulphur fuels can cause corrosion in power generation boilers; chlorine also the same effect (Raask, 1985). Coal cleaning has been employed as a means of reducing sulphur in coal and has focused on removal of mineral matter pyrite. Wet and dry gravity-based methods are effective at the removal of pyrite, and this includes density separation (Vernon & Jones, 1993).

Inorganic sulphur comprises pyrites and sulphates while organic sulphur includes thiols, sulphides, disulphides, and thiophenes. The main sulphur emission from burning coal is SO₂ and this causes acid rain and other environmental problems (Gu, et al., 2016). Sulphate compounds in the mineral matter can be released into the gas phase during coal devolatilisation (Telfer, et al., 1999). Sulphur present in the coal and coke oxidises in the raceway to create sulphur dioxide gas. It then reacts

with carbon to form compounds such as COS and CS₂. Sulphur in the charge material is released via gasification as the material descends the blast furnace. Gaseous sulphur compounds ascend the furnace and some become absorbed in the reduced iron and charge (Iljana, et al., 2013).

High concentrations of sulphur can cause formation of an FeO-FeS melt that is detrimental to blast furnace operation as it increases the size of the cohesive zone in an upward direction. This has negative implications on the blast furnace such as lowering the temperature and reducing permeability. Sulphur has been associated with swelling and contraction of iron ore pellets at low and high concentrations, respectively. Small amounts of sulphur promote the conversion of wüstite to iron but large amounts hinder the process (Iljana, et al., 2013). The presence of low concentrations of sulphur leads to formation of a porous iron layer on wüstite grains. This porosity allows reducing gases to continue to penetrate the wüstite grain. In the absence of sulphur, the iron layer is less porous (Hayashi, et al., 1984). At high sulphur concentrations FeO-FeS liquid phases were formed which impedes the passage of reducing gases to the pellet core thus hindering reduction of wüstite to metallic iron (Iljana, et al., 2013).

Sulphur exits the furnace via three routes. In the worst case, it leaves as part of the hot metal. It also leave in the gas phase as S₂, SO₂, CS₂, COS, and H₂S; and finally, in the liquid slag as CaS and FeS (IIjana, et al., 2013). Raask (1985) states that coals with high calcium can cause the sulphur to be retained in the ash rather than released as a gas. The percentage of SO₂ capture is the greatest at 1150K, but at temperatures exceeding this, reaction of calcium with aluminosilicates impedes the uptake of sulphur, thus it can be inferred that there may be a shift of sulphur to the hot metal and gas phase.

Sulfur is an undesirable impurity in high manganese austenitic steels (Lu, et al., 2010). Sulfur and phosphorus concentrations that exceed set limits reduce the toughness and increase the brittleness of low alloy steels. It is likely due to the presence of sulfide inclusions in the grain boundaries of ferrite (Rudyuk, et al., 1974). Owing to the thermodynamics, it is possible for the hot metal to absorb 0.9% sulphur, but the limit for hot metal quality is 0.02 - 0.05% (Babich, et al., 2008, p. 236). FeS, MnS, MgS, Na₂S and CaS are the sulphides that can form in the blast furnace and the stabilty of the sulphur compounds increases in the order shown. Calcium and magnesium act as the main desulphurisers in the blast furnace, although sodium also has a similar effect (Babich, et al., 2008).

2.3.5 Abrasion Due to Mineral Matter and Ash

Coal needs to be ground to a specified particle size with minimum wear on grinding plant components and minimum power consumption, in order to reduce operating costs. In a PCI facility, wear is encountered due to abrasion of mill grinding elements, and in pipework where the flow of coal results in particles impinging on pipework and causing wear. Pulveriser downtime and maintenance are determined by wear, so it is an important area to consider in coal handling. The factors affecting wear include mineral matter content and composition, particle size distribution, moisture and bulk density. Particles smaller than 100 μ m cause less wear than larger particles. The size and shape of the mineral particles in coal, the transport gas velocity and impingement angles have an effect on pipework wear (Carpenter, 2006).

The mineral matter is responsible for most of the wear on a grinding plant. The clay minerals are of a similar hardness to the organic content and these do not cause much wear. However, pyrite and quartz are much harder and are the major cause of wear to the grinding apparatus (Raask, 1985; Carpenter, 2006). High ash coals can cause abrasion and erosion of fuel handling plants, mills, burners, boiler tubes and ash pipes in power generators. Coals with high quartz (>15%) in the ash cause abrasion and erosion. Abrasion is wear caused due to surfaces rubbing together with abrasive material lodged in between. Erosion is caused by hard, rough particles impacting on a surface and removing material. Hardness index given by Mohs scale or measured methods such as Brinell, Vickers and Rockwell give a useful indication of potential abrasion or erosion causing properties for the minerals present in coals. On Mohs hardness scale, clay minerals are (2-2.5) which is similar to organic matter (1.5-2.5), whereas pyrite is (6-7) and quartz is 7. Moreover, during milling, the quartz particles fracture to produce more sharp edged particles. Usually, as clay content increases, so too does pyrite and quartz content. Therefore, clay content may be used as an indirect indicator of grindability. Water content also affects grindability to the point where grinding becomes very difficult. Clays also contain interlayer water of hydration which could reduce grinding performance (Raask, 1985).

Raask (1985) makes a distinction between the effect of inherent and extraneous mineral matter. Inherent mineral matter usually accounts for about 5% of a coal. Quartz is extraneous so makes up little of this. In contrast, pyrite, although as hard as quartz, is often found in aggregate with soft clays and organic material, thus

reducing the potential for abrasion. Removal of extraneous material reduces wear in coal plants. Erosive wear will also be reduced by removal of these substances (Raask, 1985).

Coal Grindability

Hardgrove grindability index (HGI) has been a widely used test to compare how easy different coals are to grind, however the test is criticised as not always being a good indicator of actual grinding performance. Coals are commonly blended to draw upon the strengths of the constituent coals, however, it has been found that preferential grinding of the softer coal occurs, so the grinding performance of a blend is closer to that of the harder coal (Carpenter, 2006). Shahzad et al. (2014) identified that the HGI increases with inherent moisture content. HGI is considered to be non-additive, especially as certain macerals may be unfairly represented in a pre-ground test specimen, so HGI is highly maceral dependent (Hower, 1998).

BS 1016-109:1995 Part 112 / ISO 5074:1994, describes the HGI as follows. 50 g of coal subsample that passes through a 1.18 mm mesh, but not through a 600 μ m mesh is placed into a Hardgrove grindability machine (a ball mill with a constant load of 29 kg) for 60 revolutions at 20 rpm. Then all the ground coal and residue on the machine is carefully emptied into a 75 μ m sieve. This is sieved mechanically and thoroughly and then the weight of the collected <75 μ m material is recorded and compared on an HGI chart to give a figure for the HGI. An HGI of 50 or more is preferred by pulveriser operators.

Abrasion Index

Abrasion index (AI) of coal can be measured in accordance with BS 1016-111:1998 using a piece of apparatus developed by Yancey, Geer and Price (YGP), but it has been found that this does not always correlate well with actual rates of wear in the pulveriser (Carpenter, 2006). The British Standard has since been withdrawn. The YGP apparatus shown in Figure 11 is essentially a 4-bladed spindle paddle mill that rotates in a cylindrical container of coal. Each quadrant of the paddle mill has a removable metal blade that is weighed before and after testing. The weight loss of the blades corresponds to the abrasiveness of the coal. The procedure is as follows: 2 kg of coal, prepared to a particle specification of 100% < 6.7 mm, 30% < 1 mm, is placed into the cylindrical container. The paddles are set to turn 12,000 revolutions at 1470 rpm.



Figure 11: Top view of YGP abrasion index tester (taken from BS 1016-111:1998)

Mechanism of Abrasion

Sliding abrasion wear occurs when an abrasive is caught between two loaded surfaces, and crushed. It leads to scratches, grooves and indentations in the materials. In order to resist this type of abrasion, the crushing surface should be significantly harder than the abrasive. In low stress applications, such as during the abrasion testing in this thesis, the abradant is not crushed, but cuts into the surface. It has been found that wear rate was proportional to applied load. Within a coal, the wear rate has been shown to be proportional to ash percentage, when the ash contain high quartz. Regarding erosive wear in mild steel transport lines, it was found that an impaction angle of 35° gave the highest wear rate for 125-150 µm quartz particles at 27.5 m/s, but at lesser or greater angles, the wear rate was reduced. This highlights the importance of bends with soft radii in pneumatic coal conveying plant and ideally, the larger the better. Moreover, a slight increase in impact velocity can have a marked increase in wear rate, for example, a 10% increase in velocity would double the wear. Sharp, angular grains have different effects from spherical grains, whereby the former create cutting wear and the latter induce brittle fracture in an exposed area. Again, increasing the hardness of the exposed materials gives a significant reduction in wear rates (Raask, 1985).

Effect of Heat on Mineral Abrasiveness

Clay particles vitrify, agglomerate and become spherical in a flame turning into moderately abrasive aluminosilicate particles. Quartz particles in coal are contaminated with aluminium, iron, and alkalis so can vitrify in a coal flame and the sharp edges can round off. Pyrite particles decompose rapidly and turn to spheres of iron oxides which are softer than pyrite and rounder. The effect of heating on clay particles is that they turn from soft layered minerals with a Mohs hardness of 2 to 2.5 into glassy spheres with Mohs hardness of 5. This is still less hard than quartz and pyrite at 6 to 7, but it is harder than boiler steels at 3 to 4. In some testing by Goodwin et al 1969, it was found that quartz particles of less than 5 μ m did not show any wear because they lacked momentum enough to impact a target, whereas for particles exceeding this size fraction, the wear increased with the particle size. Additionally, the small particles were more likely to be carried in the gas stream. From around 920°C to 1500°C ash becomes more abrasive as the clays become heated and turn to glassy particles. The wear rate of high temperature metals might be less than at low temperature as the materials become more ductile and may be annealed (which increases their toughness). Spheroidal ash particles have microcrystals embedded in their surfaces which will make them more abrasive than spherical glass beads (Raask, 1985). As has been discussed in the Section 2.2.4 Mineral Interactions at High Temperature, mullite forms from clays. Mullite has a Mohs hardness of 6 to 7 which is comparable to that of quartz which has a hardness of 7 (Bideaux, et al., 1995), so it is conceivable that this may lead to wear in the tuyeres. Babich (2002) states that tuyeres operate at high temperature, within high temperature gradients and under abrasion of moving solids.

2.4 Literature Review Summary

The complexity of mineral matter is apparent from this literature review, and it is clear that minerals need to be identified in order to study their effect on the blast furnace. Minerals that are present at low temperatures will be identified in order to determine the cause of the high temperature minerals. For example, the presence of haematite may be due to pyrite, siderite or ankerite. Calcium can be present in the form of calcite, dolomite or ankerite. The nature of the minerals gives greater clarity to reactions that might occur at high temperature. The mineral and elemental compositions are strongly related to the ash fusion temperature and ash fusion temperature indicates how ashes might behave in the raceway, bird's nest and beyond. Elemental analysis can be linked with the mineral analysis which enables the source of an element to be identified. For example, alkali elements reside in clays and a proportion of them are volatilised in the blast furnace. Clays are also the precursors of the aluminosilicates that are able to absorb a range of elements, including alkalis. The alkalis potassium and sodium can be released as vapours or become integrated into the aluminosilicates. This behaviour determines
whether alkalis cycle in the furnace or enter the slag. Calcium reduces fusion temperatures, up to a point, and is known to catalyse gasification. The presence of calcium and alkali in ash plays a role in increasing the reactivity of coke in the deadman and lower region of the blast furnace. The generation of fines from this increased coke reactivity is detrimental to the permeability of the furnace. A good working knowledge of the principles of the blast furnace gives relevance and background to the mineral matter effects investigated in this thesis. Kaolinite clay, and to a lesser extent illite, are responsible for the formation of mullite in ash. Mullite has a high melting temperature and is a hard mineral. It may be responsible for some form of abrasive wear, and it helps to raise the melting temperature of ash. The chemistry of the slag is dependent on the input materials and the ratio of acids to bases. Higher basicity improves the ability of the slag to capture sulphur. This is an important consideration where sulphur has a negative effect on hot metal quality and needs to be removed. However, on the other hand, an acidic slag is preferential to capture undesirable alkalis. This contradiction highlights the fact that there are compromises to be made in blast furnace operation, and that given the complex chemistry and the nature of mineral matter, there may be positive and negative effects arising from a chosen course of action.

2.5 Scope for Further Original Research

Having reviewed the literature, it is clear that coal mineral matter and ash have been extensively characterised and the effect of heat on the individual minerals has been studied. In addition, the blast furnace process and the effect of different elements within the blast furnace is well understood. However, there is limited research that experimentally investigates the effect of a high heating rate environment on coal mineral matter and relates this to the blast furnace raceway. Hence, there is scope for additional research that focusses on this area, and this is the reason for performing this PhD.

The drop-tube furnace has been used extensively to investigate the effect of high heating rate and temperature on solid fuels, however the effect of this environment on the mineral matter in coal is less well understood. The main benefit of using a drop-tube furnace for the study of coal mineral matter are that the temperature and residence time resemble that of the blast furnace raceway, especially in the tuyere region. Moreover, temperature and residence time can be adjusted to investigate the effect that this has on the mineral matter. By looking at the mineral matter as a whole system, it is expected that interactions occurring within the mineral matter will be identifiable. Hence the literature review has identified that there is scope to experimentally investigate the changes occurring to mineral matter with a focus on pulverised coal injection thus bridging the gap between what is currently known about ash and what is known to occur in the blast furnace.

The literature review facilitates the formulation of the aims and objectives detailed in Section 1.5. The following chapter details the materials and experimental methods used in this thesis to thoroughly investigate the hypotheses.

Chapter 3: Materials and Methods

This chapter is split into three sections. The first section details the materials chosen for testing, namely coal, slag, coke, and dolomite. The second section describes the background of some of the test methods, including preliminary work and lays out the methods in a step by step format. The third section surrounds processing and calculation of experimental data, with a subsection on standard deviation and error.

3.1 Materials

3.1.1 Coals

IJmuiden Samples

The majority of the testing in this thesis was carried out on five different coals supplied by Tata Steel IJmuiden, as shown in Table 3. Coals with a range of volatile matters were chosen to reflect the variety of coals selected for blends in a blast furnace as described in 1.4.5 Pulverised Coal Injection. The coals are given codes instead of names due to industrial confidentiality required by Tata Steel IJmuiden concerning their chosen blast furnace injection coals. Note that fixed carbon is calculated by difference.

Coal	Volatile Matter	Ash	Fixed Carbon
LV1	8.5	10.4	81.1
LV2	13.3	9.3	77.4
LV3	16.9	6.2	76.9
MV	20.6	7.5	71.9
HV	31.7	9.2	59.1

Table 3: Coal Proximate Analysis (%). Dried Basis.

The analysis for volatile matter, ash and fixed carbon was performed in accordance with the procedures laid out in the experimental methods. Table 1 in 1.2 Coal Formation showed the ASTM classification of coals based on fixed carbon and volatile yield. The coals in Table 3 designated as LV1, LV2, LV3, MV and HV are based upon these values. Note that the ASTM classification is specified on a mineral matter free basis. MV coal yields more than 22% volatile matter when calculated on a mineral matter free basis. Though on a dry basis, it yields 20.6% volatile matter as in Table 3. Hence, MV coal does fall into the medium volatile classification according to the ASTM. LV, MV and HV stand for low volatile, medium volatile and high volatile, respectively. The proximate analysis does not include information

about mineral matter, however it remains a convenient method of classifying coals and is used in industry by blast furnace operators.

As such, all future reference to the coal samples will be as LV1, LV2, LV3, MV and HV, and any chars and ashes produced from these coals are described accordingly using these designations.

Port Talbot Samples

Coal samples were collected from Tata Steel Port Talbot in two blast furnace trials. Trial 1 occurred on two consecutive days, and Trial 2 was a one off. Sample was collected from the granular coal injection (GCI) plant, just after the drier and prior to injection into the blast furnace. These coals were unidentified blends that were analysed at Cardiff University for combustion behaviour, mineral composition and chemistry. The proximate analysis is given in Table 4. Experimental error is discussed in Section 3.3.3. Note that ash and volatile matter tests are performed in duplicate as discussed in Section 3.2.3. Fixed carbon is calculated by difference.

Table 4: Proximate Analysis (%) of ex-Port Talbot Blast Furnace Trial Samples. Dried Basis.The standard deviation of 3 duplicates of ash testing is given in brackets.

Coal	Volatile Matter	Ash	Fixed carbon
Trial 1. Day 1	-	8.8 (±0.4)	-
Trial 1. Day 2	-	8.3 (±0.2)	-
Trial 2	11.4	7.6 (±0.1)	81.0

Proximate Analysis

The proximate analysis of coal is a convenient means of determining the percentage proportions of materials yielded by a coal sample under a standard set of heating conditions. The proximate analysis determines the yield of moisture, ash, volatile matter and fixed carbon and is described in *BS ISO 17246:2010 Proximate Analysis Description*. The three former contents are tested for and the fixed carbon is then calculated by difference. Proximate analysis can be done on several bases as follows:

- AR (as received). This uses the total weight of the coal sample as a basis for testing.
- AD (air dried). This tests the coal after it has dried in the air.
- DB (dry basis). This removes all the moisture from the coal such as surface moisture and inherent moisture.

DAF (dry, ash-free) and DMMF (dry, mineral-matter-free) can also be used.

As part of the work in this study, all proximate analyses were completed on a dry basis in accordance with the method in Section 3.2.2. Drying was performed using a prescribed method to remove inherent moisture. Since all coals were analysed from the same dried starting point, it was possible to make relative comparison of the proximate analyses from the different coals.

Ultimate Analysis

The ultimate analysis is the same as an elemental analysis. It gives absolute data of the proportion of carbon, hydrogen, oxygen, nitrogen and sulphur in a coal sample. When the ultimate analysis is performed on a coal sample, the carbon from carbonates in the ash and hydrogen from interlayer water in the clay is also taken as part of the ultimate analysis (Speight, 2013).

Coal Analysis Issues

The analysis of coal comes with certain difficulties that must be accounted for. These include: the heterogeneous nature of coal as a substance; a propensity for coal to gain or lose moisture; and to oxidise when exposed to the air. This effect will be more pronounced during high temperature drying, especially on low rank coals with higher volatile contents. Furthermore, attaining a representative sample of coal is hard to achieve because during mining, transportation and storage changes can occur to the bulk of coal. Typically, finer particles will settle to the bottom of a container, moisture and oxidation will affect the most exposed areas, and transportation will cause particle size segregation and fragmentation of coal. In the laboratory at a smaller scale, the effects of particle segregation, moisture and oxidation can still be noticed (Speight, 2005).

Experimental error was minimised by following certain procedures including thorough sample mixing (by tumbling the bag of sample), oven-drying at a specified temperature and time (without leaving samples in the oven for excessive time), placing samples into sealed containers and then into the desiccator.

3.1.2 Slag

A Port Talbot granulated blast furnace slag sample was analysed using X-ray diffraction and ICP. The purpose of the slag sample was to allow comparison between coal ash and slag to make an inference into the changes that occur in the blast furnace process between the source of mineral matter and output of amorphous material in the form of slag from the blast furnace. The slag sample was

also used in TGA testing to compare the effect of slag on coke with that of ash on coke, as described below.

3.1.3 Blast Furnace Floating Clarifier Sludge

A sample of material was collected from a gas cleaning clarifier pond at Port Talbot steelworks. This low density material was becoming caught in steelwork at the water's surface. The objective of testing the sludge was to determine the minerals and elements present to identify whether coal mineral matter related material can be found in the off gas. A proximate analysis of this material is given in Table 5. Note that fixed carbon is calculated by difference.

Table 5: Proximate Analysis (%) of Blast Furnace Floating Clarifier Sludge. Dried Basis. The standard deviation of 3 duplicates for ash and 2 duplicates for volatile matter is given in brackets.

Volatile Matter	Ash	Fixed carbon
14.6 (±0.1)	27.4 (±0.2)	58.0

3.1.4 Coke

A Port Talbot coke sample was used in TGA testing to determine whether there was any catalytic effect of ash on coke gasification.

3.1.5 Dolomite

Dolomite from Port Talbot was also used in TGA testing to compare the effect of a known catalyst (Ma, et al., 2019) with the ash and slag.

3.2 Experimental Methods

A number of experimental methods have been used in this thesis in order to create a broad and well-rounded understanding of the ash in blast furnace coals. It is typical to require many different analytical methods for mineral matter and ash (Ward, 2016), and this thesis is concerned with both physical and chemical behaviour.

In this section, the background to the experimental method is discussed. This is only done where there is significant background information or where preliminary work has been performed.

3.2.1 Grinding

The work in this thesis is closely linked with Tata Steel IJmuiden, hence all testing was performed on pulverised coals. The chosen particle specification was $100\% < 300 \ \mu m$; $50\% < 75 \ \mu m$, as agreed with the industrial sponsor.

- 1 kg of as received coal typically comprising a wide range of sizes up to around 25 mm was dried overnight on a large tray in an oven at 60°C to remove surface moisture.
- 2. This material was then placed batchwise into a TEMA bowl mill and, in the first instance, ground for 30 seconds.
- International standard sieves were stacked in order of size, top to bottom;
 mm, 1 mm, 300 μm, 150 μm, 75 μm with a cover at the top and a collecting dish at the bottom.
- 4. The contents of the TEMA bowl mill were tipped into the top 2 mm sieve and the whole stack was shaken by hand and on a vibratory shaker.
- The objective of using such a range of sizes was to reduce the amount of material in each sieve to encourage expedient particle size separation. Additionally, it made it easier to visualise the amount of material that required further grinding.
- 6. Material was collected from the 150 μ m and 75 μ m sieves and weighed to satisfy the < 300 μ m material. Material from the collecting dish was weighed to satisfy the < 75 μ m material.
- 7. Material was reground and sieved as required until the particles were sufficiently comminuted to meet the specification.

Care was taken to treat the sample as a whole and grind, sieve and regrind in batches. An easier, but less rigorous, technique would have been to: 1. Grind the bulk sample for a longer period of time; 2. Sieve as described above; 3. Collect the desired weight of material at the desired particle sizes to meet the particle specification; 4. Discard the remaining coal. Such a technique was not employed because the maceral composition of coals vary in hardness and so the softer material would be easier to grind and thus be concentrated at the smaller particle size, leaving the harder macerals concentrated at the larger particle sizes (Hower, 1998).

3.2.2 Drying

Prior to ashing and testing in the DTF, coal samples were dried in accordance with BS ISO 11722:2013 in air. Nitrogen is used for drying hard coal BS ISO 17246:2010

but air is permitted where the coal does not oxidise as described in ISO 589:2008. The coals did show some ability to oxidise (Zhang, et al., 2015a; Zhang, et al., 2015b) but they were always destined to enter a high temperature environment where combustion was going to occur. The main purpose of drying was to eliminate water from coal samples so that heat of vaporisation of water would not affect combustion in the drop-tube furnace which is a high heating environment. Samples were always specified on an air-dried basis.

- 1. Using a plastic scoop, 50 g of coal was sprinkled onto a 100-120 mm diameter watch glass so that it covered it in an even layer.
- This was placed into a preheated drying oven set at 105 °C to 110 °C, for 60 minutes.
- 3. The sample was removed from the oven and placed into a labelled sachet and then this sachet was stored in a desiccator.

3.2.3 Ashing

Ashing Background Information and Preliminary Work

The mineral matter or ash composes around 10% of the total coal material, so for the purposes of mineral matter and ash analysis they have to be separated from the carbonaceous material in order to be quantified (Gupta, et al., 2008, p. 162). Moreover, the presence of amorphous carbon can present itself on the XRD and mask the mineral material (Gupta, et al., 2008; Tian, et al., 2011).

The study of ashes is central to this work, therefore a number of different ashing techniques were used or developed.

The temperatures chosen to create ash were: 815°C which is the British Standard; 1100°C which was amendment of the British Standard; and 400°C which was developed as a medium temperature method.

High Temperature Ashing at 815°C

Coal ashing is performed in air, typically at 815°C, for the purposes of proximate analysis and calculating burnout and for coal research (Andrejko, et al., 1983). In this thesis, the British Standard ash test BS ISO 1171:2010 will be termed high temperature ash/ashing (HTA).

HTA was used in the majority of cases during this study, for the following purposes:

i. For creating ashes from raw coals to use for X-ray Diffraction (XRD) analysis, X-ray fluorescence (XRF) analysis, ash fusion testing, scanning

electron microscope (SEM) imaging, abrasion testing, bulk density and particle size analysis.

ii. For creating ashes from drop-tube furnace (DTF) chars. The DTF was run at 1100°C and 1300°C. It was decided that as HTA was much lower than DTF temperatures, it would not cause further changes in the ash properties.

Very High Temperature Ashing at 1100°C

Ashing was also performed at 1100°C, and this will be termed Very High Temperature Ash/Ashing (VHTA).

This method was devised to create ash at a higher temperature to enable a comparison to DTF char ashes, because the DTF was also run at 1100°C. Samples run through the DTF undergo very high heating rates (Lu, et al., 2001; Du, et al., 2010; Ozer, et al., 2017) whereas ashing occurs at a low heating rate. This difference was investigated using the VHTA technique.

Medium Temperature Ashing at 400°C (Preliminary Work)

For the purpose of this thesis, it was important to be able to identify components in the mineral matter from a low temperature to be able to compare these with effects at high temperature. Many of the minerals that were in the raw coal would have undergone severe enough heating during HTA that they are no longer present in their original form, due to the effects of thermal decomposition (Renton, 1982). In the literature, a common solution to this problem has been to lower the ashing temperature to 300-500°C, which provides additional information but, still, some of the minerals are altered (Gluskoter, 1975). During medium temperature ashing (MTA), the time taken for full combustion to occur is much greater than HTA: days as opposed to hours (Andrejko, et al., 1983; Steel, et al., 2001) and Ward (2002) also states that heating at 370°C can take protracted periods of time. Authors that have performed this technique include Nelson (1953) and Brown (1959) cited in (Ward, 2016, p. 4).

In pursuit of a suitable MTA procedure, preliminary work was carried out on the TGA to determine whether two coal samples LV2 and LV3 could be successfully ashed at around 350°C to 450°C. The objective was to determine the lowest possible ashing temperature whilst occurring in a reasonable timeframe of a few days. Test temperatures of 350°C, 400°C and 450°C were chosen, and the rate of mass loss is illustrated in Figure 12. The reactive gas was air at 20 ml/min.



Figure 12: TGA combustion of LV3 at 350°C, 400°C and 450°C

The heating rate was 1°C/min, thus the onset of the isothermal period is shown by the vertical dotted lines. It can be seen that mass loss begins at 300°C for this particular coal. The slight increase in mass occurring at 300°C and creating a hump is due to oxidation of the coals (Zhang, et al., 2015a; Zhang, et al., 2015b) where low heating rates on high rank coals increase this effect (Zhang, et al., 2015b). The isothermal period determines how long the sample should be left in the muffle furnace during the proposed ashing procedure. Testing at 400°C equates to 2000 minutes/33 hours, during the isothermal period, which was considered to be a practical time period to produce MTA. There is some offset between the testing at 400°C and 450°C after this 2000 minute isothermal period. This is because the mineral matter is less decomposed at the lower temperature, leading to a greater mass remaining and is discussed in Section 4.1.2, Table 9. It could possibly be due to incomplete combustion, however if this was the case, it was not a problem because any small amount remaining did not affect the clarity of the X-ray diffraction (XRD) data. The main objective of the MTA technique was to yield an ash that bore a closer resemblance to unheated mineral matter than HTA would allow. The reactivity at 350°C was considered too slow.



Figure 13: TGA combustion of LV2 at 400°C and 450°C

In order to confirm the effectiveness of 400°C ashing on a lower volatile coal, LV2 was reacted at 400°C and 450°C under the same conditions as LV3, as shown in Figure 13. At 400°C LV2 does not completely burn out in the timescale of this test, thus LV2 was less reactive than LV3, so it was decided to perform muffle furnace ashing for 48 hours to be sure of complete combustion, as opposed to the 33 hours required for coal B. This allowed any potential further mass loss to take place in less reactive coals, and enabled two runs of ash to be completed in a working week in the laboratory.

It cannot be certain that the reaction of organic matter occurs as low as 400°C as there may be localised areas of much higher temperature which could affect the mineral matter (Vassilev & Vassileva, 1996; Steel, et al., 2001). However, in order to ascertain this, a temperature probe would have to be placed into the sample, but this was not done during these MTA tests.

In summary, it was possible to create MTA in the TGA in two days. 400°C was chosen as this allowed ash to be created in a timely manner at a relatively low temperature, and it can be seen that even for the less reactive LV2, significant mass loss was achieved. It was decided to perform the test in a muffle furnace for 48 hours to give some excess time compared to the preliminary TGA work. This allowed any further mass loss to take place in less reactive coals, and enabled two runs of ash to be completed in a week in the laboratory. As a final note, it cannot be certain that the reaction of organic matter occurs as low as 400°C so there may be localised areas of much higher temperature which could affect the mineral matter (Vassilev & Vassileva, 1996) (Steel, et al., 2001). However, in order to ascertain this, a temperature probe would have to be placed into the sample, but this was not done during these MTA tests.

A Note on Low Temperature Ashing

A technique known as low temperature ashing (LTA) or plasma ashing which allows ash to be created at 120-150°C in an electrically excited oxygen plasma was developed by Gluskoter (1965). With this technique, oxygen is passed through an alternating electric field at a radiofrequency of 13.56 MHz, which creates an oxygen plasma that consists of positively and negatively charged oxygen ions, electrons, and neutral species (Rao & Gluskoter, 1973; Bogaerts, et al., 2002). The resultant oxygen plasma is reactive at low temperatures, which facilitates the oxidation of organic matter in the coal at less than 150°C and takes 72-90 hours.

This technique is said to give the most reliable method for determining the actual amount of mineral matter present (Ward, 2002), owing to minimal thermal alteration of the mineral matter, which also leads to LTA always being greater than HTA (Renton, 1982). Given and Yarzab (1978) detail that LTA has minimal effect on reactive minerals such as carbonates and pyrite, furthermore, the loss of structural OH groups and bound water from clays was shown to be very low. This view is contrasted by Vassilev and Tascón (2003, p. 272) who state that "it is an illusion that this ashing supplies a relatively unaltered <mineral matter> MM" and cite unwanted transformations such as oxidation of pyrite, dehydration of water containing minerals, and formation of sulphates to name a few. However, it was acknowledged in this paper that there are similarities to natural weathering, which is in agreement with Speight (2005).

There was not the facility to perform LTA at Cardiff University, and MTA was seen as a useful alternative. The production of LTA is time consuming, taking days, and yields small quantities, in the region of several hundred mg, of ash (Vassilev & Tascón, 2003). In addition, this thesis is based on the high temperature behaviour of mineral matter in the blast furnace so an in depth analysis of LTA was not considered essential.

Another method to leave mineral matter, known as wet ashing involves digestion of organic matter using oxidising chemicals such as perchloric-hydrofluoric, nitricsulfuric acids and hydrogen peroxide however these chemicals are particularly hazardous to work with (Andrejko, et al., 1983).

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Ashing Method

HTA was performed as per BS ISO 1171:2010, using a Carbolite HTF1700 furnace. The method below was used for ashing coal and char samples to determine ash percentages and to calculate burnout.

- Temperature resistant silica or alumina crucibles of 48 mm diameter by 15 mm high were used. Such dimensions ensured that sample loading did not exceed 0.15 g/cm².
- A clean, dry crucible was weighed empty on a 0.1 mg (4 figure) balance, and the mass m₁ was recorded.
- 3. 1 g of oven air dried sample weighed to the nearest 10 mg on the 4 figure balance was placed into the crucible. Crucibles were gently agitated by hand to ensure the sample covered the base evenly. The mass of the crucible plus sample m_2 was recorded.
- 4. Steps 2 and 3 were always duplicated for any given sample, giving two ash readings for each.
- 5. This was repeated for up to 4 sample duplicates, giving 8 crucibles in total.
- These crucibles were placed, for one hour, into a muffle furnace set at 500 °C.
- The furnace temperature was then raised to 815 °C ± 10 °C and the sample was left for a further hour.
- 8. The crucibles were removed from the furnace and placed onto a refractory surface, such as a refractory brick.
- 9. When the crucibles were around 60°C, they were cool enough to be safely handled and weighed on the 4 figure balance, but considered warm enough that they were not absorbing water from the air.
- 10. The mass of the crucible with the ash residue m_3 was recorded, and the ash percentage was calculated using the following formula:

$$A = \frac{m_3 - m_1}{m_2 - m_1} \times 100$$

Equation 24: Formula for calculating ash yield of a coal.

where:

 m_1 is the mass, expressed in grams, of the empty crucible;

- m_2 is the mass, expressed in grams, of the crucible plus the unfired sample;
- m_3 is the mass, expressed in grams, of the crucible plus the ash residue.

VHTA followed the exact same procedure as above, except that for Step 7, the furnace temperature was raised to 1100 °C instead of 815 °C.

For MTA, the procedure for HTA was followed, but Steps 6 and 7 were replaced with the following single step: the samples were placed for 48 hours in a furnace set at 400 °C.

3.2.4 Volatile Matter Analysis

The volatile test was performed in accordance with BS ISO 562:2010 in a Carbolite CWF furnace. The volatile matter test involves heating a sample of coal in the absence of air for 7 minutes at 900°C. The mass lost from the sample during this test is determined to be the volatile matter yield. Figure 14 shows the volatile matter test setup.



Figure 14: Volatile Matter Test Setup

The test method is described as follows:

- Temperature resistant silica or alumina crucibles of 25 mm diameter by 38 mm high were used. These crucibles had close fitting lids to prevent air entering whilst allowing volatile gases to escape.
- If necessary, crucibles and lids were cleaned by placing in the furnace at 900°C for 10 minutes with the lids removed, to remove combustible residue left on the surfaces from previous testing.

- A clean, dry crucible plus lid was weighed empty on a 0.1 mg (4 figure) balance, and the mass m₁ was recorded.
- 4. 1 g of oven air dried sample weighed to the nearest 10 mg on the 4 figure balance was placed into the crucible. The lid was placed onto the crucible. The mass of the crucible and lid plus sample m₂ was recorded.
- 5. Steps 3 and 4 were always duplicated for any given sample, giving two ash readings for each.
- 6. This was repeated for 2 sample duplicates, giving 4 crucibles in total.
- The crucibles, with their lids on, were placed in the purpose-made stainless steel sample rack.
- 8. Important: in the case of testing just one sample pair, the sample holder must still be filled with the remaining pair of empty crucibles plus lids as it would affect heat up rate in the furnace if the sample holder did not have all four spaces filled.
- The holder with 4 crucibles plus lids was placed, for 7 minutes, into a muffle furnace preheated to 900 °C ± 5 °C.
- 10. The holder was removed from the furnace and placed onto a refractory surface, such as a refractory brick.
- 11. When the crucibles were around 60°C, they were cool enough to be safely handled and weighed on the 4 figure balance, but considered warm enough that they were not absorbing water from the air.
- 12. The mass of the crucible with the test residue plus the lid m_3 was recorded, and the volatile percentage was calculated using the following formula:

$$V = \frac{m_2 - m_3}{m_2 - m_1} \times 100$$

Equation 25: Formula for calculating volatile matter yield of a coal.

where:

 m_1 is the mass, expressed in grams, of the empty crucible with lid;

 m_2 is the mass, expressed in grams, of the crucible with lid plus the unfired sample;

 m_3 is the mass, expressed in grams, of the crucible with lid plus the test residue.

3.2.5 Carbon and Sulphur Analysis

A partial ultimate analysis of carbon and sulphur was performed on the LECO SC144DR carbon and sulphur analyser.

The method is as follows:

- 1. The oxygen to the LECO analyser was turned on and set to 1.2 bar.
- A nickel boat liner was placed onto a 0.1 mg (4 figure) balance, and the balance was tared.
- Before using the instrument, calibration with a coal standard (QAR Certified Coal Reference Material, CRM 7, with C = 72.6%; S = 3.26%; moisture = 7.2%) was performed with the method described in steps 4 to 10.
- 4. 0.1 g to 0.3 g of sample was deposited into the nickel boat liner. This mass was dependent on the sample being tested. For high carbon samples, the mass of sample was reduced to 0.1 g to avoid unburned soot passing through the machine. Unburned soot gave an underestimation of the carbon in a sample because all carbon needs to be in the form of CO₂ before it is measurable. For ash samples, up to 0.3 g was used because amounts of sulphur and carbon were low in such samples, so more sample increased the resolution.
- 5. Experimental and sample details were entered into the desktop computer running the LECO furnace.
- 6. The mass of sample was read from the balance and entered into the desktop computer.
- 7. The nickel boat liner with sample was placed into a ceramic boat.
- The experiment was sent to run, and when the software allowed, the ceramic boat was swiftly pushed into the end of the tube furnace and the door closed.
- The experiment was complete when no further change was occurring to the continuous analysis of carbon and sulphur on the desktop computer.
- 10. The boat was removed from the furnace and allowed to cool.

3.2.6 Drop-tube Furnace

DTF Background Information

A drop-tube furnace (DTF) was chosen to create chars that were partially representative of a blast furnace raceway environment. As has been detailed in the introductory chapter, coal particles enter the raceway via oxygen-rich hot blast at around 1100°C, where they are volatilised and then char combustion occurs. During this process the temperatures reach a maximum of around 2000°C and residence times in the raceway range from 5 ms to 1000 ms. Thus the DTF can be regarded as

a simulator that creates chars most applicable to the tuyere and early raceway regions in the blast furnace.

The drop-tube furnace has been used extensively at Cardiff University to characterise coals and create chars in order to investigate the behaviour of coal in the blast furnace. The effects of: coal blends on burnout; grinding on burnout and surface chemistry; and partially burned char reactivity have been explored using chars from the DTF at Cardiff University (Steer, et al., 2015a; Steer, et al., 2015b; Steer, et al., 2018). Coal agglomeration in the blast furnace was also studied at Cardiff University using the drop-tube furnace (Sexton, et al., 2018). The drop-tube furnace has been used to study injection coals into the blast furnace and also to compare the reactivity (burnout) of different coals by numerous other authors (Lu, et al., 2001; Gupta, et al., 2006; Osório, et al., 2006; Du, et al., 2010).

In spite of differences between the blast furnace raceway and the DTF reaction environment, the DTF remains an effective technique for the testing of coals when trying to assess their performance in PCI situations with heating rates of > 10^4 K/s (Lu, et al., 2001; Du, et al., 2010; Ozer, et al., 2017). DTF temperatures are around 1300°C which is similar to the temperatures found in the blast furnace injection point, but lower than those found in the raceway (Borrego, et al., 2008).



Figure 15: Drop-tube furnace schematic diagram

The DTF is an electrically heated vertical tube furnace with a schematic shown in Figure 15 and a labelled photograph with the surrounding apparatus shown in Figure 16, where it can be seen that the DTF is a tall piece of apparatus that requires space at the bottom to insert a collector probe and access from above via a platform that is reachable with stairs around the back of the furnace.

The key parameters and features of the drop-tube furnace are as follows:

- Testable samples include powders and granules, not exceeding 2 mm.
- The DTF will run at temperatures of up to 1300°C.
- The furnace atmosphere can be air, nitrogen, carbon dioxide or a mixture of these.
- Particle feed rate is typically 0.5 g/min and this was adjusted by changing the rate of the screw feeder. Wen et al. (2016) used a particle feed rate of 0.3 g/min.
- Residence time can be adjusted from 35 ms to 700 ms. This was achieved by moving the *Water cooled collector probe* in Figure 15 in or out of the furnace to change the length of time through which the particles fell in the heated zone of the furnace.
- Water cooled feeder and collector probes ensure that heating of particles occurs within the heated zone only, and not during conveying and collection.
- The heated work tube of the DTF was made of alumina with a length of 1.36 m and a diameter of 60 mm.
- The exhaust gases leave the DTF via three lines. Each one leads to a pair of glass wool tar traps in series, and then onto a vacuum pump that draw the gases from the furnace, and discharge them into the laboratory extraction system.
- One of the three exhaust lines is connected to a SERVOMEX[®] Analyser Series 1400 that monitors the percentage of oxygen in the exhaust gases. When the sample enters into the drop-tube furnace, combustion occurs which reduces the percentage of oxygen in the reaction zone, and this can be read from the analyser. When the sample feed into the furnace is finished, the oxygen concentration rises again. Thus the analyser was used to indicate when sample reaction begins to occur and when it completes. The analyser also allowed the user to identify variance arising from different reaction temperatures and residence times, as well as a means of

troubleshooting for the drop-tube furnace for leaks. The analyser was single point calibrated at the beginning of testing using the oxygen percentage in the air (21%) as the reference. This was sufficiently accurate for this thesis where the purpose of the analyser was to identify the start and end points of testing, and to give a basic indication of the relative reactivity of different coals at different residence times.



Figure 16: Photograph of the DTF with oxygen analyser, heater control panel, and gas rotameters alongside to the left.

DTF Method

The test method for using the DTF is described thus:

- The DTF temperatures used in this thesis were 1100°C and 1300°C. This was dictated by the objective of the testing.
- 15 grams to the nearest 0.1 g of pulverised coal was poured into the screw feeder hopper (marked *Sample In* in Figure 15) using a funnel; the lid was placed onto the hopper.

- 3. The inlet gases were adjusted via a number of rotameters such that the inert supply of nitrogen to the feeder was 0.5 l/min, and the furnace atmosphere gas was 20 l/min. Combustion required the use of air; inert conditions demanded nitrogen; and carbon dioxide could be used as an inert gas or in a gasification environment, depending on the type of sample and DTF temperature setting.
- 4. The furnace exhaust gas was set via rotameter to a total of 20 l/min, such that a positive pressure was maintained in the furnace (inlet supply was 20.5 l/min as detailed in the previous step). This was important to ensure that particles were entrained in gas as opposed to being drawn through the furnace.
- 2 I/min out of the 20 I/min exhaust flow was directed to the SERVOMEX[®] Analyser Series 1400 oxygen analyser.
- 6. The collector probe was adjusted to the desired residence time. In this work, residence times of 35 ms, 100 ms, 350 ms and 700 ms were used.
- 7. The sample catch pot was attached and the screw feeder was switched on.
- 8. In the case of combustion, the oxygen analyser was monitored to identify oxygen content before, during and after the test to identify the beginning and end points of the sample feed and to indicate the extent of reaction occurring during testing. Additionally, the oxygen concentration was recorded several times during the 30 minute test.
- 9. A feed rate of 0.5 g/min was maintained for all samples.
- 10. When testing was complete, the char sample was taken from the catch pot to be weighed, and then placed into a sample pot to be stored in a desiccator.
- 11. If additional char sample was required, coal was run through the DTF again.
- 12. When testing of a sample was complete, the feeder and collector apparatus was thoroughly cleaned and vacuumed to avoid contamination of subsequent samples.

3.2.7 X-ray Diffraction

XRD Background Information

X-Ray Diffraction (XRD) mineral analysis is required in conjunction with elemental analysis in order to gather more detailed information about coal mineral matter (Ward, 2002). XRD is effective for identifying fine grained minerals and mixtures (Flohr, 1997) which makes it ideally suited to ash analysis. XRD is a widely used technique for mineral identification of coals (Rao & Gluskoter, 1973; Ward, 2016). XRD analysis of coals and chars leads to unclear mineral peaks because of noise created by the amorphous carbonaceous material; this is clearly seen in Gupta et al. (2006, pp. 463,467), and is expected given that the ash forms only a small percentage of a coal. Therefore, in all cases, ashes, not chars, were analysed under XRD, which is typical of authors in the literature.

The three dimensional structure of crystalline material is regular, repeating planes of atoms that form a crystal lattice. A crystalline material will maintain this ordered structure for billions of unit cells, and this is what differentiates it from amorphous materials, like glasses, that are only ordered for a short range (Stanjek & Häusler, 2004). When a powdered sample is exposed to a monochromatic beam of X-rays, they interact with the crystal lattice, exhibiting diffraction and, constructive and destructive interference. The X-ray diffraction angles vary with the distance (dspacing) between adjacent planes of atoms in a crystal. The distance between planes is different for all minerals which gives rise to a unique diffraction pattern for each (McReynolds, et al., 2008). The mineral can be identified according to its diffraction pattern by using standard reference materials (Flohr, 1997). Amorphous materials cannot be identified on the XRD as they do not create a distinct set of peaks. Instead, they form a broad pattern or "hump" on the diffractogram, instead of peaks (Ward & French, 2006).

XRD Method

Samples placed under the XRD were always ashes that had been prepared using the ashing procedures described in 3.2.3 Ashing. Therefore, they were dry powders. The technique is also known as X-Ray Powder Diffraction, for this reason. Given the fine ($100\% < 300 \mu$ m; $50\% < 75 \mu$ m) particle size of the coals used to create the ashes, the resultant ash was also fine. Owing to this, it was not considered necessary to grind it for XRD analysis. The clarity of the peaks was satisfactory and grinding the sample did not appear to substantially improve the quality of the results. Moreover, leaving the ash samples unground, meant that they could be used in the future for other purposes such as particle size analysis, scanning electron microscope (SEM) imaging and ash fusion testing (AFT).

Three different XRD machines were used in this project. This was owing to equipment availability and an opportunity to use a hot stage XRD.

Two Philips PW1710 diffractometers were used at Cardiff University. One was set up with a cobalt anode to give Co-K α radiation, and the other was set up with a copper anode to give Cu-K α radiation. The effect of using different types of radiation was to shift the position of the peaks on the diffractograms; the mineral "fingerprint" remained the same. Both machines were operated at 35 mA and 40 kV. The parameters of the scan were determined according to the sample. For example, an initial scan of 5° to 80° was chosen to assess an unknown sample. Following extensive analysis of ash samples from different ashing, and DTF temperature and gas environments, it was found that a scan of 5° to 40° covered all of the principal peaks for the minerals found in coal ashes, including clays, carbonates and metal oxides. The 20 step size was 0.01° and the time per step was set between 1.0 s and 1.5 s. The scan time for the sample was kept constant at about 3 hours, and the time per step was adjusted accordingly. Therefore, with the reduced scan range of 5° to 40°, there was higher resolution, which was beneficial for analysis and quantification.

Some hot stage work was performed on a PANalytical EMPYREAN X-ray diffractometer operating with Cu-K α radiation at 35 mA and 40 kV. The 2 θ step size was 0.007° scanning at 1 s per step. This diffractometer has the ability to run at 1400°C. Ashes were investigated at 400°C, 815°C and 1100°C.

A slag sample was analysed using a SIEMENS Diffraktometer D5000 using Cu-K α radiation at 40 mA and 30kV. The 2 θ step size was 0.01° scanning at 0.3 s per step. This diffractometer was used because there was an equipment change from the previous Philips unit at Cardiff University.

In all cases, the software used for mineral identification was Panalytical X'Pert HighScore Plus.

The testing procedure is as follows:

- Powdered sample was placed into a sample holder and compacted using a glass specimen slide.
- 2. This was repeated and extra sample was added at any low points in the holder to ensure that it was full and even throughout.
- 3. The holder was placed into the goniometer of the XRD analyser, and the door was attached.
- 4. The chiller for the XRD was switched on.

- 5. The XRD was switched on and the default power was set at 20 mA and 10 kV. This was turned up to 35 mA and 40 kV alternating between each setting in steps of 5. It was important to ensure that each time a button was pressed, one waited for the green light to illuminate before pressing again. This was to avoid damage to the X-ray tube.
- 6. The shutter door was opened to enable X-rays to reach the sample.
- 7. The scan program was set on the PC and the sample data was entered in.
- 8. The program was sent to the machine and the scan commenced.

3.2.8 X-ray Fluorescence Elemental Analysis

X-ray fluorescence (XRF) is a quick and convenient means of obtaining elemental data and is commonly used for coal ashes (Gluskoter, 1975). The instrument used in this thesis was an Innov-X Systems, model X-5000. It is a desktop XRF that measures dry powders, thus there is no requirement to cast the sample into a glass bead. The lightest element that it could measure was magnesium. This method was suitable for analysis of coals, chars and ashes. Where analysis of lighter elements was required, inductively coupled plasma- optical emission spectroscopy (ICP-OES) was performed, as detailed in Section 3.2.9.

The experimental method is as follows:

- The machine was switched on and logged into. Then the calibration sample of 316 stainless steel was run. Once completed, the analyser was ready to use.
- 2. A new thin-film sample support was affixed to a clean sample holder.
- Sample was conveyed with a spatula into the sample holder. Around 1 g was used, and it was ensured that the film was covered with at least 3 mm of sample.
- 4. The sample holder was placed on top of the window in the machine and the lid closed.
- The sample details were input into the machine and "Mining Plus" mode was selected.
- 6. The sample was sent to run. Analysis took 1 to 2 minutes.
- Once all samples were completed, the data was copied onto a flash drive and the machine was shut down.

3.2.9 Inductively Coupled Plasma Optical Emission Spectroscopy Elemental Analysis

Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis was performed to determine elemental compositions of coal ashes, char ashes, slag, and blast furnace sludge. The technique is commonly known as ICP. This method of elemental analysis provides greater precision than XRF, but involves performing some wet chemistry, while taking longer to perform.

The greatest proportion, by weight, of coal mineral matter and ash, and hence the most commonly analysed elements are silicon, aluminium, iron, calcium, magnesium, potassium, sodium, titanium, and sulphur, with all of these elements occurring in percentage quantities ranging from 0.4% to 46% in the coals tested in this thesis. Phosphorus can also occur in percentage quantities for particular coals, and is found in the mineral called apatite. In addition to the above elements, there are in excess of 20 trace elements found in coal comprising mostly transition elements and heavy metals (Raask, 1985; Speight, 2013). Trace elements were not investigated as part of this work. All of the common elements, plus phosphorus were measured. The test method involves acid digestion of the sample so that it is all in liquid form.

The test method is as follows:

- 1. 0.1000 g of sample was weighed to the nearest mg on a 4 figure balance.
- 2. 2 ml of reagent grade hydrofluoric acid at a concentration of 48-51% was added to the weighed sample, and left to soak overnight for 18 hours.
- 3. 3ml of 37% reagent grade hydrochloric acid and 3ml of 70% reagent grade nitric acid were added and then the sample was microwaved for 30 minutes in an Anton Parr Multiwave 3000.
- 4. The hydrofluoric acid was neutralised with 12 ml of 4% boric acid H_3BO_3 , and then replaced into the microwave for a further 30 minutes.
- 5. The final volume was made up to 50 ml with deionised water.
- These digested samples were analysed using a Perkin Elmer Optima 2100 DV ICP-OES machine.
- 7. The ICP machine was calibrated prior to each test campaign using a 28 element calibration solution with a concentration of 100 mg/l.
- 8. The solution was diluted down to 10 mg/l and 1 mg/l to perform the calibration, and the calibration curves created during this process were

used to determine the concentration of the elements in the tested ash samples.

9. Each ash sample was tested three times and the average of the three runs was determined for each element.

3.2.10 Scanning Electron Microscope Analysis

Scanning electron microscopy (SEM) provides a means of viewing samples at very high magnifications of up to 30,000 times, giving detailed surface morphology, whilst also being able to perform elemental analysis of selected points or areas of a sample (Swapp, 2017). Energy-Dispersive X-Ray Spectroscopy EDS is a technique that allows the elemental composition of a sample to be determined. When a sample interacts with an electron beam, energy is emitted from a sample in the form of x-rays with specific wavelengths according to the elements present, and these are picked up by an EDS detector and converted to a spectrum of voltages plotted against the number of counts for that voltage (Goodge, 2017). This EDS spectrum enables the ratio of detected elements to be calculated which indicates the compounds that may be present. SEM-EDS techniques have been successfully used in coal research for the purposes of morphological and elemental analysis (Ward, 2002; Van Dyk, et al., 2009; Ward, 2016).

In this work, ashes, chars, coals and sludge were examined under the SEM and the method is given as follows:

- 1. A self-adhesive carbon tab was applied to the aluminium sample holding stub.
- 2. Sample was sparingly loaded onto the self-adhesive surface and the excess was removed with a compressed air duster.
- 3. 8 sample stubs were prepared in a batch as this was the number that the SEM carousel could accommodate.
- Samples were gold and palladium coated to 7.5nm using a Quorum Q150T ES sample coater.
- 5. Analysis was done on a TESCAN MAIA 3 operating at 15kV.
- 6. EDS analysis was performed using Oxford Instruments X-Max^N.

3.2.11 Thermogravimetric Analysis

TGA Background Information

Thermal Gravimetric analysis (TGA) is a method that involves monitoring the weight changes of samples as they are heated under different conditions. Several authors have used TGA to assist in identification of the minerals in ashes, due to particular dehydroxylation or decomposition behaviour (O'Gorman & Walker, 1973; Vassilev, et al., 1995). TGA has also been used extensively to determine the reactivity of carbonaceous material (McNamee, et al., 2015; Steer, et al., 2015a) and can also be used to perform proximate analysis (Mayoral, et al., 2001; Donahue & Rais, 2009). It was used in this thesis to investigate the reactivity of coal in the presence of air and the gasification of coke in carbon dioxide. The instrument used was a Mettler Toledo TGA-DSC 3+ and a labelled photograph is shown in Figure 17.



Figure 17: Labelled photograph of the TGA.

TGA Method

An experimental method testing a single non-mixed sample is detailed as follows:

- 1. 70 μl alumina crucibles were used for all tests.
- 2. A small spatula of sample was placed into a pestle and mortar and ground so that it would pass through a 50 μ m sieve. Thus the particle size was controlled so that the variables being investigated were chemical and not physical.
- 10.5 mg of sample was weighed to the nearest milligram into a tared empty
 70 μl crucible using a 4 figure balance.
- 4. The crucible was placed into the sample holder carousel of the TGA instrument.
- 5. The desired temperature profile was inputted into the software whilst adding the reacting gas information and flowrate. Temperature may be constant or there may be a temperature gradient given in °C/min that is

increasing (positive) or decreasing (negative). Gas flow rates are given in ml/min and N₂, CO₂ or air can be safely used in the lab.

6. The experiment was sent to run, and was performed automatically after the sample robot picked the crucible and placed it into the TGA furnace.

A repeat run was performed for the work in Chapter 7.

When investigating the effect of ash on the reactivity of coal and coke in Chapter 7, ash or dolomite or slag was mixed with coal or coke at a concentration of 10%. This was performed as follows:

- 0.0030 g of ash or dolomite was weighed to the nearest 0.1 mg using the 4 figure balance, and deposited into a small agate pestle and mortar.
- 2. 0.0270 g of coal or coke was weighed to the nearest 0.1 mg and deposited into the same pestle and mortar.

The weight measured was dependent on the amount of ash. For example, if 0.0031 g of ash or dolomite was measured, the amount of coal/coke measured was 0.0279 g ± 0.1 mg, and if 0.0029 g of ash or dolomite was measured, the amount of coal/coke measured was 0.0261 g ± 0.1 mg. This ensured that a concentration of 10% was maintained as closely as possible.

3. The sample was mixed thoroughly and ground to pass through a 50 μm sieve.

Following this preparation method, the TGA method was carried out.

Two different test methods, namely combustion and gasification, were used for the work in this thesis. Combustion was performed in 50 ml/min of air at 900°C. Gasification was performed in 50 ml/min of CO_2 at 1100°C.

3.2.12 Ash Fusion Testing

Preliminary Work

Ash fusion tests are criticised for being inaccurate, partly due to subjectivity from the manual observations of ash changes, but they are a useful piece of information for problems occurring due to agglomeration (Qiu, et al., 1999). Preliminary ash fusion tests were performed in a Carbolite HTF 1700 furnace in air. Ashes from LV3 and LV2 were formed into cubes of side 5 mm, by mixing with water to form a paste. In Figure 18, it can be seen that by 815°C, drying of the ash cubes had occurred, but there was no visible fusion behaviour. At 1300°C, ash from LV3 on the left was shrinking, and this behaviour is typical of an ash that is sintering. Meanwhile, LV2 was still intact and just changing colour. By 1375°C, LV3 had reached fusion temperature i.e. melted, but LV2 was only showing moderate signs of sintering. At 1520°C, LV2 had almost melted, but required extra heating to do so fully. The temperature would have needed to be higher to cause a complete meltdown of LV2.



Figure 18: Ash fusion behaviour from preliminary testing in a muffle furnace. Left: LV3; Right LV2.

Ultimately, another method needed to be found as this method lacked precision and accuracy, and placed significant thermal stress on the Carbolite furnace as the doors needed to be opened periodically at high temperatures to check on the samples. Nonetheless, the fusion temperatures determined from this method were in agreement with those found using the following method and apparatus.

Method

Ash fusion tests were performed on a MISURA 2 HSM 1600-50 heating microscope with a maximum temperature of 1600°C and a maximum heating rate of 50°C/min. The change in shape of the ash, as it was heated, was monitored by Misura 3.32 software. The key parameters (sintering, softening, sphere, fluidity and melting) were identified automatically as the software continuously monitored changes in dimensions and proportions. An ideal representation of the stages that occur during an ash fusion test is shown in Figure 19. It can be seen that a prepared sample has straight edges and sharp corners which round off as the ash softens due to temperature. Following this, a hemispherical shape forms, and when the ash is hot enough, it melts.



Figure 19: Ideal Stages of an Ash Fusion Test

The ashes used for testing were derived from coals that had been ground to pulverised particle specification. Therefore, the ashes themselves were fine enough to be used for AFT without grinding. Moreover, it was decided that to keep the tests relevant to the environment in which the ash would be found, i.e. the blast furnace, it would be more representative to not grind them. Pellets of 2 mm diameter by 3 mm high were created using a stainless steel die as shown in Figure 20 below.



Figure 20: AFT Pellet Die

The heating microscope used to perform the ash fusion testing is shown in Figure 21. The experimental procedure is as follows:

1. A small sample spatula of ash with a typically mass of 300 mg was placed into a small dish and wetted with a small drop of water. It was then mixed into a paste.

- This ash paste was compacted into one of the holes of the die, with a hand held punch, with the plates lined up as shown in the left of Figure 20 until it was full.
- 3. The pellets were faced off by sliding the plates relative to each other, and then the uniform dimension pellet was pushed out with the punch and placed onto a small alumina slide.
- This alumina slide and pellet was placed onto the Misura using tweezers and gently slid into the horizontal tube furnace. The computer was turned on.
- 5. The focusing knobs were adjusted so that the silhouette of the pellet was in the centre of the window on the computer software, and the lighting settings were adjusted.
- 6. The coal ashes in this thesis are known to melt at more than 1200°C, thus the heating rate of the sample pellet was set at 50°C/min up to 1000°C (to save time) and then at 6°C/min thereafter. The test was continuously monitored and it was set to terminate 10°C after the melting temperature was reached.
- 7. The heating cycle was sent to run from the computer and the test was completed.
- 8. Post processing was carried out using the software and the data was exported from the computer.



Figure 21: Misura Heating Microscope used to perform ash fusion tests.

3.2.13 Ash abrasion testing

Abrasion testing was discussed in 2.3.5, however it was decided that a specific test needed to be developed for the work in this thesis. There were two constraints

which determined the nature of the testing. Firstly and most importantly, there was limited sample available for testing. For instance, to create char ash, the coal needs to be run through the DTF and the resultant char needs to be ashed in the muffle furnace. This process is time consuming and the amount of ash yielded is between 1 and 10 grams. Secondly, there was limited time to develop elaborate testing apparatus. It was ultimately decided to use an electric rotating grinding plate as shown in Figure 22. Ash was deposited onto the grinding wheel and mixed with several drops of water. Abrasion occurred when a resin blocked was rubbed on this wet ash on a rotating wheel.



Figure 22: The electric rotating grinding plate used for abrasion testing.

The method is as follows:

- Six epoxy resin cylinders measuring 20 mm diameter x 20 mm high were cast using polypropylene moulds. The tradename of the epoxy resin used was Huntsman Araldite 2020.
- The cylinders were left to cure for 3 days in a Belling heated drying cabinet at 50°C.
- One of the faces of the cylinder was prepared on a rotating grinding plate, with silicon carbide grits of increasing fineness ranging from 220 to 600, to produce a uniform, flat surface for ash abrasion testing.
- 4. The mass of the resin cylinder was measured on a 4 figure balance.
- 0.2 g of ash sample was weighed out into a dish, and then deposited into the middle of the grinding plate.
- 6. 8 drops of water were added to the ash sample using a pipette.

- The resin cylinder was held with the intended wear surface facing downwards towards the ash then subsequently used to mix the water with the sample until a paste was created.
- The paste was thinly spread in a circular motion, with minimal pressure, about the centre of the grinding plate until it covered a third of the area of the wheel.
- The machine was switched on and pressure was applied by hand while simultaneously reciprocating the sample across the face of the wheel in a linear motion from edge to edge, while the wheel was spinning, see Figure 23.
- 10. After 30 seconds, the machine was switched off and a further 8 drops of water were added with a pipette, to the sample on the plate.
- 11. This water was mixed with the sample on the plate and step 9 was repeated for 30 seconds.
- 12. The machine was switched off and the resin block was rinsed in water to remove adhering sample, and dried with a paper towel. The grinding plate was also cleaned of sample and dried.
- The resin cylinder was reweighed on the 4 figure balance, and the weight loss due to abrasion was determined.
- 14. For each ash sample, the test was repeated three times.



Figure 23: Reciprocating movement of resin cylinder on a rotating grinding plate.

There were several challenges that had to be overcome when using this method, however the most obvious is the application of constant force by hand. During the testing, the application of force on the resin cylinder by a person was not a perfect solution but was considered necessary given the constraints of the test, namely the small sample amount and simple apparatus. The effect of human error due to inconsistent force was mitigated by restricting effort to 30 seconds at a time to prevent hand fatigue, and by repeating runs three times for each sample. Care, concentration and a good level of manual dexterity were advantageous in producing consistent force.

Repeatability of the test methods was verified by performing six repeats on a standard sample of silicon carbide grit thus creating, in effect, a calibration test. It was found that there was consistency between individual runs of the calibration test, and between different days when the same calibration procedure was performed, as shown in Table 6. It should be noted that the calibration test followed the exact same procedure as for the ashes being investigated, except that silicon carbide is used instead of ash and runs are repeated six times instead of three.

Date	Average mass loss for 6 runs (g)	Relative Standard Deviation %
24.01.2019	0.0285	10.30
27.02.2019	0.0286	6.93
25.03.2019	0.0293	6.83

Table 6: Calibration tests demonstrating repeatability and percentage standard deviationof the ash abrasion method.

Further challenges relate to the sample itself and four of these are as follows: variable ash physical properties; sample being cast from the plate; sample drying during testing; and the resin cylinder dragging during testing. All of these issues are related and further discussed.

The physical properties of the ash can be classified as two main groups. The first group contained ashes of low bulk density, typically with lower particle size, angular, acicular particles. The second group comprised ashes of a higher bulk density and higher particle size with more spherically shaped particles as well as spherical irregular. There were also ashes that possessed characteristics of the two groups.

The former group absorbed more water than the spherical ashes, which caused difficulties when adding the same number of drops of water to ashes of varying physical properties, because some may be too dry and others may be too wet.

This leads onto the second issue of sample being cast from the rotating plate, since when a sample was too wet, as was likely in the case of sandy ashes, when the grinding plate was switched on, the sample would run to the edge of the plate and be cast off the side. This was not a problem with powdery ashes as they formed a paste that better adhered to the plate.

Regarding the third issue: the ash samples would dry out, under test, if insufficient water was added in the first place. This was especially likely with the powdery ashes that formed a paste because most of the water is absorbed into the ash, leaving less free water available, as the paste was worked over the grinding plate during the test.

The fourth problem was that when the ash sample became too dry, the friction would increase causing the resin block to drag and snatch rather than glide across the surface of the grinding plate which gave erroneous results for abrasion. Sandy ashes were less prone to drying out, and much easier to manage in all respects.

The aim of testing a suite of different ashes was to maintain a constant addition of water to dry ash sample, in an effort to maintain consistency in experimental variables across a range of ash types. Following comprehensive method development, it was found that 0.2 g of ash provided sufficient sample to perform a test. It was also found that adding 8 drops of water, then running the test for 30 seconds before adding another 8 drops of water and then running for a final 30 seconds was sufficient to alleviate the sample related problems discussed above. It is worth mentioning that the addition of water to the ash was necessary to ensure that a paste was created that would cover the grinding plate and make sure there was always ash sample between the plate and the resin cylinder. Dry ash would simply be thrown off of the rotating plate, and also be swept off by the resin cylinder. Reciprocating movement of the resin cylinder across the plate ensured that fresh sample was encountered at the abrading interface of the resin cylinder and the plate. It was considered to hold the resin block stationary with a fixed load placed upon it, but this simply caused the ash sample to be ploughed away by the block and left no scope for conveyance of fresh sample to the abrading interface.

The hardness of the resin cylinder is a factor that was contemplated. It was considered that a resin might continue to harden over the course of several days even though the manufacturer states that full curing takes place in 24 hours. As a safeguard, abrasion testing was not begun until the resin had been allowed to cure for 7 days.

3.2.14 Bulk density

Bulk density was performed on chars and ashes as a means of differentiating between different coals and ashes.

The method is as follows:

- 1. A 300 μl crucible was placed onto a 4 figure balance and tared.
- 2. Sample was poured onto a sheet of paper and then funnelled into a 300 μ l crucible until it was heaped and overflowing.
- 3. The crucible was held with a pair of tweezers and tapped gently on a hard surface three times.
- If the level of the sample had settled lower than the edge of the crucible, more sample was added with the paper.
- 5. Excess, heaped sample was gently skimmed off with a spatula to leave a flat surface.
- 6. The sample was weighed on a 4 figure balance.
- 7. Steps 1 to 6 were repeated so that the testing for each sample was completed in duplicate.
- The density was calculated by dividing the mass over the volume, and this data was recorded into a spreadsheet.

3.2.15 Particle Size Analysis

Particle size analysis was performed on coal chars and ashes using a Malvern Mastersizer 3000 laser particle sizer. It is a useful technique to investigate differences in particle size of chars and ashes from effects such as agglomeration or fragmentation. Additionally, it enables the particle size from coal grinding and sieving to be verified.

In terms of representing particle size, Dv10, Dv50 and Dv90 are often given as a single number answer to a particle size distribution. Respectively, these represent the particle size where 10%, 50%, and 90% of the population lies below this value as shown in Figure 24. Hence, Dv50 is the median particle size (HORIBA Instruments, Inc., 2010). Dv90 particle size distribution was chosen for the purposes of this thesis because it takes account of the larger sized particles, which is particularly relevant to abrasion testing where the larger particles are more responsible for abrasive behaviour than the smaller ones.



Figure 24: Dv10, Dv50, Dv90 particle size distribution. Taken from HORIBA Instruments, Inc. (2010).

Particles can be represented in terms of volume density, number density and area density. Assuming an equal number of "small" particles and "large" particles, then the large particles would occupy a greater volume, and the same number of small particles would occupy a lesser volume. In number density, the number of small and large particles is the same. Thus in volume density, a greater number of particles are required at a smaller particle size to occupy the same volume as fewer large particles, thus this is indicative of the mass of particles present of a given size. Laser diffraction particle sizes are reported on a volume basis (HORIBA Instruments, Inc., 2010).

It is important to understand that a single number for particle size data does not give information about the distribution of particle sizes, and this is an important point to consider when quoting particle size information. However, in the case of this thesis, plotting a bar chart of single number particle sizes enabled several coals and ashes to be conveniently compared.

The method used is as follows:

- A small spatula of sample was placed into a 500 ml beaker of deionised water. Note that for substances that do not mix easily with water, it was necessary to add a small amount of surfactant and to mix the sample in a much smaller vessel to help it to wet.
- 2. The software for the Malvern instrument required the sample refractive index, absorption index and particle density to be entered. For coals and
chars the respective values were 2.42, 1, and 1 g/cm³ respectively. For ashes it was 1.65, 0.1, and 1 g/cm³ respectively.

- The software was adjusted such that 6 repeats were performed for each sample, with each one taking around 1 minute. The 6 repeats were automatically averaged.
- 4. The repeatability of the 6 repeats could be identified on the software. For example, if the particle sizes of the consecutive repeats were seen to be decreasing, this would indicate particles dissolving or agglomerated particles breaking apart.

3.3 Experimental Analysis

In a minority of cases, the information provided from the experimental methods required some sort of analysis to make useable numerical data.

3.3.1 Ash Tracer Method to Calculate Drop-Tube Furnace Burnout

Ash tracer method was used in this thesis to calculate the extent of burnout of coal chars collected from the DTF. Calculating the burnout was essential to being able to compare the reactivity of the selected coals, and to allow comparison between DTF residence times, temperatures and gas environments. It has been used by many authors (Lu, et al., 2001; Borrego, et al., 2008; Du, et al., 2010; Steer, et al., 2015a; Zou, et al., 2017) and assumes that the amount of ash remains constant in a coal or char, thus being able to track the burnout of combustible material relative to non-combustible material.

Burnout % =
$$\frac{10^4(A_1 - A_0)}{A_1(100 - A_0)} 10^4(A_1 - A_0)$$

Equation 26: Ash Tracer Method Percentage Burnout (Steer, et al., 2015a).

Where A_1 = ash yield of the char; and A_0 = ash yield of the original coal.

Suzuki, et al. (1984) compared ash tracer method with a titanium tracer and gas analysis. Ash tracer is susceptible to errors, for instance, in the incomplete collection of ash during combustion; vaporisation; condensation; and high temperature transformations. A titanium tracer was found to be more accurate at high temperatures as it is more stable under these conditions and does not vaporise, unlike ash. They found gas analysis to be dependent on whether O_2 or CO_2 was measured and in addition, this did not account for CO, H_2 and H_2O formation.

In spite of this, ash tracer was chosen on account of its simplicity and successful use by many authors. Importantly, the addition of a titanium tracer would have contaminated the ash samples with a foreign mineral, thus affecting the XRD results, ash fusion behaviour, particle size and other variables investigated in this thesis. In addition, there was a significant number of chars from different reaction conditions. The addition of a tracer would have complicated the experimental process. There was not access to a gas analyser from the DTF for this work. Moreover, DTF burnout was not the main focus of this work.

3.3.2 X-ray Diffraction Semi-Quantification

Background Information

Quantitative mineral analysis of mineral matter is a challenge owing to the variability of composition (Ward, 2002). Nonetheless sufficient information can be drawn from a diffractogram by performing semi-quantification of the minerals by measuring the height of the main peaks, or the area of the main peaks in a diffractogram and it provides a convenient means of comparing data from samples that have undergone the same test method using the same XRD instrument (Vassileva & Vassilev, 2005). Semi-quantification is a recognised term used when quantifying XRD data that takes account of the uncertainty in the actual measurement of the mineralogy and its subsequent analysis. It is possible to attain accurate quantitative data by using Rietveld refinement method but this requires creating a mathematical model that replicates the pattern of the measured diffractogram. The calculated pattern is achieved by using different graphical functions as well as inputting the crystallographic parameters into the computer software. In the case of mixtures of minerals, it is necessary to calculate a diffraction pattern for each of the individual mineral phases, and then to fit all of the calculated information to the measured pattern (Rietveld, 1969; Misture & Snyder, 2001). Although this method is valuable, it would have been highly timeconsuming given the number of different samples analysed in this thesis, and also given the nature of ashes as a mixture. It was decided that time was not best spent on overanalysing the XRD data, so a simpler semi-quantitative method was adopted. This type of method has been used by Stanislav Vassilev who has published numerous papers in the field of coal ash and mineral analysis. McReynolds et al. (2008) describe such a semi-quantitative method as an acceptable method when comparing similar sample types in a single study, which is the case with this thesis. Li et al. (2017) determined that XRD repeatability was found to be 15%. It was also stated that if limited minerals can be found, the remaining material must be amorphous.

Minerals were manually semi-quantified by measuring and calculating the area of the main peak for each identified mineral. Peak area was calculated using FWHM (full width at half maximum) as shown in Figure 25. The total of the areas for all the minerals was taken to be 100%, hence each mineral represents a percentage of these calculated areas. This technique is known as the *100% approach*, and makes the assumption that all minerals have been identified and it does not account for amorphous material (Kahle, et al., 2002).



Figure 25: FWHM to calculate peak area.

Vassilev et al. (1995) performed a similar method as described, however the peak height of the main peaks was used, as opposed to the area. There was good reproducibility using this method with a relative deviation of less than 7% for quartz. There are several caveats to the technique which are described as follows. This method of quantification is approximate because it does not account for different mineral absorption coefficients. In addition, there are issues regarding crystallite size, preferred orientation, overlapping and reflection of X-rays. Clay minerals are highly variable, often with poor crystallinity, and inconsistent compositions which makes it difficult to unmistakably identify a clay mineral (Gupta, et al., 2008). Another challenge to contend with was the overlapping of peaks within an XRD diffractogram. This sometimes meant that it was difficult to distinguish between peaks, so it was often easier and more accurate, to use a secondary peak, unless the two peaks could be disseminated. For minerals such as quartz and anhydrite, the data was more reliable as the clarity of these peaks was greater, owing to higher crystallinity (Vassilev, et al., 1995). According to Renton (1986), XRD works well so long as the crystallinity of the sample is high, and that the unknown mineral in coal is a good match for the known standard in the

database. Unfortunately, both of these requirements are not typical of coal mineral matter, which means that analysis is semi-quantitative with percentage errors of \pm 10% (Renton, 1986). Vassileva and Vassilev (2002) states that some quartz may not be detected by XRD (because it may be amorphous), which would give the appearance that there is less quartz than actuality.

When quantifying clay minerals in an XRD diffractogram, it is necessary to multiply the peak intensity by a mineral intensity factor (MIF) / weighting factor depending on the type of clay present. This is because clays have varying abilities to diffract Xrays and so the intensity and area of the peaks cannot be used as a direct representation of the amount present in a sample. All the other mineral phases in an XRD sample e.g. hematite and quartz, have a weighting factor of 1, so these do not need to be adjusted. Mineral intensity factors are discussed in depth by Kahle et al. (2002) where a list of MIFs from various authors is compiled. Table 7 shows simplified list of MIFs.

Mineral	Weighting Factor
Kaolinite	2
Illite	1
Chlorite	2
Smectite (montmorillonite)	4

Table 7: Clay Mineral Weighting Factors. Information from (Biscaye, 1965).

In the case of this thesis, the mineral intensity factor for kaolinite was the most important, and any calculation of peak area was given a double weighting prior to presenting the semi-quantitative data.

Method

The semi-quantification method, involving the use of FHWM, is described as follows, and an example quantification is shown in Figure 26.

- 1. Determine background of the chart using the software.
- 2. Subtract the background to bring the chart down a zero baseline.
- 3. Use y=0 as the baseline for quantifying the peaks.
- 4. Measure the peak height from the baseline.
- 5. For 100% peaks with no overlap, use FWHM method to calculate the area.
- 6. For peaks with overlap, either calculate the effective peak size of just the single peak by drawing the other peak in, or choose a lower intensity peak

that does not have any interference. Remember to scale up the lower intensity peak relative to the 100% peak.



Figure 26: Example of XRD Mineral Semi-Quantification

3.3.3 Standard Deviation and Standard Error

An important consideration in this thesis was the presentation of experimental error. Typically, in large datasets, standard deviation and standard error are used and applied to data points on graphs, such as points on a curve or bars in a bar chart. Population standard deviation is calculated using the following formula:

$$\sigma = \sqrt{\frac{\sum (x_i - \mu)^2}{N}}$$

Equation 27: Population standard deviation formula.

The *population* standard deviation is used when the population of data points is a known quantity, for instance if many data points have been taken, and the value of all of them is known. *Sample* standard deviation is calculated as above except that the numerator is divided by the number of data points minus one. This increases the value for the standard deviation, and is used when not all of the data points are known, for instance when a subset of a dataset is being investigated. Thus, the objective of raising the standard deviation in this case is to account for uncertainty of the unaccounted data points in the dataset (Khan Academy, 2019).

Standard error is calculated by dividing the standard deviation by the square root of the number of data points as follows (Radford University, 2004).

Standard Error = $\frac{\sigma}{\sqrt{N}}$ Equation 28: Standard error formula.

Error bars of plus or minus one standard error gives a 68% chance that the mean of a sample set will lie within the published value. Two standard errors increases this chance to 95%, and three increases it to 99.7% (Galarnyk, 2018). Standard deviation also follows the 68-95-99.7 rule but this applies to the percentage of the *data* lying within the mean (Hertzog, 2017).

The methods described above are usually employed on large datasets. However, in this thesis, the nature of the work has meant that the majority has been repeated twice, and in some cases three times, thus the datasets are small. It was seen as more authentic to present the data in terms of a mean value accompanied by the maximum and minimum deviation from the mean, rather than applying statistical tools. Equation 27 achieves this objective, since the equation is simply a way of calculating deviation from the mean. In this thesis error bars are plotted on bar charts in terms of maximum and minimum deviation from the mean, and additional information is given where necessary.

Chapter 4: Results of Mineral and Chemical Analysis of Ash and their Effect on Ash Fusion Behaviour

This chapter aims to fully characterise the mineral matter present in blast furnace injection coals with a view to allowing an operator to make a more informed choice based upon the coal mineral matter composition. The effect of heating conditions in a muffle furnace and drop-tube furnace was investigated.

Mineral matter was analysed using X-ray diffraction (XRD) and quantification of the minerals was performed. Inductively coupled plasma (ICP) elemental analysis and X-ray fluorescence (XRF) elemental analysis were used to analyse the coal ashes. The mineral and elemental compositions, are explored and linked with possible effects in the blast furnace.

For instance, the clay composition and carbonate composition is connected to the elemental chemistry and fusion temperature of the coal ashes. These findings may be of interest to operators looking to control the effects of ash fusion behaviour. In addition potential for catalytic activity can be related to the minerals and elements present in ash.

Coals were run through a drop-tube furnace (DTF) to investigate the effect of reaction conditions, such as temperature, residence time, and gas environment on the melting temperature of the ash. These conditions are particularly relevant to the blast furnace raceway where high heating rates, variable residence times and changing gas compositions occur.

In this chapter, although much information can be obtained from coal ash analysis, it became apparent that owing to the highly variable nature and the complex interplay of interactions, that are not fully understood, it was not possible to conclusively infer ash behaviour from solely elemental analysis or mineral analysis. It is however possible to obtain an indication of what may occur, and given that blast furnace operators largely use volatile matter as a metric for a good or bad coal, any additional information is helpful.

This chapter relates to the hypothesis by aiming to determine the effect of heating conditions on ash fusion temperature. It is also interested in determining the effect of elements on the ash fusion temperature.

4.1 XRD Diffractograms

Numerous XRD diffractograms were produced in order to generate the semiquantitative data presented in this chapter. Several of these diffractograms are selected and annotated to give a visual representation of the minerals present in the ashes, and the mineral changes that occur due to heating.

4.1.1 Identification Example

Figure 27 shows a labelled diffractogram for LV3 400°C ash created using Cu-Ka radiation. A distinct set of peaks corresponds to a given mineral, and in this case there are five confirmed minerals in the ash, namely quartz, kaolinite, illite, calcite and dolomite thus these sets of peaks overlay each other. It can be seen that the ash contains a complex assemblage of minerals which makes identification and quantification a challenge. For each mineral, there is a principal peak with a 100% intensity, and the other lesser peaks for the minerals in question are a relative proportion of this main peak. The 100% peaks for quartz, kaolinite, calcite and dolomite are 26.6°, 24.8°, 29.5° and 31° respectively. Illite has peaks that approach 100% at 9°, 20°, 26.5°, and 35°. Thus illite overlaps with the principle peak for quartz and this makes quantification of both clays in general, and mineral mixtures, challenging. XRD crystallographic information can be found from a reference library and in the Panalytical X'Pert HighScore Plus software that was mentioned in Section 3.2.7. For coal mineral analysis, it was found that principle peaks for the minerals could be identified within the first 40° of the scan, thus many diffractograms in this chapter show this scan range. Gypsum is a commonly found mineral in low temperature ashes (Mitchell & Gluskoter, 1976) and are indicated by '(G)' in Figure 27. It can be seen that each of the gypsum peaks coincides closely with peaks from the other identified minerals. It is highly likely that gypsum is present in the ashes of the coals in this thesis, owing to the prevalence of this mineral in the literature, but the overlying peaks makes it problematic to semi-quantify this mineral. It is known that sulphur is present in 400°C ash from work in Chapter 5. The likely form of this sulphur is gypsum or bassanite. Peaks for bassanite and haematite are identified although issues such as overlap and an incomplete peak pattern meant that it could not be conclusively confirmed that these were present. Bassanite (CaSO₄. ½H₂O) is partially or semi hydrated gypsum, where gypsum is hydrated calcium sulphate (CaSO₄.H₂O); this is detailed in Table 2.



Figure 27: Labelled XRD Diffractogram of LV3 400°C Ash. Q = Quartz, C = Calcite, K = Kaolinite, I = Illite, D = Dolomite. (G) = Gypsum, (B) = Bassanite, (H) = Haematite.

The minerals identified in LV3 400°C ash are typical of other authors who investigated ash created at the same temperature. For example, Filippidis et al. (1996) also observed quartz, kaolinite, illite, calcite, and dolomite. Mitchell and Gluskoter (1976) found pyrite, gypsum and sphalerite in addition to these minerals. Pyrite was not observed in the coals of this thesis on account of pyrite decomposition, which occurs at less than 400°C as discussed in Section 2.2.3. Gupta et al. (2008) report quartz, kaolinite, illite, calcite, dolomite, pyrite, siderite, bassanite, goyazite, apatite and anatase as common minerals in coking coals.

LTA (low temperature ashing) as discussed in Section 3.2.3 is often used for the identification of mineral matter owing to its lower temperature leading to less destruction. In addition to the minerals identified in MTA, LTA allows determination of pyrite (FeS₂) (Matjie, et al., 2011; Tian, et al., 2011). LTA was not used in this thesis, however it can be seen from Figure 27 that the minerals identified in the thesis are comparable to those found in the literature. The detection of the significant clay minerals and carbonates is evidence for the effectiveness of the MTA technique used in this thesis. It is discussed in Section 4.1.2 that high temperature ashing (HTA) at 815°C causes significant changes in the mineral matter such that the original minerals would be unidentifiable.

4.1.2 The Effect of Ash Determination on Mineral Matter

This section is concerned with the effect of high temperature ashing at 815°C on the mineral matter in coal. Firstly, a visual representation of the changes that occur during ashing by displaying an annotated XRD diffractogram is given, for the purposes of familiarising the reader with the typical changes that occur in the mineral matter due to ashing of coal. The second part relates these changes to the comparative ash yield under MTA and HTA conditions.

Changes in an XRD Diffractogram

Figure 28 gives a clear visual representation of the mineral changes occurring between MTA and HTA. The diffractogram was created using Co-K α radiation therefore the peaks are shifted to the right when compared with Figure 27 which used Cu-K α radiation. The diffractograms of MV coal were chosen to depict the mineral changes as this coal contains a more uniform composition of the mineral phases as indicated by the semi-quantitative analysis of the MTA in Section 4.2.1, Table 10, thus the peaks for each mineral are large and clear which aids in showing the changes occurring. Kaolinite, calcite and dolomite that are present in MTA are not present in the HTA diffractogram. Dehydroxylation of kaolinite clay leads to the formation of meta-kaolinite which is a non-crystalline material. The heat is sufficient for decomposition of the carbonate minerals. Haematite forms from the decomposition products of iron-containing carbonates. Anhydrite peaks become apparent due the decomposition products of gypsum and also the reaction of calcium from calcite decomposition and sulphur from pyrite decomposition (Matjie, et al., 2012). An organic source of calcium available to react with sulphur can also give rise to anhydrite (Ward, 2016).



Figure 28: Diffractograms of MV MTA and HTA, showing the effect of ashing temperature on the mineral matter.

Similar minerals found in the MTA of the coals in this thesis were found in LTA by Tian et al. (2016) who also observed a change in relative intensity of the peaks under different ashing temperatures which shows that the proportion of the minerals is changing. This gives confidence in the identification and quantification in this thesis.

Change in Ash Yield with Ashing Temperature

In the literature, it is widely stated that the mass of ash yielded decreases as the ashing temperature increases (Gupta, et al., 2008). Typically, the mineral matter weighs around a third more than the high temperature ash yield (Rao & Gluskoter, 1973). Andrejko et al. (1983) combusted nine different types of peat under four temperature conditions: LTA, 375°C, 550°C and 750° and found that the ash yield decreased with increasing temperature, however the effect diminished at higher temperatures. The data in Table 8 are in agreement with the literature. There is around a 20% higher yield of ash at 400°C than at 815°C. This is due to decomposition and dehydration of minerals such as pyrite, clays and carbonates. It

could be argued that the mass loss is due to incomplete ashing, but in work by Filippidis et al. (1996) it was observed that all the carbonaceous material in two lignite coals was fully combusted at temperatures exceeding 400°C. It was also observed that the greatest mass loss is between 400°C and 500°C with further loss to 1200°C being comparatively lower. A number of changes occur in the mineral matter when it is heated from room temperature up to 400°C. These include loss of adsorbed water from 55°C to 110°C, dehydration of gypsum (hydrated calcium sulphate) from 130°C to 180°C. In addition, clays lose interlayer water and structural OH groups (Vassilev, et al., 1995). There may also be oxidation of pyrite (FeS₂) to haematite (Fe₂O₃) and decomposition of siderite (FeCO₃) to haematite (Steel, et al., 2001). In addition, clays lose interlayer OH groups. It is worth considering that the local reaction temperature of the coal will be higher than 400°C; Steel et al. (2001) found that at a nominal temperature of 370°C, the actual temperature of the reacting zone was in excess of 600°C. If this is the case, other decomposition reactions such as that of calcite to calcium oxide and carbon dioxide, which typically occurs at >625°C, with a weight loss of 44%, (Gluskoter, 1975), could also be causing a loss in mass of the mineral matter as shown in Table 8 and Table 9. Thus the range of decomposition reactions occurring lead to a significant proportion of mineral matter being lost in the form of gases such as SO₂ and CO₂, as well as water vapour (Andrejko, et al., 1983).

	LV1	LV2	LV3	MV	HV
400°C Ash (wt%)	12.61	11.31	7.07	9.30	10.90
815°C Ash (wt%)	10.44	9.32	6.17	7.52	9.18
1100°C Ash (wt%)	10.37	9.35	6.12	7.36	8.59
Increase in ash yield at 400°C vs 815°C (%)	20.8	21.4	14.6	23.7	18.7

Table 8. Comparison of ash yield under different ashing temperatures.

The change in the mass of ash with temperature was an important consideration in terms of ash tracer method when performing burnout calculations of DTF chars. It has been shown in Table 8 that the mass of ash decreases with temperature, however the effect is most pronounced between 400°C and 815°C. The difference in mass between 815°C and 1100°C ash is much lower. For all of the ashes, except HV, the change occurs within one decimal place. This means that at the high temperatures experienced during HTA and the DTF, the relative changes in the mass of the ash are small. Regarding HV, this is a high volatile, high reactivity coal

as shown in Section 5.1.3. Differences in ash yield have a smaller effect on the burnout result at high conversion when compared to low burnout conditions where a small change in ash percentage has a stronger effect on the burnout result. Therefore the burnout error is minimised in the case of HV where the coal has a high reactivity.

Table 9 shows the ash percentages at the different ashing temperatures in the TGA. It can be seen that as the temperature is increased, the ash percentage reduces therefore it is expected that the majority of the decomposition reactions occur in this temperature range.

	LV2	LV3
400°C Ash (wt%)	14.0	8.2
450°C Ash (wt%)	11.9	6.9
500°C Ash (wt%)	11.3	6.0

Table 9: The effect of ashing temperature on ash yield in a TGA at 400°C, 450°C and 500°C.

4.1.3 Drop-Tube Furnace Conditions

MV coal was run through the DTF at 1100°C for 100 and 350 ms, and the chars produced were ashed at 815°C. Figure 29 shows how the amount of mullite increases with DTF residence time. Mullite possesses a peak at 19° and double peaks around 30°, as indicated by the purple arrows. It can be seen that an increase in DTF residence time increases the amount of mullite in the char ash. Mullite is not found in 815°C muffle furnace ash, see Figure 28, as formation of crystalline mullite does not begin to occur until at least 1050°C (Chakraborty, et al., 2003). The formation of mullite occurs due to crystallisation of the amorphous decomposition product of kaolinite, and to a lesser extent, illite.

Regarding other minerals, in Figure 29 it can be seen that illite is almost completely decomposed by 350 ms. The illite scheme in Figure 9, Section 2.2.3 by McConville and Lee (2005) shows that full conversion of illite to spinel and mullite does not occur until 1100°C, hence why it is still possible to see illite in the DTF char ash. Moreover, anhydrite is present in both char ashes but experiences a slight reduction by 350 ms due to decomposition which is typical at temperatures exceeding 1100°C. It can be seen that haematite increases with residence time, which also occurs at these temperatures (Vassileva & Vassilev, 2005).



Figure 29: Diffractograms of MV 100 ms and 350 ms char ash showing mullite formation in DTF chars at 1100°C.

4.2 Mineral Quantification

Table 10 shows the quantification results of the minerals present in MTA for LV1, LV2, LV3, MV and HV. The semi-quantitative analysis gives useful information, however its limitations have been discussed in Section 3.3.2. It is only possible to identify crystalline materials using this technique and the sum of the identified minerals is assumed to be 100%. Thus, when comparing an ash with a small number of minerals to an ash with a large number of minerals, this can give an inflated quantification when there are fewer minerals to identify. This can be seen in the change from MTA to HTA, where in HTA, the amount of quartz and illite are increased due to there being fewer minerals present in those ashes. There are fewer minerals in the HTA owing to conversion of clays, carbonates etc. to amorphous material, which cannot be quantified in the same way as the crystalline peaks. Identifying quartz on a diffractogram is straightforward owing to the high,

recognisable 100% peak however, owing to this, quartz can become overrepresented during the quantification analysis as the peak is particularly high. This should be kept in mind when using the quantification data. A mineral intensity factor (MIF) to reduce the apparent concentration was not applied to the quartz results, since, in the literature MIFs were only used for clays.

In this work, the amorphous material (glass phase) was not quantified. It has already been discussed that XRD is suitable for measuring crystalline materials and that amorphous materials become represented as broad patterns (humps) that cover a large angular range on a diffractogram. Under low ashing temperatures, the majority of material is as crystalline minerals. However, it is discussed in Sections 4.4.4 and 4.5.1 that the presence of amorphous material in ash samples increases with temperature. With regard to the quantification in this section, it means that the presence of unaccounted amorphous material will have an impact on the accuracy when making comparisons between sample conditions. It is not possible to compare the mineral quantification of MTA with HTA or DTF Ash because the proportion of amorphous material is unknown so we cannot be certain of the amorphous material is an area of uncertainty and may contain some elements that are of particular interest to blast furnace operators.

4.2.1 Medium Temperature Ashing

Table 10 shows that with the exception of LV1, the MTA contains quartz, kaolinite, illite, calcite and dolomite; as shown in the diffractogram of LV3, Figure 27. LV1 does not contain the carbonates calcite and dolomite, however it does contain an apatite mineral, namely fluorapatite which is calcium phosphate with a formula of $Ca_5F(PO_4)_3$. Phosphorus is a particularly undesirable element with strict limits on its input rate into the blast furnace (Geerdes, et al., 2009). Therefore being able to identify minerals such as these before they enter the blast furnace is important.

Mineral	LV1	LV2	LV3	MV	ΗV
Quartz [SiO ₂]	20	43	27	38	33
Kaolinite [Al₂Si₂O₅(OH)₄]	51	7	32	14	12
Illite [K _{1.5} Al ₄ (Si _{6.5} Al _{1.5})O ₂₀ (OH) ₄]	19	43	8	19	6
Calcite [CaCO₃]		2	27	10	14
Dolomite [(CaMg)(CO₃)₂]		4	5	19	35
Fluorapatite [Ca₅F(PO₄)₃]	10				

Table 10: XRD mineral quantification for MTA (medium temperature ash) at 400°C (%).

LV2 contains a low concentration of carbonates and hence low calcium. It is also noticeably lower in kaolinite than the other coals. Clays such as kaolinite and illite are a source of silicon and aluminium and are typically found in greater abundance in higher rank (lower volatile) coals (Vassilev, et al., 1995; Vassileva & Vassilev, 2002). The converse is true of alkaline components such as calcium and magnesium (Vassilev, et al., 1995; Pisupati & Krishnamoorthy, 2017). High clay contents are indicative of high fusion temperatures and high carbonate contents reduce the fusion temperature. This is also related with the elemental analysis. Table 10 is in agreement with the literature in that the sum of the illite and kaolinite clays decreases with lower rank coals, and that the amount of calcite and dolomite typically increases with lower rank coals; in Section 4.3, it is found that there is some correlation with fusion temperature for the work in this thesis. In terms of application for the blast furnace operator, this would indicate that the volatile matter metric that is commonly used to select coals could also link to the relative proportion of clays and carbonates, which could lead to inference of the fusion temperature, where high volatile coal ashes typically have lower fusion temperatures components (Pisupati & Krishnamoorthy, 2017). A larger sample set of ashes would greatly benefit this theory, however the limited findings in this thesis are in agreement with the literature.

4.2.2 High Temperature Ashing

Table 11 shows the minerals present in HTA in all five ashes are quartz, illite, haematite and anhydrite; this is typical of other authors (Qiu, et al., 1999; Song, et al., 2009). It has already been examined that kaolinite, calcite and dolomite are not present in HTA, while peaks for anhydrite and haematite appear. Illite persists in HTA, as discussed in the literature. It was not possible to identify sulphur compounds in MTA, however the presence of anhydrite in HTA is important information when looking to minimise sulphur input into the blast furnace. In Section 5.2.1, it is discussed that LV3 and HV which have a high proportion of anhydrite, also possess high sulphur content, which is persistent at high temperature and not readily lost into the gas phase. Performing XRD of HTA could provide operators with a convenient means of determining the mineral form of sulphur in injection coals, where it was not possible to identify in MTA.

Table 11: XRD mineral quantification for HTA (high temperature ash) at 815°C (%)

Mineral	LV1	LV2	LV3	MV	HV
Quartz [SiO ₂]	38	32	45	41	53
Illite [K _{1.5} Al ₄ (Si _{6.5} Al _{1.5})O ₂₀ (OH) ₄]	34	54	24	40	13
Haematite [Fe ₂ O ₃]	9	5	9	8	13
Anhydrite [CaSO₄]	5	10	22	11	22
Fluorapatite [Ca₅F(PO₄)₃]	15				

4.2.3 Drop-tube Furnace Char Ash

Table 12 shows that in the DTF 350 ms char ash, there is quartz, mullite, haematite and anhydrite in all samples. Similar minerals were observed by Song et al. (2009) and Tian et al. (2011). LV1 contains a small amount of illite and some fluorapatite. Mullite forms from the decomposition products of kaolinite, and to a lesser extent illite. Hence the MTA technique was useful in being able to identify the minerals in the coal that are responsible for some of the minerals created under high temperature conditions. Mullite is a hard mineral with a high melting temperature and it is possible that if mullite is formed in the tuyere, it could initiate wear, however, this would be dependent on there being sufficient temperature and residence time in this region, for this effect to occur. Also, in terms of wear, quartz is a mineral that has a melting temperature of 1710°C, and is present in HTA and DTF Char Ash, so it is likely that the resilient nature of this mineral could lead to wear of the tuyeres, even under high temperature conditions. In addition, fluorapatite is present. This is a mineral that does not begin to change phase until 1350°C (Reifenstein, et al., 1999).

Mineral	LV1	LV2	LV3	MV	HV
Quartz [SiO ₂]	30	74	45	65	61
Mullite [3Al ₂ O ₃ .2SiO ₂]	27	11	12	20	15
Haematite [Fe ₂ O ₃]	25	6	26	7	13
Anhydrite [CaSO ₄]	2	9	16	8	11
Illite [K _{1.524} (Si _{6.5} Al _{1.5})O ₂₀ (OH) ₄]	8				
Fluorapatite [Ca₅F(PO₄)₃]	9				

Table 12: XRD mineral quantification for 350 ms DTF char ash (%).

4.3 Ash Fusion Temperature

Ash fusion temperature is an important factor to consider in the context of the blast furnace because it has an effect on how the ash generated from pulverised coal interacts with coke. According to (Khairil, et al., 2002), sticky ash that is blown to*wards the bird's nest and deadman can attach to the coke and act as a binder and it is proposed that this has the potential to reduce the permeability of the furnace. Ichida et al. (Ichida, et al., 2001) states that a reduction in deadman permeability can cause the temperature to reduce leading to an increase in slag viscosity. Thus a high melting temperature ash is more like to adhere to the coke, whereas low melting temperature ash flows off of the coke to enter the slag. However, work by Zou et al. (2017), found that low melting temperature ash is more able to penetrate the coke pores, which is likely to increase the reactivity of the coke. The effect of ash on coke reactivity is investigated in Chapter 7.

Table 13 shows the ash fusion temperatures performed in accordance with the method in Section 3.2.12 for coal ashes that have undergone different ashing conditions. The ashing conditions of MTA, HTA, and VHTA appear to have little effect on the AFT. Most of the ashes investigated in this thesis were performed at 815°C. The full dataset for the fusion temperatures at 815°C HTA is discussed as follows due to being able to form comparisons between the five coals. HV ash with the lowest melting temperature of 1194°C also had the highest amount of carbonate material when looking at the quantification of medium temperature ash minerals in Table 10. Conversely, LV2 with the highest melting temperature of 1526°C had a particularly high amount of quartz and illite, which are known to increase ash fusion temperatures (Vassilev, et al., 1995). It is proposed that although LV1 contains high quartz and clay minerals, as determined from the XRD results, the presence of calcium from fluorapatite was reducing the fusion temperature.

In terms of applying melting temperature to the blast furnace, work in Chapter 7 determined that the low melting point ash HV possessed catalytic behaviour, due to its elemental composition. On the other hand, the LV2 was significantly less catalytic. LV2 had a high melting temperature thus may be more likely to stick to the surface of the coke so may effect permeability, but is less likely to cause coke degradation, owing to its lower catalytic chemistry. It should be pointed out that the catalysis is not due to low fusion temperature. The catalysis is due to calcium content, which is also responsible for low fusion temperature. Therefore it is possible to indirectly link fusion temperature to catalytic behaviour.

Table 13: Ash fusion temperature (°C) for ashes under different ashing temperatures.

Sample	LV1	LV2	LV3	MV	HV
400°C MTA	-	1510	1318	-	-
815°C HTA	1300	1526	1316	1298	1194
1100°C VHTA	1308	1502	1308	-	-

Table 14 introduces the effect of DTF residence time on ash fusion temperature. Coal samples were run through the DTF at 1100°C for 100 ms and 350 ms, and the chars were subsequently ashed at 815°C. The melting temperature of HTA has already been shown in previous tables, however it is used again in this table to act as a point of reference for the DTF char ash fusion temperatures. An increase in DTF residence time led to an increase in melting temperature for all ashes except LV2. LV2 ash has a particularly high melting point and it is evident that the drop-tube furnace was unable to cause a further increase. Two runs were performed for LV2 100 ms and LV2 350 ms. The deviation from the mean is shown for these values, and it can be seen that this deviation is greater than some of the perceived differences in the other coal ashes melting temperatures. However for the coal ashes with mid to low melting temperature, there is a consistent increase in fusion temperature as a result of DTF treatment.

Table 14: Ash fusion temperature (°C) for 1100°C 100 ms and 1100°C 350ms DTF Char Ash, compared to HTA. Note that two runs were performed for LV2 and the deviation from the mean is stated for these results.

Sample	LV1	LV2	LV3	MV	HV
815°C HTA	1300	1526	1316	1298	1194
DTF Char Ash 1100°C 100ms	1348	1484 (±18)	1314	1306	1222
DTF Char Ash 1100°C 350ms	1336	1469 (±27)	1326	1314	1250

4.3.1 Factors Affecting Ash Fusion Temperature

Mineral Effects

A link can be made between the ash fusion temperature and the semi-quantitative mineral analysis shown in Table 10. It has already been discussed in Section 2.2.7 that minerals such as quartz, kaolinite and illite contribute to higher AFT, while minerals such as calcite and dolomite reduce the melting temperature. Looking at the mineral composition for MTA, it can be seen that the ash with the lowest

melting temperature, HV, has the highest proportion of calcite and dolomite. LV2 has a very high AFT and this corresponds with a large proportion of quartz and clay and a minor proportion of carbonates which is in agreement with other work where an absence of calcite was observed at high AFT (>1500°C) (Qiu, et al., 1999). LV3 and MV have a moderate balance of refractory and fluxing minerals, and they also possess an AFT somewhere between the two extremes of LV2 and HV. LV1, however, does not follow the trend of the other 4 coals, as this possesses a large proportion of refractory minerals, but without such a high AFT to match, it was proposed that this is due to the presence of calcium in the fluorapatite mineral. Thus, in most cases, there is a clear correlation between mineralogy and melting temperature, however, it would be incorrect to use the mineral matter composition as a secure predictor of AFT.

Elemental Effects

Table 15 shows the ICP elemental analysis of the 815°C ash of the 5 coals. The elemental analysis was converted to the oxide form as shown in the table. In the literature, this method is typically used and was chosen in this work for two reasons. Firstly, it allows direct comparison of the findings of this work to the literature. Secondly, acid to base ratios and slag basicity are commonly used literature and industry parameters that use the relative proportion of oxides. The oxides were used in all of the results in this thesis to maintain consistency across all of the data. It is understood that in real ash samples, the elements may not exist in the oxides forms expressed in Table 15.

The effect of each element has been discussed in 2.2.7, and it was determined that elements with the strongest effect on melting behaviour are silicon, aluminium, and titanium which have refractory properties that increase AFT, meanwhile iron, calcium and sulphur have fluxing properties that lower the AFT. Other components such as potassium, sodium and magnesium also have a fluxing effect, but these are more marginal. LV2 contains the highest silicon, high aluminium and the lowest iron, calcium and potassium, and this is reflected in its high fusion temperature. HV contains low silicon and very low aluminium compared to the other samples, thus the chemistry is in agreement with the low AFT experienced by HV. LV3 contains low silicon and aluminium but the highest iron, high calcium and the highest sulphur. Disregarding aluminium, LV3 has a similar chemistry to HV coal, yet possesses a fusion temperature that is 120°C higher.

Table 15: ICP element oxide (%) for HTA

	SiO₂	Al ₂ O ₃	Fe₂O₃	CaO	MgO	K₂O	Na₂O	TiO₂	SO₃	P₂O₅
LV1	38.95	28.71	7.45	6.65	1.03	2.61	0.58	0.87	0.89	4.79
LV2	48.75	28.07	6.09	2.59	1.08	1.11	1.79	1.00	1.20	0.84
LV3	34.99	20.83	12.74	9.62	1.72	1.82	0.52	1.02	3.35	0.13
MV	45.19	22.58	6.93	7.19	2.56	1.74	0.36	0.78	1.77	0.67
ΗV	35.31	16.32	8.14	10.92	3.70	1.37	2.29	0.99	2.65	1.05

LV3 and HV contain the highest proportion of sulphur and this is also reflected in the mineral quantification where the 815°C ash is much higher in anhydrite than the other coals. LV1 contains a high proportion of aluminium, potassium and phosphorus. Potassium and phosphorus are both undesirable elements in the blast furnace, therefore, the loading limit for potassium is 1-1.5 kg/tHM and for phosphorus there is a limit of 0.06-0.13% in the hot metal produced. Phosphorus that enters into the blast furnace leaves via the hot metal (Geerdes, et al., 2009, p. 59), so it is imperative that blast furnace operators identify this mineral before it is injected into the blast furnace to ensure that loading limits are not exceeded.

Acid to Base Ratio Correlations

In this section, a number of different acid to base ratios are assessed as a means of categorising coal mineral matter. The objective was to determine whether any of the metrics from the literature were able to provide a convenient metric for the blast furnace operator to be able to estimate the fusion temperature of a particular coal based upon its ash elemental analysis.

Table 16 displays several different elemental ratios as informed by the literature review in Section 2.2.7. The elemental analysis given in Table 15 was used to calculate these ratios. The columns are defined as follows:

- 1. In the column entitled 'Acid to Base', $(SiO_2 + Al_2O_3 + TiO_2)$ is divided by $(Fe_2O_3 + CaO + MgO + K_2O + Na_2O + SO_3)$. This is representative of all the typical coal mineral elements.
- 2. The detrital to authigenic index relates to the manner in which the mineral matter was formed, as discussed in Section 2.2.1, and is represented by $(SiO_2 + Al_2O_3 + K_2O + Na_2O + TiO_2) / (Fe_2O_3 + MgO + CaO + SO_3)$ (Vassileva & Vassilev, 2002). It can be seen that the detrital to authigenic index differs from the acid to base index in that two alkali bases are included in the

detrital matter. This is because detrital materials include clays that are rich in potassium and sodium.

- 3. The next column calculates $(SiO_2 + Al_2O_3 + TiO_2) / (Fe_2O_3 + CaO + SO_3)$. These elements were selected in accordance with the literature review on account of them having the most pronounced effect on ash fusion behavior.
- SiO₂/Al₂O₃ (S/A) ratio has been discussed by Yan et al. (2017). However, it relates better with the viscosity of the liquid phase where a higher S/A ratio gives higher viscosity.
- Vincent's formula (Gray, 1987) was used to calculate a predicted ash fusion temperature. It is described in the literature in Section 2.2.7 and uses all of the element oxides in Table 15.

	Measured AFT of HTA (°C)	1. Acid to Base	2. Detrital to Authigenic	3. (SiO ₂ + Al ₂ O ₃ + TiO ₂) / (Fe ₂ O ₃ + CaO + SO ₃)	4. (S/A)	5. Vincent's Formula AFT Prediction (°C)
LV1	1300	3.57	4.48	4.57	1.36	1812
LV2	1526	5.62	7.37	7.88	1.74	1811
LV3	1316	1.91	2.16	2.21	1.68	1690
MV	1298	3.34	3.83	4.31	2.00	1768
ΗV	1194	1.81	2.21	2.42	2.16	1679

Table 16: Correlating the AFT of HTA with Acid to Base ratios from the literature.

In Table 16, it can be seen that the indices 1, 2, and 3 correlate with the AFT. This could be used as an indicator of fusion temperature in industry. LV2 and HV which possess the highest and lowest fusion temperature respectively, also possess the highest and lowest respective acid to base ratios. For LV1 and MV, which have an average AFT around 1300°C, the elemental ratio lies somewhere between that of LV2 and HV. However, LV3, in spite of having a melting temperature of 1316°C, exhibited an index value similar to that of HV. Thus, it was not possible to correlate LV3 with an element oxide ratio, and it appears that it cannot be categorised with this technique.

The S/A ratio does not show any correlation with fusion temperature. Given that SiO_2 and Al_2O_3 are both acidic oxides which contribute to high melting temperature ashes, it is unsurprising that dividing them between each other did not yield a noteworthy outcome. In terms of the literature, the ratio of acids to bases, (ratio

number 1) needs to be constant in order for the (S/A) ratio to subsequently show an effect on FT (Shi, et al., 2018).

Vincent's formula was not accurate for the ashes investigated in this thesis. The predicted fusion temperatures correlate poorly compared to the simple element ratio in the preceding columns. In the case of the HTA in this thesis, Vincent's formula overestimates by around 20% and notwithstanding, they are still inaccurate even if a factor of 20% is taken account of.

Thermochemical software such as FactSage can be used to calculate fusion temperatures of ash mixtures. FactSage is a software that calculates kinetic changes in substances. It contains an extensive database of information about solid, liquid and gaseous substances. The FACT database contains critically evaluated thermodynamic data for numerous metal oxides and several non-metal oxides. Phase diagrams can be created for substances using this software (Bale, et al., 2016). The focus of this PhD was experimental, so although the use of a thermochemical software would be useful in being able to calculate fusion temperatures, it was not undertaken in this thesis.

Ashing Conditions vs Acid to Base Ratio

Li et al (2017) determined that there was a higher proportion of sintering and fluxing minerals in 550°C ash when compared to the 815°C ash, which was accompanied by a lower fusion temperature. However, in this thesis, a lower melting temperature was not observed in the MTA, and neither was there a higher proportion of fluxing materials in MTA. Table 17 shows a comparison of the AFTs between HTA and MTA, and it appears that ashing temperature does not affect fusion temperature. The acid to base ratios for the HTA and MTA were calculated using the ICP elemental data. There is not a trend towards higher basicity for MTA. In the case of LV1 and HV, the ratios for MTA and HTA are almost identical, and for the other three ashes LV2, LV3 and MV, there is an increase in acidity of MTA which is linked to more refractory behaviour.

	AFT of MTA (°C)	AFT of UTA (°C)	Acid to Base	Acid to Base Ratio for HTA	
	AFT OF WITA (C)	AFI OI HIA (C)	Ratio for MTA		
LV1	-	1300	3.58	3.57	
LV2	1510	1526	6.44	5.62	
LV3	1318	1316	2.02	1.91	
MV	-	1298	3.46	3.34	
HV	-	1194	1.80	1.81	

Table 17: AFT of HTA and MTA with the Acid to Base ratio of the respective ashes

4.4 The Effect of DTF Conditions on Ash Fusion Temperature

An investigation into the effect of DTF temperature, residence time and gas environment on the ash fusion temperature of LV1 was performed. LV1 was chosen for testing as it exhibited a pronounced change in fusion temperature with residence time as was determined in Table 14, and contained a high proportion of kaolinite, which is known to change into mullite under high temperature, and is thought to be responsible for increasing fusion temperature owing to its high melting point (Vassilev, et al., 1995). Thus, it was expected that observable increases in mullite formation would be detected with change in DTF environment.

Coal was run through the DTF to create char. The char was ashed under HTA conditions and analysed. In this section, ash fusion tests are performed, mineral matter is analysed using XRD, and elemental analysis is performed using XRF in order to provide elemental information for calculation of the acid to base ratios.

The DTF conditions are described as follows:

- Temperature of 1100°C and 1300°C to replicate regions of the tuyere and raceway.
- 2. Residence times of 100 ms and 350 ms, to mimic the effect of a char residence time in the raceway.
- 3. Gas environment of:
 - a. Air to produce a combustion environment where particle temperatures are high
 - b. Nitrogen to investigate the effect of heating in an inert atmosphere with no combustion effect.
 - c. Carbon dioxide to compare the results with nitrogen and determine whether this gas has an effect on mineralogy under DTF conditions.

It is important to provide some blast furnace background in justification of the above parameters, and to highlight limitations. The particulars of blast furnace raceway conditions are detailed in Section 1.4.3. Firstly, the temperature in the tuyere region is around 1100°C to 1300°C, due to the hot blast, but this quickly increases as the particles enter the raceway, thus the DTF is particularly effective for characterising coal behaviour the early stages of devolatilisation and combustion. Secondly, residence time in the raceway is typically lower than that used in the DTF, however changing the residence times between 100 ms and 350

ms gives a useful indication of how the ash might change as it travels through the raceway. Thirdly, the gas conditions are highly dynamic starting with an abundance of oxygen at the point of coal injection, followed by rapid devolatilisation and combustion in the raceway and moving to a reducing environment as particles leave the raceway.

Thus it cannot be expected to fully replicate real-world conditions with the laboratory conditions used in this thesis, nonetheless, the techniques can be expected to make well-founded and justifiable findings. However, in the following work, it was noticed that increasing the residence time had a similar effect to increasing the temperature, with respect to fusion temperature, mullite formation and clay decomposition. This finding is particularly useful for blast furnace operators who are interested in replicating the raceway conditions as closely as possible. It means that increases in residence time in the DTF may allow researchers to extrapolate effects that occur at much higher temperatures, but much lower residence times, in the raceway. Thus, in a regard, increased residence time can be used as a proxy for the higher temperatures experienced in the raceway.

4.4.1 Ash Melting Behaviour

Ash fusion temperatures are plotted in Figure 30 for all the samples. With the exception of 1100°C 100 ms air, an increase in residence time leads to an increase in the melting temperature. The melting temperature is significantly higher in air than in the non-oxidising gases. An increase in temperature corresponds with a slight increase in fusion temperature in all cases. It appears that a limit to the fusion temperature is reached by 1300°C 350 ms in air, where further increases in temperature and residence time would yield little to no further increase in AFT.



Figure 30: The Effect of DTF Gas Environment, Temperature and Residence Time on Ash fusion temperature for LV1. Four of the samples have error bars which show the deviation from the mean for two runs.

This is promising in terms of using the DTF to characterise the raceway because even though there are lower temperatures in the DTF compared to the raceway, it implies that the limits of some of the mineral transformations may be reached at these lower temperatures. For example, mullite formation begins to occur at more than 1000°C, but mullite is a stable mineral with a high melting temperature of >1800°C. It is expected that further increases in temperature will increase the rate of mullite formation, but once the full extent of mineral transformation from metakaolinite to mullite has occurred, then the mullite will remain in the same form with further increases in temperature. In addition, decomposition products of clays leads to amorphous aluminosilicates, after which they form a melt. Increase in temperature is expected to increase the amorphous component of the ashes (Gupta, et al., 2008) and this can also be observed in Figure 33, Section 4.4.4.

Carbon dioxide was chosen as well as nitrogen to be an inert gas. It was also chosen due to the possibility of the reverse Boudouard reaction at high temperature, where carbon reacts with carbon dioxide thus producing carbon monoxide in an endothermic reaction (Steer, et al., 2018). The existence of an endothermic reaction would reduce particle temperatures, which would affect the results of this study, namely, the resultant char ashes should possess a lower fusion temperature, and a lower proportion of mullite, when compared to nitrogen, which behaves solely as an inert gas in this testing. No observable difference in fusion temperature and mullite formation was observed between nitrogen and carbon dioxide, however, this is unsurprising given that the reverse Boudouard reaction occurs over a long residence time of several hundred minutes in the TGA (Steer, et al., 2018) and long residence time is not a feature of the drop-tube furnace. In addition, Liu (2009) observed in TGA combustion testing, that there was little difference in using CO_2 or N_2 as a non-reactive gas mixed with varying percentages of oxygen at varying heating rates.

Four of the samples, namely nitrogen 1300°C 100 ms; nitrogen 1300°C 350 ms; carbon dioxide 1100°C 100 ms; and carbon dioxide 1300°C 100 ms; were performed in duplicate, and the absolute deviation from the mean is depicted by the error bars. It can be seen that the deviation extends beyond the difference in melting temperature for 100 ms and 350 ms samples, although the difference between the reactive and non-oxidising gases was much higher than the deviation, which means that these differences are statistically significant. Performing a number of repeats for each sample would improve the accuracy of the results and reduce the standard deviation, however, each fusion test takes several hours for the heat up and cool down times and the equipment used was not located at Cardiff University, so there was limited time available on the instrument. Nonetheless the findings from this study of LV1 are consistent with the previous results in this thesis looking at the effect of DTF residence time on AFT.

Given that the high temperature environment in the DTF leads to ash with a high fusion temperature, this indicates that the muffle furnace ashing performed in Table 13 may not be a sufficient indicator of the behaviour that might occur in the blast furnace. The high heating rate of the drop tube furnace aims to simulate that of the raceway, and the increase in ash fusion temperature observed may affect how the ashes behave in the deadman, with regards to the ash interaction with coke that was discussed earlier.

4.4.2 XRD Analysis

Table 18 shows the semi-quantitative results for the minerals present in LV1 char ash for all of the reaction conditions. All samples, except for 1300°C carbon dioxide, were repeated on the DTF, and mineral quantification was performed for these repeats. In the case of the repeated samples, the absolute deviation from the mean of the two runs is shown in italics to the right of the mineral value.

Table 18: XRD Mineral Semi-Quantification of LV1 Char Ashes under various DTF conditions. Where duplicates were performed, absolute deviation from the mean is shown in brackets to the right of the data point.

Temperature (°C)	Residence Time (ms)	Gas		% Quartz (SiO ₂)		% Hematite (Fe ₂ O₃)	% Fluorapatite	% Fluorapatite [Cas(PO4)3F]		[K1.5Al4(Si6.5Al1.5)O20 (OH)4]	% Anhydrite (CaSO₄)		% Mullite (3Al ₅ O3.	2SiO ₂)
1100	100	Air	37.5	(±4.0)	13.5	(±0.3)	14.4	(±0.3)	21.6	(±1.7)	10.1	(±3.7)	2.8	(±2.1)
1100	350	Air	34.1	(±4.4)	23.0	(±2.0)	8.0	(±0.2)	5.2	(±3.2)	2.2	(±0.1)	27.5	(±0.7)
1300	100	Air	33.7	(±0.8)	25.4	(±1.2)	7.6	(±0.8)	3.1	(±0.5)	5.4	(±0.8)	24.9	(±1.6)
1300	350	Air	26.6	(±1.6)	31.5	(±1.4)	6.5	(±0.4)	1.4	(±1.4)	5.1	(±3.2)	28.9	(±4.3)
1100	100	N ₂	39.1	(±2.0)	12.2	(±5.2)	12.0	(±0.6)	33.0	(±3.4)	3.8	(±0.4)	0.0	
1100	350	N ₂	37.7	(±5.9)	10.9	(±0.0)	14.9	(±1.3)	31.1	(±1.6)	5.5	(±3.0)	0.0	
1300	100	N ₂	39.5	(±7.4)	11.4	(±0.6)	13.4	(±0.9)	25.5	(±0.6)	10.2	(±5.3)	0.0	
1300	350	N ₂	37.9	(±2.7)	21.5	(±1.6)	20.9	(±1.8)	4.7	(±1.4)	5.1	(±0.9)	9.8	(±5.2)
1100	100	CO2	37.0	(±2.5)	10.0	(±1.6)	13.6	(±0.1)	33.4	(±1.5)	6.0	(±2.4)	0.0	
1100	350	CO2	36.7	(±1.1)	10.5	(±1.5)	15.1	(±0.5)	32.8	(±2.7)	4.9	(±0.6)	0.0	
1300	100	CO2	39.6		14.3		16.7		23.9		5.5		0.0	
1300	350	CO2	27.4		18.3		18.4		10.7		13.9		11.3	

Quartz, haematite, fluorapatite, illite, anhydrite and mullite are detected in the DTF char ash samples. The quartz content remains broadly similar under all reaction conditions, which is as expected given that quartz is largely unaffected by temperature, as discussed in the literature. Given that quartz is a hard mineral, this implies that there remains the possible of erosive wear in the tuyeres, even at high temperature. It can be seen that the illite content decreases as the temperature and residence time in the DTF increases, nonetheless, illite is still present in the 1300°C 350 ms air test. Tian et al. (2016) observes that clay mineral dehydroxylation is not complete at a DTF temperature of 1050°C moreover, included clay minerals may be protected from full decomposition, especially in less reactive low volatile coals, as they may be shielded within unburned carbon (Tian, et al., 2016). This point is illustrated in Figure 31. It can be seen that the raw coal at the top contains flecks of mineral matter within the coal matrix; these are predominantly clay minerals. The image on the bottom left is of a 1300°C, 100 ms char reacted in air and the bottom right is at 700 ms. At 100 ms, the mineral matter is oozing out of the char in small globules, however the bulk of the char is not fully combusted, therefore it is likely that there are sheltered clay minerals within the char matrix thus giving rise to the detection of illite, even at high temperatures. The image at 700 ms shows much more advanced combustion of the char with the coalescence

of ash occurring and formation of potassium iron aluminosilicates. In this case, the illite has converted to potassium aluminosilicates at high temperature. Illite is a source of potassium to the blast furnace. If the clay particles remain sheltered within unreacted char matrices, this may mean that they are released as finer particles into the blast furnace, as char consumption occurs outside of the raceway, which could possibly increase the potential for catalytic potassium to make contact with the burden further up the furnace. Although Figure 31 shows significant coalescence of ash at high residence time, it is likely that the nature of the mineral matter released from the coal is dependent on the residence time in the blast furnace because the mineral matter still exists as very small particles in the 100 ms char.





Figure 31: SEM Images for LV1. Top: Raw Coal; Bottom Left: Air 1300°C 100 ms Char; Bottom Right: Air 1300°C 700 ms Char.

The last column of Table 18 shows that the formation of mullite increases at higher temperatures in the DTF. This is in agreement with Tian et al. (2011) and Tian et al. (2016) who observed a stronger mullite peak at 1250°C compared to 1050°C under DTF conditions. Mullite is only present in nitrogen and carbon dioxide at the highest temperature and longest residence time. Therefore the formation of mullite is temperature dependent, and in the non-oxidising gases, it requires the most intense environment for it to form. An important factor to consider is that the particle temperature may exceed the reacting gas temperature by several hundred

degrees due to the exothermic nature of combustion (Senior & Flagan, 1982) which promotes the formation of mullite, hence the samples in air contain a higher proportion than the other gas environments. LV1 contains kaolinite and illite clay minerals in the MTA as detailed in the semi-quantification of Table 10, and it was described in the literature review in Section 2.2.3 that such clays are the precursors of the mineral mullite, which is formed at high temperature. Thus, the high proportion of mullite occurring in LV1 DTF char ash is likely related to the amount of kaolinite and illite clay determined in the MTA. The formation of mullite could pose a wear issue in the blast furnace tuyere, but only if the mineral can form in the short time that is available for a mineral transformation to take place.

In a similar trend to mullite, haematite increases with temperature and residence time in most cases, which indicates that amorphous iron enters a crystalline phase. Vassileva and Vassilev (2005) described that haematite increases with temperature up to 1100°C to 1200°C. This change in form of iron in the ash is interesting. Iron is a known catalyst for gasification (Gupta, et al., 2008) and the change in phase may affect its catalytic activity. Also, the ability for iron from the ash to be reduced into iron may be improved if it is in the form of haematite, which would present benefits in terms of keeping iron in the slag low, but to investigate this hypothesis would require thermodynamic modelling of ash which was beyond the scope of this thesis.

The amount of fluorapatite is relatively stable in the cooler inert conditions but there is a decrease at higher residence time and higher temperature environments in air. Anhydrite is also affected by the temperature in the DTF, and although the results in Table 18 are inconclusive, it is expected that anhydrite should start to decompose at temperatures exceeding 1200°C (Filippidis, et al., 1996). Fluorapatite is a phosphate mineral that is an undesirable source of phosphorus to the blast furnace.

In terms of relating the mineralogy to the fusion temperature, it can be seen that there is a link between mullite formation and higher fusion temperatures. Mullite possesses a melting temperature of 1810°C, and its occurrence in ash (Li, et al., 2016), along with other high melting temperature materials such as quartz, titanium oxides and aluminium oxides (Vassilev, et al., 1995), increases the fusion temperature. An increase in kaolin clay increases fusion temperatures (Li, et al., 2016; Li, et al., 2017) Thus, it is possible to link the MTA kaolinite content, the DTF char ash mullite content, and the ash fusion temperature.

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4.4.3 Elemental Ratios

In Figure 32, the ratio of acidic to basic components is plotted for each of the DTF reaction conditions. XRF elemental analysis data was used as this provided a means of quick and convenient elemental analysis for the twelve DTF reaction conditions investigated. The XRF data was repeated at least twice for each ash sample, and the deviation from the mean is indicated by the error bars. All of the error bars are central to the mean value, however, some of the small error bars appear to not be central to the mean and this is due to graphics and printing. The ratio of $(SiO_2 + AI_2O_3 + TiO_2)$ to $(Fe_2O_3 + CaO + SO_3 + K_2O)$ was chosen due to the results of the previous work on elemental ratios and due to the literature review detailing how these elements have a strong effect on fusion temperature. Potassium, sodium and magnesium have more of a marginal effect on AFT, but potassium was chosen as part of this ratio because it is known to devolatilize under high temperatures, and it was measurable by XRF. Sodium and magnesium were not detectable by the XRF analyser that was used in this thesis.



Figure 32: Acid to Base Ratio. $(SiO_2 + Al_2O_3 + TiO_2) / (Fe_2O_3 + CaO + SO_3 + K_2O)$. Deviation from the mean for duplicate tests is shown by the error bars.

It can be seen that there is some correlation between the ratio of the acids to bases and the ash fusion data in Figure 30. This indicates that the conditions within the DTF are affecting the chemistry of the ash. The DTF is a high temperature environment, and the heating rate is high, therefore fluxing elements such as potassium and sulphur are volatilised easily. In comparison, a low heating rate, high residence time environment would either allow these elements to remain in the solid phase, or it would allow more time for such elements to recombine with aluminosilicates. In both situations, they would be less likely to be lost from the ash as a gas. Thus as the chemistry of the ash changes, it is likely that this is one of the factors driving a change in melting temperature.

4.4.4 Amorphous Material

Amorphous material represented by a broad pattern or "hump" in an XRD diffractogram is caused by non-crystalline glass (Ward & French, 2006) and is typically centered around 26° to 27° for Co-K α radiation. Although not quantified in this thesis, the hump gives an indication of the amount of aluminosilicate glass that is present in an ash sample (Ward & French, 2006). Aluminosilicate glass material forms from the decomposition of clays (Matjie, et al., 2012; Creelman, et al., 2013).

The blue circled region in Figure 33 demonstrates an increase in the size of the amorphous hump as the temperature and residence time in the DTF increases. The equivalent diffractograms are shown in Figure 34, except that these have been reacted in nitrogen. The occurrence of amorphous material is much lower, to the extent that there is only a particularly noticeable amorphous hump in the 1300°C 350ms nitrogen char ash. Thus it can be deduced that the increased temperature arising from combustion in the air environment has promoted the formation of amorphous material, when compared to the nitrogen environment. The importance of the amorphous material in a blast furnace context is that although the chemistry of an ash may be known, and an estimation of fusion temperature may be made, this could be inaccurate if amorphous material has not been accounted for, because it has been observed in the DTF which has a high heating rate environment similar to the raceway that the fusion temperature of the ash has increased.



Figure 33: XRD diffractograms showing the increasing size of the amorphous hump with DTF residence time and temperature for LV1 reacted in air.



Figure 34: XRD diffractograms showing the increasing size of the amorphous hump with DTF residence time and temperature for LV1 reacted in nitrogen.

Similar features have been detected in the diffractograms of other authors. Tian et al. (2011) detected significant amorphous humps centred around 23° for DTF char ash. Tian et al. (2016) also observed that in 1250°C DTF ash, the diffractogram shows a broad, symmetrical hump centered around 25° (Cu-K α) that is caused by amorphous material, whereas with muffle furnace ash, the amorphous feature on the diffractogram was minimal.

Qiu et al. (1999) observed that the XRD pattern of an ash sample with the highest melting temperature in excess of 1500°C possessed a broad, gentle hump at around 25°, near the quartz principle peak. Meanwhile, two other samples with AFTs of

around 1400°C did not have this feature in the XRD patterns. Thus there is evidence from other authors that the presence of amorphous material is a common occurrence, especially in the DTF, that it is likely linked with high fusion temperature.

Another factor to take into account when relating fusion behavior to amorphous material is (NBO/T): the ratio of non-bridging oxygen atoms to tetrahedrally coordinated cations 'T' (Tian, et al., 2016) where T = Si, Al, and Ti. NBO is an oxygen bonded to only one T atom. In a fully polymerised melt, all of the oxygen atoms in a TO₄ tetrahedron are linked to other tetrahedra, thus NBO tends to zero. As the NBO/T ratio increases, the degree of polymerisation reduces which results in lower melting temperature (Wang, et al., 2014). Thus a glass can vary in this ratio, but this cannot be detected from a chemical analysis, and the amorphous hump does not contain this information, making it challenging to determine the melting temperature by looking at this information alone.

4.5 Relating Ash Mineralogy to Blast Furnace Output Materials

4.5.1 Blast Furnace Slag

In order to draw a relationship between the input and output materials of the blast furnace, a slag sample and a wet off gas cleaning residue were analysed and compared to the mineralogy and elemental analysis of the coal mineral matter investigated in this chapter.

Figure 35 shows a diffractogram of a slag sample with a large amorphous hump centred around 30°. Note that the hump occurring at less than 14° is due to the plastic sample holder, and not the slag material. The hump of amorphous material in the slag is much greater than in the high residence time, high temperature DTF char ash in Figure 33, which shows the change of crystalline material to amorphous material as minerals progress through the blast furnace. Thus this relate the changes that occur in the drop-tube furnace char ashes to the slag output of the blast furnace,



Figure 35: XRD of Port Talbot Slag Sample

The chemistry of this slag is given via an ICP analysis as shown in Table 19. The four main elements present in the slag are silicon, aluminium, calcium and magnesium (Tänzer, et al., 2015). There are minor concentrations of iron, potassium, sodium, titanium and sulphur.

	SiO2	Al ₂ 0₃	Fe ₂ 0 ₃	Ca O	MgO	K₂O	Na₂O	TiO ₂	SO3	P ₂ O5
Ground										
Granulated										
Blast	32.35	11.42	0.55	34.42	6.09	0.64	0.37	0.55	1.01	0.01
Furnace										
Slag										

Table 19: ICP element oxide (%) for slag sample.

When comparing the slag to the elemental analysis of HTA from coal in Table 15, the coal ash contains much higher iron, potassium, sodium and sulphur than the slag. The objective of a blast furnace is to produce hot metal, so achieving low iron in the slag is preferable. Potassium is an undesirable element in the blast furnace, that has been discussed in the literature, and identified in LV1. Potassium that does not enter the gas phase is preferable, as this prevents it from cycling within the blast furnace. From the slag data, it is evident that some of the potassium reports to the slag, and the same is true of sodium. Sulphur is another element that is volatilised in the raceway, however, it can be seen from the slag analysis that some sulphur is found in the slag. This is promising because sulphur in the gas phase is responsible for iron ore degradation, and hot metal quality is affected by too much sulphur. There is almost no phosphorus in the slag which supports all accounts that

phosphorus makes its way into the hot metal. This information highlights the importance of performing an elemental analysis of the feed materials to identify undesirable elements. Analysis of this slag sample enables us to understand what happens to materials that enter the blast furnace.

4.5.2 Blast Furnace Floating Clarifier Sludge Analysis

A floating clarifier scum product of the off gas wet cleaning process was analysed in this section to identify the types of material that travel into the flue gas, in order to determine whether some of these materials have origins from the coal injection.

Blast furnace sludge originates from the off gas of the blast furnace. The off gas undergoes a dry cleaning stage with a gravity dust catcher or more recently a cyclone, and then moves onto a wet gas cleaning stage (Lajtonyi, 2011). The dry material is known as flue dust and the wet material is known as sludge. The outflow of the wet cleaning stage enters a clarifier pond where it settles to form sludge that sinks to the bottom. However, in the case of this thesis, the material that was collected was floating on the surface of the pond and becoming trapped in metalwork near the surface of the clarifier pond, hence it was floating scum. The proximate analysis reiterated in Table 20 shows the clarifier floats to contain 27.4% ash and 14.6% volatile matter yield with a high proportion of carbon. The volatile matter yield was high, especially in proportion to the total amount of carbonaceous material. According to Leimalm et al. (2010) the off gas flue dust consists of Fe₂O₃ particles arising from the burden at the top of the stack, and coke dust particles from within the stack. Meanwhile, the sludge is composed of haematite, magnetite, chemically formed particles of SiO₂ and MgO, alkalis, soot and partially burned char. The amount of carbon in sludge increases with pulverised coal rate, thus is originated from the high temperature region around the raceway (Leimalm, et al., 2010). Therefore it is possible that the high volatile content observed in Port Talbot sludge is derived from partially burned chars. In order to successfully utilise coal injection and maximise injection rates, to gain the benefits described in the literature, reducing partially burned char is of paramount importance. The effect of ash on char combustion is explored in Chapter 7.

Table 20: Proximate Analysis (%) of Floating Blast Furnace Clarifier Sludge. Standard deviation is given for 2 duplicates for volatile testing and 4 duplicates for ash testing.

Volatil	e Matter	Ash	Fixed carbon		
14.6	(±0.14)	27.4 (±0.20)	58		
The carbonaceous material was amorphous and gave unclear mineral results under XRD, therefore the sludge was ashed at 815°C and analysed using XRD. The majority of the ash was composed of iron oxide as shown in Table 21.

	SiO ₂	۶0²Al	Fe ₂ O ₃	CaO	MgO	K₂O	Na₂O	TiO2	۶O3	P ₂ O5	Ouz
Blast Furnace Sludge	5.62	2.99	60.78	2.66	0.94	2.83	0.44	0.20	3.13	0.06	4.57

Table 21: ICP element oxide (%) for blast furnace floating clarifier sludge ash.

This is corroborated by Figure 36 which shows the minerals present to be haematite, magnetite and a minor concentration of quartz. An additional observation relates to the background of the diffractogram. There is no amorphous hump observed which indicates that amorphous material from the mineral matter is not present in significant quantity in the sludge, and instead enters the slag.



Figure 36: XRD mineral analysis of blast furnace floating clarifier sludge ash.

Regarding other elements, the sludge ICP results in Table 21 show high potassium and sulphur. This is particularly interesting because it gives evidence for the occurrence of alkali volatilisation and the presence of sulphur in the off gas which is investigated in the following chapter. The absence of an amorphous hump in Figure 36 indicates that the potassium and sulphur present in the slag are more likely to be volatilised species rather than integrated into amorphous aluminosilicates. The concentrations of potassium and sulphur in the sludge ash are treble that of the slag, and around double that of the injection coal ash, which does support the finding that sludge is made of chemically formed products (Leimalm, et al., 2010). Nonetheless, there is insufficient evidence to conclude that the majority of the alkalis and potassium are vaporised, since blast furnace sludge makes up a small proportion of the furnace output. However, knowing the rate of coal injection, and all other inputs, along with the rate of all outputs, one would be able to make an informed estimate of the rate of alkali volatilisation providing that accurate chemical data for all the inputs and outputs were available.

4.5.3 Blended Coal Mineral Matter

All of the information thus far has been about the effect of individual coals, however, in the blast furnace a blend of different coals is used to try and lessen the undesirable effects of each particular coal. Table 22 represents the ash chemistry of typical blends for a blast furnace coal. When comparing this information with the elemental compositions of individual coals, as shown in Table 15, it can be seen that the blended coal represents an average of the extremes found in the individual coals. Aluminium is higher, but silicon and the other elements represent an average of coals tested thesis. The blended coal ash also possesses low potassium, sulphur and phosphorus, which is essential for successful blast furnace operation.

	SiO2	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K₂O	Na₂O	TiO ₂	SO₃	P2O5	ZnO
5 th December 2017	37.44	26.39	6.42	5.22	1.42	1.15	0.88	1.10	1.12	0.99	0.03
6 th December 2017	38.11	26.62	7.20	4.99	1.40	1.12	1.07	1.13	1.21	1.13	0.03
March 2018 Full Hour	40.48	26.39	6.98	3.28	1.12	1.09	0.76	1.27	1.01	1.19	0.04

Table 22: ICP element oxide (%) for HTA of Tata Steel Port Talbot coal blends.

Given the elemental information of the blended coals in Table 22, it was decided to calculate the acid to base ratios using $(SiO_2 + Al_2O_3 + TiO_2) / (Fe_2O_3 + CaO + MgO + K_2O + Na_2O + SO_3)$. Table 23 compares the five coals used in the thesis, with the blended coals that are highlighted. The acid to base ratio for the blends is 4.01, 3.88, and 4.78 respectively. When comparing these ratios with the five thesis coals and their fusion temperatures, it may be inferred that the melting temperature of the blended coal may be around 1350°C to 1400°C.

	Measured AFT of HTA (°C)	1. Acid to Base Ratio
LV1	1300	3.57
LV2	1526	5.62
LV3	1316	1.91
MV	1298	3.34
HV	1194	1.81
5 th December 2017		4.01
6 th December 2017		3.88
March 2018 Full Hour		4.78

However, a major limitation to this prediction is that the fusion temperature of blended coals is not additive (Qiu, et al., 1999; Li, et al., 2017). This is illustrated in Table 24 where HTA was blended 50:50 for some of the thesis coals. The melting temperature of the blend of LV2 and LV3 is 1330°C which is very close to LV3 and not halfway between the two individual coals. Likewise, the blend of MV and HV is disproportionately close to the higher AFT MV ash. The reason for this is due to the formation of eutectics with variable melting points (Qiu, et al., 1999). This was a useful exercise from a blast furnace operator's point of view because it highlights the complexity of the system, even when elemental information is known. It also indicates that the fusion temperature of individual coals may be more predictable than blends.

Table 24: AFT of Blended Coals

Sample	AFT (°C)
LV2:LV3 50:50 HTA Blend	1330
MV:HV 50:50 HTA Blend	1278

Finally, in terms of mineralogy of a blended coal, a mineral analysis for HTA is given in Table 25. In comparison to the mineral analysis of individual coals in Table 10, it can be seen that this blend contains less quartz, more illite and similar proportions of anhydrite and haematite. This high proportion of illite does support the elemental ratio in terms of this blend having a medium high fusion temperature.

Table 25: Mineral Ana	lysis of Coal Ash Blend
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Mineral	Quartz	Illite	Anhydrite	Hematite
Percentage	28.8	51.0	12.0	8.2

4.6 Chapter Summary

Typical minerals observed in coal ash created at 400°C included quartz, kaolinite, illite, calcite, dolomite and gypsum. Fluorapatite was also observed in one of the injection coals and this is a source of phosphorus to the blast furnace, for which there is stringent regulation. In spite of the limited sample set, there was a correlation between the volatility of the coal and the type of mineral matter, which can also be found in the literature. The low volatile coals contained higher concentrations of quartz and clay, which contains silicon and aluminium, and can be correlated with high fusion temperature. Conversely, the high volatile coals contained more carbonate minerals, such as calcite and dolomite, which contain calcium, and is linked to lower fusion temperature. Thus, it may be possible to use the regular coal parameter of volatile matter that is favoured by blast furnace operators, to gain an approximation of the mineral matter type.

Ash fusion temperatures ranged from 1194°C to 1504°C for the coal ashes tested. This was related to mineralogy and ash chemistry. Minerals such as kaolinite and illite were found in greater abundance in the higher melting temperature ashes, whilst minerals such as calcite, dolomite and other calcium containing minerals, such as fluorapatite were found in the lower melting temperature ashes. In terms of chemistry, higher concentration of silicon and aluminium are found in ashes with high melting temperature, whereas calcium and iron can be seen at low melting temperature. LV3 showed uncharacteristic behaviour when relating chemistry to melting temperature which became particularly apparent when calculating the acid to base ratios, where it was unable to be correlated.

According to the literature, ash fusion temperature determines how the ash might behave in the blast furnace. High melting temperature ash is more likely to adhere to coke and could act as a binder reducing permeability in the deadman. Low melting temperature ash with a low viscosity is more likely to flow off of the coke and run into the slag (Khairil, et al., 2002).

The findings of the elemental composition in the ash relate to effects on the slag chemistry. Minerals with more silicon and aluminium will lead to a higher acidity slag that is more viscous and have a higher melting point, but be able to absorb alkalis better. Minerals containing higher calcium will help to create a basic slag that is less viscous, less effective at alkali absorption, but better at sulphur absorption (Babich, et al., 2008). Running coal through the DTF provoked some interesting changes in mineralogy. The formation of mullite began to occur in the DTF at 1100°C 100 ms and became prominent by 1100°C 350 ms. A small amount of mullite, 3%, was observed when coal was reacted in air at 1100°C, 100 ms and this increased to around 30% at 1300°C, 350 ms. In the unreactive gases of nitrogen and carbon dioxide, mullite was not formed until 1300°C, 350 ms at which point there was around 10%. Thus the formation of mullite was temperature dependent. According to this investigation, the limit of mullite formation from ash was likely reached in the drop-tube furnace, therefore, this makes the drop-tube furnace a useful technique for simulating the raceway, without having to test at higher temperatures. One of the concerns levelled at the drop-tube furnace is the difference in temperature between it and the raceway. The limit of mullite formation may help to allay some of the concerns.

Mullite has a high melting point of >1800°C and a hardness of 6-7 on the Mohs scale. The formation of mullite in coal ash may be possible for wear in the blast furnace tuyere region, but that would only be the case if mullite is able to form in the high temperature region between the injection lance and the tuyere tip. Quartz was observed to be unaffected by ashing conditions, and also appeared to be unaffected in the DTF. Quartz has similar properties to mullite and likely remains unchanged in the coal from ambient temperature to tuyere temperature, so it is likely that this will cause tuyere wear.

The occurrence of clays such as kaolinite are linked to an increase in the formation of mullite in coal ash which is a factor in increasing the ash fusion temperature. Therefore, if high ash fusion temperature is considered undesirable in the blast furnace, then coals with low clay content should be chosen. A low clay coal will produce a low melting temperature ash which is likely to reduce deposits in the deadman and lead to a low viscosity slag. However, from the results of this chapter, it was observed that such a coal is likely to have a high carbonate content, and therefore contain catalytic calcium which could lead to higher coke degradation, and a low fusion temperature and low viscosity which will enable it to enter the coke pores. Thus the desire for a given positive property must be tempered with the likelihood of a negative property. This will be a recurring theme in this thesis and it will become clear that compromise needs to be met when selecting coals for the blast furnace.

Specific elements have a strong tendency to affect the AFT, but it is not possible to make a sound prediction of AFT based on elemental analysis alone. This has been

discussed in the literature (Vassilev, et al., 1995; Ward, 2016) and it is clear that a combination of sources of mineral information are required to create a more comprehensive understanding. In terms of categorisation for a blast furnace operator, it was not possible to unequivocally link the mineralogy or chemistry to the melting behaviour of a particular ash, as observed when blending ashes, but knowing the element data can give a good indication of behaviour that might occur. Knowledge of the elemental analysis is also useful for identifying undesirable elements such as potassium, sulphur and phosphorus, and it can be used to inform upon how the slag chemistry may be affected by identifying the amounts of silicon, aluminium, calcium and magnesium in an ash sample.

It would be strongly recommended to perform elemental analysis of current and prospective blast furnace coals and to perform a fusion temperature on the ashes, with the aim of relating the fusion temperature to the acid to base ratios. If a database of this information were continually built upon, it would be possible to make a stronger correlation between elemental analysis and ash melting behaviour for typically used blast furnace coals. It would also be valuable to identify coals that do not fit the correlation, such as LV3. For the time being, blast furnace operators will still be able to gain useful information if they use the element data and perform a simple check of acid to base ratio.

Chapter 5: Results of the Ash Volatilisation Study. Alkalis and Sulphur.

This chapter is divided into two parts. The first part investigates alkali volatilisation using the DTF. The second part investigates the release of sulphur from coal mineral matter using the LECO carbon sulphur analyser and the DTF. Alkali and sulphur in the gas phase presents similar negative consequences for the blast furnace. A paradox exists in terms of promoting alkali and sulphur into the slag, which is the desired outcome (Babich, et al., 2008). Alkali fixation requires an acidic slag that is low in basic elements and calcium, whereas sulphur fixation requires a basic slag that is high in calcium and alkali metals. The conditions for removal are discussed in this chapter.

The drop-tube furnace was run at 1100°C and 1300°C and the amount of alkali in the char ash was measured using ICP. The degree of alkali volatilisation was determined from the change in the amount of alkali present in the char ashes from different conditions. The rates of volatilisation in terms of conversion relative to HTA are presented, and suggestions are given to mitigate the effect.

Sulphur release was investigated in the same way as the alkalis. The DTF was used to investigate sulphur release in a high heating rate environment representing that found in the raceway. This allowed a relationship to be made to the potential sulphur behaviour occurring in the blast furnace. In addition, sulphur analysis of ashes was performed using the LECO analyser, and the profiles of sulphur release into the gas phase were analysed. It was found that the rates of sulphur release varied between coals, which indicated that sulphur was present in the ash in different forms. The purpose of analysing the sulphur release profiles generated by the LECO analyser was to determine the fine differences occurring between different ashes as sulphur is released. Measuring the sulphur in a DTF char ash gives a final sulphur output that can be compared to the input coal, but it does not help to explain the process.

Volatilisation of the alkalis potassium and sodium is a significant problem in the blast furnace. Alkalis catalyse the gasification of coke and are also responsible for the swelling of iron ore, pellet and sinter, leading to fines generation. Alkalis also cause erosive damage to the blast furnace refractory lining and scaffold formation on the refractory inside the stack (Slizovskiy & Tangstad, 2010; Dastidar, et al., 2018). Sulphurous gases are responsible for the breakdown of the iron ore burden.

Sulphur reduces the hot metal quality leading to a more brittle product (Rudyuk, et al., 1974). Sulphur exits the furnace as: part of the hot metal; in the gas phase; and in the liquid slag as calcium sulphide (CaS) and iron sulphide (FeS) (Iljana, et al., 2013). The preferred exit for sulphur is via the slag. CaS in the slag is a stable compound (Babich, et al., 2008).

The aim of this chapter was to determine the extent of volatilisation and release of alkalis and sulphur, and then to relate this to the raceway.

5.1 Alkali Volatilisation

5.1.1 DTF Char Ash Study

LV1, LV2, LV3, MV and HV coals were run through drop-tube furnace at 1100°C and 1300°C at residence times of 100 ms, 350 ms and 700 ms and the char produced was ashed at 815°C. The char ashes were analysed on the ICP for the amount of potassium and sodium present. This was converted to oxide form and is presented in Figure 37 for 1100°C and Figure 38 for 1300°C. The results were used to infer the extent to which potassium and sodium volatilises for the different coals. The x-axis allows comparison between the samples and across the drop-tube furnace residence times, however there is no trend occurring from LV1 to HV. Figure 37 shows that most of the char ashes consistently undergo a decrease in the percentage of potassium and sodium which indicates higher rates of volatilisation with increasing residence time. LV3 and HV show a particularly strong trend of devolatilisation with residence time. However, LV1 has the highest potassium content of all the char ashes but this is not accompanied by an increase in volatilisation with residence time. Given that the clay minerals such as illite remain, even at high residence time, within the char matrix of LV1 as shown in Figure 31 in Section 4.4.2, it is likely that volatilisation of potassium was limited by the ability of the clays to leave the char matrix. The content of potassium and sodium appears to be unrelated to the volatile matter yield of the coal, therefore blast furnace operators cannot use volatile matter content as a predictor of alkali content. Potassium and sodium are present in the coal mineral matter in the clays. Illite contains high potassium, and montmorillonite contains high sodium and this can be observed from the chemical formulas in Table 2 in Section 2.2.1.



Figure 37: ICP Analysis of K_2O / Na_2O (%) in 1100°C DTF Char Ashes at 100 ms, 350 ms and 700 ms

Figure 38 shows the effect of residence time on the char ash potassium and sodium contents at 1300°C in the drop tube furnace. The extent of devolatilisation at 1300°C is greater than at 1100°C, however this difference is better illustrated in Figure 39 which compares the two temperatures in terms of potassium volatilisation relative to HTA. In Figure 38, it is interesting to note that the increase in devolatilisation with residence time occurs less sharply as compared to 1100°C. This implies that the process of alkali volatilisation occurs quickly and reaches a limit more quickly at higher temperature. The effects observed are not isolated to potassium. In spite of variation in the absolute concentrations, Figure 37 and Figure 38 show that the behaviour of sodium volatilisation is broadly similar to the behaviour of potassium, although in terms of the blast furnace the negative effects of sodium are not as significant as those of potassium (Narita , et al., 1981).



Figure 38: ICP Analysis of K₂O / Na₂O (%) in 1300°C DTF Char Ash at 100 ms, 350 ms and 700 ms

Figure 39 shows relative amounts of potassium in DTF char ash with respect to the potassium content of HTA. The scale on the y-axis starts at 0.50 to improve readability of the trends. As was discussed above, the alkali volatilisation increases with DTF temperature. It is proposed that as the ashes approach and exceed fusion temperature, as they would in the DTF at 1300°C, the possibility for potassium and sodium to become reintegrated into the aluminosilicates increases, thus at higher residence times there are no further loss of these elements from the char ash. Evidence of this can be seen in MV and HV where there is a significant difference in potassium content at 700ms when comparing 1300°C with 1100°C. Comparing this to LV2, it can be seen that there is a consistent decrease of potassium in the char ash as the residence time increases in the 1300°C test. LV2 has a very high melting temperature, so it is put forward that this may be limiting the ability of LV2 ash to reabsorb alkalis. This is interesting for the blast furnace operator because it introduces ash fusion behaviour as a variable to consider when investigating the ability of coal ash to release alkali into the gas phase. The potential for low fusion temperature ashes to retain alkalis bears a parallel with the capacity of low viscosity slag to perform the same effect (Yang, et al., 2000).



Figure 39: Loss of K₂O in DTF Char Ash relative to HTA. Testing performed in the DTF for 100 ms, 350 ms and 700 ms at 1100°C and 1300°C.

5.1.2 Alkali Reabsorption

In the blast furnace, a commonly employed method of increasing the uptake of alkalis into the slag is the adjustment of slag chemistry to a less basic state (Babich, et al., 2008; Dastidar, et al., 2018). In relation to ash chemistry, this will mean that ashes of higher fusion temperature are likely to possess the preferred chemistry for removal of alkalis. Addition of kaolin has been employed to reduce the tendency of alkali volatilisation (Ozer, et al., 2017), although this effect diminishes above 1100°C (Li, et al., 2016). It can be seen in Table 26 that LV1 and LV2 HTA possess low basicity which is beneficial for alkali retention, while LV3 and HV HTA possesses high basicity, which is not helpful for alkali retention. Therefore the proposed effect of lower ash fusion temperature leading to decreased alkali volatilisation in the DTF and the preferred chemistry of the ashes to absorb alkalis, are not in agreement, however, an increase in the MgO content of the slag is also a means of retaining alkali in the slag (Yang, et al., 2000; Babich, et al., 2008); this can be achieved by adding dolomite [CaMg(CO₃)] (Yang, et al., 2000). Thus, it can be seen in Table 26, that the MgO content is particularly high for MV and HV, both of which show an effect of reduced alkali volatilisation at 1300°C 700 ms. In addition to the low fusion temperature, the magnesium content may be a contributory factor.

	Slag	MgO
	Basicity	Content
LV1	0.11	1.03
LV2	0.05	1.08
LV3	0.20	1.72
MV	0.14	2.56
HV	0.28	3.70

Table 26: Slag basicity and MgO content of HTA

5.1.3 Effect of Temperature on Coal Burnout

From the information thus far, it can be deduced that a simple method to reduce the effects of alkali volatilisation would be adjust operating parameters in the blast furnace such as lowering the temperature (Yang, et al., 2000), however such a measure would reduce furnace productivity and pulverised coal burnout would suffer. This can be observed in Figure 40 where a comparison of burnout at 1100°C and 1300°C in the DTF is shown for LV1, MV and HV. The burnout increases with temperature and the demonstrated increase in burnout with coal volatility is concordant with the literature (Steer, et al., 2015a; Steer, et al., 2015b), and with the burnout comparison of the five thesis coals presented in Figure 65, Section 7.1.1.



Figure 40: Comparison of the burnout (%) of LV1, MV and HV in the DTF at 1100°C and 1300°C. Note that some of the data points were not investigated and are therefore not plotted.

DTF repeats were performed for 12 data points at several different residence times and temperatures and the average absolute deviation from the mean for burnout was determined to be 1.2 burnout percentage points. The minimum deviation was 0.1% and the maximum was 4.1%. This was considered a good level of deviation which gives confidence in the DTF as a means of coal char preparation. The error bars were not plotted on the burnout charts because it would not have been possible to see them.

Suzuki, et al. (1984) describes incomplete collection of ash during combustion; vaporisation; condensation; and high temperature transformations, as limitations of the ash tracer method. This relates to the burnout shown for LV1 being zero. Hence, this is likely an artefact of the DTF cyclone collection system and is expected to be dependent on the physical relationship between the mineral and the char, for instance the presence of extraneous mineral matter that may escape collection. Based upon this, it is suggested that the effect should be consistent for coal types, as each coal possesses its own properties. Thus the reason for the apparently low burnout at low residence time for LV1 is that potential for error increases due to a combination of low burnout and incomplete collection of ash.

5.2 Sulphur Investigation

Investigation of the behaviour of sulphur was performed by investigating raw coal, MTA, HTA and VHTA on a LECO carbon sulphur analyser, the method as described in Section 3.2.5. In addition, DTF char ashes were analysed. Analysis of the change in sulphur content with DTF residence time and temperature was performed in the same way as the alkali volatilisation work.

5.2.1 LECO Analyser Study

According to Vernon and Jones (1993), during coal combustion, the majority of sulphur is released into the gas phase, predominantly as SO_2 and 1-2% as SO_3 . Around 10% is retained in the ash, although this is dependent on the alkali content of the ash. In this work it will be discovered that although this statement is broadly true, in the coal ashes investigated, there is significant variation in how easily sulphur release occurs, and variation in the amount of alkali retained in the ash, and these factors are determined by the ash chemistry.

Sulphur Analysis of Raw Coal, MTA, HTA and VHTA

Table 27 shows the LECO analysis of sulphur in raw coal, MTA, HTA, and VHTA (1100°C Ash). It can be seen that MTA has a lower proportion of sulphur in the ash than the HTA. In Chapter 4, it was observed that HTA has lower mass than MTA, so it is proposed that sulphur occupies proportionately more of the HTA.

LV1 is an exception to this observation, which shows a reduction in sulphur between MTA and HTA. In coals, sulphur dioxide evolved from the decomposition of pyrite reacts with calcium released from carbonates and calcium released from organic sources to produce anhydrite (Matjie, et al., 2012). However, as seen in Section 4.2, LV1 does not contain carbonates in its mineralogy. In addition, LV1 consistently contains the lowest anhydrite (in HTA and DTF Char Ash) of the 5 coals investigated, as seen in Section 4.2, which demonstrates a lower occurrence of this sulphur compound in the ash compared to the other coals. The combination of this information indicates that the high sulphur intially present in compounds in LV1 coal is gasified at comparitively low temperature to form SO₂, without a source of calcium to absorb it. Since fluorapatite does not decompose until 1100°C 350ms in the DTF, it can be assumed that the calcium from fluorapatite is not liberated to be able to absorb sulphur at the comparitively low temperatures encountered during the MTA and HTA processes. The sharp peak of sulphur removal as shown in Figure 42 corrobarates the comparitive ease with which sulphur is lost from LV1 MTA. In terms of the blast furnace, the sulphur behaviour of LV1 is undesirable since it is readily released into the gas phase.

	LV1	LV2	LV3	MV	HV
Raw Coal	0.98	0.43	0.78	0.25	0.76
MTA 400°C Ash	1.07	0.56	1.41	0.44	1.50
HTA 815°C Ash	0.66	0.68	1.68	1.18	1.69
VHTA 1100°C Ash	0.00	0.00	1.03	0.77	0.99

Table 27: LECO Analysis showing % Sulphur Content of Raw Coal, 400°C, 815°C and 1100°C Ashes.

The sulphur behaviour of MV is particularly interesting. It indicates that concentration of sulphur in the ash occurs under MTA conditions, but becomes particularly pronounced under HTA conditions. It is uncertain to what this effect is owing, as a cursory check of the elemental analysis does not show abnormally high levels of calcium, sodium or magnesium, in comparison to the other coals. Note that calcium, sodium and magnesium possess a strong capacity for fixing sulphur (Babich, et al., 2008, p. 237). It may be that MV contains a high proportion of organic sulphur which is more readily fixed into the ash at higher ashing temperatures.

Comparing the percentage of sulphur in the raw coal to that in the ash gives an indication of whether sulphur is more concentrated in the ash or the coal. Assuming that the sulphur is evenly distributed between the ash and the coal, the percentage of sulphur in the coal and the ash should be equal. However, if either ash or coal shows a higher percentage of sulphur, this indicates sulphur is more concentrated in ash or the organic matter, respectively.

Table 27 shows a tendency for the sulphur to be more concentrated in the ash. It is possible for sulphur from the organic material to become fixed into the inorganic material (ash), largely due the action of calcium-based carbonates. In this work, the effect of sulphur fixation increases with calcium content of the mineral matter (where LV3, MV and HV contain high calcium and high carbonate content as discussed in Section 4.2 and 4.3). The occurrence of anhydrite in HTA, as semi-quantified in Section 4.2.2 correlates well with sulphur content of HTA from the LECO analysis, which gives confidence in the semi-quantitative data. By contrast, LV1 and LV2 which contain little to no carbonate material show only a small increase when comparing the MTA with the raw coal, which provides further confidence in the proposed effect of carbonate material to fix sulphur. In the literature, the addition of dolomite during gasification to coal and other alternative solid fuel blends was a highly effective means of retaining sulphur in the solid phase (Pinto, et al., 2008, p. 1054).

Regarding the VHTA, sulphur is no longer present for LV1 or LV2. It is believed that the low carbonate content of both of these coal ashes is an important factor. By contrast, LV3, MV and HV retain significant amounts of sulphur in the ash. In terms of the blast furnace, this means that low carbonate coals have a tendency to readily release sulphur at lower temperatures which is a negative factor that should be considered by blast furnace operators when selecting coals. By extension, this implies that the volatile matter yield of the coal bears some relation to the sulphur release behaviour, where in Chapter 4, it was proposed that the higher volatile matter coals contain higher amounts of carbonate minerals.

Sulphur Loss Profiles

The following profiles were obtained from the LECO carbon sulphur analyser. The label on the y-axis of each chart is signal in millivolts. In terms of the LECO analyser, the millivolt signal is integrated across the profile to give the area, which is converted into a percentage of sulphur. In terms of this research, the units of the

y-axis was arbitrary, and the focus was on analysing the profiles to determine how sulphur was lost from the samples.

Figure 41 shows the sulphur release profile from MTA when using the LECO analyser. An important observation is the relative readiness with which sulphur is removed from a raw coal when compared to the ashes. Sulphur loss is complete by 80 seconds for all the coals, but takes 240 seconds for the ashes in Figure 42 to Figure 44. The presence of combustible organic material will raise the particle temperatures which will increase the rate of sulphur release.



Figure 41: LECO Analysis Profile of Sulphur Release from Raw Coal

It was stated in the literature by Iljana et al. (2013), that sulphur can also enter the gas phase as CS₂ and COS, as well as SO₂. Thus in the case of the raw coal testing, sulphur is possibly reacting with carbon to form compounds such as COS (carbonyl sulphide) and CS₂ (carbon disulphide) leading to an increase in sulphur release rate when compared to ashes. COS and CS₂ are both flammable compounds (PubChem, 2019a; PubChem, 2019b), so subsequent conversion to SO₂ in the high temperature oxidising environment of the LECO analyser will ensue. In this thesis COS and CS₂ were not measured, so this theory presents an additional potential cause, based upon the literature, of why the sulphur release was faster in the presence of carbonaceous material.

The implication of the increased sulphur release in the presence of carbon is that sulphur contained as part of a char is likely to be more easily lost than sulphur from ash particles. Additionally, it may be possible that ash particles that encounter carbon (such as coke) elsewhere in the blast furnace can potentially release sulphur, which is undesirable in terms of preventing sulphur entering into the gas phase in the blast furnace.

Figure 42 shows the sulphur release profile for MTA. With the exception of LV1, the removal of sulphur from the coals is bimodal with an initial peak at around 5 to 25 seconds and a prolonged phase from roughly 100 to 200 seconds. As was discussed earlier, owing to an absence of calcium carbonate to fix sulphur, sulphur from LV1 is quickly lost in a strong peak at 5 to 25 seconds. LV2 shows similar behaviour, although to a lesser extent than LV1. The prolonged phase of sulphur removal arising after 100 seconds is most possibly due to the decomposition of anhydrite which begins at 1200°C (Filippidis, et al., 1996).



Figure 42: LECO Analysis Profile of Sulphur Release from MTA

In Figure 43 the sulphur release from HTA is presented. It can be seen that the initial peak of sulphur removal at 5 to 25 seconds, observed in Figure 42, is no longer present. It is expected that the presence of readily removable sulphur is no longer a possibility after HTA conditions have taken place because this sulphur has either been released during ashing or converted to a more stable form. Hence the testing takes about 240 seconds. LV1 and LV2 contain the lowest sulphur of all the samples which is probably due to a lack of calcium to fix sulphur into the anhydrite phase.



Figure 43: LECO Analysis Profile of Sulphur Release from HTA

Further identification of minerals is required in order to ascertain why the highest rate of sulphur removal occurs at different points for the different coals. It may be related to chemical form of the sulphur or potential interactions between other minerals within the ash that effect the removal of sulphur, for example catalytic effects. It has been investigated by several authors that additives such as silica, alumina and ferric oxide (in that order) increase the rate at which anhydrite is decomposed (Swift, et al., 1976) although in this thesis no relationship could be observed between the onset of sulphur release and the elemental composition of the HTA. The sulphur removal for HV coal at 150 to 200 seconds is irregular. It is possible that several different chemical reactions may be occurring and that they may be interrelated.

Figure 44 shows that LV1 and LV2 do not contain sulphur in VHTA. The sulphur release profile peaks are much tighter than those of the HTA release in Figure 43 which indicates that the form of sulphur is more uniform. The form of sulphur is evidently more stable than in HTA because the onset of release occurs 80 seconds into the test compared to 40 seconds for HTA. The peak of MV occurs later in VHTA than HTA which indicates that the process of ashing is changing the form of sulphur.



Figure 44: LECO Analysis Profile of Sulphur Release from VHTA

Regarding the blast furnace, the behaviour of LV3, MV and HV is favourable in terms of the ability for the sulphur to remain in the ash because it is less likely to cause sulphurous gas related issues in the blast furnace. Calcium and magnesium are the main desulphurisers in the blast furnace, but sodium also performs the same function. They form sulphides such as CaS, MgS and Na₂S which leave with the slag (Babich, et al., 2008). It can therefore be deduced that regarding ash properties, the amount of calcium, sodium and magnesium in the ash have an effect on the tendency of the sulphur to remain fixed in a solid phase. Further analysis of the ash to identify these sulphide compounds would be a useful study.

Blast Furnace Floating Clarifier Sludge

The mineralogy and chemistry of the floating clarifier sludge was discussed in Section 4.5.2. The carbon and sulphur analysis performed in the LECO furnace for the floating blast furnace clarifier sludge and its ash is given in Table 28. Owing to the relative proportions of carbon and sulphur in the sludge and the sludge ash, it can be deduced that nearly all of the sulphur is found in the sludge following ashing. This could show that either the sulphur is found in the inorganic component of the sludge prior to ashing, or that during ashing sulphur originally present in the organic material reacts with the sludge ash, becoming fixed. In terms of chemistry, the formation of FeS is possible owing to the majority iron content of the sludge ash, as determined in Table 21, Section 4.5.2. Moreover, the sludge ash contains calcium, magnesium and sodium which also has the potential to fix sulphur, however, peaks for anhydrite were not observed in Figure 36, Section 4.5.2. This means that any sulphur fixed into these elements would possibly be in the ash in the form of FeS, CaS, MgS and Na₂S.

	Carbon	Sulphur
Sludge	66.94 (±0.46)	0.49 (±0.03)
Sludge Ash	0.38 (±0.01)	1.53 (±0.00)

Table 28: LECO Carbon Sulphur Analysis of Blast Furnace Floating Sludge (%). Standarddeviation of two runs is given in brackets.

Figure 45 shows the LECO furnace profile of sulphur release from the sludge. Two sharp peaks are evident within the first 50 seconds and these indicate easily releasable sulphur. It was observed that although the sludge contained high carbon, the rate of sulphur release was significantly slower than with the raw coal testing in Figure 41, where it was proposed that coal combustion increased the temperature leading to faster desulphurisation. This is indicative that the sulphur is associated with the "ash" rather than the carbon, since the majority of organic sulphur compounds can be released at 400°C to 500°C with unreactive aromatic sulphur being released at less than 1000°C (Gu, et al., 2016); these experiments were performed in hydrogen, inert gas and carbon dioxide.



Figure 45: LECO Analysis Profile of Sulphur Release from Blast Furnace Floating Clarifier Sludge.

The following equations detail reactions between anhydrite, carbon, calcium sulphide and oxygen (Ropp, 2012, pp. 139-140). Ropp (2012) states that calcium sulphide is formed in burning coal heaps; it also decomposes upon contact with water.

Carbothermic reduction of anhydrite is an endothermic reaction that occurs between carbon and anhydrite to give calcium sulphide as follows:

 $CaSO_4 + 2C \rightarrow CaS + 2CO_2$

Equation 29: Carbothermic Reduction of Anhydrite

However it should be noted that the LECO test occurs in oxygen, so anhydrite is likely to be reacting with CO or CO_2 although Swift et al. (1976, p. 2) states that the products are the same. Anhydrite can react with calcium sulphide to form calcium oxide and sulphur dioxide as follows:

3CaSO₄ + CaS → 4CaO + 4SO₂ Equation 30

In the following reaction it can be seen that heating calcium sulphide with oxygen leads to the formation of calcium sulphite and oxygen which converts to anhydrite.

 $2CaS + 3O_2 \rightarrow 2CaSO_3 + O_2 \rightarrow 2CaSO_4$

Equation 31

These equations give an insight into the reactions that may be occurring in the LECO furnace. It appears that the reaction of calcium sulphide in oxygen may not be a straightforward decomposition to calcium oxide and sulphur dioxide gas, and it is likely that once the sulphur enters the sulphide form, it is difficult to find a direct reaction pathway for it to be released. Swift et al. (1976, p. 16) details that calcium sulphate can be reduced to calcium oxide and sulphur dioxide in gases such as CO and CO₂ but this occurs at very high temperatures greater than 1800°C. It is clear from a basic analysis of the chemistry that the release of sulphur from the samples investigated in this thesis is a complex chemical process that merits further investigation. Regarding the blast furnace, although predominantly a reducing environment, it is probable that calcium sulphide undergoes similar difficulty in being released in the gaseous phase, which is positive in terms of sulphur maintaining a solid state in the blast furnace.

Figure 46 shows the sulphur release profile for ash created from the sludge. It can be seen that the first peak at less than 20 seconds is in a similar location to that of the sludge in Figure 45, which indicates that this is the same form of sulphur. The principal broad pattern in Figure 46 is possibly due to a large amount of a single form of sulphur. The tests in Figure 45 and Figure 46 on the sludge and sludge ash show that the release of sulphur is not completed within 250 seconds, whereas, for the coal ashes tested in the LECO furnace, the test does manage to complete. The settings for the analyser were the same for all the tests in this chapter. This shows that the sulphur in the sludge and sludge ash is more tightly bound than the sulphur in the VHTA of Figure 44, which indicates that processes in the blast furnace tend to increase the stability of sulphur that enters the solid phase.



Figure 46: LECO Analysis Profile of Sulphur Release from Blast Furnace Floating Clarifier Sludge Ash.

A notable difference between the sludge derived samples and the coal derived samples is that coal ash contains SiO_2 and Al_2O_3 in quantities that are not matched by the sludge ash sample. The catalytic effect of these components in the removal of sulphur has already been mentioned (Swift, et al., 1976), and it is possible that this is having an effect on the rate of removal, when comparing the sludge with the coal. In addition, Gu et al. (2016) describe the catalytic effect of kaolin on the removal of organic sulphur compounds.

5.2.2 DTF Char Ash Study

Chars were prepared in the drop-tube furnace at 1100°C and 1300°C from all five thesis coals. These were ashed at 815°C and the char ashes were analysed using ICP. The DTF approach differs from the LECO profile analysis approach. The DTF provides useful information about how a char behaves in a high heating rate environment, so this information is applicable to raceway conditions, and indicates how much sulphur might be expected to enter the gas phase in the blast furnace. Profile analysis aims to determine the process that is occurring as sulphur is lost from an ash, with a view to relating this to chemical changes.

Figure 47 shows the percentage of SO_3 identified in 1100°C and 1300°C DTF char ashes respectively, using ICP Analysis. With each increase in residence time, the amount of sulphur present in the char ashes decreases. DTF conditions are interesting because the char ashes demonstrate a much greater loss of sulphur in the DTF, when compared to the high amounts of sulphur still present in VHTA as measured by the LECO furnace. Figure 41 showed how the sulphur release occurred quickly in the LECO furnace in a raw coal due to the presence of carbon. In the DTF, the heat generated by char combustion has exposed the minerals to a higher temperature and it is probable that this has caused the release of sulphur to increase. The samples tested in the LECO furnace were ashes that had undergone a combustion process at a far lower heating rate than the DTF. Hence, it is proposed that high heating rates of the DTF are causing greater sulphur release. Higher rates of sulphur loss under DTF conditions are likely due the limited opportunity given for sulphur to react with mineral matter and become fixed in the ash phase. Therefore, sulphur release from injection coals is likely to be a concern at the high heating rates experienced in the raceway.

An increase in DTF temperature causes the amount of sulphur released from the char ashes to increase, with a few exceptions, as follows. Comparing the sulphur contents of the char ashes between 1100°C and 1300°C, it can be observed that at 1300°C 700 ms for LV3 and MV, there is more sulphur than in the respective samples at 1100°C 700 ms. This is also the case for the LV3 350 ms sample. Evidently, there is less release of sulphurous gas which indicates that some form of sulphur fixing is occurring more strongly in the DTF at 1300°C than 1100°C. Reduction of calcium sulphate to calcium sulphide can occur with carbon or carbon monoxide as has been discussed in the text around Equation 29. This is an endothermic reaction which would occur at an increased rate at higher temperature, and may be the reason for increased sulphur retention at 1300°C for the samples in question.

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Figure 47: Percentage of SO $_3$ in 1100°C and 1300°C DTF Char Ashes at 100 ms, 350 ms and 700 ms

At increasing DTF residence time the difference in the sulphur release between 1100°C and 1300°C narrows. This is possibly due to the proposed effect of conversion to a more stable form of sulphur such as calcium sulphide. It is evident that the DTF environment is effective at releasing sulphur from the coals. The DTF bears similarities to the blast furnace raceway, where it is likely that similar sulphur release behaviour will be noticed. The differences observed in the 700 ms samples for LV3 and MV may prove promising in the raceway if higher temperatures lead to the formation of calcium sulphide instead of sulphur in the gas phase.

A chart showing the conversion of sulphur relative to HTA for the 1300°C DTF testing is shown in Figure 48. Due to the sulphur changes that occur between a raw coal, MTA and HTA, as discussed in Section 5.2.1, it can be complicated to calculate a representative conversion. It was not possible to convert back to the raw coal because ICP data was not available for this, and it would be erroneous to use the LECO analyser data, as this is a different instrument that operates on a different principle. Thus it was decided to plot the conversion relative to the HTA, which was a reasoned approach considering that the DTF chars underwent this same process to remove char carbon prior to ICP analysis. Figure 48 shows that the proportion of sulphur remaining in solid phase as a proportion of the original ash is the greatest in LV3, MV and HV, especially at low residence time. As has been discussed in Section 5.2.1, LV1 and LV2 release the majority of their sulphur, and do so much

sooner than the other coals. Thus, Figure 48 corroborates the findings in Table 27 and Figure 44 from the LECO investigation, where LV1 and LV2 did not contain sulphur in VHTA, meanwhile LV3, MV and HV contained a significant amount.



Figure 48: Amount of SO₃ in 1300°C Char Ashes relative to HTA

5.3 Chapter Summary

In this chapter, alkali volatilisation and sulphur release into the gas phase were investigated using the drop-tube furnace and the LECO carbon-sulphur analyser, with a view to relating the heating environments with the alkali volatilisation effects and sulphur loss profiles. The information obtained was important in being able to answer how the varying chemistry and mineralogy of the ashes effects these behaviours.

Increasing the temperature in the DTF caused an increase in the alkali volatilisation and at the lower temperature of 1100°C investigated, the loss of alkali also increased with residence time for the majority of the coals tested, however char structure may limit the ability of alkalis to be volatilised as hypothesised for LV1. This was possibly due to clays (which contain alkalis) being locked within the char structure.

When the DTF temperature was increased, the effect of residence time reduced. This was considered to be on account of volatilisation being more of a temperature dependent process like vaporisation where further increases in residence time did not necessarily increase the volatilisation. Testing the effect at another temperature point greater than 1300°C would confirm whether further increase in temperature shows residence time to have less effect again on alkali volatilisation. In terms of the blast furnace, the findings of this chapter showed that raceway temperature is likely to have a greater impact on alkali volatilisation than residence time. The residence time in the raceway is short and difficult to determine, but this may not be an overriding factor for the volatilisation of alkalis. Reducing the temperature of the blast furnace can limit alkali volatilisation (Yang, et al., 2000) and the work in this chapter confirmed this. Although lowering the temperature of the DTF reduced alkali volatilisation, it also led to reduced char burnout. An effective means of reducing alkali volatilisation would be to select low alkali coals and this was confirmed in Section 4.5.3 where the elemental analysis of the HTA of typical coal blend showed low alkali content.

It was found that the ashes with the higher proportions of bases, such as calcium, were predisposed to alkali volatilisation meanwhile the acidic ashes that were high in silicon and aluminium, such as LV2 showed lower volatilisation. It was discussed in the literature in Section 2.2.4 that ash aluminosilicate melts absorb alkalis. The findings of this work suggest a similar effect whereby high silicon and aluminium ash has a stronger affinity to alkalis in the DTF, than high calcium ashes. This suggestion is supported by the contrasting behaviour of LV3 and HV which have lower Si and Al, and higher Ca, and showed higher rates of volatilisation than LV2.

Differences in ash fusion behaviour may also influence the degree of alkali volatilisation. It was proposed that ashes with a low fusion temperature may promote alkali to be integrated into the ash aluminosilicates instead of being volatilised. If this is the case, then the relationship between coal volatile matter, elemental analysis, and fusion temperature could also relate to alkali behaviour. In terms of slag chemistry, an acidic slag (high in Si and Al) is effective at removing alkalis, however, this is at odds with the slag chemistry required to remove sulphur from the hot metal. In industry, the typical approach is to periodically increase the acidity to remove alkalis and maintain an acceptable alkali level. For most of the time a favourable environment for slag sulphur formation is maintained (Babich, et al., 2008). Hot metal is produced continually, so long term changes that improve alkali fixation at the expense of increase sulphur hot metal content would not be constructive. Blast furnace operators should look for feed materials with low alkali to reduce the root cause of the problem.

A basic slag that is rich in calcium is effective for sulphur removal from the hot metal, and the findings of this work relate to how an increasing calcium content in the ash is likely responsible for the sulphur fixing behaviour observed in the ash samples. In this chapter the calcium content is related to the carbonates present in the minerals, and the frequent referral to the carbonate content calculated from the XRD semi-quantification of MTA provides strong justification for the development of MTA as a technique and underscores the importance of a robust method of XRD quantification.

LV3 showed prominent behaviour in terms of its tendency to release alkalis and to retain sulphur. Even though, it was not possible to correlate acid to base ratios of LV3 with fusion temperature, the high basicity / low acidity as determined by its elemental analysis in Section 4.4.3 did correlate with the alkali and sulphur behaviour discussed in this chapter.

The analysis of blast furnace sludge determined that the sulphur within both the sludge and the sludge ash was of a more stable form than the coal ashes. From this it was possible to conclude that processes within the blast furnace led to their stability, and it was considered that part of the sulphur may be in the form of iron sulphide, although further analysis is required for a deeper understanding.

The LECO and DTF showed similarities in terms of LV3, MV and HV having a greater tendency to retain sulphur, however, a notable difference was how the high heating rate of the DTF released sulphur in greater quantities. This occurrence of sulphur release is undesirable in the raceway as sulphur in gas form is responsible for iron-ore burden degradation in the blast furnace, and the preferred outlet for sulphur is as calcium sulphide in the slag. LV1 and LV2 were shown to release sulphur in the gas phase more readily than other samples, so in this regard, they are less desirable. However, an additional factor that must not be overlooked is the amount of sulphur present in the raw coal itself. Low sulphur coals are preferable, but a coal that manages to fix sulphur, even if the sulphur content is higher, may still be acceptable for use in the blast furnace. There is also the possibility to use additives high in calcium and magnesium, such as dolomite to control sulphur behaviour (Pinto, et al., 2008).

It is an interesting paradox that the ash chemistry required to reduce alkali volatilisation is one of high acidity, and the ash chemistry required to reduce sulphurous gas release is one of high basicity. Thus, it appears not possible to possess favourable properties in both areas and that a compromise has to be met between the two behaviours. However, magnesium may hold the key to attaining favourable behaviour for simultaneous removal of both the undesirable groups.

Chapter 6: Results of the Physical Properties of Ash. Abrasion, Particle Size and Bulk Density.

All five of the thesis coals were run through the DTF at 1100°C for 35 ms, 100 ms, 350 ms and 700 ms. The chars were collected and ashed at 815°C. The factors affecting wear include mineral matter content and composition, particle size distribution, moisture and bulk density (Carpenter, 2006). The abrasiveness, particle size and bulk density of the ashes were investigated to determine changes that occur with residence time. The aim of this chapter was to determine whether the abrasiveness of ashes increases with residence, in light of the chemical changes and ash fusion temperature changes discussed in Chapter 4. It was hypothesised that the formation of mullite in ash might lead to ashes with increased abrasiveness. It was considered that an increase in ash abrasiveness might increase the occurrence of erosive wear to the tuyeres where coal particles are injected at high velocity into the blast furnace. Particle size and bulk density were investigated with respect to DTF residence time and temperature. It was expected that changes in particle size and bulk density could affect the path of the particles in the raceway. For example, large particles with high bulk density might be expected to travel to the back of the raceway, whereas small particles with low density might be expected to follow the gas flow of the furnace (Ichida, et al., 2001). It was considered that differences in the particle size and bulk density could be related to the melting behaviour, and hence the ash chemistry, as discovered in Chapter 4, and that this behaviour might change with residence time.

6.1 Abrasiveness

It should be noted that although ash abrasiveness was investigated during this chapter, the majority of wear in the coal handling plant and blast furnace tuyeres is due to erosion which has a different wear mechanism than abrasion. The wear mechanisms are discussed in Section 6.1.1. Abrasive wear will occur during coal grinding. Erosion wear occurs in the pipework that conveys the coal to the blast furnace. In addition, tuyeres can become worn due to fast moving solid particles.

An ideal situation would have been to measure erosion in an experimental setup, however this would have required an abundant supply of ash. The abrasion tests in this thesis were devised to require a minimal sample of ash whilst still being able to give a comparison of the abrasiveness of the ashes from different coals and heating conditions. In itself, this information was useful, and the difference in abrasiveness could be related to the morphology of the ashes. It is expected that the abrasiveness information might give an indication of the potential for erosion.

6.1.1 Reference Samples

Abrasiveness was measured in accordance with the method described in Section 3.2.13 where a resin cylinder was abraded on a rotating grinding wheel using the sample under investigation (coal or ash) as the abrasive medium. The cylinder was weighed after a set amount of time and the mass loss was used to create the graphs in this section. Therefore, the level of abrasiveness was determined from the mass loss due to abrasion. Each sample was repeated three times; the error bars drawn onto all charts are the deviation from the mean based upon these three runs.

It is important to define the terms abrasion and erosion and to indicate where they are likely to occur. Abrasion can occur under high stress or low stress situations. Under high stress situations, when an abrasive is located between two loaded surfaces, and the applied stress causes the abrasive to be crushed, high stresses are placed at the point of abrasive contact which causes the surfaces to undergo plastic deformation. This type of abrasion typically occurs during milling. Low stress abrasion is where the abrasive is not crushed but acts as a cutting tool as it rubs against surfaces. This occurs on the walls of coal chutes and bunkers (Raask, 1985, pp. 49-51). It was likely that both modes of abrasion occurred in the samples used during the abrasion testing for this chapter, since the abrasive sample appeared to become comminuted during testing. This was a consequence of the test, rather than the aim.

Particle impaction erosion occurs when particles collide against a surface. Hard, abrasive angular particles such as quartz result in cutting erosion, whereas round particles, such as glass beads, cause surface deformation until such a point as pieces of material break off. In practice, both types of erosion occur simultaneously (Raask, 1985, pp. 51-53). In terms of the testing used in this chapter, it was necessary to link the abrasiveness results obtained to potential instances of erosion in the blast furnace.

Prior to performing testing on coals and ashes, the abrasiveness of some reference materials was considered to be a helpful indicator against which to compare the coals and ashes being tested. This was especially important given the novel nature of the test method used in this thesis. A low abrasiveness reference of graphite was used. This material was a sample used for LECO calibration, namely Graphite flake, natural, -325 mesh, 99.8% (metals basis). It was decided to use this material because it was a carbon rich sample with no mineral matter. Therefore, it was expected to be less abrasive than coal, whilst still possessing some similarities. An SEM image of the graphite in Figure 49 shows the material to be particles that are composed of flakes. The graphite flakes were tested in accordance with Section 3.2.13 and, as expected, found to have a mass loss of 0.0009 g as shown in Figure 51, which demonstrates a low level of abrasiveness.



Figure 49: SEM of graphite showing that it is composed of flakes

A high abrasiveness reference of 600 grit silicon carbide was used. It was used to confirm whether the test was being formed consistently between different days so was an indicator of repeatability, as well as a reference for high abrasiveness. As shown in Table 6 in Section 3.2.13, the average mass loss from the resin cylinder was 0.0285 g, 0.0286 g and 0.0293 g with a standard deviation of 0.0029 g, 0.0020 g and 0.0020 g respectively for 6 repeats per calibration test. This was considered a good level of repeatability for a manually performed test. Silicon carbide has a high hardness and the SEM image in Figure 50 shows that at high magnification it is composed of stony fragments of irregular shape and with sharp edges.



Figure 50: SEM image of 600 grit silicon carbide

The non-abrasive and abrasive samples in Figure 49 and Figure 50, respectively, show similar physical characteristics to SEM images of low abrasiveness kaolin and mica, and high abrasiveness quartz and pyrite as shown in Raask (1985, p. 46).

Table 29 shows Mohs hardness for typical coal minerals and ash components. The abrasive minerals within a coal are quartz and pyrite, typically 7 and 6-7, respectively, and these cause the majority of wear during grinding (Raask, 1985; Carpenter, 2006). Clays, carbonates and the coal substance are much softer.

Constituent	Mohs Hardness Number			
Coal Minerals				
Coal Substance	1.5-2.5			
Quartz	7			
Pyrite	6-7			
Kaolinite	2-2.5			
Illite	2-2.5			
Muscovite	2-2.5			
Calcite	3			
Siderite	4			
Ash Compo	onents			
Haematite	5-6			
Anhydrite	3-3.5			
Mullite	6-7			
Fluorapatite	5			
Aluminosilicates Glass (from clays)	5			

Table 29: Mohs hardness number for coal substance and minerals in coal (Reproduced
from Raask 1985). Ash mineral hardness data from (mindat.org, 2019).

6.2.1 Raw Coal and Ash Abrasion

Figure 51 shows the mass loss due to abrasion of the raw coals, with graphite shown as comparison. In the figure, graphite had a much lower abrasiveness than the coals. This was expected given that the graphite did not contain mineral matter and was composed of soft particles made up of flakes. LV3 was the least abrasive of the coals and this is likely due to its smaller particle size.



Figure 51: Abrasiveness of Raw Coals determined from the mass loss of a resin block. The error bars show standard deviation from the mean for 3 test runs.

Figure 52 shows Dv90 particle size distribution plotted against mass loss due to coal abrasion. A clear positive correlation can be seen where an increase in mass loss due to abrasion of the raw coal occurs due to increasing coal particle size.



Figure 52: Correlation of Dv90 Particle Size Distribution with Mass Loss due to Coal Abrasion.

It is known that quartz and pyrite play a strong role in the abrasiveness of a raw coal, however coal abrasion did not correlate with the amount of quartz as identified in the MTA mineral quantification. Coal grinding systems run for 1000-

2000 hours, before observing a change in mill output (Raask, 1985). In an industrial system running for such long periods of time, it would be expected to be able to observe differences between coals, when compared to this test where samples were tested for 1 minute. In a coal, the abrasive ash component constitutes only around 10% of the coal sample, with the abrasive minerals (quartz and pyrite) constituting less again. Thus it was challenging to be able to disseminate fine differences in an already pulverised sample, and the abrasion test in this chapter would benefit from occurring over a longer time period. The abrasion index of coals has been investigated in the past and is detailed in Section 2.3.5, where BS 1016-111:1998 used a piece of apparatus developed by Yancey, Geer and Price (YGP), but application of this test to actual pulveriser wear rates did not always correlate well (Carpenter, 2006). The British Standard was removed. From this, it can be deduced that it is challenging to measure the abrasiveness of coals.

Nonetheless, the abrasion testing in this thesis was able to determine that there was a correlation between abrasiveness and particle size, under the conditions of this test. However, although it is likely that the large particle sizes are more responsible for wear, in terms of the steelworks this needs to be balanced with other issues such as the energy consumption of the grinding plant and the burnout achieved in the blast furnace. It takes more energy to grind particles to a smaller specification, and this may lead to reduced wear in the pipework. It also leads to increased coal burnout (Guo, et al., 2005), which is a priority for injection coals.

The mass loss due to abrasion of the coal ashes is shown in Figure 53. The abrasiveness of the ash was considerably greater than that of the coal, with around 0.0100 g of mass loss from the resin cylinder for the ash, compared to 0.0020 g for the coal. This was due to the concentration of abrasive material that occurs during the ashing process after the carbon has been burned off. Generally the abrasiveness of HTA was greater than MTA. This is to be expected as many of the softer minerals such as clays and carbonates decomposed from MTA to HTA, as was discussed in Section 4.1.2, leading to further concentration of abrasiveness between the different coals was similar for MTA and HTA. This shows that the differences observed between the coals were unlikely to be due to experimental variabilty, and more likely to be due to relative differences in the ash properties.



Figure 53: Abrasiveness determined from the mass loss of a resin block of 400°C MTA and 815°C HTA muffle furnace coal ashes. The error bars show standard deviation from the mean for 3 test runs.

Figure 54 shows a plot of percentage quartz in MTA as determined from XRD semiquantification against the mass loss due to MTA abrasion. There is a positive correlation with the abrasiveness of MTA and the percentage of quartz identified from XRD diffractograms. Particle size and amount of quartz are two of the known factors that affect abrasiveness (Raask, 1985; Carpenter, 2006). Regarding HTA, it is likely that both of these factors were impacting the abrasiveness simultaneously. LV1 had a high ash particle size and yet possessed an abrasiveness that was not amongst the highest, and this may be in part due to its lower quartz content as observed in Section 4.2. Conversely, LV2, had a low ash particle size but a high quartz content, and posessed the highest abrasiveness of the raw coal ashes in Figure 53, as well as of the char ashes in Figure 55 in Section 6.1.3, when compared to the other samples. LV3 had a low ash particle size (similar to LV2), and it also had a relatively low quartz content, which led to the lowest abrasiveness. Thus it can be seen that the particle size and quartz content both have an impact.



Figure 54: Correlation of Quartz (%) in MTA with Mass Loss due to MTA Abrasion.

The absolute error of the abrasiveness for the raw coals was lower than that of the ashes and the char ashes however, the relative error was greater because the mass loss due to coal abrasion was small. The error in the DTF char ashes in Figure 55 was lower than muffle furnace coal ashes in Figure 53. It was found that the muffle furnace coal ashes were more difficult to test owing to the presence of fine particles and clay minerals that would cause the resin block to stick rather than glide on the abrasive wheel. Fewer problems were experienced with DTF char ashes, especially the ashes from high residence time conditions where some fusion had begun to occur, giving the ash a predictable "sandy" characteristic.

6.1.3 DTF Char Ash Abrasion

Figure 55 shows the abrasiveness of char ashes prepared from the five thesis coals at 1100°C in the DTF at 35 ms, 100 ms, 350 ms and 700 ms. Under DTF conditions the heat causes changes to occur to the mineral matter as discussed in Chapter 4, and some of these are responsible for the formation of hard materials, that were not present in the unheated mineral matter. These include the formation of mullite from kaolinite and illite and the formation of aluminosilicate glasses from the products of clay decomposition. Thus, it can be expected for the abrasiveness of ashes from the DTF to be greater than the muffle furnace ashes presented in Figure 53. Figure 55 shows that at low residence times of 35 ms and 100 ms, the DTF char abrasiveness was greater than both the MTA and HTA, with the exception of MV at 100 ms. For the subsequent residence times, the abrasiveness of the ashes increases for LV2 and decreases for LV1, LV3, MV, and HV. This is interesting behaviour, since it is known from Chapter 4 that the proportion of mullite and the proportion of glass increases for chars tested at 350 ms compared to 100 ms, and so it would be expected that higher residence times lead to an increase in ash abrasiveness. The decreasing trend in abrasiveness with increasing residence time was determined to be due to the formation of less abrasive spherical aluminosilicates as the ashes began to fuse. This effect is further discussed.

As a general observation across all the residence times, LV1 and LV2 are the most abrasive char ashes, meanwhile LV3 is the least abrasive. Thus if ashes are able to form in the tuyere region, this implies that LV1 and LV2 would be more likely to cause erosion, whereas LV3 would be the least likely to cause erosion. It can also be deduced that although mullite and potential high melting temperature aluminosilicate glasses form, as determined from Chapter 4, these may not present problems in terms of increasing abrasion effects in the blast furnace, due to the

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formation of spherical beads, however LV2 may be an exception owing to its high melting point.



Figure 55: Abrasiveness determined from the mass loss of a resin block. Samples are ashes prepared from 1100°C DTF Chars at 35 ms, 100 ms, 350 ms and 700 ms for LV1, LV2, LV3, MV and HV. The error bars show standard deviation from the mean for 3 test runs.

Figure 56 shows the SEM images of all char ashes produced in the DTF at 700 ms. LV2 shows minor formation of ash agglomerates with the majority of the ash not showing signs of fusion. This was due to the high ash fusion temperature of >1500°C as determined in Section 4.3. The morphology of HV DTF char ash which had the lowest fusion temperature ash of <1200°C is different. It was predominantly composed of fused aluminosilicate beads which were able to form in the DTF where there was sufficient temperature for ash fusion to occur for this low melting temperature ash. For the other three samples, LV1, LV3 and MV which possesded
moderate fusion temperatures of around 1300°C, significant formation of fused aluminosilicate beads can be observed, although not to the extent of HV.

In terms of abrasiveness as shown in Figure 55, LV2 char ash which underwent minimal fusion in the DTF showed an increasing trend of abrasiveness up to 350 ms, whereafter there was a slight decrease. This is likely to be attributed to the fusion of a minor proportion of the ash leading to less angular particles, thus slightly lower abrasiveness. The other samples, LV1, LV3, MV and HV all show decreasing abrasion with residence time and this is attributed to the reduced abrasiveness of the aluminosilicate beads compared to irregularly shaped ash particles expected at lower residence time. Mullite is known to form in all the samples under high residence time DTF conditions, as observed from the XRD quantification in Chapter 4. It is possible that mullite was absorbed into the aluminosilicate beads of the lower fusion temperature ashes. LV2 possessed only a small amount of fused material, which would give limited capacity to absorb mullite, so the increased abundance of unabsorbed mullite could be a factor in the higher abrasiveness of this particular sample, across all residence times. There was variation in the abrasiveness of samples that contained aluminosilicate beads. This could be due to the relative difference in hardness between the types of aluminosilicate or the surface morphology of the aluminosilicate beads, where beads with rough surfaces and embedded material should be more abrasive than smooth surfaces. These factors were not investigated in the PhD.



Figure 56: SEM images of DTF 1100°C 700 ms char ashes. Top left: LV1; top right: LV2; bottom left: LV3; bottom right: MV; bottom centre: HV. The view field was ~270 μm for all images in this figure.

Even though there was formation of harder material under DTF conditions as determined in Chapter 4, the shape of these minerals was less abrasive because ash fusion processes at high residence time led to more rounded particles. In terms of the blast furnace, this means that any abrasion effects may not be increased with residence time, although, this does not rule out the negative effect of erosion due to the impacting of beads. It is possible that ash particles that have been through the raceway are present in the off gas and they may pose a threat of erosion wear to off gas handling systems. It is considered that small particles which did not undergo fusion may be able to follow the gas flow up through the furnace and form part of the off gas. However, it needs to be considered that the raceway is in excess of 2000°C and the cohesive zone is between 1100°C and 1400°C so it is also expected that the many particles of ash and unburnt char would become stuck in the cohesive zone. Unburnt char from the raceway has the potential to become caught further up in the blast furnace stack (Bennett & Fukushima, 2003; Steer, et al., 2018), or exit the furnace as a dust (Bennett & Fukushima, 2003).

Figure 57 shows that unburnt chars contain particles of ash, confirmed via SEM to be aluminosilicates with integrated metals. Ash carried within chars could still find its way to other areas of the blast furnace. It should also be noted from this figure that LV1 contains visibly more ash than LV3 owing to its higher proximate ash yield. It is considered that these particles of ash will possess the same properties as the char ashes investigated in this section and therefore, the carriage of unburnt chars through the blast furnace presents another way in which ash may leave the raceway, and could find themselves in other areas of the blast furnace such as the flue gas, or attached to coke where they affect the gasification reactivity, as discussed in Chapter 7.



Figure 57: SEM images of DTF 1300°C 100 ms char. Left: LV1; Right: LV3 showing the relationship between the ash and the char. The light coloured globules are aluminosilicate ash particles found on the surface of the char.

An additional point to consider is the effect of blending coals. As was observed from the blends presented in Section 4.5.3, the resultant fusion temperature was not additive. Likewise for the ash abrasion testing, it is probable that mixing of different ash types could mitigate or promote the effects of abrasiveness observed with the SEM images in Figure 56 due to earlier or later onset of ash agglomeration.

6.2 Particle Size

Figure 58 shows the Dv90 particle size distribution of raw coal and 815°C ash (HTA).

The purpose of this chart was to determine the relationship between coal and ash particle size. This information was used to infer whether grinding of the coal was responsible for a reduction in the size of the mineral matter. Figure 58 shows little correlation between the particle size distribution of the coal and the ash. This implies that grinding of the coal has a limited effect on the size of the mineral matter.

For example, the particle size of LV1 coal ash is not dissimilar from the particle size of the coal. By contrast, the particle size of the ash is much lower for the LV2, MV and HV coals. LV2 and LV3 have disparate coal grinding sizes but similarly sized ashes. For the blast furnace, this suggests that the fineness of the coal grinding has limited impact on the size of the mineral matter, unless the coal is ground to a smaller particle size specification than the mineral matter particle size, which is unlikely given that these samples were ground to pulverised specification. The reason for the smaller than usual coal particle size distribution for LV3 was because during laboratory preparation particle agglomeration made this coal problematic to sieve which made it difficult to determine when the particles were ground small enough. Thus, some additional grinding occurred.

This work suggests that coal and mineral matter particle size might not be closely related. Therefore the mineral matter particle size distribution is more of an inherent characteristic of the coal that should be analysed separately to the particle size distribution of the coal, to determine the potential for abrasion in the coal handling facility at a steelworks.



Figure 58: Dv90 Particle Size Distribution (μm) of raw coals compared to 815°C HTA.

Figure 59 and Figure 60 show the Dv90 Particle Size Distribution of char ashes from the DTF at 1100°C and 1300°C, respectively. There is a clear correlation of an increase in particle size with residence time for LV1, MV and HV at both temperatures. This is likely because increasing the particle residence time allows more opportunity for fusion effects and agglomeration to occur. However, LV3 shows little increase in particle size with residence time in spite of having a moderate fusion temperature that was shown to be affected by the DTF in Figure 56. This is possibly owing to its low ash content and the char structure where individual ash particles had limited opportunities to agglomerate, as shown in Figure 57.

In terms of the blast furnace, ash particles that increase in size with residence time due to agglomeration will necessarily be heavier and carry greater momentum within the raceway and this is likely to affect their direction of travel. Guo, et al. (2005) and Wu et al. (2019) observed that large coal particles (200 μ m and 130 μ m respectively) tended to continue in their direction of travel whereas small particles followed the gas streamline. The same effect is proposed for the larger and denser ash agglomerates; that they may be more likely to travel in the direction of motion of the tuyere blast, and if so they will aim for the bird's nest, as seen from the raceway diagram in Section 1.4.3 by Chen et al. (2007).

The type of ash more likely to undergo agglomeration is a low melting temperature variant lower in quartz, clays and high melting temperature minerals, and higher in calcium, carbonates and low melting temperature minerals, as determined from Chapter 4. This means that it will probably have a catalytic effect as described in the literature in Section 2.2.5, and in Chapter 7. Therefore the concentration of a catalytic effect at this region might lead to an increase in raceway depth due to increased coke gasification reactivity. In this case, there may also be preferential centre flow of gas with the proposed increase in raceway depth. On the other hand, the bird's nest may be overcome with low melting temperature, catalytic ash that will flow down into the slag.

In Figure 59 and Figure 60, LV2 does not show the same level of increase as the other coals with residence time or temperature. This is likely owing to its high fusion temperature that allowed limited opportunities for agglomeration as could also be seen in Figure 56. Therefore, if the ash is less likely to agglomerate into large particles with greater momentum, it may travel with the gas flow in the furnace and become trapped in the cohesive zone (Ichida, et al., 2001). This could alter the

chemistry of the ash in this region leading to an increase in dripping slag viscosity, due the potential concentration of high fusion temperature ash in this part of the furnace.

It can also be observed from Figure 59 and Figure 60 that the particle size increases with temperature for the agglomerating ashes. Therefore changes in reaction temperature in the raceway, and hot blast temperature, can be expected to affect ash agglomeration in the blast furnace, hence particle size.

A final point relates to the effect of char compared to ash. All of the above ideas assume that the char has burnt out sufficiently that the ash has been liberated. Char burnout in the raceway is difficult to measure owing to the turbulent environment and extreme conditions. If char burnout is not sufficient, then the ash will travel as part of the char, and char physical properties will be more likely to determine how the particles travel.



Figure 59: Dv90 Particle Size Distribution (μ m) of DTF Char Ashes at 1100°C



Figure 60: Dv90 Particle Size Distribution (μm) of DTF Char Ashes at 1300°C.

6.3 Bulk Density

The bulk density of DTF char ashes, coals and chars was investigated to determine changes that occur with residence time and differences in the density of coals and chars. This work was performed to identify additional factors that may impact on the behaviour of ash in the blast furnace. The chars were investigated to determine whether there was a link between char behaviour and char ash behaviour.

Figure 61 and Figure 62 show the bulk density of char ashes prepared from the DTF at 1100°C and 1300°C, respectively. Bulk density measurements were performed twice for each sample and the error bars show the absolute deviation from the average of the two results. It has been shown that ashes undergo mineral agglomeration and spheroidisation inside the drop-tube furnace. This was linked to the observed increase in particle size with temperature and residence time. The bulk density of the char ashes shows a similar trend to the particle size distribution work, where there is an increase with residence time, and this is expected to occur due to particle softening and agglomeration where particles become more compact, therefore on a bulk basis, they occupy less volume leading to an increase in bulk density. In terms of the blast furnace, bulk density is expected to have the similar effects to those discussed in the previous section whereby higher density material travels into the back of the raceway, while less dense material follows the air flow of the furnace and circulates within the raceway.

The figures show that when comparing 1100°C with 1300°C, the bulk density of the char ashes showed minimal increase at 100 ms and 350 ms, however at the highest residence time of 700 ms the increase in bulk density with temperature was significant. It is suggested that the increase in particle size was not entirely correlated to the increase in bulk density because particle size can increase by particles agglomerating, but this does not necessarily increase the bulk density because the agglomerated particles may still possess similar void fraction. However, at the highest residence time the particles themselves melted considerably which decreased their void fraction and increased their bulk density, especially at 1300°C.



Figure 61: Bulk density of 1100°C DTF char ashes at 35 ms, 100 ms, 350 ms, and 700 ms.



Figure 62: Bulk density of 1300°C DTF char ashes at 100 ms, 350 ms, and 700 ms. The error bars show standard deviation from the mean for 2 test runs.

Figure 63 shows the bulk density of the raw coals used in this thesis. There is weak correlation between the particle size and the bulk density. LV3 was ground to the smallest particle size and does show a reduced bulk density compared to the other coals, however in general, the bulk densities of the coals are similar. In terms of the blast furnace, this means that coals that are milled to the correct particle specification should not occupy a disproportionate volume of the blend. It is possible that if a certain type of coal occupied a disproportionately greater volume of a blend, when being injected into the furnace, it may react preferentially to the other coals if it is more dispersed in its gas environment due to a more plentiful supply of reacting gas.



Figure 63: Bulk density of raw coal. The error bars show standard deviation from the mean for 2 test runs.

The char bulk density is shown in Figure 64. When compared to the coal bulk density in Figure 63, the char bulk density is lower, with the exception of LV1. This reduction in bulk density from the coal to the char indicates swelling occurring in the DTF. Swelling behaviour is typical of bituminous coals and more likely to occur at higher heating rates (Yu, et al., 2003). Swelling leads to coal agglomeration (Shampine, et al., 1995) which may cause blockages to occur during coal injection into the blast furnace (Sexton, 2019). Following an occurrence of swelling behaviour upon entering the DTF at 35 ms, there does not appear to be any observable trend with increasing residence time for any of the coals. As char consumption occurs, it might be expected for the bulk density of the coal to decrease with residence time as material is consumed, however on the other hand, ash is denser than organic matter, and this ash may concentrate in the shrinking char structure thus offsetting the decrease in bulk density occurring due to char consumption. It can be observed that for HV, there is a large increase in bulk density at 700 ms. This is likely owing to breakdown of the char structure to the extent that the char is predominantly formed of agglomerated ash. The DTF char from HV at 1100°C 700 ms, was in fact composed of 77.6% ash, so this is highly likely to be the reason.



Figure 64: Bulk density of DTF chars prepared at 35 ms, 100 ms, 350 ms, and 700 ms. The error bars show standard deviation from the mean for 2 test runs.

6.4 Chapter Summary

This chapter investigated the abrasiveness of coal, ash, and char ash. It made links between the abrasiveness with particle size. The bulk density of coal, char and char ash was briefly investigated. The abrasiveness of muffle furnace ashes and DTF char ashes was investigated in this chapter in order to determine the effect of heating regime on ash abrasiveness.

Coals were found to be significantly less abrasive than the ash. It is important to emphasise the difference in abrasiveness of the coal and the mineral matter or ash. Coal itself is not very abrasive, whereas mineral matter or ash can be very abrasive. Nonetheless, there was a correlation between the particle size of the coal and the abrasiveness, where smaller particle size resulted in lower abrasion. This suggests that smaller particle size coals will cause less abrasion to the tuyere region. In addition, smaller particles combust more fully (Guo, et al., 2005) which helps to achieve the objective of more complete combustion of pulverised coal in the raceway. It was not possible to link coal abrasiveness to mineral matter content and composition. Therefore, it was suggested that the test method lacked the sensitivity to be able to determine the fine differences exerted by the mineral matter composition when contained as part of the coal organic matter. Accurately quantifying abrasiveness of coals and applying this to real situations has proved to be problematic using abrasion index with YGP apparatus (Carpenter, 2006).

Muffle furnace ashes were investigated and there was some evidence to suggest that smaller particle sizes led to less abrasive ashes. The amount of quartz in an ash was also an important factor, as this was the principal abrasive in muffle furnace ash. In terms of correlation, it was determined that for ashes, a combination of particle size and quartz content affected the abrasiveness. For example, a large particle size in conjunction with a high quartz content gave high abrasion. In the case of LV2, which possessed a particle size similar to the other char ash samples, it had the highest abrasiveness, and this was considered to be due to the quartz content. Similar findings were detailed by Raask (1985, p. 368), where abrasion index was calculated and found to increase with increased amounts of larger particle size quartz.

Regarding the effect of heating regime on abrasiveness, it was found from Chapter 4 that the types of material generated in the DTF included mullite and aluminosilicate glasses, and it was hypothesised that these would lead to increased abrasiveness of DTF ash. An increase in abrasiveness was observed in DTF char ashes at low residence time when compared to muffle furnace ashes. At high residence time, the behaviour was determined by the ash fusion temperature. The ashes with low to medium fusion temperature formed aluminosilicate beads at increased residence time which reduced the abrasiveness of the ash. The high abrasiveness silicon carbide reference specimen was composed of irregular, angular particles that lead to a noticeable cutting action during abrasion. The aluminosilicate beads that formed at high residence time, although likely to be hard, lacked the appropriate shape for cutting abrasion, hence the abrasion reduced as they became more numerous in the char ash. Regarding the sample with the highest fusion temperature, namely LV2, the abrasiveness of the ash increased with residence time up to 350 ms. There was a slight decrease at 700 ms, likely due to ash fusion effects rounding the sharp edges of angular, abrasive minerals such as quartz thus reducing their abrasiveness. Raask (1985, p. 369), observed the similar findings as in this thesis, where ash became more abrasive as the clay material converted to glassy particles, and then subsequently less abrasive as quartz particles started to round off at higher temperature.

The difference between erosion and abrasion was discussed in this chapter. Abrasion occurs when abrasive particles are lodged between two moving surfaces or when abrasive particles slide against a surface such as in a coal chute. Erosion

occurs due to particles that are carried in a stream and impinge with a surface causing wear.

It is known that hard minerals such as mullite form in the DTF, and these will also form in the raceway, but it is not known whether they would form in the short distance between the coal injection lance and the end of the tuyere. Notwithstanding, the abrasive mineral quartz will still be present, as this is generally unaffected by temperature. It would be interesting to determine whether abrasion increases as a result of increased hot blast temperature, as increased hot blast might increase the rate of combustion in the tuyere leading to a higher concentration of abrasive ash in the material that is travelling within that region. On the other hand, increased hot blast temperature might enable quartz to soften and become less abrasive. Extraneous quartz minerals are likely to contribute to tuyere wear, especially as they would be unlikely to lose their sharp edges at the lower temperatures in the tuyere region. In order to further the knowledge gained in this chapter and to more thoroughly investigate tuyere wear, it would be recommended to investigate the abrasiveness of different types of char, as this is more likely to be the form in which the material in the tuyere is found.

It is considered that the results of this chapter are more applicable to pulverised fuel boilers where the temperatures are lower and the residence times are higher (Ishii, 2000). These conditions allow greater opportunity for coal burnout, and subsequent formation of the ash structures observed in this chapter. Abrasive, quartz containing fly ash is produced from pulverised coal fired boilers and abrasion / erosion is commonly encountered on comparatively low temperature steam containing boiler heater tubes usually when ash flue gas temperatures are below 1000°C (Raask, 1985).

DTF char ash particle size and bulk density were investigated. They were related to the fusion temperature of the ash, where lower AFT generally led to larger particles at higher temperature and residence time as a result of increasing ash agglomeration. For LV2 which possessed the highest fusion temperature, the increase in particle size and bulk density with temperature and residence time was more gradual.

In terms of the blast furnace, this means that lower melting temperature ashes are more likely to form larger particle size agglomerates with higher bulk density. These ash particles will have greater momentum and may be more likely to travel in the

direction of blast to the back of the raceway. They may be less susceptible to following the gas flow through the furnace. These low fusion temperature particles are likely to have a catalytic chemistry with increased levels of calcium, as discussed in Chapter 4. Therefore, if they do accumulate in the back of the raceway, as this work suggests, then any catalytic effect would increase coke gasification in this region and may change the size of the raceway and the permeability. Ash catalysis is investigated in Chapter 7.

High fusion temperature ash will more likely have a lower particle size and bulk density due to lower levels of agglomeration and fusion. This material may be more likely to travel through the furnace with the gas flow and either become stuck in the cohesive zone or deposit on the burden. The likelihood is that such ashes will contain less catalytic material which could be beneficial in terms of reduced coke degradation in the cohesive zone and beyond.

Chapter 7 Results of the Effect of Ash on Coal Combustion and Coke Gasification in the TGA.

The effect of ash on the combustion of coal and the gasification of coke using a Thermal Gravimetric Analyser (TGA) is investigated in this chapter. Ash has been described as a diluent to the combustion process (Ward, 2016), and also as a catalyst (Tomita, 2001). This chapter will determine the extent to which those statements are true. This chapter aims to determine whether the ash behaves as a catalyst during coal combustion in air, and during coke gasification in carbon dioxide. Alkali metals, calcium, iron and other transition metals are known catalysts of gasification that are contained in different proportions in coal mineral matter (Nomura, et al., 2006). Catalytic mechanisms are discussed in Section 2.2.5.

The findings of this work will provide information to the blast furnace operator about whether ash is a beneficial coal constituent to have during combustion in the raceway, and also the extent to which the gasification of coke is catalysed, for example in the coke surrounding the raceway, in the deadman and further up the furnace. Coke degradation is undesirable since this causes the generation of fines which leads to a loss of permeability in the blast furnace.

Coals are injected in the form of blends into the blast furnace, and each coal ash has different chemical properties which can affect the reaction. During combustion in the raceway, the ash formed can be intimately mixed and in close proximity to the carbonaceous material. This chapter examines the effect of ashes created from three of the five thesis coals to determine their effect on the combustion reaction of two out of the five thesis coals. The ashes and coals are selected based on their properties observed during this thesis, for example, catalytic or non-catalytic ash chemistry. During testing they are mixed at a rate of 10% ash to 90% coal / coke. An improvement in combustion due to the presence of ash would be positive for the blast furnace in terms of increasing burnout and reducing the negative effect of partially burned chars in the blast furnace.

The first half of this chapter investigates the effect of ash on coal combustion, and the second half investigates the effect of ash on coke gasification.

7.1 Sample Selection

7.1.1 Coal Selection

Figure 65 shows the burnout of the five thesis coals at 1100°C in the DTF. This informed the choice of coals to be used for the TGA combustion investigation in this chapter. Low reactivity LV2 coal and high reactivity HV were chosen. These two coals were chosen to determine whether the addition of a potential catalytic ash additive might have a stronger effect on a coal with an intrinsically low reactivity when compared to a coal with a higher reactivity. In spite of having the lowest reactivity, LV1 was not chosen because its ash contained a moderate concentration of calcium, so it was decided that this might create confusion when trying to assess the impact of the additive versus the inherent calcium content of the coal. Lines are drawn through the data points to enable visual comparison between the different coals, rather than to identify a trend. The lines do indicate a trend of increasing burnout with residence time but more data points would enable more confidence in a trend. The data show that coal burnout in the DTF increases with volatile matter designation, which affirms the literature and indicates that higher volatile coals will burn out faster in the raceway, so in this regard, higher coal volatility is beneficial to the blast furnace operator. There is interesting behaviour occurring between LV3 and MV, where the reactivity is higher at lower residence times and similar at higher residence times. LV3 was found to possess a lower particle size than the other coals in Section 6.2, and this is likely a factor in its reactivity being higher than might be expected for its volatile yield in relation to the other coals.

The zero burnout for LV1 was discussed in Section 5.1.3, and it was determined that a combination of low levels of combustion with incomplete ash collection led to a situation where error was increased. The DTF burnout repeatability error was also discussed in Section 5.1.3, and found to be at a low level.



Figure 65: Burnout (%) of LV1, LV2, LV3, MV and HV at 1100°C in the DTF with points at 35 ms, 100 ms, 350 ms and 700 ms.

7.1.2 Additive Selection

Combustion Test Additives

Firstly, the coal samples were tested without additive to act as a control. Following this, 815°C ashes from three of the five thesis coals were chosen as additives for all testing in this chapter. The term "additive" was used because it was unsure whether or not the effect would be catalytic. The ash additives were produced from LV2, LV3, and HV coals. These ashes were selected based upon their potential for catalytic behaviour. Low and high catalytic chemistry coals were used.

LV2 ash contains low amounts of catalytic elements while LV3 ash and HV ash comprise high levels of catalytic elements. The ICP data for elements of interest are reiterated in Table 30. LV2 ash contains around a third of the calcium of MV and HV, and a lower iron content. HV ash contains the highest proportion of basic elements including calcium content compared to LV2 and LV3. LV3 was a reactive coal in terms of burnout as shown in Figure 65, but not as reactive as HV. The element oxide analysis indicates that HV ash should be more catalytic than LV3 ash.

	Fe₂O₃	CaO	MgO	K₂O	Na₂O
LV2	6.09	2.59	1.08	1.11	1.79
LV3	12.74	9.62	1.72	1.82	0.52
HV	8.14	10.92	3.70	1.37	2.29

Table 30: ICP element oxide (%) for LV2, LV3 and HV HTA.

For the combustion tests, the ashes were added to the coal samples as MTA and as HTA. It was determined in Section 4.1.2 that catalytic minerals such as calcite and dolomite are present in MTA but decompose to oxides as they are heated up to HTA conditions. Clays contain potassium which is potentially catalytic; the form of clays change to dehydrated amorphous material as they are heated to HTA conditions. MTA and HTA were both used as additives to the coal to determine whether the different mineral forms would affect the catalytic ability.

Dolomite was also used as an additive to enable comparison of a known catalyst with the selected ash additives. An elemental oxide composition of pure dolomite is 30.41% CaO and 21.86% MgO (webmineral.com, 2019). Comparing to the elemental analysis of the coal ashes in Table 30, this is around three times the amount of CaO contained in LV3 and HV, and around ten times the amount of MgO. Dolomite is known to be a catalyst for the gasification of coal and biomass blends (Ma, et al., 2019). All additives were added at a rate of 10% additive to 90% coal.

Gasification Test Additives

For gasification tests, DTF char ashes from LV2, LV3, and HV were used to investigate the effect of potential catalytic ash elemental composition on gasification. The differences in elemental composition were discussed in the previous section. Chars were created in the DTF at 1100°C for 100 ms and 700 ms, and subsequently ashed at 815°C. The objective of using char ashes, as opposed to muffle furnace MTA and HTA, was to provide a more representative ash material with which the coke might interact in the raceway. The two residence time DTF char ashes, 100 ms and 700 ms, were investigated to determine whether this would alter the behaviour of the ashes. In the blast furnace raceway, particle residence time is uncertain, so the use of two different DTF residence time char ashes as additives was undertaken to identify whether this affected coke gasification reactivity.

Slag formed from coke ash, iron ore gangue and coal ash drains through the coke in the deadman. Therefore a sample of slag was used as an additive during a gasification experiment to allow a comparison to the effect of the coal ashes. As with the combustion experiments, dolomite was also used as an additive to enable comparison of a known catalyst with the selected char ash additives, and all additives were added at a rate of 10% additive to 90% coke.

7.2 Coal Combustion Experiments

Figure 66 shows the combustion mass loss profiles of the two selected coals, LV2 and HV, performed in the TGA. It can be seen that HV is more reactive than LV2 in the TGA, which is in agreement with the DTF burnout in Figure 65. " t_{50} " was the metric used to compare reactivity of all tests in this chapter, both combustion and gasification. t_{50} is the time taken for 50% conversion compared to the original mass, and is used by other authors when stating gasification reactivity (Cempa & Smoliński, 2017; Wang, et al., 2017). In this thesis t_{50} was also used for combustion reactivity. This chart provides a baseline for the reactivity of LV2 and HV with no ash additive. The t_{50} was 6162.0 seconds and 5697.5 seconds respectively.



Figure 66: TGA Combustion of LV2 and HV Coals.

In Figure 67 the TGA combustion of HV coal is shown with no ash additive and with addition of 10% of 400°C ash (MTA) from LV2, LV3, and HV. The ash additives do not improve combustion when compared with HV with no additive. Addition of LV2, LV3 and HV ash gave respective t_{50} times of 5728.5 seconds, 5777.5 seconds and 5744.0 seconds, compared to 5697.5 seconds for no additive. Therefore, it can be seen that addition of ash is causing combustion to take marginally longer. This is likely due to the energy required to heat the 10% of additional ash. Moreover, referring to the t_{50} times, the addition of LV2 ash appears to be slightly less negative than the ashes of LV3 and HV. There may be an underlying endothermic effect such as carbonate decomposition in LV3 and HV coals that caused this difference, since LV3 and HV contain higher proportions of carbonates than LV2.



Figure 67: TGA Combustion of HV Coal mixed with 10% of 400°C Ash from selected coals.

Figure 68 shows the TGA combustion of HV coal with no ash additive and with addition of 10% of 815°C ash (HTA) from LV2, LV3, and HV. As with the experiment in Figure 67, it can be seen that there is no catalytic effect due to the addition of ash. The respective t_{50} combustion times with the aforementioned additives were 5837.5 seconds, 5793.0 seconds and 5799.0 seconds respectively. When compared to the HV with no additive taking 5697.5 seconds, 815°C HTA has a marginally more negative effect on combustion than 400°C MTA with the combustion taking longer.



Figure 68: TGA Combustion of HV Coal mixed with 10% of 815°C Ash from selected coals.

In Figure 69, the low reactivity coal, LV2 was tested with no additive and with 10% 400°C ash from LV3 and HV 400°C. It can be seen that the ash additives do not increase the rate of combustion. The t_{50} time taken for the respective samples with additives was 6276.0 seconds, 6261.0 seconds, compared to 6162.0 seconds with no additive. Therefore, the reactivity of LV2 coal was not improved by the addition of potentially catalytic ashes, in spite of being less reactive in the DTF than HV coal. The results of the coal combustion with ash additives in the TGA showed no improvement in all cases, irrespective of the original reactivity of the coal, and irrespective of the potentially catalytic chemistry of the ash additives used.





Figure 70 and Figure 71 show the TGA reactivity with the addition of dolomite to LV2 and HV coal. There was no catalytic effect due to the addition of dolomite. Dolomite which contains around three times the amount of calcium as LV3 and HV, did not improve the coal reactivity, thus the process of combustion was not improved by the presence of calcium for the combustion tests performed in this chapter. When dolomite additive was used, there was an increase in t_{50} for LV2 and HV of 1.7% and 0.8% respectively. The endothermic effect of dolomite decomposition is likely responsible for the perceived decrease in reactivity. There is a feature in the TGA mass loss curve for the samples with dolomite addition that can be seen between 6000 and 8000 seconds. After 8000 seconds, further mass loss does not occur. This feature is due to decomposition of dolomite and is occurring between 550°C and 700°C.

It could be argued that the end point of combustion should have been taken before the complete decomposition of dolomite, as decomposition was not part of the combustion process being investigated. However, there are also carbonates and clays within coal ash that will decompose and break down at similar temperatures. In order to representatively remove the effect of additive decomposition it would be necessary to accurately quantify the amount of decomposition occurring in the coal ash, as well as the dolomite, and then recalculate the desired end points of TGA mass loss accordingly.

In spite of these concerns, the onset of mass loss and the gradient for the mass loss is broadly the same whether or not the additive is present, which shows that the rate of reaction was not improved by the addition of dolomite under TGA conditions. Moreover, in an industrial process, the points of interest are more likely to be the start and end points, to determine whether there was an overall positive or negative effect. For instance, if in the blast furnace, the catalyst improves the combustion reaction but then requires significant energy to melt or decompose, the net effect may not be so attractive from an industrial perspective.



Figure 70: TGA Combustion of HV Coal mixed with 10% of dolomite.



Figure 71: TGA Combustion of LV2 Coal mixed with 10% of dolomite.

Table 31 shows the t_{so} combustion times for all of the samples investigated in the TGA combustion experiments. The TGA mass loss figures have already been discussed and some of the data from the table have been used to describe the figures. All tests were performed in duplicate, and low deviation from the mean is consistent for all. In percentage time terms, the deviation for the duplicate runs was a fraction of one percent, with a range of 0.01% to 0.35%. This low level of error gives confidence in the findings of the TGA combustion experiments.

Combustion reactivity of LV2 coal and HV coal was not improved by the addition of ash. The combustion reaction t_{50} took around 1-2% longer with addition of MTA or HTA for both coals. Note that positive percentage change in time indicates that more time was taken. Although it has been stated that there was no catalytic effect upon combustion due to the addition of ash additives, it might be expected that the potentially catalytic ashes (LV3 and HV) were marginally less ineffective than the ash that was expected to be less catalytic (LV2). This was not observed to be the case and looking at the results as a whole, all ash additives behaved similarly.

The results of the TGA combustion experiments do not exhibit a strong inhibitory effect on combustion. However, in all cases, they do increase the t_{50} . The energy required to heat up and decompose material in the additives is the most likely explanation for the small perceived reduction in reactivity. In terms of absolute reactivity, it is likely that the ash did not affect the combustion mechanism, but simply acted as a diluent.

		HV Coal	HV Coal	HV Coal	
	HV Coal.	+ 10%	+ 10%	+ 10%	HV Coal
HV Coal plus 400°C Ash-	No	1/2	1/3	HV	+ 10%
			400°C	400°C	Delemite
	additive	400 C	400 C	400 C	Dolomite
		Asn	Asn	Asn	
t₅o Combustion Time (s)	5697.5	5728.5	5777.5	5744.0	5742.0
Percentage Change from HV Coal. No additive.		0.5	1.4	0.8	0.8
Deviation from the mean of two runs (s)	8.5	10.5	13.5	4.0	10.0
		HV Coal	HV Coal	HV Coal	
		+ 10%	+ 10%	+ 10%	
HV Coal plus 815°C Ash:-		LV2	LV3	HV	
		815°C	815°C	815°C	
		Ash	Ash	Ash	
t₅o Combustion Time (s)		5837.5	5793.0	5799.0	
Percentage Change from					
HV Coal. No additive.		2.5	1.7	1.8	
Deviation from the mean					
of two runs (s)		0.5	7.0	13.0	
				LV2 Coal	
	1.1/2		LVZ CUai	LVZ CUdi	
			+ 10%	+ 10%	
LV2 Coal plus 400°C Ash:-	Coal. No		LV3	HV	+ 10%
	additive		400°C	400°C	Dolomite
			Ash	Ash	
t₅o Combustion Time (s)	6162.0		6276.0	6261.0	6268.0
Percentage Change from LV2 Coal. No additive.			1.9	1.6	1.7
Deviation from the mean of two runs (s)	8.0		22.0	19.0	2.0

Table 31: TGA Coal Combustion of HV and LV2 Coal with selected ashes and dolomite.Relative Standard Deviations are given for duplicate runs.

7.3 Coke Gasification Experiments.

Coke gasification begins to occur in the blast furnace at 900°C and the rate increases with temperature. The reaction of coke carbon with carbon dioxide is known at the solution loss or reverse-Boudouard reaction and is shown in Equation 3; the product is carbon monoxide gas.

The reverse-Boudouard reaction is an endothermic reaction, and as well as temperature, the rate of reaction is highly dependent on the structure of the carbon. When the carbon is highly crystalline, it is less reactive. Additionally, pore structure plays an important role in determining the reactivity of carbon (Tomita, 2001).

In this thesis, gasification was performed in the TGA at 1100°C in carbon dioxide. This temperature was determined to be high enough that the reaction completes in around four hours whilst allowing differences in reactivity to be identifiable. This condition is typical of those used by other authors when performing coke gasification (Nomura, et al., 2006; Gupta, et al., 2008).

Figure 72 shows the reaction of coke with no additive and with 100 ms char ash from LV2, LV3 and HV. The reaction of coke with no additive is the slowest, however with addition of the char ashes, the rate is increased. Coke with no additive takes 5599 seconds for t₅o to occur. With the addition of 100 ms char ashes, this reduces to 5425.5 seconds, 4702.0 seconds and 4768.0 seconds for LV2, LV3 and HV, which represents a percentage decrease in t_{50} of 3.1 %, 16.0 % and 14.8 %, respectively. LV2 was expected to have a low catalytic activity in accordance with its elemental analysis and the literature. It can be seen that the catalytic effect of LV3 and HV on coke gasification was significantly higher than LV2, and this is likely owing to the high content of catalytic components such as calcium, iron and alkalis. These findings are consistent with the literature where gasification rate increases with the sum of the basic components in ash (Ozer, et al., 2017). It should be reiterated at this point that the catalytic gasification of coke is generally not a desirable property to have in the blast furnace as this leads to a reduction in the size of the coke and the increased generation of fines, both of which decrease the permeability in the blast furnace (Díez, et al., 2002).



Figure 72: TGA Gasification of coke mixed with 10% of 100 ms DTF Char Ash from selected coals.

Figure 73 shows the reaction of coke with no additive and with 700 ms char ash from LV2, LV3 and HV. The trend is similar to that of the 100 ms char ash additives as shown in Figure 72, where LV2 is a less effective catalyst than LV3 and HV. This behaviour is similar to that observed at 100 ms, and it appears that there was not a significant difference in reactivity between the different residence time char ashes.



Figure 73: TGA Gasification of coke mixed with 10% of 700 ms DTF Char Ash from selected coals.

Figure 74 shows the mass loss curves for coke gasification with 100 ms LV2 char ash and 700 ms LV2 char ash. The curves show that there is no significant difference between the two. The results from LV3 and HV char ashes at 100 ms and 700 ms are similar. In terms of the blast furnace, this means that changes in char residence time in the raceway are unlikely to have a strong effect on the reactivity of the ashes produced.



Figure 74: TGA Gasification of coke. Comparison of 100 ms with 700 ms LV2 DTF Char Ash.

Figure 75 shows a comparison of the gasification rates for coke with no additive, compared to coke with: ground slag; LV3 100 ms char ash; and dolomite. The increased reactivity observed with ground slag is interesting because this indicates that the environment in which the coke below the cohesive zone finds itself is intrinsically catalytic. Coke strength after reaction (CSR) test is performed to determine how a coke might behave in the reactive environment of the blast furnace, especially at the bottom where weakening due to its reaction throughout the furnace may lead to the generation of fines. This test is performed by reacting a sample of coke in carbon dioxide at 1100°C for 2 hours and then tumbling the reacted sample in a drum, thereafter determining the proportion of fines (Nomura, et al., 2007). The reaction does not occur in the presence of a catalyst, however the findings of this TGA work show that coke reactivity in slag is likely greater than under CSR test conditions. This may be important to consider when selecting coke, as coke reactivity in the presence of catalytic materials might present a more objective assessment when the material is used in the blast furnace environment where catalytic materials are present.

In Figure 75, dolomite shows the greatest effect on increase in reactivity, compared to the other additives. However, there is a feature in the mass loss curve at the early stages of reaction. It can be seen that there is a mass decrease at around 2000 seconds followed by a mass increase at around 3000 seconds for the "Coke + 10% Dolomite" curve. This is due to dolomite decomposition followed by partial carbonation at 3000 seconds, which leads to a subsequent increase in mass. In CO₂, dolomite decomposes into MgO and CaO at 700°C, with a mass reduction. Carbonation of this decomposed CaO occurs leading to the formation of low crystallinity calcite (CaCO₃), with a subsequent mass increase. This material then decomposes at 925°C and the mass reduces again (Valverde, et al., 2015). Since gasification was carried out in carbon dioxide, this has led to the decrease then increase of mass observed in Figure 75. By comparison, the reaction of coal in air with dolomite additive in Figure 70 and Figure 71 does not show this behaviour.

LV3 100 ms char ash, which was shown to be reactive in previous work is less reactive than dolomite but more than slag, which was to be expected.



Figure 75: TGA Gasification of coke. Illustrating the effect of dolomite and ground slag additives.

The data for the TGA gasification experiment are shown in Table 32. All tests were performed in duplicate, and although low deviation from the mean is consistent for all duplicates, the error is slightly greater than for the combustion experiments. In terms of percentage time, the deviation for the duplicate runs was usually lower than one percent, with a range of 0.11% to 1.42%. This low level of error gives confidence in the findings of the TGA gasification experiments.

Gasification reactivity of coke was catalysed by the addition of all the additives tested. The additive with the most catalytic effect on coke gasification in the TGA was dolomite which reduced the t_{50} by 30.0 %. The next most reactive additives were LV3 and HV DTF char ashes, which reduced t_{50} gasification time by around 15%. It was observed that the char ash residence time (100 ms and 700 ms) did not have a strong influence on the catalytic effect of these ashes. In terms of the blast furnace, this means that the ash retains its catalytic effect on gasification regardless of its residence time in the raceway. As expected, LV2 was a less effective catalyst on the gasification of coke and a t_{50} reduction of 2% to 3% was observed.

The behaviour of slag was interesting as this reduced the t_{50} by around 4%, which was more than the effect of LV2 char ash. It is perhaps unintuitive to think of slag in terms of a catalyst, but looking at the ICP oxide content in Section 4.5.1 shows the slag to have a CaO content of 34% and an MgO content of 6%, but a low iron content of 0.55%. In terms of composition, this is most similar to the dolomite, but evidently, the chemical structure is very different. Likewise, the structure of char ash must be different from that of slag. The calcium and other catalytic components in slag are fixed into aluminosilicates, and possibly as sulphides, so they are not available in the same form as in dolomite and the ashes. Deactivation of potassium catalyst due to interaction with inherent aluminosilicates as observed by Radovic, et al. (1984) supports the theory that the calcium in slag is not in a very catalytic form. Moreover, it was discussed (Mckee, 1983) that carbonates, oxides and hydroxides are effective catalysts. Slag does not match this description.

Table 32: TGA Coke Gasification with DTF char ash additives, dolomite and ground slag. Relative Standard Deviations are given for duplicate runs.

	Coke. No additive	Coke + 10% Dolomite	Coke + 10% Ground Slag				
t₅o Gasification Time (s)	5599.0	3918.5	5380.5				
Percentage Change from Coke. No additive.		-30.0	-3.9				
Deviation from the mean of two runs (s)	34.0	4.5	31.5				
100 ms Char Ash Tests:-	Coke + 10% DTF LV2 Char Ash 100ms	Coke + 10% DTF LV3 Char Ash 100ms	Coke + 10% DTF HV Char Ash 100ms				
t₅o Gasification Time (s)	5425.5	4702.0	4768.0				
Percentage Change from Coke. No additive.	-3.1	-16.0	-14.8				
Deviation from the mean of two runs (seconds)	25.5	7.0	44.0				
700 ms Char Ash Tests:-	Coke + 10% DTF LV2 Char Ash 700ms	Coke + 10% DTF LV3 Char Ash 700ms	Coke + 10% DTF HV Char Ash 700ms				
t₅o Gasification Time (s)	5497.5	4668.0	4823.5				
Percentage Change from Coke. No additive.	-1.8	-16.6	-13.9				
Deviation from the mean of two runs (s)	65.5	22.0	68.5				

7.4 Chapter Summary

There are many accounts in the literature detailing the effect of alkalis and transition elements on gasification reactivity. However, the effect of these elements on combustion was less certain and the coal combustion work in this chapter provided useful information in this area. Ash is known to contain catalytic elements such as calcium, iron and alkalis, and the effect of ash on blast furnace feed materials was investigated in this chapter. During coal combustion in air, it was found that ash did not have a significant effect on combustion reactivity in the TGA, and that it was not catalytic. The effect of ash was slightly negative with a 1% to 2% reduction in t_{50} for all the additives tested, including dolomite. This negative effect

was considered to be the energy requirements to melt and to decompose the additives, rather than a definite inhibitory effect.

Coke gasification in carbon dioxide was performed with additives of LV2, LV3 and HV DTF char ashes, ground slag, and dolomite. The reaction with additives was compared to a control where no additives were used. With the addition of additives the t₅₀ time was reduced in all cases, hence there was an increase in gasification reactivity. The reaction with dolomite was the most catalytic with a 30% reduction in t_{50} gasification time. The reactivity of the DTF char ashes was dependent on the ash chemistry where ashes with the highest content of iron, calcium and basic components showed the greatest catalytic effect on gasification reactivity. LV3 and HV decreased t_{50} by around 15% whereas LV2 decreased t_{50} by only 2 to 3%. 100 ms and 700 ms char ashes were used and it was found that this had little effect on the catalytic ability of the ash, thus, the effect of ashes was highly dependent on their ash chemistry. It has been discussed that breakdown of coke lower down in the blast furnace can lead to problems with permeability. Thus, increased gasification reactivity of coke is generally seen as negative behaviour. The findings of this chapter regarding the effect of ash on coke gasification reactivity are of interest to blast furnace operators who are looking to minimise the effects of ash catalysis on coke gasification when choosing different coals for injection. Increased rates of coke gasification due to the catalytic effects of ash may be responsible for coke degradation in the back of the raceway (the bird's nest) and further into the deadman. Conversely, according to Zou et al. (2017), the effect of char and ash may not be so negative, since unburnt char reacts preferentially to coke which protects the coke surface, and a small amount of ash on the surface may not enter the pore surface, but instead protect the coke, however it is observed that prolonged interaction between coal ash and coke surface leads to increased pore size with subsequent reduced coke strength. The fluidity of the ash was determined to be an important factor in penetration into coke pores, so this would be an additional factor to study in future ash catalysis work. The results from Chapter 6 relating to the agglomeration and increasing particle size of lower melting temperature ash links well with this chapter, where it might be expected for the catalytic material to be more likely to travel into the bird's nest area.

During gasification in carbon dioxide, addition of ground slag to coke led to a t_{50} decrease of 3.9% which was greater than LV2 char ash. This behaviour was interesting because slag is not associated with being a catalyst, however, the

elemental composition of the slag used in this thesis was similar to dolomite with around 34% of CaO as determined from ICP analysis, yet the effect on coke reactivity was significantly less than that of dolomite. This indicates that the chemical form of calcium in dolomite is very different from the chemical form in slag, where it is expected to be incorporated into aluminosilicates. This finding is similar to that of Chapter 4 where the elemental composition of ashes was insufficient to solely determine ash fusion temperature which also was found to be dependent on the chemical structure of ash constituents. The catalytic effect of slag on coke gasification brought about an interesting point about coke strength after reaction (CSR) testing. CSR is performed in a non-catalytic environment, but coke within the blast furnace is surrounded by catalytic materials such as iron, calcium and alkalis. If even the slag has been shown to be catalytic, then perhaps catalysis is an important aspect to consider when determining coke strength. According to Tomita (2001), the reaction between coke and carbon dioxide occurs at it fastest in the melting zone of the blast furnace, which is partly attributed to high alkali concentration. Clearly the catalytic environment that exists within the blast furnace is different from the CSR test conditions.

Char burnout in the raceway is an important factor in the blast furnace, and the effect of partially burned chars as they travel outside of the raceway is a matter of interest and concern (Steer, et al., 2018). There is a reducing environment outside of the raceway where partially burned char can be expected to gasify in the same way as investigated with coke. Although char gasification was not investigated in this thesis, it is clear from the increased reactivity seen in coke mixed with ash, that chars are likely to display similar behaviour under gasification conditions. It has been observed that ash acted as a diluent under combustion conditions, which is an undesirable effect. However, char gasification reactivity outside of the raceway may be increased as a result of ash. If this potential increase in char reactivity due to ash is greater than the diluting effect of ash during char combustion, then there is a net benefit. This is an effect that needs to be considered in more detail, but it does provide a positive impact to the presence of ash in coals that blast furnace operators might wish to consider. However, any benefit of increased char reactivity may not outweigh the negative effects observed in increased coke gasification reactivity. This would be challenging to quantify in real life and would require extensive multi-facetted correlation in the blast furnace conditions. Therefore, the findings of this chapter present useful information to consider in the context of the blast furnace, but with no definitive answer as to the overall effect of ash.

The reactivity of the thesis coals when tested for burnout in the DTF could be correlated closely with their volatile matter content. The lowest volatile coal, namely LV1, had the lowest rate of burnout and the burnout of the successive thesis coals occurred in sequence with their volatile matter designation i.e. LV2, LV3, MV, HV. However, there was some overlap between LV3 and MV, which was likely due to a difference in particle size. Using the information within this thesis and in this chapter, and in light of the TGA investigation of the effect of ash on combustion, it is clear that the ash within the coal is having little to no impact on combustion, and is likely acting as a diluent. Therefore, the volatile matter metric commonly employed by blast furnace operators is a good measure of coal reactivity in terms of combustion.

Chapter 8: Discussion and Conclusion

8.1 Relating the Academic Findings to the Blast Furnace

This thesis assessed the impact of coal mineral matter on the blast furnace by performing extensive testing in the laboratory and relating these findings to processes and effects in the blast furnace. The following is a discussion surrounding the findings of this thesis. It describes how the effects observed due to the ash properties are often interrelated.

Mineralogy and elemental composition of coal ashes was analysed and linked to ash fusion temperatures. It was determined that elements such as silicon and aluminium were responsible for high ash fusion temperature, whereas elements such as iron, calcium and magnesium were responsible for low ash fusion temperature. Increased proportion of carbonate minerals was linked to lower fusion temperature. In addition, increased proportions of clay minerals were linked to high fusion temperature. It was also observed that other sources of calcium such as fluorapatite reduced the ash fusion temperature, where the clay content otherwise suggested a high melting temperature. This highlighted the importance of calcium compounds in particular. It was also determined that elemental and mineral analyses could not be correlated with fusion temperature in all cases owing to the complexity of the ash system, and this was especially true of LV3 which in spite of having a high iron and calcium content, had a higher than expected fusion temperature. For the blast furnace operator looking to control slag chemistry, the elemental composition of the PCI ash is an important consideration. Following careful study of the literature, the effect of ash fusion temperature was linked to the blast furnace. It was suggested that high fusion temperature ash particles that are blown into the coke surrounding the raceway might adhere to the coke and cause adhesion between coke lumps leading to a reduction in gas permeability, whereas low fusion temperature ash would be more likely to run off of the coke and enter the slag (Khairil, et al., 2002).

An observation was made regarding the mineral composition and the volatile matter yield of the coal. It was proposed that with decreasing coal rank (increasing volatile matter yield), the amount of calcium and magnesium carbonates (calcite and dolomite) increased, while the amount of clays decreased. Aside from reduced fusion temperature with increasing carbonates, as already discussed, the presence of carbonate material was linked to other notable behaviours observed in the

thesis. These included the ability of calcium carbonates to fix sulphur into the ash phase, and the catalytic effect of calcium on coke gasification. For LV3, MV and HV at high DTF temperature and residence time of 1300°C, 700 ms, there was less sulphur released than at 1100°C 700 ms, which indicated that the calcium from carbonates were responsible for fixing sulphur into the solid phase. For the coals with little to no carbonate mineral (LV1 and LV2) no fixing was observed under these conditions. LV3 which had the highest proportion of sulphur also showed the greatest ability to fix sulphur of all the coals. In addition, the readiness with which sulphur was released from coal ashes was observed to be dependent on the presence of calcium in carbonate form. LV2 contained minimal carbonate minerals, and released sulphur easily. LV1 contained calcium in the mineral fluorapatite, but swift sulphur release was observed under DTF and LECO furnace conditions. An ash's ability to fix sulphur was linked to the presence of anhydrite in the 815°C HTA. The link between the volatile matter, calcium-based carbonate content, and ability to fix sulphur is useful for the blast furnace operator seeking to use volatile matter yield is a convenient metric to assess whether sulphur is likely to enter the gas phase or be retained in the ash.

An additional finding in this thesis, related alkali retention to fusion temperature. In most cases, alkali volatilisation increased with temperature and residence in the DTF. However, it was observed in MV and HV that at 700 ms, there was less alkali volatilisation at 1300°C than at 1100°C, which was an interesting finding considering that volatilisation is expected to increase with temperature. It was proposed that the decrease in volatilisation was due to alkali retention by the partially molten ash that was determined to have existed under the high temperature, high residence time DTF conditions. It was also considered that magnesium content played a role in improved retention of alkalis because the occurrence of alkali retention behaviour was linked to increasing magnesium content in the ash. High magnesium content in slag has been shown to improve alkali retention (Yang, et al., 2000), however lower calcium in slag is also beneficial to alkali retention. It is suggested in this thesis that lower ash fusion temperature was the factor that facilitated alkali retention, therefore, the possibility to indirectly link the volatile matter metric to the fusion temperature may also be of interest in terms of providing a rough indicator as to whether alkali volatilisation might occur in the raceway. However, it should be noted that the sample set of the coals used in this thesis was small, and in order to gain more confidence in the relationship between coal volatile matter and mineral matter content, more different coals should be assessed. In this way, it may be possible for the blast furnace operator to be able to more accurately use the volatile matter designation as an indicator of potential sulphur release and alkali volatilisation in the raceway.

Having examined the different ash effects in this thesis, it was determined that several paradoxes were presented in terms of ash chemistry and desired outcome. For example, low fusion temperature ash is positive for blast furnace permeability, as it runs off the coke rather than sticking (Khairil, et al., 2002) but the catalytic chemistry of this type of ash is more likely to enhance the reactivity of coke as was observed from the TGA study in this thesis which compared the reactivity of different ashes on coke gasification. On the other hand, the same high calcium ash chemistry has potential for catalysing the gasification reactivity of unburnt char, which is beneficial to trying to fully utilise the coal that has been injected into the furnace.

The slag chemistry is a point of contradiction for the removal of alkalis and sulphur. Alkali into the slag requires an acidic slag that is high in silicon and aluminium and low in basic elements including calcium. In this regard, high fusion temperature ash such as LV2 would be beneficial as it contains higher proportions of silicon and aluminium, and so would alter the slag chemistry in favour of alkali removal. On the other hand, the removal of sulphur requires a basic slag with a high calcium content, and hence calcium rich and low fusion temperature ashes such as LV3 and HV might be more appropriate. Regarding the ash behaviour itself, high calciumbased carbonates are effective at converting the sulphur into anhydrite form, as observed in this thesis, and to calcium sulphide, as determined from literature. Additionally, high calcium ashes typically have lower fusion temperatures, which in the drop-tube furnace study, improved the retention of alkalis. This seems inconsistent with the first point of this paragraph explaining that slag chemistry should be low in calcium. However, the difference in composition between slag chemistry and ash chemistry is different. The slag investigated in this thesis contained 34% calcium, whereas a "high calcium" ash in this thesis was around 10% calcium, therefore, it is conceivable that alkalis can be fixed into a coal ash, however, it is expected that lowering the calcium of a coal ash would improve alkali retention, all other things being equal.

An important point regards the behaviour of ash during combustion in the raceway. It was considered that the presence of ash within a coal could be catalytic during combustion, however following an investigation in the TGA, it was determined that

this was not the case and that the ash was, at best, acting as a diluent that required additional energy to heat up and decompose. In terms of coal combustion in the blast furnace raceway, it recommended to minimise the mineral content of the coal as it did not appear to offer any improvement in combustion performance. The volatile matter metric commonly employed by blast furnace operators is a good measure of coal reactivity as determined in the DTF burnout charts.

Coal abrasiveness was positively correlated to coal particle size. Ashes were around five times as abrasive as coals under the conditions of the testing in this thesis. In terms of coal handling it is expected that the quartz and pyrite contents are the most likely contributors to wear, and this was inferred from the relative abrasiveness of muffle furnace ash compared to coal, as well as information from Raask (1985). It should be noted that although correlations between particle size and quartz content were made in this thesis, the abrasion measurement of relatively low abrasiveness substances like coal was challenging to determine accurately. Due to the high abrasiveness of ash compared to coal, it was determined that blast furnace tuyere wear was more likely to be due to the ash from the coal or char in that region, where the most abrasive constituent of ash at these temperatures is quartz. It was known from Chapter 4 that the formation of mullite and aluminosilicate glass occurs in the DTF and increases with residence time. Mullite is a hard mineral with a high melting temperature that forms from kaolinite and illite clay, and aluminosilicates are relatively hard glasses that form from the products of clay calcination. Clays are soft minerals, so the effect of DTF heating conditions was to transform soft minerals into a more abrasive material. DTF char ashes were investigated and at low residence time they were more abrasive than muffle furnace ashes. However, at high residence time, the abrasiveness decreased. In light of the findings of mineral changes due to heating, this decrease was counterintuitive, however, under the SEM it was observed that abrasiveness decreased due to the formation of fused aluminosilicate beads, which were less abrasive due to their round shape. Abrasion due to ash was determined not be a significant problem in the blast furnace, due to fusion effects where the ashes are likely to be soft, or even liquid.

An increase in ash particle size was observed with increasing DTF temperature and residence time, however the extent of this increase was related to the fusion temperature of the ashes. The increase in particle size with residence time was greater for lower fusion temperature ashes due to higher levels of agglomeration.
For higher fusion temperature ashes, the increase in particle size was more gradual owing to lower levels of agglomeration. It was suggested that this behaviour might govern the path of ash through the raceway, where larger, heavier agglomerated particles might be more likely to travel in their initial direction of travel given by the hot blast and land in the back of the raceway. Meanwhile, the higher fusion temperature ashes that were less susceptible to agglomeration might be more likely to follow the direction of gas flow in the blast furnace. It was determined that this might lead to a form of ash segregation where the lower fusion temperature, more catalytic ash is blown to the back of the raceway and the higher FT, less catalytic material either becomes caught in the cohesive zone, or travels further up the furnace. If this effect does occur, it could affect the size of the raceway, the chemistry of the cohesive zone, and the nature of the ash found further up the furnace and within the flue dust. This particle agglomeration effect is interesting because it relates to the fusion temperature of the ash which relates to the original mineralogy and chemistry of the coal.

8.1.1 Elemental Considerations for the Blast Furnace

The effects of the different elements in mineral matter were studied in this thesis through experimentation and literature. It is important to evaluate the effects of each element to answer the question of which are desirable, and which are undesirable. Alkalis in the gas phase in the blast furnace are responsible for many negative effects and can accumulate if the slag chemistry is not appropriate for their removal. This makes it especially important to monitor alkalis and take steps to ensure that they are removed as part of the slag. Sulphur enters the blast furnace in relatively low concentrations, yet sulphurous gases are responsible for negative effects in the blast furnace and reduce the quality of the hot metal. It is beneficial for sulphur to leave in the slag. Magnesium has several positive effects in the blast furnace. Magnesium reduces the viscosity and liquidus temperature of the slag which helps to remove silicon and sulphur from the hot metal. Magnesium helps to maintain alkalis in the slag. Calcium has been shown in this thesis to reduce ash fusion temperatures, which should improve slag formation. It was also determined that calcium provides favourable conditions to fix sulphur. Calcium increased coke gasification reactivity, but potential increase in reactivity of partially burned chars would be beneficial. Silicon and aluminium do not share the same negative effects as alkalis and sulphur, but are responsible for higher ash fusion temperature which may affect the ashes' ability to run off the coke and become part of the slag. Phosphorus is negative element and nearly all of it reports to the hot metal, as described in the literature and deduced, in this thesis, from the absence of phosphorus in blast furnace slag and clarifier scum from the wet gas cleaning process.

Having assessed each element, it can be deduced that some of the elements do not possess any positive properties. Amongst these are potassium, sulphur and phosphorous. Sodium has potential for desulphurisation but it is considered that this is outweighed by its negative behaviour; additionally, there are more positive alternatives such as calcium and magnesium for sulphur mitigation. In terms of recommendations for blast furnace practice, phosphorus and alkali input should be minimised; analysis of the coal blends in Section 4.5.3 shows this to be already the case. Sulphur should also be minimised, but calcium and magnesium are able to manage the negative effects of sulphur.

8.1.2 Summary

The study of the effect of mineral matter from pulverised coal injection in the blast furnace has enabled observation of the many different effects that can occur due to the composition of elements and minerals in coal mineral matter. This thesis has shown that observed effects can be related to the initial composition and mineralogy. A larger sample set of coals and additional test conditions will make it possible to gain more insight and more confidence in the results obtained in this thesis. From an industry perspective, it is undesirable to have to perform extensive analysis to understand a coal sample. The tools used in the PhD have enabled an understanding of the effects of temperature and residence time on the constituents of the ash. It is hoped that with information about the volatile matter content, elemental composition and mineralogy, the blast furnace operator will be able to make more informed decisions about the types of coals that they are injecting into their blast furnaces.

8.2 Implications for Industry

Having performed an extensive experimental study into ash behaviour at high temperature, there are experimental outcomes that can be applied to industry and some recommendations that can be made.

In the sample set of coals tested in this thesis, there was a link between the volatile matter yield of the coal and the types of mineral matter present in it. It was found that with increasing volatile matter yield, coals possessed an increasing proportion of carbonate minerals such as calcite and dolomite and a decreasing proportion of clays such as kaolinite and illite. This could be related to ash fusion behaviour where high clay, low carbonate ashes had higher fusion temperatures. Coals with carbonate-rich mineral matter were able to fix sulphur into the solid ash phase, and these sulphur compounds were tightly bound to the ash, even under high temperature conditions. Coals with low carbonate content were unable to fix sulphur. Blast furnace operators looking to improve the tendency for sulphur to remain in the solid phase may wish to choose coals with high carbonate content, and according to this work, with high volatile content.

The importance of the link between mineral matter composition and volatile matter is that blast furnace operators may attain an indication of the mineral behaviour based upon the coal volatile matter yield. It is recommended that blast furnace operators create a record of all the coals that they use with the proximate analysis, mineral analysis and elemental analysis as key information. Using this information, it would be useful to correlate the volatile matter yield with the mineral composition, namely, clay and carbonate content. This will build upon the work in this thesis and allow blast furnace operators to attain a more comprehensive understanding of their injection coals, and to look for trends, as they add more coals to the record.

This PhD has used a DTF to investigate the effect of high temperature on mineral matter behaviour and interactions that occur within the mineral matter. The temperature in the DTF is lower than in the raceway and this is a point of contention with blast furnace operators. In this thesis, the limit of mullite formation appeared to be reached in the DTF at 1300°C so it may not be necessary to perform even higher temperature tests. Coal mineral matter undergoes amorphisation with increasing temperature to form aluminosilicate glass and other mineral phases. Higher temperatures would give additional information but it is clear from this thesis that mineral behaviour could be established at the temperatures tested. Moreover, to an extent, increased residence time did act as a proxy for increased temperature.

The temperature in the raceway is likely to have a strong effect on alkali and sulphur volatilisation. A high raceway temperature is required to maximise coal combustion and to minimise the effects of partially burnt char carryover. Hence, an effective means of reducing alkali input into the blast furnace would be to select low alkali coals, because this does not involve interventions that alter the blast furnace

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operating parameters. High silicon and aluminium ashes are more effective at maintaining alkalis in the solid phase.

In terms of the physical properties, higher coal and ash particle size is responsible for greater levels of abrasive wear. Ash agglomeration may influence the path of ash in the blast furnace. Ash agglomeration was related to fusion behaviour.

Regarding potentially catalytic behaviour, in this study, ash had no impact on combustion behaviour, merely acting as a diluent. Coals with mineral matter that contain a high proportion of calcium and iron increase the gasification reactivity of coke. Coals that contain a low proportion of catalytic elements exhibit a far lower tendency to catalyse gasification. Therefore, coals with catalytic ashes can be expected to increase the char gasification reactivity which will be beneficial for the consumption of partially burnt char in other parts of the blast furnace.

The desire for a given positive property must be tempered with the possibility of a negative property, for example high volatile coals may combust faster, and have other positive properties, but these types of coal have a lower coke replacement ratio, and are less effective at fixing alkalis. However, there is the potential for magnesium to have a positive effect in the blast furnace in terms of being able help fix both alkalis and sulphur, but this requires further investigation.

In short:

- Low volatile coal, high clay minerals, low carbonate minerals, high silicon and aluminium, higher fusion temperature, ability to retain alkalis in the solid phase, weak catalytic properties.
- 2. High volatile coal, low clay minerals, high carbonate minerals, high calcium and iron, lower fusion temperature, ability to fix sulphur in the solid phase, catalytic properties.

8.2.1 Assessment of the Five Thesis Coals

The following is an assessment of the five coals used in the thesis. The information given below is drawn from the test methods used in this thesis, and serves to provide the blast furnace operator with a convenient reference for the type of behaviour observed in each of the coals.

<u>LV1</u>

Least reactive of all the coals in the DTF.

High clay content, especially kaolinite, with strong mullite formation. Likely low quartz.

High aluminium, potassium and **phosphorus**. Lowest sulphur and magnesium of all the coals.

No carbonates observed on XRD, hence low ability to fix sulphur.

Sulphur readily lost into the gas phase on LECO furnace, however low initial sulphur.

Increased temperature and residence time did not appear to increase potassium volatilisation.

Moderate ash fusion temperature of 1300°C, likely due to mineral calcium phosphate (fluorapatite).

Moderate ash abrasiveness. Large ash particle size.

<u>LV2</u>

Low to moderate coal reactivity.

High silicon and aluminium. Very low calcium. Low iron, magnesium, potassium and sulphur.

High clay and likely high quartz content, low carbonate content.

Very high fusion temperature 1526°C.

Sulphur readily lost into the gas phase on LECO, however low initial sulphur. Some sulphur retained as anhydrite in 815°C ash, however limited ability to fix sulphur.

Moderate tendency to volatise potassium.

Most abrasive of all ashes tested. More abrasive at high temperature due to high AFT.

Low catalytic effect on coke gasification.

<u>LV3</u>

Reactive in the DTF.

High calcium, iron and sulphur. Moderate magnesium and potassium. V. low phosphorus.

Strong tendency to potassium volatilisation.

Low to moderate silicon and aluminium.

High calcite and likely low quartz.

Moderate fusion temperature 1316°C. FT not predictable with acid to base ratios.

Strong ability to fix sulphur.

Low abrasiveness. Low ash particle size.

High catalytic effect on coke gasification.

MV

Reactive in the DTF

High silicon. Moderate aluminium, potassium, sulphur

Low iron and sodium.

Low to moderate calcite, moderate dolomite.

Moderate clay and quartz.

Moderate fusion temperature 1298°C.

Low tendency to volatilise potassium

Strong sulphur fixing behaviour in the LECO, less strong in the DTF.

Moderate ash abrasiveness.

HV

Very reactive in the DTF

High carbonate content. High dolomite. Low clay. Moderate quartz.

Low aluminium and potassium.

High calcium, magnesium and sodium. Moderate high sulphur and iron.

Low to moderate alkali volatilisation.

Low to moderate fusion temperature 1194°C.

Strong sulphur fixing behaviour in the LECO, less strong in the DTF.

High catalytic effect on coke gasification. Marginally lower than LV3.

Moderate ash abrasiveness.

8.3 Conclusions

The conclusions are listed in this chapter in the form of bullet points. Four of the main conclusions that may be more valuable to blast furnace operators are written in bold text.

- Ashing at 400°C, medium temperature ashing (MTA) was a valuable technique to create an ash where most of the minerals original present in unburnt coal were still intact and possible to view as discrete minerals. This enabled them to be identified in the five thesis coals and then to be related to the elemental analysis and the properties of the ash.
- Investigation of MTA determined that the ashes contained quartz, kaolinite, illite, calcite, dolomite, fluorapatite, and likely gypsum.
- The mass of 815°C ash (HTA) was lower than 400°C ash due to loss of water and carbon dioxide from decomposition of kaolinite, calcite and dolomite. Decomposition of ash requires energy, and this may reduce combustion efficiency.
- The ash fusion temperature was affected by the elemental composition of the ash. High silicon and aluminium increased the chance of ash having a high fusion temperature, and high calcium, iron and alkalis were responsible for a lower fusion temperature. Acid to base ratios of these elements correlate with ash fusion temperature in many cases.
- The fusion temperature was affected by mineral composition of the ash, and this was directly related to the elemental composition. Minerals that were responsible for high fusion temperature included quartz, kaolinite and illite. Minerals that were responsible for lower fusion temperature included calcite, dolomite, and fluorapatite.

- In some cases, it was not possible to accurately predict the fusion temperature of an ash on the basis of its mineral and elemental composition. Ash behaviour is complex and related to other factors such as the interaction of the elements, minerals and amorphous material, so it cannot be possible to fully understand it based solely on mineral and elemental composition.
- Blending ashes did not lead to additive results for fusion temperature. This
 is important to consider since blast furnace operators use blended coals for
 injection. The behaviour of ash in the blend might be different and less
 predictable than original coals.
- A relationship was observed between coal volatile matter designation (LV1, LV2 etc.) and ash mineralogy and chemistry. Higher volatile coals possessed higher levels of calcium based carbonates, whereas lower volatile coals possessed greater levels of clay minerals. This was considered important for the blast furnace operator who seeks a convenient means of approximating the mineral behaviour of a coal without having to perform complex analysis.
- Drop-tube furnace conditions led to the formation of mullite in coal char ashes. Formation of amorphous material was also observed in the DTF. Both effects increased with temperature and residence time. The formation of mullite required 1300°C for 350 ms to form in non-oxidising gases such as nitrogen and carbon dioxide compared to 1100°C for 100 ms in air. This confirms the effect of temperature on mullite formation.
- Drop-tube furnace conditions resulted in char ashes that had higher melting temperatures, this was attributed partly to the formation of mullite, and partly to the increase in amorphous glass material. It was recognised that there are other factors that were not investigated in this thesis that affected the melting temperature.
- Alkali volatilisation was observed in the DTF and found to increase with DTF temperature, and to a lesser extent, residence time.
- Fixing of alkalis was observed in low fusion temperature ashes with high magnesium content. Magnesium content in ash may help to reduce the extent of alkali volatilisation.
- Sulphur from ash was released into the gas phase under DTF conditions and the effect increased with temperature and residence time.

- Ashes containing high calcium in the form of carbonates fixed sulphur, thus reducing the amount released into the gas phase. This effect was apparent in the DTF and in the LECO furnace. Anhydrite (calcium sulphate) was the mineral form of sulphur observed in 815°C muffle furnace ash and DTF char ash.
- The sulphur in blast furnace clarifier floating scum took high energy to remove in the LECO furnace. This represents a stable compound of sulphur that is possible to be iron sulphide.
- Abrasiveness of coal was correlated with particle size. It was not possible to correlate coal abrasion with the mineral matter composition.
- Abrasiveness of coal ashes was correlated with quartz content but it was also observed that particle size had an effect.
- Lower residence time DTF char ashes were more abrasive than muffle furnace ashes and this was expected to be due to the formation of mullite and hard aluminosilicate glasses. At high DTF residence time, ash fusion temperature affected the abrasion of DTF char ashes. Low fusion temperature ashes were able to form fused aluminosilicate beads which led to lower abrasiveness. The high fusion temperature ash retained higher abrasiveness owing to absence of fused glass beads.
- Particle size and bulk density increase with DTF temperature and residence time, but the effect is more pronounced for lower AFT ashes. These larger, heavier particles may be more likely to travel in the direction of the blast to the coke in the bird's nest and this might affect coke gasification reactivity, especially as low fusion temperature ashes have a more catalytic chemistry. The higher fusion temperature ashes are less likely to agglomerate into large, heavy particles which may mean that they are more likely to be swept upwards into the blast furnace.
- Coal grinding did not appear to reduce the size of mineral matter in proportion to the coal particle size specification. Thus it is concluded that the mineral matter particle size is more of an inherent characteristic of a coal. It may be possible to measure this in prospective coals to reduce the risk of coal plant abrasion by selecting coals with smaller particle size mineral matter.
- Addition of ash to coal was shown to marginally increase the time for coal combustion in the TGA. This was attributed to the energy requirement to heat it and decompose it. It was not attributed to a definite inhibitory

process. Dolomite, catalytic ash, and low catalytic ash all showed the same slight negative effect.

Addition of ash, slag, and dolomite was shown to reduce the time for coke gasification in the TGA. Dolomite showed a 30% reduction in t₅₀. Whereas catalytic ash was around 15%, non-catalytic ash was 2-3% and slag was 4%. The catalytic effect was mostly attributed to calcium content.

8.4 Suggestions for Future Work

Having performed many experiments and investigations to understand the effect of pulverised coal ash in the raceway, several areas were identified to improve the quality of the existing work and to advance the knowledge and understanding of the topics discussed in this thesis.

- A larger sample set of coals that shows a greater range of elemental composition and mineral composition would allow trends to be more confidently created, and to identify coals that do not lie within the behaviour of the trend. Furthermore, the work where ash fusion behaviour was correlated with mineralogy and chemistry would benefit from a larger number of samples. By extension, other conclusions drawn, such as the effect of sulphur fixing due to carbonate content, decrease in alkali volatilisation due to fusion temperature and magnesium content, the effect of ash fusion temperature on particle agglomeration, and effect of ash chemistry on coke gasification, would be reinforced with the use of more coal samples.
- A more robust method of XRD mineral quantification that takes account of amorphous material and effects such as the overrepresentation of the strength of the quartz peak would add confidence to quantification data.
- A greater number of blast furnace input and output materials, such as coke, iron ore, dust and sludge, that were used at the same time as the injected coals may allow some correlations to be drawn between the blast furnace materials flow, the properties of these materials, and the observed operational behaviour. Access to a range of these materials would enable a mass balance to be drawn between the input and output of materials which would be especially interesting for alkali and sulphur behaviour.
- Testing the effect of additives such as calcium compounds and sodium compounds on sulphur fixing in the solid or liquid phase as opposed to

being released in the gas phase, would enable greater understanding of the fixation observed in the carbonate rich ashes.

- Coals are injected into the blast furnace as blends. Therefore investigating the effects observed in this thesis regarding fusion temperature, sulphur behaviour, and alkali volatilisation in terms of blended coals would be relevant to the feed coals entering the blast furnace.
- Much of the work in this thesis was performed on samples of ash. In the case of ash analysis and fusion temperature, this is necessary, however there are many instances in the blast furnace where the behaviour of char is more likely to dominate. For instance, the effect of wear on tuyeres is likely to occur due to the action of a char, thus it would be useful to perform abrasiveness tests on chars. Investigating the effect of sulphur loss from chars in the LECO furnace would provide useful information in the context of chars. Moreover, there is likely to be a significant amount of char that is swept into the coke surrounding the raceway. Investigating the char interactions with coke, such as catalytic behaviour, is am important factor to consider.
- The LECO furnace was used to investigate sulphur release profiles. It could also be used to infer the forms of carbon by observing carbon release profiles. The forms of carbon are interesting because these can provide useful information about the relative reactivity of different types of char. This relates to char consumption within and outside of the raceway which is an important topic where the aim of coal injection is to utilise the chars to the maximum possible extent, and to reduce the amount of partially burned char accumulating in the blast furnace.
- Future work involving the investigation of sulphur and alkali release under a CO₂ environment would be valuable in determining these effects deeper in the raceway where a reducing environment dominates.

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