Identification of sintering and slagging materials: Characterization of coal, ash and non-coal rock fragments

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DECLARATION

I, Tshifhiwa Maphala declare that this research report is my own unaided work. It is being submitted for the degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

.....

(Signature of Candidate)

.....day of.....year.....

ABSTRACT

During a coal-conversion process, some components of the mineral matter in the coal such as organic minerals, organically-bound and inorganic elements and extraneous rock fragments may interact with each other to generate submicron ash particles, volatile compounds and ash clinkers, and can give rise to fouling, slagging, abrasion, stickiness and corrosion within coal conversion units.

It is proposed that some fluxing minerals such as pyrite, calcite, and ankerite and to a lesser extent dolomite or inorganic elements present in the extraneous rock fragments such as sandstone, siltstone, mudstone and carbonaceous shale could react with free aluminium silicates (clays) at elevated temperatures to form a melt, and contribute to the slagging problems during coal-conversion. In order to manage this, and hence to minimise its effects, it is important to better understand the chemical and mineralogical properties of the individual rock fragments included in the feedstock coal.

In this study, a detailed characterization of rock fragments was undertaken in order to better understand their chemical and mineralogical properties. A mineralogical characterization on the feed coal and corresponding ash clinker was conducted in order to understand the mineral composition, and compared to the determined mineralogy of rock fragments mineralogy.

Crystalline phases (minerals) qualification and quantification were determined using powder X-ray diffraction (PXRD). Different Rietveld based methods were used for quantification of minerals and compared to each other. Quantitative evaluation of minerals by scanning electron microscope (QEMSCAN) and normative methods were used as a comparative tool and confirmation of minerals discrimination. The major minerals determined were quartz, kaolinite and muscovite/illite with minor occurrences of feldspar in the form of microcline.

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LIST OF ABBREVIATIONS

AFT –Ash Fusion Temperatures

BSE – Back-scattered electrons

CCSEM – Computer Controlled Scanning Electron Microscopy

CQA – Coal Quality Assessment

CSIRO – Commonwealth Scientific and Industrial Research Organisation

EVA – Evaluation software

HTA – High temperature ashing

HT-XRD – High temperature X-ray diffraction

HS – Hemispheric temperature

ICP-AES - Inductively Coupled Plasma-Atomic Emission Spectroscopy

ICSD – Inorganic Crystal Structure Database

ID-Initial deformation temperature

LTA – Low temperature ashing

LOI –Loss on ignition

MAUD – Mineral Analysis Using Diffraction

PXRD – Powder x-ray diffraction

QEMSEM – Quantitative evaluation of materials by scanning electron microscopy

S – Spherical temperature

SEM – Scanning Electron Microscope

VAC – Van Alphen Consultancy

XRD – X-ray diffraction

XRF – X-ray Fluorescence

CHAPTER 1: INTRODUCTION

1.1 Coal quality

Coal is currently the number one global energy source with about 36 percent of the total fuel consumption of the world's electricity production. About 77 percent of South Africa's primary energy needs are provided by coal[1]. It seems unlikely that any other resource will overtake coal for at least the next 50 years. But coal as a resource faces its own challenges, as have been witnessed lately with the current power cuts (or "load shedding") in South Africa by the state's main power supplier, ESKOM. One of the main factors that were identified by ESKOM, was the low quality coals that the coal suppliers have been supplying[2]. ESKOM stated that "it had emerged that coal quality (its energy values, particle sizes and dryness) was a major problem for just about every power station at present....as proving to be the major reason for many of the unplanned outages or lower-than-normal generation performance" [2]. South Africa is not unique to the coal quality problem as it is a global problem.

To put the coal quality problem into context, coal should be understood as a chemical material rather than a mineral resource. Coal is defined as a heterogeneous solid and complex combustible layered metamorphic rock of >50% carbonaceous material[3]. The ≥50% material is carbonaceous shale and mineral matter. Figure 1.1 illustrates the relationship between coal quality and mineral matter composition. As the mineral matter in a coal increases, the quality of the coal decreases, as there is a lower percentage of combustible material per mass of coal. If the mineral matter content is >50% then the material is classified as carbonaceous rock or shale. The combusted mineral matter residue is commonly known as ash. In this report, these terms will be used in their correct context as graphically depicted in Figure 1.1:

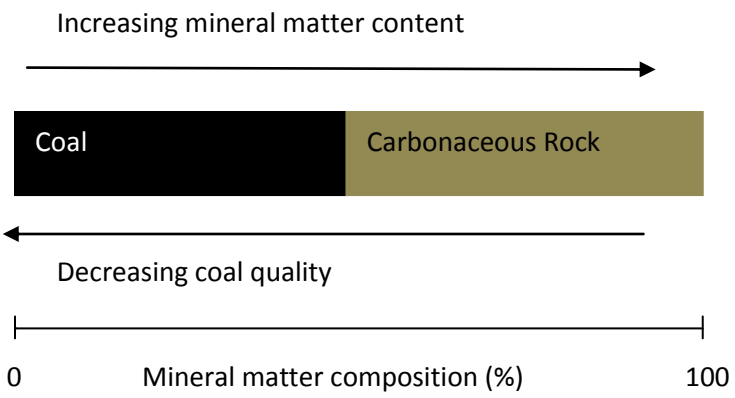

Figure 1.1: A scheme showing the relationship between coal quality and mineral matter composition

South Africa is endowed with large coal reserves but the majority of these reserves are rich in inorganic constituents (mineral matter), commonly referred to as high ash coals. The amount and type of inorganic constituents present in coal play a major role in the design, maintenance and availability of coal-fired plants[4]. With the current global demand for coal, most coal producers mine and beneficiate the remaining high quality coals for export and the low quality coals are used for local consumption, as in the example with the local power supplier. Snyman and Botha studied South African coal reserves and classified them according to grade (Table 1.1) [5]. As indicated in the table, the majority (>46%) of South African coal has >30% ash yield. With Snyman's work having been reported in the early 90's, a large proportion of the >30% ash yield is likely to have been mined. Most South African coal users are faced with the challenge of having to develop their coal conversion technologies such that they are able to cope with the high ash coal feedstocks.

Table 1.1: South African in-situ coal reserves according to grade[5]

	% Ash yield	% of reserves
	10 -15	1.6
	15 -20	10.5
	20 -25	18.7
	25 -30	23.1
	30 -35	46.1
Average	27.6	100

There are different coal grade requirements for different coal users (Table 1.2). For most users, <20% ash yield per mass of coal is required (except for Sasol-Lurgi gasifiers which can take coal of over 40% ash and certain ESKOM boilers which can take over 45% ash yield coals). South African reserves of <20% ash yield is very minimal if not depleted (Table 1.1) . Most of the coal users including ESKOM, Sasol, and smaller industries that use coal as a feedstock for their boilers, need to find ways of using the available high ash coals or face being out of business.

Table 1.2: Coal grade requirements for different coal users [5]

Use	% Ash yield
General trade	< 20
Blend and straight coking coal	< 14
Export: steam coal	< 16
Export: high grade coal	< 7.5

1.2 Problems associated with mineral matter in coal during coal conversion

Most coal conversion technologies (including combustion and gasification) face common challenges caused by mineral matter in coal; namely slagging, fouling and clinker formation. This is true for those coal conversion technologies that have not been designed handle slags. Slags and clinker are caused by the agglomeration of ash materials in boilers and gasifiers which occur as a result of mineral matter transformation, forming a melt at high temperatures.

The process of ash formation is an unavoidable product of combustion or gasification. There are essentially two factors controlling clinker formation, slagging and fouling in coal conversion processes; i) operating conditions of the coal converting process, and ii) the minerals that contain fluxing inorganic elements (K, Na, Ca, Fe, Mg, etc) in the coal[6]. During combustion, the mineral matter is transformed into fly ash, which is deposited on heat transfer surfaces in the downstream sections. Deposition of ash on furnace walls is called slagging when the deposit is in highly viscous state, forming a liquid layer, generally occurring in the radiant section. It is called fouling when the deposit is built up by the condensed species, forming a dry deposit, generally in the convective section[6] of the boiler. Clinkering is the process by which ash forms partially fused solid material.

The agglomeration of ash particles is not an entirely undesirable characteristic of ash as it provides the desired porosity of the ash bed for adequate agent (steam and oxygen) flow and distribution in certain coal processing units i.e fixed bed gasifiers[6]. It is when there is excessive slagging that channel burning, pressure drop problems or unstable operation is caused. This can result in cut backs on the coal processing unit load, which implies a direct loss in production[6]. In the design of coal conversion furnaces, boilers and gasifiers, one has to take into account the ash melting behaviour. Failure to do so can result in inefficient boilers, furnaces and gasifiers. In fact, all coal conversion technologies are designed on the predicted AFT ranges of the coal feedstock. Any feedstock that has AFTs outside that range can drastically affect the performance the technology.

Abrasion of mills is considered to be one of the technical issues associated with certain mineral matter in coal[7]. Quartz and to some extent pyrite are the main minerals suspected to be

associated with abrasion of mills[8]. In the actual furnaces or gasifiers, quartz is known to have a high fusion temperature of around 1800°C. This implies that quartz is non-reactive in gasification and combustion environments where maximum temperatures of 1600°C are reached. And because it is inherently hard mineral, course-grained quartz (non-spherical shaped) thus represents an abrasion or erosion hazard in gasifiers and combustion furnaces, and reports to the ash fractions[8].

With the current global emphasis on coal efficiency improvements and environmental sustainability, there is a great challenge for those in the coal industries to develop clean coal technologies. But clean coal technologies require a deep understanding of coal, including mineralogy and its behaviour at high temperatures. For example, the occurrence of sulphur (whether organic or inorganic, pyritic or elemental) is important as it has direct implications on its behaviour during coal conversion and SOx formation. The ability to characterise and understand mineral matter in coal will be great contribution in the fight against global air pollutants and other environmental issues associated with coal.

But the understanding of mineral matter in coal, just as in any engineering or science field, is only as good as techniques being used in the study of the material under investigation. The development of many analytical techniques has given engineers and scientists the opportunity to gain knowledge and understanding of mineral matter in coal, and the transformation of these minerals during combustion and gasification.

It is suspected that fluxing minerals (pyrite, calcite and to a lesser extent dolomite) or fluxing elements (e.g. K, Na, Ca, Fe, Mg) present in the extraneous rock fragments (sandstone, siltstone, mudstone and carbonaceous shale) could react with free aluminium silicates (clays) to form a melt and contribute to the slag or clinker formation during coal conversion process.

1.3 Aims and objective of study

This investigation forms part of a detailed project investigation on clinker formation in a coal conversion process. The aim of this investigation is to identify sintering and slagging components, leading to clinker formation, in non-coal rock fragments samples.

The main objective of this study is to undertake a detailed characterization of non-coal rock fragments, ash and coal to better understand their chemical and mineralogical properties. A secondary objective is to link this information to clinker formation in coal conversion processes, and hence to minimise their effects. X-ray fluorescence (XRF) and powder X-ray diffraction (PXRD) have been used for chemical and mineral characterization respectively. The ash and feed coal were characterized and minerals were quantified using Rietveld methods. The study focused on the science of mineral matter in non-coal rock fragments and not on the conversion technology.

CHAPTER 2: BACKGROUND AND LITERATURE REVIEW ON COAL MINERALOGY

In this chapter two coal processing technologies are briefly reviewed followed by a more detailed discussion on minerals in coal and associated strata, and analytical techniques to quantify and qualify the mineral matter.

2. 1 Coal conversion technologies

Two main coal conversion technologies are combustion and gasification. In South Africa, low grade coal is primarily used for power generation (combustion) and gasification (liquid fuels and chemicals).

2.1.1 Combustion

Combustion takes place when coal reacts with oxygen in air to produce heat. The heat created by the burning of coal is used in the operation of equipment such as boilers, furnaces, and kilns[7]. Along with heat, CO_2 (carbon dioxide) and H_20 (water) are formed as byproducts of the exothermic reaction. The heat generated is used to heat water and the steam generated is then used to turn turbines generating electricity. The chemical reactions (simplified) describing combustion is as follows[10]:

$C + O_2 \rightarrow CO_2$ + Heat……..(1)

$2H_2 + O_2 \rightarrow 2H_2O$ + Heat……..(2)

There are many varieties of coal being used in combustion processes around the world; the most widely used are anthracite, bituminous coal, sub-bituminous coal, and lignite. From equation 1 it is clear that burning coal leads to a considerable amount of carbon dioxide being generated.

2.1.2 Gasification

Coal gasification is the conversion of coal with insufficient oxygen to turn all the chemical energy into heat[8]. There are many gasification technologies, but the commercial scale technologies all fall under the umbrella of three gasification technologies, namely i) fixed-bed (also known as moving-bed), ii) fluidized –bed gasification, and iii) entrained flow gasification . Apart from underground gasification, most gasification technologies are a modified version of the above mentioned gasification technologies.

2.1.2.1 Fixed-bed gasification

Fixed bed (or moving bed as referred to in the United States) gasification consist of beds of fuel through which the air or oxygen for gasification is blown[11]. The solids move slowly towards the bottom of the gasifier, transforming the mineral matter in coal to ash/slag on the way. In counter-flow versions, the gas exits at the top of the gasifier[6] (Figure 2.1)

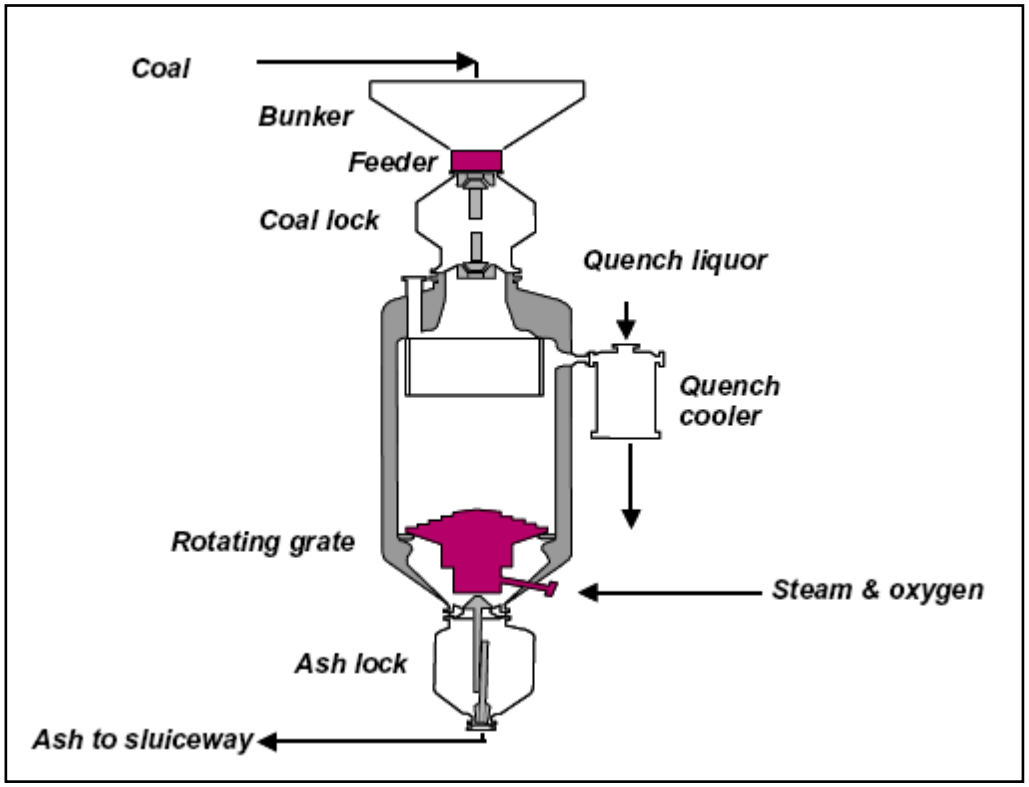

Figure 2.1: An example of a fixed-bed gasifier: Sasol–Lurgi fixed bed dry bottom (FBDB) gasifier[12]

2.1.2.2 Fluidised-bed gasification

Fluidized beds use coal crushed to a few millimeters in diameter[13]. The particles are kept in motion by blowing air or oxygen through the particle bed. Most of the bed material can be (and usually is) ash. Limestone can be added to remove sulphur during the gasification process. Careful temperature control and good mixing of the bed are required to achieve adequate rates for the gasification reactions without local overheating and slagging of the fluidized bed. It is difficult to achieve high carbon conversions with this sort of gasifier unless the coal is of high reactivity or a circulating system included. It is perhaps best suited to low-ash brown coals, particularly if the ash is sufficiently alkaline to retain the sulphur[14]

2.1.2.3 Entrained flow gasification

Entrained systems use pulverized coal blown into the gasifier vessels in a similar manner to pulverized coal powered stations. Oxygen or highly enriched air is the usual oxidizing agent, rather than air. A low nitrogen concentration is important as the gasifier exit temperature is high, meaning a high ratio of sensible heat to chemical energy in the product gas. Nitrogen further increases this sensible heat/chemical energy ratio and hence is particularly undesirable in this form of gasifier. High temperatures are achieved which usually means good carbon conversion efficiency, whatever the fuel, and the production of molten ash. The technology has developed in parallel for coal, petroleum coke and oil feedstocks[11].

The current growing demand for energy has led to renewed interest in the use of these 3 coal conversion technologies, as a possible replacement for oil as a source of energy. This means that much investment is being placed on the development and enhancements of these technologies. There are many challenges, including the behaviour of mineral matter.

2.2 Mineral matter in coal

A brief discussion on the occurrence, abundance and technological impact of major minerals in coals from both the Northern and Southern Hemispheres follows. It is assumed that Australian, Indian and South African coals are a good representation of the Southern Hemisphere coals and that the USA, Turkish and Bulgarian coals are a good representation of the Northern

Hemisphere coals. The mode of occurrence of these minerals requires discussion as this may have great implications on the characterization and utilization of the coal and on the behaviour of minerals at high temperatures.

There are more than 100 minerals that have been identified in coal [15]. Vassileva and Vassilev[15] studied minerals and mineral phases in Bulgarian subbituminous and bituminous coals and their oxidation and combustion products (Table 2.1, see next page). This table provides an indication of some of the major minerals that commonly occur in coals around the world. Coals differ significantly across the world) both organically and inorganically, with different coals have different mineral matter composition. Just as coals in the Southern hemisphere will differ significantly in maceral composition to Northern Hemisphere coals, so will the mineral composition differ. For example, in Southern Hemisphere coals the major iron-bearing mineral is usually siderite {$Fe(CO_3)$}, while Northern Hemisphere coals typically contain pyrite {FeS_2}[7,8].

2.2.1 Northern Hemisphere coals

Northern Hemisphere coals are known to be different from the Southern Hemisphere coals from a quality point of view. This is because that these coals formed at different geological times. Northern Hemisphere coals formed in the equatorial conditions in Carboniferous times (300-350 million years ago) whereas the Southern Hemisphere coals formed in cold to cool temperate conditions in Permian times (280-300 million years ago)[16]. Thus Northern Hemisphere coals are of older age and are more matured than the Southern Hemisphere coals. These times affect the depositional systems which are the current make-up of the mineral matter distributions in coals. This has resulted in the Northern Hemisphere coal generally having a lower percentage of mineral matter[16].

Table 2.1: Occurrence and probable origin of minerals and phases identified in Bulgarian subbituminous and bituminous coals and their oxidation and combustion products (OCPs)[15]

Mineral phase	Formula	Origin		
		Primary	Secondary	Tertiary
Sulphides				
Pyrite	FeS_2	•	○	
Marcasite	FeS_2	•		
Carbonates				
Calcite	$CaCO_3$	•	○	○
Dolomite	$CaMg(CO_3)_2$	•	○	
Ankerite	$Ca(MgFe)(CO_3)_2$	•		
Siderite	$FeCO_3$	•	○?	
Sulphates				
Gypsum	$CaSO_4{\cdot}2H_2O$	•	○	
Bassanite	$CaSO_4{\cdot}0.5H_2O$	•		
Anhydrite	$CaSO_4$	○	•	
Jarosite	$KFe_3(SO_4)_2(OH)_6$	•	○	
Oxides and hydroxide				
Hematite	$\alpha\text{-}Fe_2O_3$	○	•	
Magnetite	$FeFe_2O_4$	•		
Goethite	$\alpha\text{-}FeOOH$	•	○?	○?
Corundum	Al_2O_3	•		
Lime	CaO	•		
Silicates				
Quartz	SiO_2	•	○	
Cristobalite	SiO_2	•		
Tridymite	SiO_2	•		
Kaolinite	$Al_2Si_2O_5(OH)_4$	•	○?	
Illite+	$(KH_2O)Al_2$	•	○?	
	$(AlSi)Si_3O_{10}(OH)_2$			
Muscovite	$KAl_2AlSi_3O_{10}(OH)_2$			
Montmorillonite	$(NaCa)_{0.3}$	•		
	$(AlMgFe)_2Si_4O_{10}(OH)_2{\cdot}xH_2O$			
Chlorite	$(MgFe)_5Al_2Si_3O_{10}(OH)_8$	•	○?	
Plagioclase	$NaAlSi_3O_8\text{–}CaAl_2Si_2O_8$	•	○	
K-feldspar	$KAlSi_3O_8$	•	○	
Mullite	$Al_6Si_2O_{13}$	•		
Organic matter		•	○	
Amorphous		○?	•	
Clay minerals				
Glass		○	•	

Primary—original mineral in coal; secondary—new phase in OCP formed during coal heating; tertiary - new mineral or phase formed during storage of OCP.
(P—primary; S—secondary; T—tertiary;·•— dominant; ○ — subordinate)

2.2.2 Southern Hemisphere coals

Southern Hemisphere coals are known for their relatively high ash content as compared to Northern Hemisphere coals, which are known for their low ash content[17]. Snyman and Botha studied mineral matter in Highveld coals (Table 2.2)[5].

Table 2.2: A table showing the most abundant mineral matter in South African coals[5].

Mineral	Variation (%)	Median %
Illite	0 - 87	6
Kaolinite	0 - 45	16
Quartz	0 - 38	10
Calcite	0 - 24	4
Pyrite	0 - 10	4
Dolomite	0 - 9	3
Siderite	0 - 6	2

From Table 2.2, clay minerals (illite and kaolinite) are the most abundant mineral in South African coals, followed by quartz and sulphides with carbonates in the form of dolomite and siderite as the minor minerals.

2.2.3 Non-coal rock fragments

Coal mined typically contains additional mineral constituents derived from bands and other concentrations of non-coal material within the coal seam. The coal mined may also include some fragments of the non-coal rock derived from contamination of the mined product by roof or floor strata (Figure 2.2).

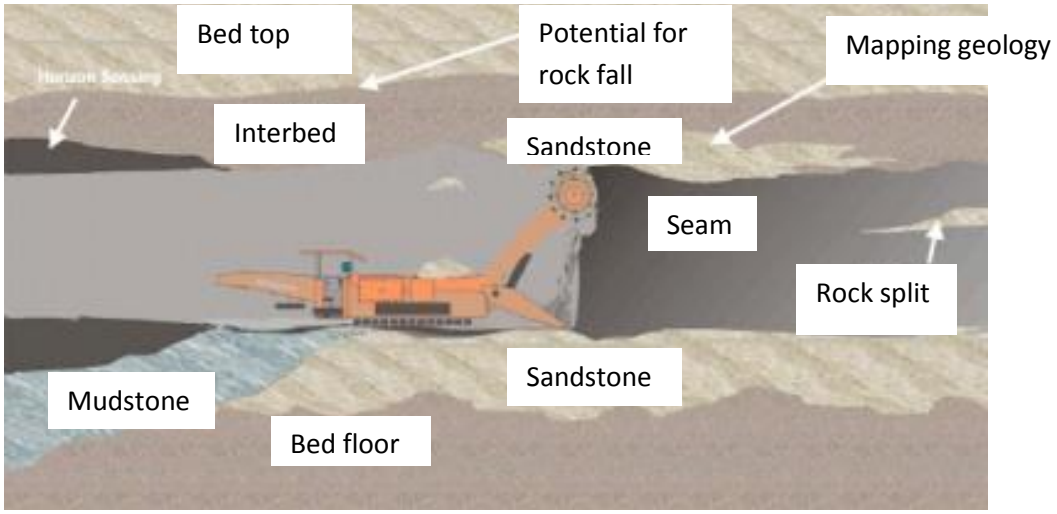

Figure 2.2: A cross-section view of coal strata showing the coal seam, interburden, and floor and roof, mudstone and sandstone[18]

Much of the non-coal mineral matter can be removed in beneficiation plants, but for certain processes some of the non-coal rock fragments are purposefully allowed in the feed coal[19].The rock fragments may be included as feedstock together with coal because they contain fluxing minerals (pyrite, calcite and to a lesser extent dolomite). Fluxing minerals play a significant role in controlling the ash fusion temperature of coals[19].

2.2.4 Mineral types/groups

Minerals in coal occur in types or groups as indicated in Table 2.1. The abundance and mode of occurrence these mineral groups play a role of determining how the minerals behave under different conditions. In this section different mineral groups are discussed in terms of their origin, relative proportions in coals of different regions, mode of occurrence, and their behaviour under normal combustion and gasification conditions.

2.2.4.1 Silicates

In a study of occurrence, abundance and origin of minerals in some Turkish coals, Vassileva[16] observed that the approximate quantitative distribution of mineral classes in coal is generally: Silicates>carbonates>oxyhyroxides>sulphides>sulphates>phosphates>others. This holds true for many other coals even those that are not from the Northern Hemisphere. In fact the above

findings can be taken as a true representation for the occurrence of mineral matter in all coals with a few exceptions[16].

Quartz {SiO_2}

Of all the silicates, quartz is the most abundant mineral matter in coal followed by the clay minerals[12,15,17,20]. It is thus the most common mineral in all coals, Northern and Southern Hemisphere, and is both detrital and authigenic in origin[16]. In some silicified coals and some of the floor strata, quartz may represent more than 70% of the total mineral matter[21]. Quartz is also a relatively abundant mineral in the interseam sandstone and shale beds.

Quartz in the Indonesian coals, and for most Southern Hemisphere coals, occurs as microcrystalline infillings of cell lumens, or as infillings of cracks within the macerals[22]. The silica in such cases may have come from diatoms and other biogenic sources in the original peat, from transformation of clay minerals, or possibly from the alteration of volcanic ash falling into the peat swamp. Quartz is known to be nonreactive during coal conversion and often reports in bottom ash[12]. For example, as was reported by Martjie *et al*[12], quartz in coarse ash was determined to have originated from coarse-grained sandstone rock fragments. Included quartz was determined to have originated from siltstone/mudstone rock fragments, and not from crystallisation during cooling of the ash slag, as was suspected[12].

Clay minerals

Illite and kaolinite are the most dominant clay minerals in coal, in both Southern and Northern Hemisphere coals[24,25]. The molten phase of illite tends to stick the molten phase of pyrite, and adheres to heat transfer surfaces to form deposits in the radiant section of boilers[26]. Although common in the associated non-coal shaly sediments, illite is relatively rare in the mineral matter of Australian coals generally[24]. Illite which is abundant in US bituminous coals melts under typical combustion conditions to form molten silicate particles[26]

Gaigher[25] found that low rank Witbank and Free State coals had similar clay compositions to Australian coals but higher rank Natal coals typically contained considerably more illite. The clay mineral distribution of the latter coals was similar to that of Illinois coals from the US, where it was observed that the clay minerals in high volatile coals tended to contain kaolinite

as the principal clay mineral, whereas the anthracites were high in illite[25]. In addition Susilawati and Ward[22] who determined that kaolinite is not as abundant in the mineral matter of the higher rank or heat-affected coals of Indonesian sub-bituminous coals, and that there is a tendency for the proportion of kaolinite to decrease as the rank of the coal increases[22].

2.2.4.2 Carbonate minerals

Carbonates occur mostly as authigenic minerals in coal[27]. According to Volkova and Bogdanova[27], a Ca/Mg ratio of <1 classifies the coals as having formed in a marine environment, while the above ratio with value of >10 classifies the coals as having formed in a fresh water environment[27]. The main carbonate mineral in Northern Hemisphere bituminous coal is calcite {$CaCO_3$}. Dolomite {$CaMg(CO_3)_2$} and ankerite {$Ca(Mg,Fe,Mn)(CO3)_2$} are frequently associated with calcite. Siderite {$FeCO_3$} is more common in Southern Hemisphere coals, although the other carbonate minerals may also be present[28]. All carbonate minerals lose CO_2 during combustion, and form agglomerates of small oxide particles with compositions reflecting the parent mineral[29].

Dolomite {$CaMg(CO_3)_2$}

Dolomite and other calcium minerals such as unaltered calcite and aragonite fragments are mostly of detrital occurrence and originate from coarse-grained carbonate rocks of source areas[16].

Siderite {$FeCO_3$}

Siderite is present as massive and fine-grained lenses, nodules and layers or infillings of essentially syngenetic origin. It is believed to be formed in the absence of significant sulphate, from CO_2 released by organic matter decomposition[30]. Siderite is common in coal seams where freshwater sedimentation occurred, while ankerite and calcite occur in seams overlain by both freshwater and marine rocks[16].

2.2.4.3 Sulphides

Sulphides are characteristic authigenic minerals in coal. Coals, particularly with a marine influence, are commonly enriched in Fe sulphides, primarily pyrite[16]. Epigenetic pyrite and marcasite are occasionally more abundant than their syngenetic occurrence.

Pyrite {FeS_2}

Pyrite in coals occurs as typical syngenetic framboidal, euhedral and massive cell-filling forms[31]. It is thought to form mainly from the bacterial reduction of sulphate-rich waters permeating through the peat bed[32]. Included and excluded pyrite grains behave differently during coal conversion. When pyrite occurs as excluded grains, it tends to fragment and oxidize to form magnetite and hematite[7]. The terms included and excluded have to do with the whether a mineral is organically or inorganically associated respectively. Pyrite, together with illite, is commonly found in US coals and is often associated with slagging problems. Pyrite grains have been found to decompose to form pyrrhotite which melts at combustion temperatures (900˚C - 1500˚C) and is oxidized exothermically to form molten oxysulfide particles[33, 22].

2.2.4.4 Summary

In summary, different mineral groups display different behavior under similar environments of gasification and combustion. Their behavior is not only determined by the mineral group they belong to, but is also determined by their occurrence, whether syngenetic or epigenetic, as well.

2.2.5 Identification of mineral matter in coal

Ash is the residue left after coal combustion and originates from minerals. In other words, ash is that it is the transformed high-temperature product of mineral matter. This description of ash is important for the coal analyst in the selection of coal analyses. To identify minerals from ash can sometimes lead to inaccurate interpretations as the minerals may have gone through many transformations before forming ash. Thus, before analyses are done, a decision has to be made whether to analyse the mineral component in coal as is, or to study the ash. Each has their own advantages and disadvantages and in most of the cases the decision is dependent on

the analytical technique available. Some techniques can only analyse liquid samples which would require ashing and/or dissolution. Others such as Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSEM) can analyse whole coal samples[34]. The most accurate method is to characterize the mineral matter in coal without ashing. In this section methods for detailed mineral matter analysis and characterization are discussed.

2.2.5.1 Ashing

Ash is prepared by the combustion of coal in a furnace. There are two methods for preparation of ash, namely high temperature ash (HTA) and low temperature ash (LTA). HTA is prepared by the combustion of a coal sample at temperatures between 400 and 800 °C in an electric furnace. LTA is prepared by combustion of a coal sample at temperature below 200 °C in electronically excited oxygen plasma[35]. The ash is assumed to represent the mineral matter in the coal sample, and thus is used for fusibility tests and the mineralogical characterization However; the mass of the ash formed may differ from that of the minerals in the coal. The difference is primarily due to loss of carbon dioxide and water of crystallization in minerals[36]. It has been empirically estimated that mineral matter in coal is 1.1 times the ash determined from the laboratory analysis of the coals[36].

2.2.5.2 Ash fusion tests (AFT)

The determination of ash fusion temperatures (AFTs) is a one of the most important tests used in order to predict the behaviour minerals at different temperatures during utilization. AFT is one of the many methods that are used to predict the slagging propensity of coals. AFT predictions are dependent on the knowledge of the minerals in the coal sample, which means that predictions are only as good as the characterization of the ash. Thus AFTs, in combination with the information obtained from the methods discussed below, is able to predict the behaviour of the minerals at high temperatures.

As the ash sample is heated, particles sinter and fuse and may eventually form a liquid slag. These changes provide a basis for characterizing the fusion processes (Figure 2.1). The AFT operator observes changes in a standard ash cone as it is heated through the temperature range expected in a furnace. Initial deformation temperature (ID) is the temperature at which

the rounding of the tip of an ash cone is noted, and this has been accepted as the temperature where the ash first softens and may become sticky[38]. The softening temperature (S) is taken to be when the height of the cone equals the width of the cone. The hemisphere temperature (HS) is when the cone height is half the cone width[38]. The flow temperature (FLOW) is when the sample height is about 1.5 mm. The temperature range involved is 1000-1600°C.

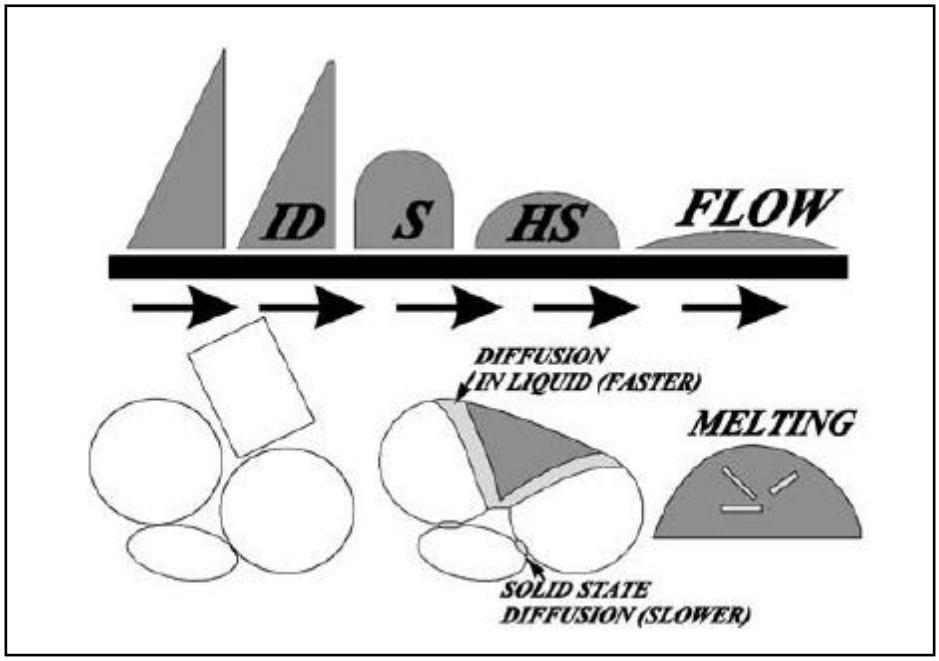

Figure 2.3: The processes taking place during AFT test[39]

Vassilev *et al*[40] studied the relationships between AFTs and the mineral and chemical composition of coals and coal ashes from a wide variety of deposits. The study was done using a melting test, X-ray diffractometry (XRD), light microscopy, differential-thermal(DTA), thermogravimetric (TGA) and chemical analyses. Vassilev *et al*[40] concluded that "it is possible to make a reliable explanation and prediction of ash-fusion characteristics when the coal and coal-ash minerals, their quantities, as well as their refractory and fluxing action behaviour during heating, are known".

A more reliable way of predicting high temperature behaviour of minerals would be to study specific species and then deduce their collective behaviours at higher temperatures. In the work on mineral species-specific information on ash properties and the specific affect on AFT,

van Dyk[41] showed that factors like CaO/MgO ratio and other elements like Fe, Na, and K are the major factors affecting AFTs. This work confirmed what other researchers suspected, that "ash composition on its own does not explain the AFT behavior of coal accurately"[42].
In summary, ash fusion tests are useful as an indicator of the behavior of mineral matter in coal. The tests are unable, on their own to correctly predict the behavior of mineral matter at high temperatures. The tools that provide the coal analyst with more information are discussed in the next section.

2.2.5.3 X-ray Fluorescence (XRF)

The most widely used X-ray method for elemental analysis in coal literature is X-ray fluorescence (XRF). The reasons for this wide usage is because XRF is a versatile and relatively common laboratory instrument. Current instruments are fully automated and can do multiple analysis[3]. In addition, the relative ease of sample preparation gives XRF an edge over other elemental analysis methods.

A typical chemical analysis of coals from the Highveld region in South Africa is shown below (Table 2.3). The major elements are Si and Al with minor compositions of fluxing elements Fe, Ca, and Mg.

Table 2.3: Table showing typical chemical composition for Highveld coals in South Africa (from different sources) determined by XRF

Chemical	Coal 1(%)[33]	Coal 2(%)[34]	Coal 3(%)[9]
SiO_2	54.3	45.61	56
Al_2O_3	28.2	27.51	26.1
Fe_2O_3	2.21	9.23	3.4
CaO	7.79	5.86	1.1
MgO	2.91	1.58	9.1
TiO_2	1.3	1.38	3
Na_2O	0	0.48	0.9
K_2O	0.6	0.61	0.4
MnO	0.05	-	-
P_2O_5	1.25	0.61	-
SO_3	1.44	5.89	-

2.2.5.4. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) is an emission spectrophotometric technique, exploiting the fact that excited electrons emit energy at a given wavelength as they return to ground state. The fundamental characteristic of this process is that each element emits energy at specific wavelengths unique to its chemical character. Although each element emits energy at multiple wavelengths, in the ICP-AES technique it is most common to select a single wavelength (or a very few) for a given element. The intensity of the energy emitted at the chosen wavelength is proportional to the amount (concentration) of that element in the analyzed sample. Thus, by determining which wavelengths are emitted by a sample and by determining their intensities, the analyst can quantify the elemental composition of the given sample relative to a reference standard[44,45].

2.2.5.5 Powder X-ray Diffraction (PXRD)

Elemental analysis is not enough if one wants to know how the mineral phases occur in the coal. Elemental composition only informs the analyst about “how much” of the element or compound is found in the coal (quantitative), but not about how they occur in the structure (the phases). Powder X-ray diffraction (PXRD) has been used extensively for many years in the analysis of coal minerals. It is used mainly for its ability to quantitatively characterise minerals phases[6, 8, 9, 34].

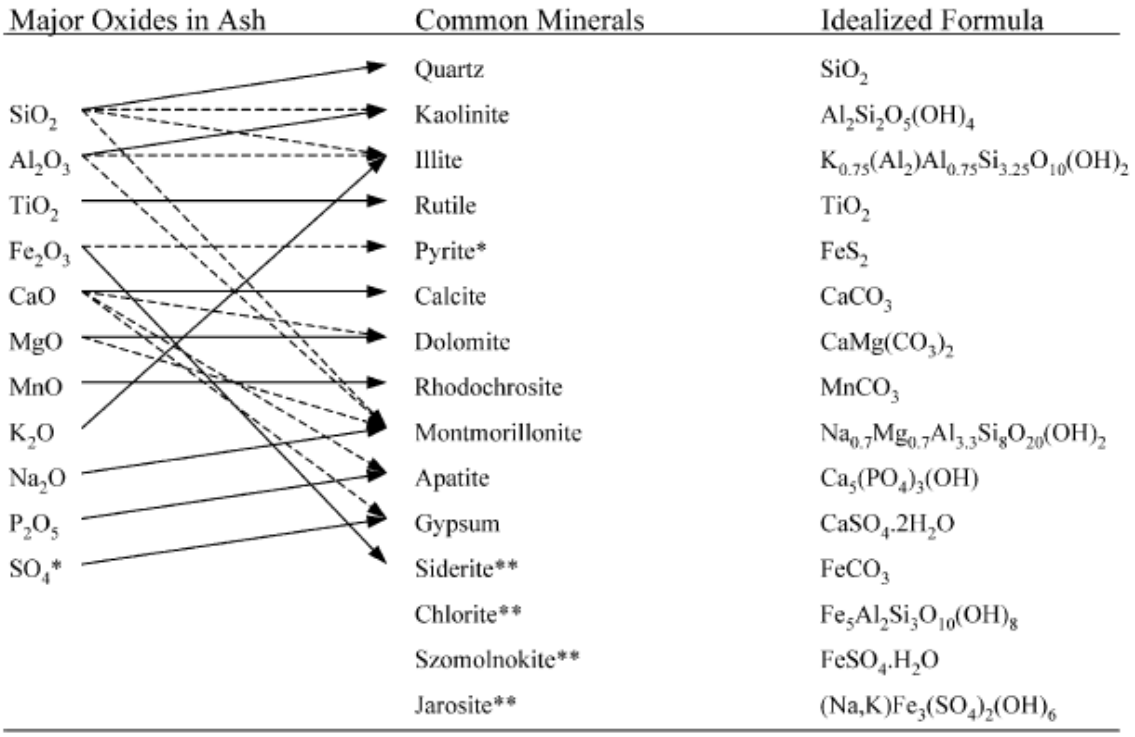

Figure 2.4: The elemental composition of ash on the left as opposed to the mineral phases on the right[46]

In Figure 2.4, the major oxides on the left are the oxides in ash which are easily analysed quantitatively using XRF, ICP-AES or any other elemental analysis technique. So far XRD is the only reliable and most trusted technique for this type of analysis. It is able to not only **qualitatively** analyse the mineral phases but its strength lies its ability to also **quantify** those mineral phases[6, 8, 47] by way of a profile refined developed by Rietveld called Rietveld refinement, or method.

Qualitative mineral analysis

PXRD's phase qualitative analysis abilities are used beyond coal mineral matter analysis. It is used in almost all industrial analysis where materials are used. The method of PXRD is one based on the nature of atoms in crystalline materials. These order themselves on a plane which when irradiated with x-ray form a diffraction pattern, acts a fingerprint for each individual mineral. A diffraction pattern is obtained when constructive interference occurs. Braggs law: $\lambda = 2d \sin \vartheta$ (where λ is the wavelength of the x-ray, d is the spacing between planes of atoms in

the solid, and θ is the angle of incidence) is used as a criterion for constructive interference of the x-ray waves. PXRD patterns are then generated that act as fingerprints for each different material because each material has atoms in a unique way. The way in which these atoms are arranged in a crystalline solid is called a phase. Some materials will have the same composition but different phases, hence the limitation of other techniques in phase identification since they are designed to determine the composition of the material.

Quantitative mineral analysis

In 1969, H.M Rietveld published a paper on entitled "A profile refinement method for nuclear and magnetic structures" [48]outlining how a powder XRD pattern can be used to determine many aspects of the material's structure. Rietveld used a least squares approach to refine a theoretical line profile (the height, width and position of these peaks) until it matched the measured profile. Since then the method has been further developed and with the advent of computer-based data collection and processing, this approach has been extended to evaluate mineral percentages in a mixture from the overall XRD pattern[37]. The extension of Rietveld methodology in this way allows a calculated XRD profile of each mineral phase to be generated from its refined crystal structure, and the sum of all calculated patterns to be fitted to the observed XRD profile of a multi-mineral mixture by least-squares analysis to find the optimum phase scales. The phase scales are then used to determine the individual mineral percentages represented in the sample[37].

High Temperature XRD

The above mentioned X-ray techniques are mostly performed at room temperature. However XRD performed at higher temperatures (HT-XRD) is rapidly growing in importance especially in coal mineral analysis[49]. The need to simulate actual coal conversion process for mineral matter transformations studies has been the main reason for this growth. The traditional approach to understanding mineral matter behaviour in coal at high temperatures is based on AFTs and elemental oxides, as discussed earlier. These methods have not been successful in predicting the actual behaviours of mineral matter at higher temperatures as was discussed earlier. HT-XRD is rapidly becoming the instrument of choice for accurate simulation coal conversion

processes for mineral matter investigation purposes. This is mainly because of the availability of intense x-ray sources and position sensitive detectors which make it possible for rapid acquisition of x-ray diffraction data at high temperatures[37]. Current instruments are able to reach temperatures of up to 2400°C, and 1600°C in oxidising atmosphere. When used in conjunction with a Rietveld-based analysis such as SIROQUANT[a], quantitative abundance data can be obtained not only for the crystalline phases but also for any solid or liquid amorphous phase that may be formed.

In summary, PXRD is the instrument of choice for qualification and quantification of mineral matter in coal and HT-XRD will continue to be the instrument of choice for studies of mineral matter transformations. The technique of importance for this study is the normal temperature PXRD which has been used to identify and quantify mineral matter in coal.

2.2.5.6 CCSEM/QEMSCAN

The nature and distribution of minerals in coal have a fundamental effect on the behaviour of coals when used for various purposes[50]. This "nature and distribution" is primarily the mineral grain size, and whether the mineral grains are within the coal matrix or extraneous[43].
Pioneering work using computer controlled scanning electron microscope (CCSEM) for the study mineral matter in coal was done by White and co-workers[52], and the technique has been further developed as evidenced by its current success in coal analysis. It is mostly used to study the nature and distribution of mineral matter in coal and has been used in coal analysis with great success [34]. The CCSEM technique uses an automated scanning electron microscope (SEM) and is programmed to scan preselected areas of a sample to capture the back scattered emission image (BSE) image. A particle recognition and characterization program is then used to locate an individual coal/ash/mineral particle, and to determine its size and chemical composition.
In 2005 researchers at the Commonwealth Scientific and Industrial Research Organisation (CSIRO) in Australia developed the CCSEM technique for the mineral matter characterization

[a] SIROQUANT – A Rietveld-based mineral quantification software developed by CSIRO, Australia.

with the introduction of a QEMSCAN [50]. QEMSCAN[b] is a special variety of the CCSEM technique originally known as QEMSEM (quantitative evaluation of materials by scanning electron microscopy). QEMSCAN determines the association of chemical elements at individual points on a coal polished section from the output of several X-ray analyzers directed at each point under the SEM. The development of faster X-ray detectors, stable scanning electron microscopes, high-resolution BSE detectors, and good processing software has improved the analytical capabilities of automated scanning electron microscopes based techniques like QEMSCAN.

Summary of Chapter

In summary, coal conversion technologies will continue to be in demand. But many of these face many challenges that could determine their success or failure as technologies of choice for future application. One of these challenges is the management of mineral matter in coal. Many characterization techniques have been developed and continue to be developed towards the achievement of this goal. PXRD and QEMSCAN are gaining popularity among coal specialists for mineral matter investigations and mineral associations respectively. Developments in these methods will provide the necessary knowledge and understanding of mineral matter in coal and hence the ability to manage the processes associated with mineral matter in coal.

[b] QEMSCAN – a modified version of QEMSEM – developed by CSIRO, Australia.

Chapter 3: METHODS AND INSTRUMENTATION

Chapter 2 discussed the analytical methods that are used for investigation of mineral matter. Much of the literature study discussed in chapter 2 dealt with only mineral matter in coal. Non-coal rock fragments, although not included in the literature study, form the main part of the study. The aim of the investigation is to characterise the mineral matter in samples, including non-coal rock fragments samples, using different analytical techniques and ultimately to understanding the role of these minerals play in clinker formation and/or slagging.

3.1 Sample Selection

The approach to understanding the role that mineral in rock fragments play was through a complete analysis of all the sources of minerals in clinkers (Figure 3.1). This was done by collecting a coal sample, ash clinker sample and non-coal rock fragment samples.

3.1.1 Coal and Ash

A grab sample of a clinker is a complex mixture of i) high temperature transformation products of minerals (included minerals and fluxing minerals), and (ii) the high temperature transformation products of minerals from non-coal rock fragments (also known as extraneous minerals).

The coarse coal entering a coal conversion processe was sampled on an hourly basis and the coarse ash every three hours over a 24-hour period.

3.1.2 Non-coal rock Fragments

Non-coal rock fragments were the main focus of the study. One of the reasons for this is because they may contain low concentration of organic matter. Excessive amounts of organic matter in coal can be a stumbling block to mineralogical analysis in various ways which make the detection of minerals in low concentrations difficult (Figure 3.1).

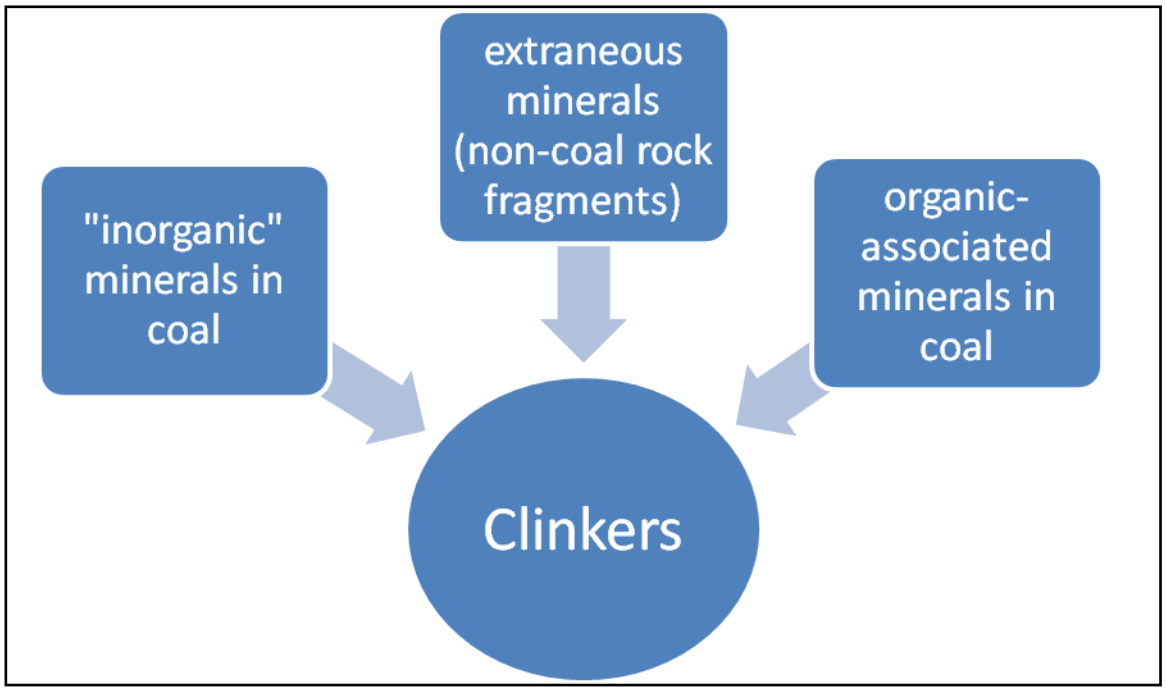

Figure 3.1: A scheme showing the relationship between the clinker mineralogy and coal mineralogy.

The non-coal rock fragment samples were obtained from run off mine (ROM) at stockpiles of certain mines in the Highveld coalfields.

3.2 Analyses

A detailed mineralogical examination using XRD, XRF and QEMSCAN on the coal, non-coal rock fragment samples and clinker samples was conducted as outlined (Figure 3.2). The blocks below the dotted lines indicate expected outcome of the characterisation study.

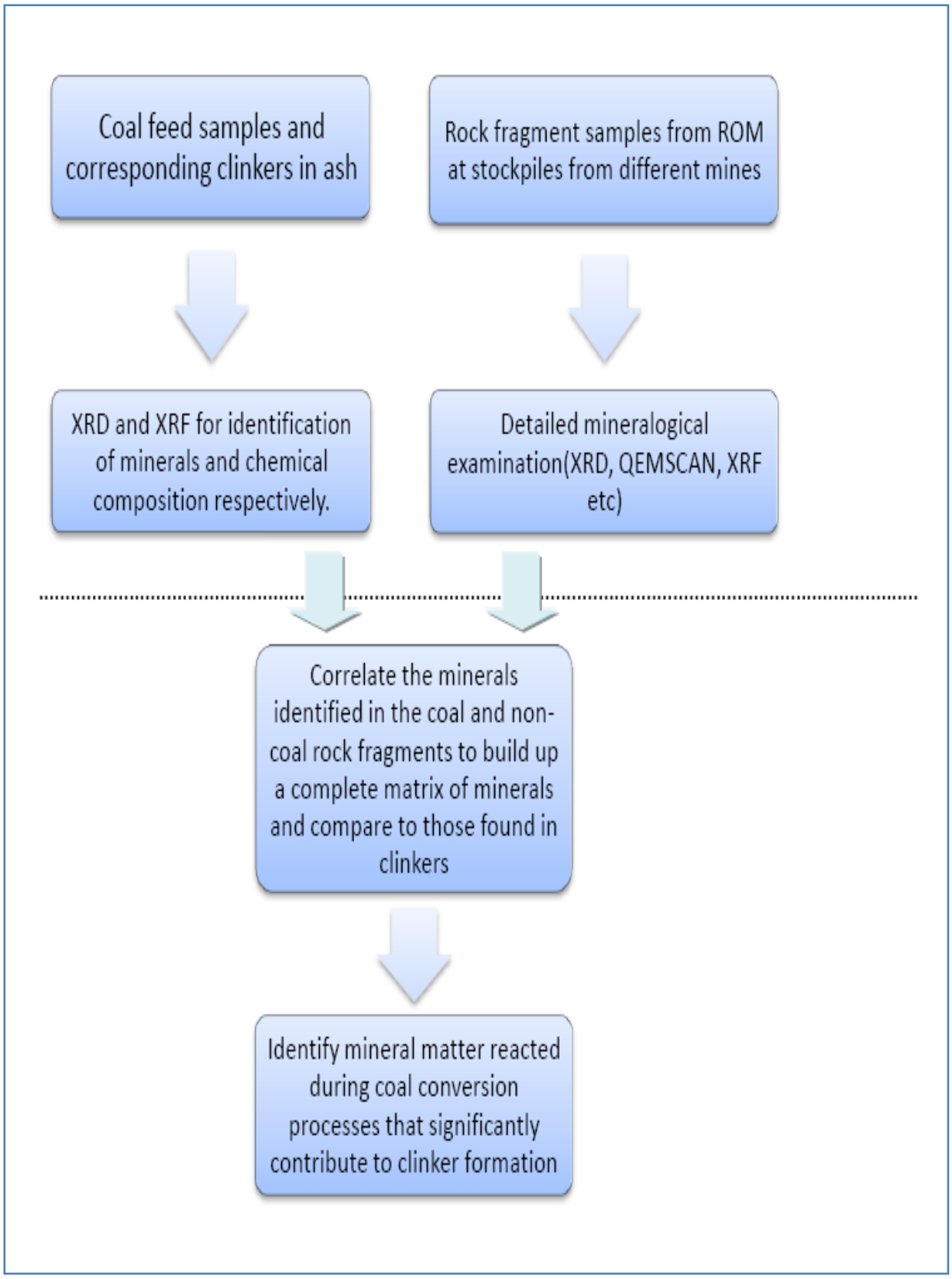

Figure 3.2: A scheme showing the methodology used in the study

3.2.1 Analyses: Coal and Ash

Analyses on the coal and ash clinker samples were performed to correlate mineral matter in coal with the transformed mineral matter in the ash clinker sample. Two samples were submitted for qualitative and quantitative XRD analyses: coarse coal feedstock and corresponding coarse ash/clinker (Figure 3.3).

Figure 3.3: An image of a hand-picked sized sample of a coarse gasification ash/clinker similar to the one used[12]

The samples were crushed and were subsequently milled to very fine powder (<10µm) using McCrone automatic grinder, to be suitable for quantitative XRD analysis. In order to determine the non-crystalline content of the samples, an internal standard (CaF_2) was added to each sample. Then each sample with and without internal standard was exposed to X-ray diffraction.

3.2.1.1 Proximate and ultimate analysis

Coal and clinker/ash samples were submitted to the SABS laboratories for the proximate and ultimate analysis.

3.2.1.2 Powder X-ray Diffraction (PXRD)

Representative fractions of crushed coal feedstock and coarse ash clinker (100% <1mm particles) were submitted to the Sasol Technology Research and Development (Material Characterisation Group), and facilities of the Structural Chemistry laboratory at Wits University were used for the qualitative and quantitative characterisation of the samples. At Sasol Technology, a Panalytical X'Pert PRO Multi-purpose Diffractometer (MPD) was used to record XRD patterns. Four hour scans were applied in order to achieve the best accuracy of results. Each sample was measured twice: without and with a CaF_2 internal standard to determine non-crystalline content. The overall composition of the glassy (amorphous) phase in each case was then estimated by subtracting the proportion and inferred composition of the crystalline phases from the bulk ash composition, following procedures described by Ward and French[53]. Rietveld-based SIROQUANT software was the used for the quantification of mineral matter.

At Wits University, the PXRD data were collected using a Bruker AXS D8 with a primary beam Gobel mirror, a radial Soller slit, a V Antec-1 detector and using Cu-K radiation (40kV, 40mA). Data were collected in the 2θ range 5 to 90 in 0.007 steps, using a scan speed resulting in an equivalent counting time of 439.2s. The samples in this case were not spiked with an internal standard for non-crystalline content determination. Rietveld-based TOPAS was used for the quantification of mineral matter. The two Rietveld-based methods were then compared to each other for evaluation of:

(i) Accuracy between the two software programs (SIROQUANT and TOPAS)

(ii) Difference between the spiked and non-spiked samples

3.2.2 Analyses: Rock fragments

Rock fragments are the major source of extraneous mineral matter and as such represent the main part of the study. Different types of non-coal rock fragments (sandstone, siltstone, mudstone, carbonaceous shale) from ROM at stockpiles of individual of Highveld mines were hand picked. The samples were numbered as follows according to the location and characterised as follows:

Solid 2 : Micaceous sandstone
Solid 3 : Unidentified
Solid 4 : Gritstone
Soild 5 : Siltstone
Solid 6: Unidentified
Solid 7: Sandstone

3.2.2.1 X-ray Fluorescence (XRF)

An XRF spectrometer (ARL9800XP (SIM-SEQ) at SABS was used to determine the elemental compositions of the rock fragments. For quantification, the intensity of characteristic lines of the element to be analysed was measured. Coal ash typically contains Fe, Al, Mg, Mn, V, Ti, Si, Ca, Na, K, P, S and Cr, which are reported as metal oxides by default (Fe_2O_3, Al_2O_3, MgO, MnO, V_2O_3, TiO_2, SiO_2, CaO, Na_2O, K_2O, P_2O_5, SO_3 and Cr_2O_3).

Each solid sample was initially ground to 100% passing 212 µm. The powdered sample was then calcined at 850°C in air for 4h in order to remove all organic compounds and water originally contained in the sample. The calcined sample was then converted into a solid solution by fusion with lithium tetraborate ($Li_2B_4O_7$).

The prepared solid solution and standard (NIMN from Mintek) were placed in the sample holders. The sample holder was then placed in the sample compartment of an XRF spectrometer. The intensity of a characteristic line of element to be determined was measured and the concentration of the element in the sample was calculated from the intensity measured

3.2.2.2 PXRD

For the non-coal rock fragments powder X-ray diffraction data were collected using a Bruker AXS D8 equiped as in section 3.2.1.2 above with a primary beam Gobel mirror, a radial Soller slit, a V Antec-1 detector and using Cu-K radiation (40kV, 40mA). Data were collected in the 2θ range 5 to 90 in 0.007 steps , using a scan speed resulting in an equivalent counting time of 439.2s.

Peak identification was performed using Bruker Eva search/match software. Quantitative X-ray diffraction analysis was performed using an open software called Material Analysis Using Diffraction(MAUD), a quantitative X-ray diffraction analysis software package that uses Rietveld procedures to generate a synthetic pattern which is then matched to the experimental data using a least squares minimisation fitting procedure. The crystalline phases were identified by comparing the peak positions and intensities with those in the ICSD data files.

MAUD is a Rietveld based mineral quantification software. It is freely available online and was used as learning tool for quantification of mineral matter. It is much easier to use than the other more advanced commercial Rietveld based methods namely TOPAS[3] and SIROQUANT. The more advanced commercial software programs were used for their accuracy and ability to manage large data input.

3.2.2.3 QEMSCAN

QEMSCAN™ is an automated electron beam image analysis instrumentation package based upon a scanning electron microscope. Unlike Computer Controlled Scanning Electron Microscopy (CCSEM), particles are initially located using a backscattered electron image, then analysed on a pixel by pixel basis using energy dispersive X-ray analysis with a combination of up to four detectors. The pixel spacing can be set by the operator and can vary from a fraction of a micrometre to tens of micrometres (Figure 3.4) The X-ray spectral information is used to assign an individual pixel to a particular mineral species by comparison with a look-up table to produce a phase composition map of the sample. The output from QEMSCAN is an image in which each mineral or phase type is labeled with a different color to represent different species and a table minerals and mineral phases present in the sample. In this study, QEMSCAN analysis was conducted by Van Alphen Consultancy in South Africa but the data was collected at CSIRO Australia.

[3] TOPAS – a Rietveld based mineral quantification software program – developed by Bruker.

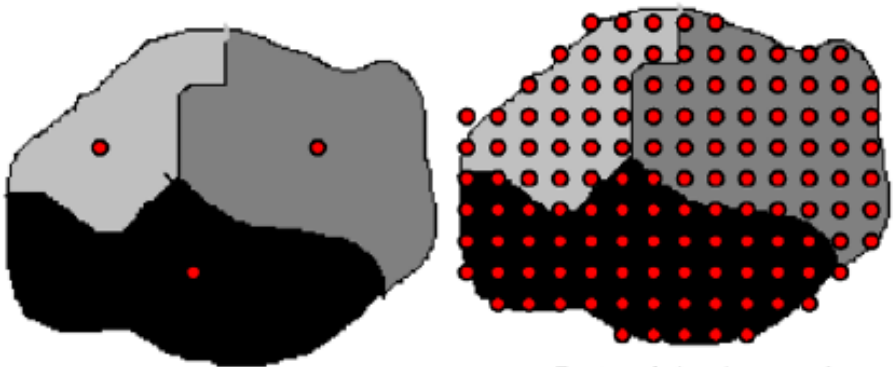

Figure 3.4: QEMSCAN' s electron beam positioning. Centroidal on the left or raster of closely spaced points on the right[34]

3.2.2.4 Normative analysis

Normative methods were also used for the discrimination of mineral matter in rock fragments. Normative methods utilize elemental proportions to predict mineral proportions (both crystalline and non-crystalline material). X-ray fluorescence (XRF) and atomic absorption (AA) spectrometry were used for the elemental proportions input data. The predictions from XRF and AA were compared. Normative methods are normally used as verification tools to verify mineral proportions determined by QEMSCAN or PXRD. In this study they were used to verify and compare QEMSCAN results.

Van Alphen Consultancy Coal Quality Assessment (VAC CQA)

Van Alphen Consultancy Coal Quality Assessment (VAC CQA) is a coal quality assessment (CQA) prediction spreadsheet that uses mineral proportions based on known mineral compositions. A good example is in the prediction of K-bearing orthoclase and muscovite/illite. In predicting these proportions, the normative method assumes certain ratios. Since there is more than one mineral containing K, such as microcline, muscovite and illite, it is assumed that 50% of the K-bearing minerals is microcline and 50% is muscovite/illite. These assumptions are prone to introducing a lot of errors in calculations. This is because of the distribution K-bearing minerals which might not be same as the assumed percentages.

Summary of Chapter

In this chapter methods used for the identification of minerals in coal sample, ash clinker sample and non-coal rock fragments were discussed. First, basic coal analysis methods namely proximate and ultimate analysis was determined. Elemental proportions were determined by using XRF and AA (for normative method comparison). Finally, detailed mineralogy was determined by PXRD, QEMSCAN, and normative methods. Different Rietveld-based methods were used for the quantification of minerals and were compared (Figure 3.5).

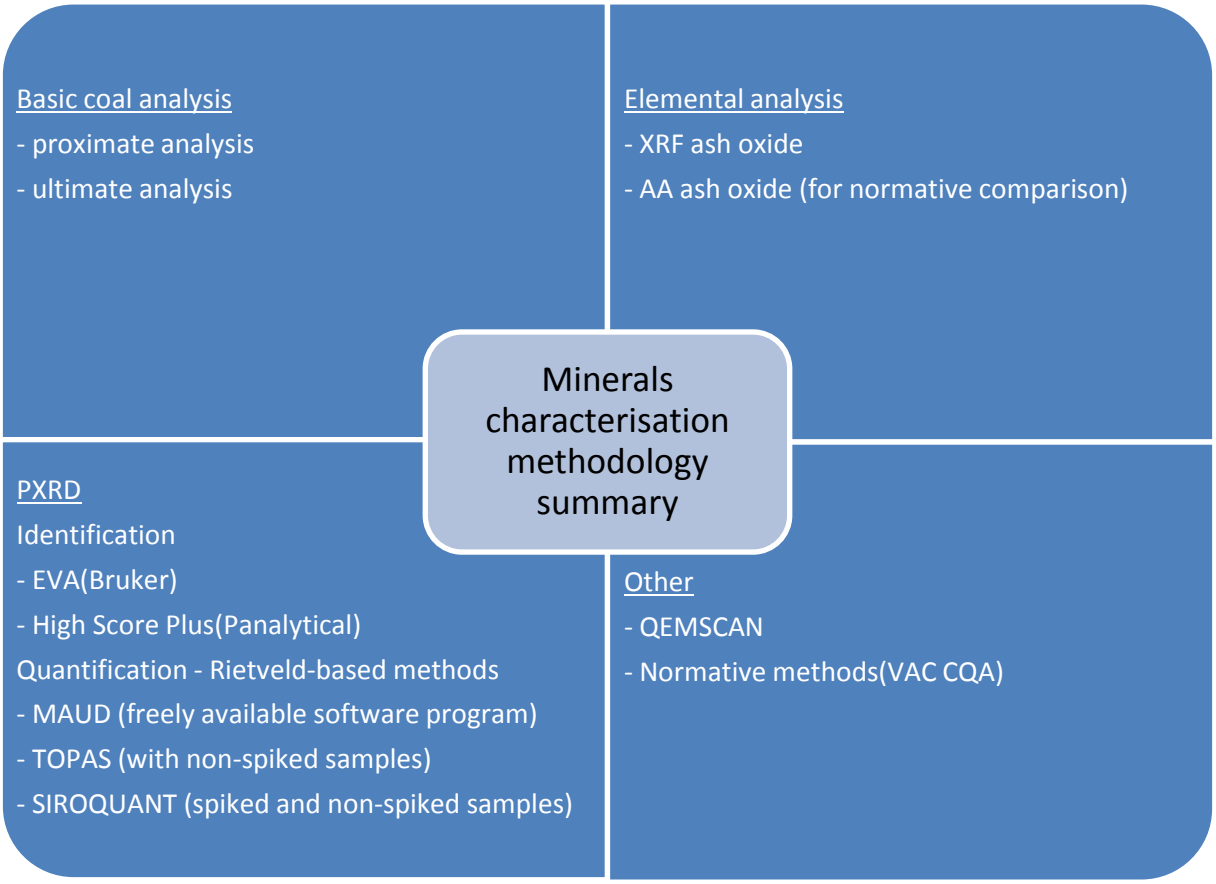

Figure 3.5: A summary of the analytical methods for the study

Chapter 4: RESULTS AND DISCUSSION

In this chapter results from the chemical and mineralogical analysis of the coal, ash and the rock fragments are presented. In the first and second sections results are presented and discussed for the coal, ash analysis and rock fragments respectively. The chapter concludes with discussions of the results and their implications, if any, on clinker formation.

4.1 Coal and Ash

Mineral matter content in coal, coupled with operation conditions of coal conversion processes, is important in initiating and controlling clinker or slag formation. By studying the mineral matter in coal certain conclusions can be drawn about formation and behaviour of clinker. In the next section, the basic coal and ash analysis are discussed. The coal analysis was conducted mainly for comparative reasons and the ash clinker analysis was conducted to better understand the source of the mineral matter present in the ash clinker. Because the coal conversion facility from which samples were taken operates under pressure, it is practically impossible to obtain samples from the operational unit. Instead the role played by mineral matter in coal is inferred from examining the feed coal and corresponding ash clinker. Coal and ash clinkers results are discussed initially followed by a thorough study on non-coal rock fragments which are the main focus of the study.

4.1.1 Proximate and ultimate analysis

Knowledge of the basic coal properties is important in roughly predicting how the mineral matter in coal will behave in coal conversion processes. Although proximate analysis of coal does not reveal much about the mineralogy of the coal, it does give an indication of the suitability of a coal for a certain process. There has been a trend shown to exist between coals of certain volatile matter content and their mineral composition as was discussed by Gaigher[25]. The proximate and ultimate analysis of feed coal and ash clinker samples are reported in Table 4.1.

A proximate analysis of the ash sample is not really necessary as it is 96.8% ash but an analysis was done for comparative reasons. The coal sample is typical of a Highveld coal were ash

values typically lie between 30% and 35%. A volatile matter content of 20.8% is moderate for these coals. As discussed (section 2.2.2) these types of coal usually have clay minerals which contain kaolinite as the principal clay mineral[25].

Table 4.1: The proximate and ultimate analysis of a coal sample and its corresponding ash sample from Highveld Coalfields

Sample	Coal sample	Ash Sample
Proximate Analysis(%)		
Inherent Moisture (H_2O)	5.00	0.20
Ash	31.1	96.8
Volatile Matter	20.8	0.60
Fixed Carbon	43.1	2.40
Total Sulphur	1.39	0.34
Ultimate Analysis(%)		
Carbon	50.4	2.84
Hydrogen	2.69	0.06
Nitrogen	1.39	0.28
Total Sulphur	1.39	0.34
Oxygen	8.08	0.00

4.1.2 Ash Oxide analysis (XRF)

XRF analysis was undertaken to determine the elemental composition expressed as oxides of the metals relate proportion of different minerals in the coal and ash clinker and will be compared to that of the non-coal rock fragments.

XRF chemical analysis results for coal and ash samples are comparable (Table 4.2). The results have been normalised for loss on ignition (LOI). The major elements determined Si, Al, Ca and Fe. Minor compositions of fluxing elements Na, Mg and K present in both samples. The high percentage composition of the acidic species suggests a high alumino-silicates or clay composition.

Table 4.2: A table showing ash axide composition for coal and ash samples (XRF).

Ash Analysis	Coal sample(%)	Ash sample(%)
SiO_2	51.20	50.60
Al_2O_3	22.30	25.50
Fe_2O_3	6.90	6.61
P_2O_5	0.66	0.80
TiO_2	0.74	0.88
CaO	9.37	10.40
MgO	1.88	2.02
K_2O	1.34	1.09
Na_2O	0.43	0.57
SO_3	5.54	0.43

The similarity in elemental compositions may also suggest that the mineral phases that these elemental species occur in may be inert to the temperatures achieved during coal conversion environment.

Coal has a higher percentage of sulphur (reported as SO_3) than in the ash sample. The nature of S (organically-bound, free or mineral-bound) was not determined at this stage. This makes it difficult to predict its behaviour upon heat treatment but it is safe to assume that the most the difference in S is mainly due to it being oxidised and vaporised in the combustion zone of the coal processing unit; to SOx. SOx is further treated to meet emissions regulations or emitted to atmosphere if it occurs in trace amounts.

4.1.3 PXRD analysis

X-ray diffraction patterns for analysed samples are presented in Figures 4.1 and 4.2. Only portion of scans is presented for clarity. The data is available in APPENDIX C. Data relating to quantitative mineral analysis by TOPAS is also included in APPENDIX C.

4.1.3.1 Qualitative analysis

XRD patterns for coal and ash samples were obtained using a Panalytical X'Pert PRO Multi-purpose Diffractometer (MPD). Mineral crystalline phase composition of the samples was

determined using X'Pert HighScore Plus software, which applies search-match algorithm through the ICDD PDF database.

The XRD pattern for the coal sample (Figure 4.1) has a very high background noise due to the high percentage of amorphous carbon (and non-carbon) material. The major peaks (at 14.2˚2θ, 23˚2θ, 23.7˚2θ, 24.7˚2θ, 25.2˚2θ and 29˚2θ) are kaolinite peaks and quartz (25.2˚2θ, 31.1˚2θ and other low intensity peaks). Other minor peaks for pyrite, dolomite, aragonite, muscovite and calcite were also identified

The XRD pattern for the ash sample (Figure 4.2) had major peaks for quartz [SiO2] (2θ=31˚2θ and 24.2˚2θ), without any kaolinite peaks. A mullite [$Al_6Si_2O_{13}$] peak was observed instead of kaolinite [$Al_2Si_2O_5(OH)_4$]. This is due to coal minerals undergoing phase transformation during the high temperatures in a gasification and combustion environment. Mullite is known to be a mineral derivative of metakaolinite which is an amorphous phase of kaolinite.

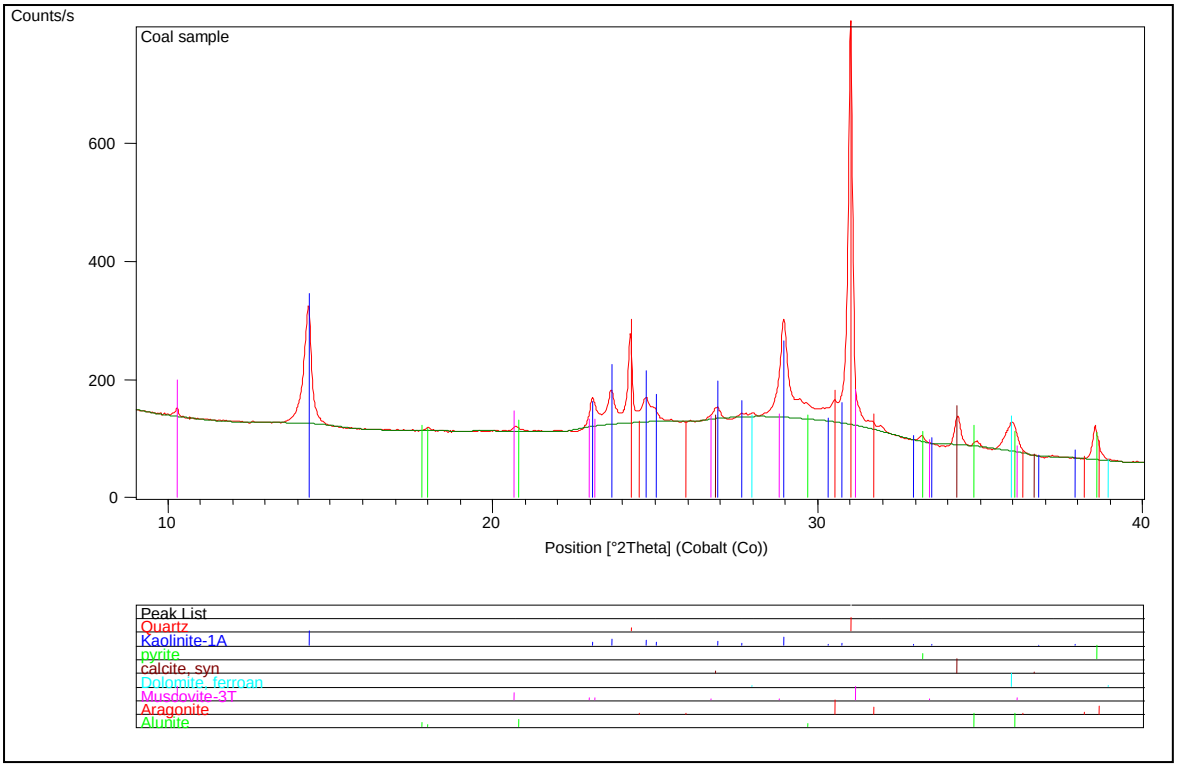

Figure 4.1: A figure showing an XRD pattern for the feed coal.

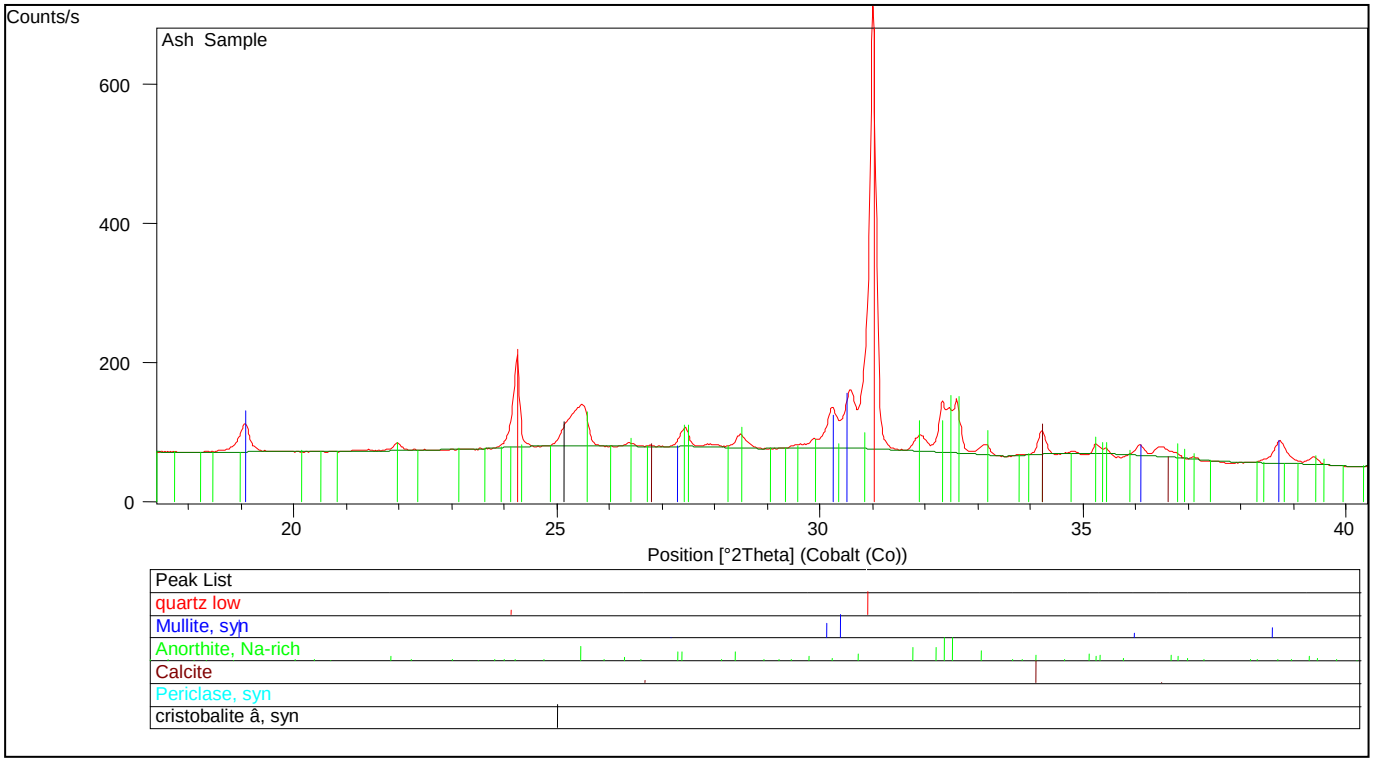

Figure 4.2: A figure showing an XRD pattern for the ash clinker sample

One of the other major crystalline phases identified in the coal sample was sodium (Na) rich anorthite. Anorthite ($Na_2O.Al_2O_3.6SiO_2$) is known to be the main solid phase upon cooling below 1300[12]. Cristabolite (SiO_2) is a high temperature form of silica.

4.1.3.2 Quantitative Analysis

Mineral phase quantification for coal and ash clinker samples was performed using SIROQUANT and TOPAS. Both these software programs allow for the proportions of different minerals in a mixture to be quantified from a conventional PXRD pattern using Rietveld techniques[37]. The different crystallographic parameters for each mineral can be adjusted interactively, to allow for variations due to atomic substitution, layer disordering, preferred orientation and other factors in the standard patterns used[37].

SIROQUANT

Phase quantification for coal and ash samples was performed by Rietveld analysis using SIROQUANT software. The minerals identified in the raw coal samples (Table 4.3) represent only the components actually present as crystalline phases in the original coal. They do not

include any mineral artifacts derived from destruction of the organic matter. Non-crystalline content was determined by spiking samples with a calcium fluorite (CaF_2) internal standard and by application of SIROQUANT software. Results below about 2% should be taken with caution.

Table 4.3: A table showing the mineral quantity for coal and ash samples as determined using SIROQUANT

Mineral	Chemical Formula	Coal(%)	Ash(%)
Quartz	SiO_2	8.2	17.8
Kaolinite	$Al_2(Si_2O_5)(OH)_4$	14.2	-
Muscovite/Illite	$KAl_2Si_3O_{10}(OH)_2$	0.6	-
Pyrite	FeS_2	1.5	-
Calcite	$CaCO_3$	1.2	0.4
Dolomite	$CaMg(CO_3)_2$	2.6	-
Aragonite	$CaCO_3$	0.6	-
Alunite	$KAl_{3(}SO4)_{3(}OH)_6$	0.3	-
Mullite	$Al_6Si_2O_{13}$	-	22.2
Anorthite	$CaAl_2Si_2O_8$	-	13.6
Cristobalite	SiO_2	-	3.8
Periclase	MgO	-	0.2
Non-crystalline content/carbon		70.8	42.0
Total		100.0	100.0

Major minerals present in the coal sample are kaolinite (14.2%) and quartz (8.2%), with minor carbonates (dolomite, calcite, aragonite, total 4.4%) and pyrite (1.5%), and traces of muscovite and alunite. Interestingly, two polymorphs of calcium carbonate ($CaCO_3$) namely calcite and aragonite were identified. The non-crystalline content (mostly organic material in coal) is equal to 70.8%.

In the ash sample the most abundant crystalline phase is mullite (22.2%). Unaltered quartz originally present in the coal sample survives high temperatures in the coal conversion process (17.8%). Anorthite (calcium alumino-silicate) is 13.6%. Cristobalite (high temperature form of silica) was also identified with an amount of 3.8%. Traces of periclase (magnesium oxide) were detected with very low concentration. It is possible that the remains of calcite are still present

in the ash; within accuracy of XRD analysis (main calcite peak overlaps with 20% intensity anorthite peak). The calcite could be due to descrete unburned carbon in the ash which contains remnant calcite. Non-crystalline content in the ash sample is equal to 42% most of which is amorphous carbon and glassy material

TOPAS

The samples analysed at Wits University were quantified using Rietveld-based TOPAS software. The minerals identified in the raw coal samples (Table 4.4) represent only the components present as crystalline phases in the original coal. The non-crystalline/carbon content is assumed to be the same as the one determined by SIROQUANT for simplicity of interpretation. The results presented belowhave been normalised to account for the non-crystalline/carbon .

Table 4.4: A table showing the mineralogical composition for coal and ash by TOPAS

	Chemical formula	Coal(%)	Ash(%)
Quartz	SiO_2	17.4	0.66
Kaolinite	$Al_2(Si_2O_5)(OH)_4$	9.9	-
Muscovite	$KAl_2Si_3O_{10}(OH)_2$	4.2	-
Arnothite	$CaAl_2Si_2O_8$	-	43.1
Mullite	Al_6SiO_{13}	-	14.3
Non-crystalline/carbon*		70.8	42.0
Total		100.0	100.0

*=from SIROQUANT

The major minerals present in the coal sample are quartz (17.4%), and kaolinite (9.9%) and with minor phases of muscovite/illite (4.2%). In the ash sample the most abundant crystalline phase is anorthite (43.1%) and mullite (14.3%). Trace amounts of quartz (1.14%) were also present.

4.2 Non-coal rock fragments

Chemical and mineralogical analyses of coal are important for understanding the mineral behaviour under different coal conversion processes as was mentioned earlier. But it is of equal importance to understand the mineralogy of the included non-coal rock materials because these materials play a major role in the transformation of minerals (both coal and

non-coal minerals) during sintering, slagging and ash clinkers formation in gasifiers and boilers. In this section, findings on the characterisation of non-coal rock fragments are discussed.

4.2.1 Ash oxide analysis (XRF)

The XRF data for major elements in the non-coal rock fragments were expressed as weight percentages of the respective oxides (Table 4.5), with the values obtained from the whole-coal samples normalised so that the major element oxides usually found in coal ash total 100%.

Table 4.5: A table showing ash oxide of the non-coal rock fragments.

	Solid 2(%)	Solid 3(%)	Solid 4(%)	Solid 5(%)	Solid 6(%)	Solid 7(%)
Fe_2O_3	1.27	5.01	4.76	1.57	0.75	2.79
MnO	0.01	0.01	0.04	0.01	0.01	0.01
Cr_2O_3	0.02	0.02	0.03	0.03	0.01	0.05
V_2O_5	0.01	0.01	0.01	0.02	0.01	0.02
TiO_2	0.68	0.23	0.35	1.06	0.51	0.59
CaO	0.26	0.53	0.06	0.24	0.06	0.22
K_2O	1.75	2.52	1.01	1.16	2.72	2.71
P_2O_5	0.02	0.01	0.01	0.03	0.01	0.11
SiO_2	54.30	72.06	77.46	45.61	74.60	63.03
Al_2O_3	27.94	8.13	5.32	21.58	13.42	14.27
LOI	12.43	8.23	6.42	25.02	4.41	14.28

All the samples have a high composition of SiO_2. The other major chemical composition is Al_2O_3. The rock fragments with a SiO_2 of <50% are characteristic of sandstones or siltstones. The elemental proportions of SiO_2, Al_2O_3 and Fe_2O_3 are important as they can give useful information on the phases that these elements occur.

4.2.2 Non-coal rock fragment mineralogy

Non-coal rock fragments are suspected to contain a high percentage of fluxing minerals. Fluxing minerals reduce the ash fusion temperatures of coals[41]. Hence it is important that mineral matter in non-coal rock fragments is well characterised. In this section results pertaining to the mineral matter as determined qualitatively and quantitatively are presented.

4.2.2.1 Qualitative XRD

For non-coal rock fragments PXRD data were collected using a Bruker AXS D8. Peak identification was performed using Bruker Eva search/match software. The crystalline phases were identified by comparing the peak positions and intensities with those in the Inorganic crystal structure database (ICSD) data files.

As expected, the major minerals in the hand picked non-coal rock fragments are kaolinite, quartz, muscovite/illite and orthoclase. Below (Figure 4.4) are XRD patterns for the samples analysed for non-coal rock fragments. The most intense peaks are for quartz correlating to the ash oxide composition where quartz is the most abundant mineral. Most of the peaks for the clay minerals overlap and there was difficulty in distinguishing the difference between certain minerals. Examples of this are the illite and muscovite peaks. They both are minerals of the same family of mica clay minerals and diffract x-rays at almost similar angles.

Considering Figure 4.3 the first peak is characteristic of muscovite/illite. The next peak is that of kaolinite. Because of the chemical structure of these clay minerals being similar, most of their peaks were found to overlap. The peaks at $2\theta > 30^{\circ}$ are mostly quartz peaks and were not labeled for clarity purposes. Microcline is identified by the peak at $27^{\circ}2\theta$ close to the highly intense quartz peak.

The peaks have different intensities which correspond to the mineral compositions. These intensities are confirmed by the mineral matter quantitative analysis results which are discussed in the section to follow (section 4.2.2.2). The sharpness of the peaks also confirms that non-coal rock fragments contain a lot of crystalline material.

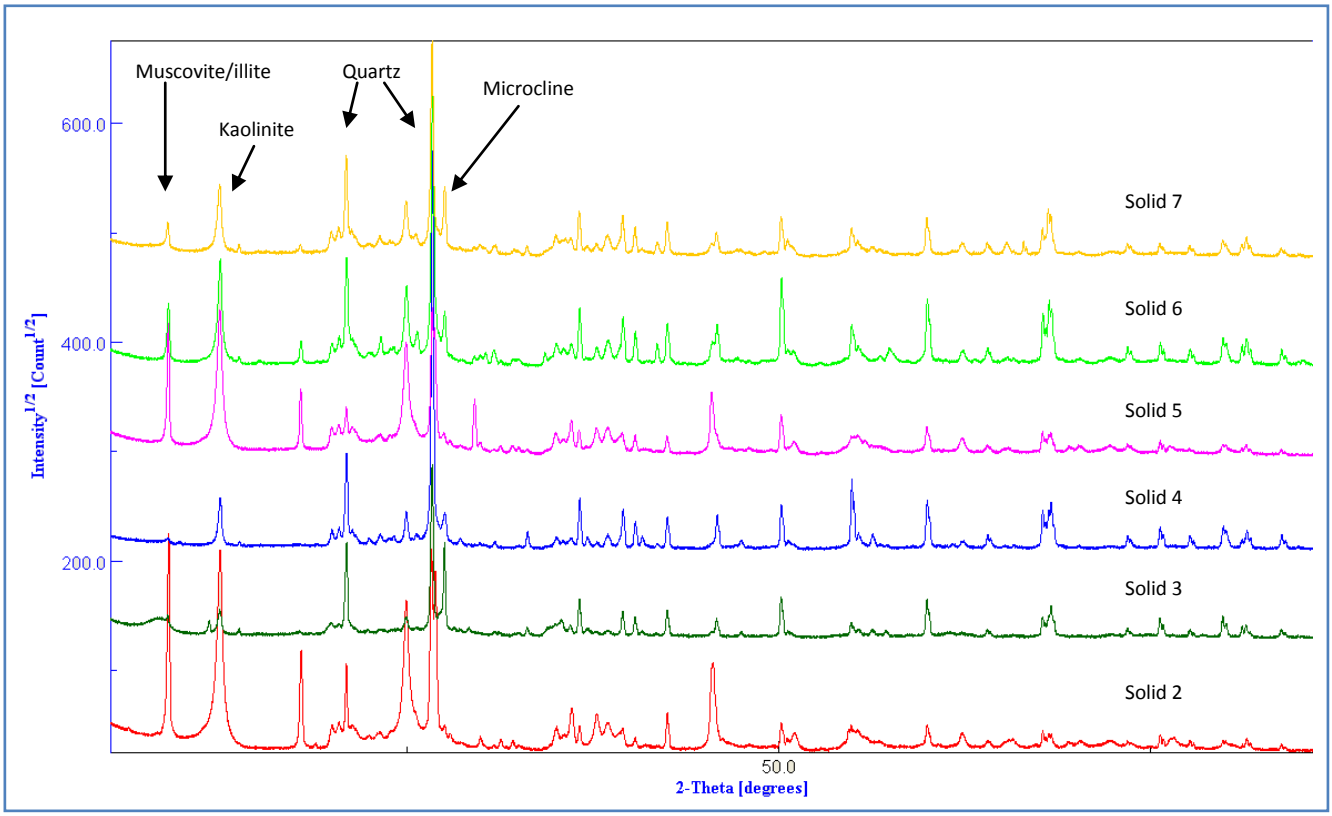

Figure 4.4: An XRD pattern for the non-coal samples analysed

The background peak of an XRD pattern is another characteristic of PXRD patterns that can give invaluable information on the relative composition of amorphous material. But the background can also make it difficult to identify crystalline phases if the amorphous content is very high; therefore subtracted in the above patterns to make the analysis easier. According to the non-subtracted background XRD patterns (which was deducted by observation), most of the non-coal rock material analysed did not have a high organic matter material. The subtraction of the background for the above patterns removed with it a lot of valuable information on the organic matter content in each of the above patterns.

4.2.2.2 Quantitative analysis

PXRD is a very useful tool to qualify and quantify crystalline phases present in the samples. But it should be remembered that XRD is only able to quantify crystalline material. One of the main reasons for studying rock fragments was to understand its low non-crystalline material content. Quantitative phase analysis was performed on the rock fragments using Rietveld-

based analysis softwares MAUD and TOPAS. So the following quantitative results should be taken with caution as they were normalised to 100% crystalline material.

MAUD

Before the actual operation of the MAUD program, raw files from the EVA program(generated by the x-ray diffractometer) were converted to a format compatible with MAUD as UXD files. The actual operation of the MAUD program involves interactive adjustment and best-fit matching of the PXRD profiles for the individual minerals in the CIF file to the observed X-ray powder diffraction pattern after the background removal and calibration processes. Overall intensities of the individual mineral phases, together with unit-cell dimensions, line widths and preferred orientation for the minerals, were progressively refined under operator instructions to fit the full profile of the sample's XRD pattern. Weight percentages of the different minerals were calculated at each stage of the process, along with the overall standard deviation expressed as the sigma value between the observed and computed profiles (Table 4.5).

The results of the MAUD analysis (Figure 4.5 for solid 7) represents the final output from the refinement, when the best possible fit had been achieved between the observed and calculated XRD patterns(see APPENDIX B for profile outputs for solid samples 2 – 6). The blue marked pattern represents the observed pattern whereas the black marked pattern represents the calculated pattern with refinements. Below the patterns are minerals which were being quantified. The numbers 63315 ICSD and 9542 ICSD are the database numbers for quartz and kaolinite respectively. ICSD is an international crystallographic structural database from which the calculated pattern was computed from. The red marks represent the positions of the peaks for each of the minerals being quantified. The profile at the bottom part of the figure represents the difference pattern between the observed and calculated profiles.

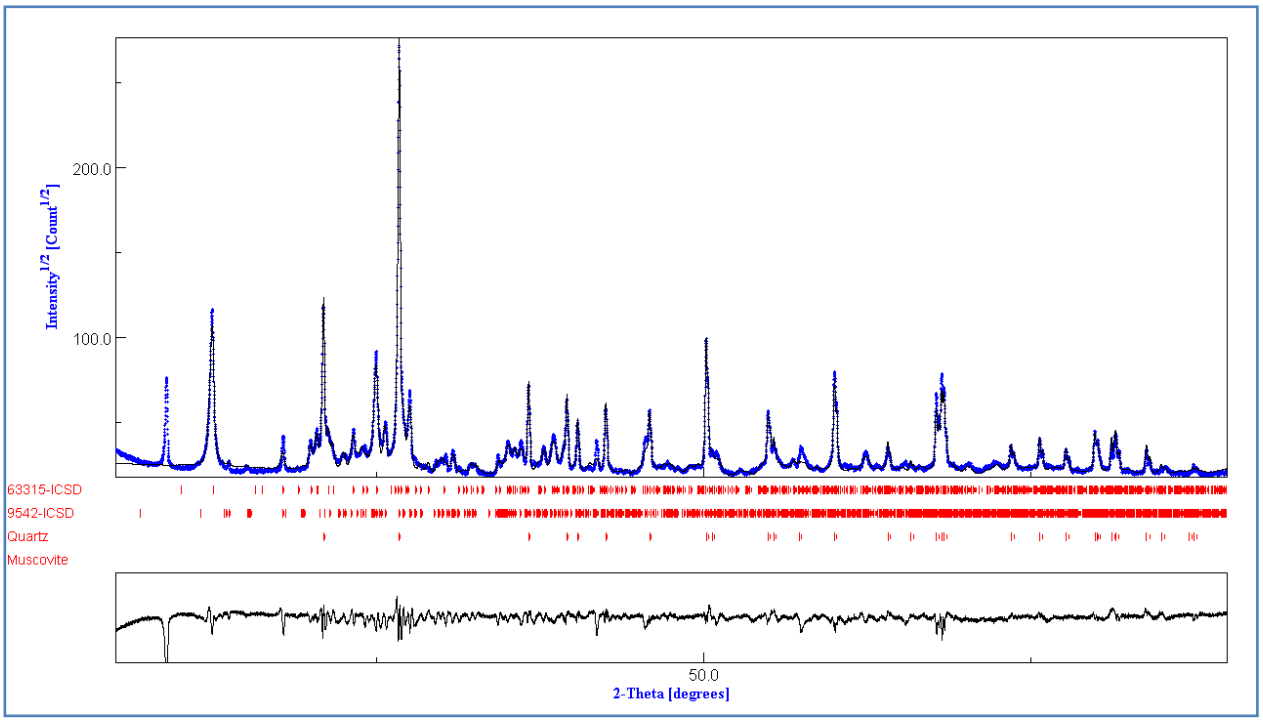

Figure 4.5: A MAUD program output for solid 7

Quantitative results for non-coal mineral matter are shown on Table 4.7 below. The most important parameters are the final *Rw* and *sigma* values. These values represent the standard deviation. An acceptable standard deviation has values of *Rw<15.0* and *sig<2.0.* For almost all the refinements done, the standard deviation was higher than these confidence values with the highest value being for solid 2 with *Rw* = 36.9 and *sigma* =15.9 and the best fit having *Rw*= 11.0 and *sigma* = 4.3. The errors in these refinements could not be accounted for but it was suspected that the MAUD program might not have been able to quantify the number of minerals required. This is evident considering that when the program was instructed to determine four or more phases in the profile, it was only able to quantify three mineral phases. This usually occurred when there was more than one mineral where peaks would overlap (clay minerals). The program's refinement was unable to distinguish between some of these overlapping peaks as can be seen for muscovite in Figure 4.5. The muscovite peaks have been somehow been excluded from the refinement. The only analysis where four minerals were quantified was for solid 6.

The other reason suspected for the high standard deviation percentage was the composition of mineral components that are in small proportions and quantification is below the resolution of

the Rietveld technique[47]. These minerals are the minerals that were confidently qualified during the search/match exercise. They include minerals such as pyrite, dolomite, microcline and siderite. The results below have been normalized to a 100% but should be taken with caution for reasons mentioned above.

Table 4.6: A table showing XRD quantitative minerals composition for non-coal rock fragments as determined using MAUD

	Solid 2(%)	Solid 3(%)	Solid 4(%)	Solid 5(%)	Solid 6(%)	Solid 7(%)
Kaolinite	51.0	0.0	0.0	0.0	30.4	36.2
Quartz	40.1	48.3	74.2	73.9	54.1	42.5
Muscovite/illite	8.89	34.3	2.2	0.0	2.47	0.0
Microcline	0.0	17.4	6.9	26.1	13.4	21.3
Total	100	100	83.2	100	100	100
Sig	15.9	5.2	7.5	9.0	5.4	4.3
R_w	36.9	11.2	18.6	27.6	16.7	11.0

Taking into consideration the above concern, the major minerals present in the non-coal rock samples are kaolinite, quartz, and with minor feldspar in the form of microcline, and traces of muscovite/illite in almost all the samples. This observation is consistent with the ash oxide composition results where SiO_2 was the most abundant mineral. Solid samples 4 and 5 have very high quartz content (74.2% and 73.9% respectively) which is consistent with the chemical composition of sandstones. Amorphous material was not quantified. The 0% kaolinite in solid samples 3, 4, and 5 could not be explained. It was suspected that the anomaly could have resulted from a software error.

TOPAS

Quantitative analysis methods using TOPAS were also compared for non-coal rock fragments. A TOPAS quantitative method was performed in similar manner as was discussed for MAUD above. The only difference between the two methods is mainly the calculation capabilities of the methods with TOPAS being able to handle a larger amount of data.

Figure 4.6 below shows a profile output for TOPAS with the actual quantitative phase results displayed on the top right corner.

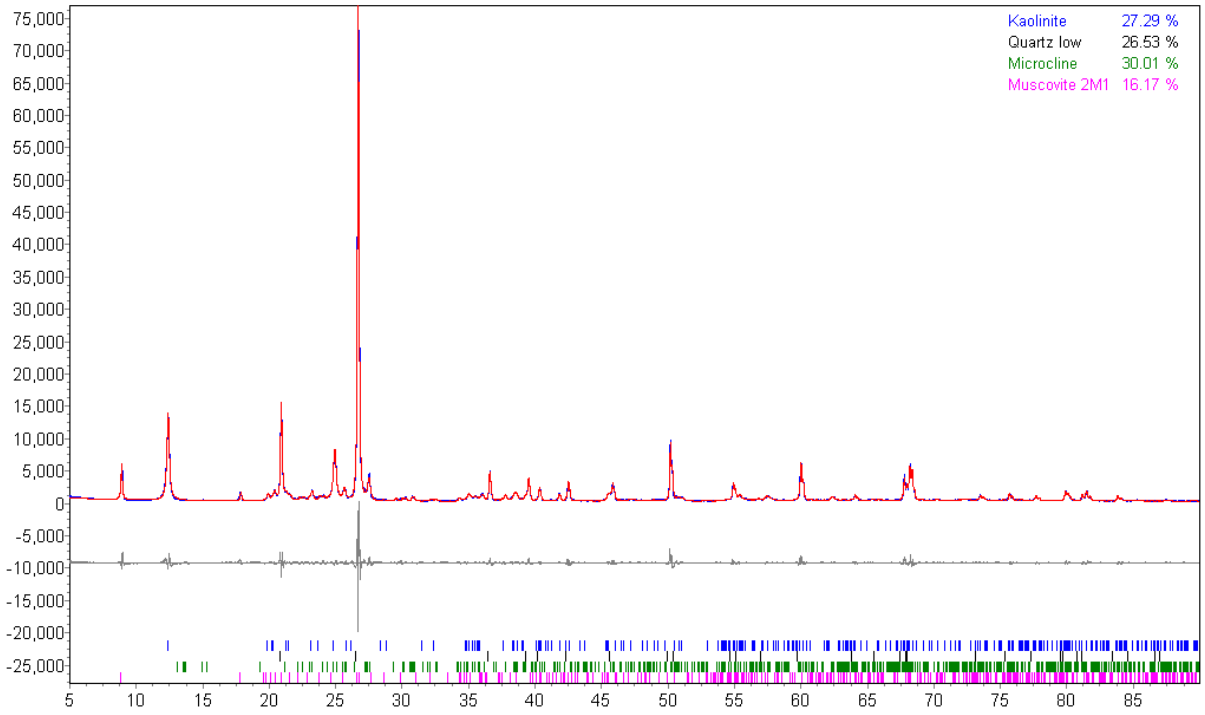

Figure 4.6: A figure showing a profile output for non-coal rock fragments using TOPAS

The complete quantitative results of all the non-coal rock fragments are displayed in Table 4.8 Note the major differences in the quantitative results of the two methods (Table 4.9). This is mainly due to the errors in calculation as explained in interpretation of MAUD quantitative results. TOPAS can account for all the peaks identified (standard deviation ≤3 obtained in most cases) as compared to the ≥6 standard deviation for MAUD.

Thus TOPAS results can be accepted with much more confidence because of their reproducibility when compared to MAUD. Comparisons with data from QEMSCAN are discussed below.

The fluxing minerals (dolomite, calcite, and pyrite) have been included in the results even though they were undetected. This was done to show just that, non-coal rock fragment contain little or no fluxing minerals, or the values are below the detection limit of the equipment.

Table 4.7: A table showing the quantitative results for non-coal rock fragments using TOPAS

Mineral	Solid 2(%)	Solid 3(%)	Solid 4(%)	Solid 5(%)	Solid 6(%)	Solid 7(%)
Quartz	13.2	3.4	26.5	1.9	26.5	19.6
Kaolinite	73.5	30.7	69.8	46.1	27.3	24.2
Muskovite/illite	13.3	38.7	<0.1	22.0	16.2	19.0
Microcline	<0.1	27.2	3.7	30.0	30.0	37.1
Dolomite	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Calcite	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pyrite	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Aragonite	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Siderite	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Total	100	100	100	100	100	100

When considering the mineral compositions of most rock fragments, (based on literature) the above quantitative results in Table 4.7 are more acceptable than those expressed in Table 4.6, although a high composition of quartz was expected for sandstones and a high kaolinite composition was expected for siltstones (solids 3 and 5). It is suspected that a similar problem to the one encountered with MAUD was encountered when attempting to resolve for quartz and kaolinite peaks. The use of standards is advised for future studies. This will enable the distinguishing and correct quantification of peaks belonging to kaolinite and quartz.

4.2.2.3 QEMSCAN

The mineral proportions determined by QEMSCAN showed that the major minerals are the same as the minerals quantified by the Rietveld based MAUD and TOPAS program. The major minerals are highlighted in Table 4.8, being quartz, kaolinite, muscovite/illite and minor minerals of feldspar in the form of microcline. The "coal" proportion is based on ash% and the carbon value from proximate and ultimate analysis.

Table 4.8: A table showing the mineral proportions calculated from QEMSCAN

Mineral	Solid 2(%)	Solid 3(%)	Solid 4(%)	Solid 5(%)	Solid 6(%)	Solid 7(%)
K-alteration	0.04	1.3	0.3	0.1	0.02	0.6
Pyrite	0.1	3.6	7.0	1.3	0.5	4.0
Calcite	0.4	0.3	0.05	0.2	0.1	0.2
Dolomite	0.01	0.00	0.01	0.1	0.00	0.04
Apatite	0.01	0.01	0.04	0.1	0.04	0.1
Microcline	2.4	13.7	6.7	2.8	14.3	14.5
Muscovite/Illite	15.2	11.7	1.9	10.0	6.6	7.5
Kaolinite	59.4	9.4	9.5	46.5	22.3	24.0
Quartz	20.5	57.9	73.1	22.1	54.4	41.8
FeOxide/Siderite	0.03	0.13	0.04	0.02	0.1	0.04
Anatase	0.6	0.5	0.7	1.1	0.6	0.8
Other	0.1	0.6	0.14	0.08	0.2	0.2
Coal	1.3	0.8	0.6	15.7	1.0	6.3
Total	100.0	100.0	100.0	100.0	100.0	100.0

There are major differences though between the mineral proportions from QEMSCAN and XRD. As XRD is technically a semi-quantitative analytical technique this can be expected. The anomalies between the two mineral quantification techniques are in the actual values, as highlighted in Table 4.9.

Table 4.9: Comparison of mineral proportions calculated by TOPAS, MAUD and QEMSCAN for Solid 7

Mineral	QEMSCAN(%)	TOPAS(%)	MAUD(%)
Microcline	2.4	0.1	21.3
Muscovite/illite	15.2	13.3	0.0
Kaolinite	59.4	73.5	36.2
Quartz	20.5	3.4	42.5

The mineral proportions for certain minerals, microcline and quartz, indicate how the methods are incomparable. The ranges for muscovite/illite and kaolinite are too high for any correlation between the two instruments to be made.

In comparing TOPAS results with the inferred mineral matter proportions from XRF in Table 4.8 and QEMSCAN below, SIROQUANT results are the most accurate. The precision for TOPAS is good when considering the goodness of fitting of the least square curve. The goodness of fit for the ash was 1.42 and 1.82 respectively. A perfect fit is equal to 1 but anything less than 2 is considered good.

4.2.2.4 Comparison of QEMSCAN and normative analysis

Through the use of either ternary diagrams or normative methods, elemental proportions can be very useful tools for mineral proportions. Below (Table 4.10) is a table showing mineral proportions determined using VAC CQA prediction spreadsheet, mineral proportions are based on known mineral compositions.

Table 4.10: VAC CQA prediction based on XRF elemental proportions

Mineral	Sample 2(%)	Sample 3(%)	Sample4(%)	Sample 5(%)	Sample 6(%)	Sample 7(%)
Pyrite	0.1	3.6	4.7	1.3	0.1	4.0
Calcite	0.4	1.1	0.1	0.4	0.1	0.1
Dolomite	0.0	0.0	0.0	0.0	0.0	0.0
Apatite	0.0	0.0	0.0	0.1	0.0	0.3
Microcline	5.8	8.2	3.3	3.9	9.0	8.7
Muscovite/Illite	8.3	14.0	5.6	5.7	12.7	14.0
Kaolinite	61.9	7.0	9.2	50.7	18.2	22.6
Quartz	20.1	59.8	70.5	19.9	57.2	42.7
Siderite/Fe-oxide	1.8	5.3	3.8	1.1	1.0	0.7
Rutile	0.7	0.2	0.3	1.1	0.5	0.6
Coal	0.8	0.8	2.4	15.7	1.1	6.3
Total	100.0	100.0	100.0	100.0	100.0	100.0

For verification purposes QEMSCAN results were compared to normal normative analysis. Tables 4.10 and 4.11 below show the VAC CQA predictions based on XRF and AA (See Appendix A) elemental proportions respectively. This data was used in comparing VAC CQA predictions based on XRF and AA against QEMSCAN mineral proportions (Figure 4.11)

Table 4.11: VAC CQA prediction based on AA elemental proportions

	Solid 2(%)	Solid 3(%)	Solid 4(%)	Solid 5(%)	Solid 6(%)	Solid 7(%)
Pyrite	0.1	3.6	4.8	1.4	0.1	4.1
Calcite	0.0	0.0	1.0	0.1	0.0	0.0
Dolomite	1.0	1.8	0.1	0.9	0.3	0.7
Apatite	0.1	0.1	0.1	0.1	0.0	0.3
Microcline	6.1	7.2	2.8	3.9	6.9	8.4
Muscovite/Illite	8.6	12.4	4.9	5.8	9.7	13.8
Kaolinite	57.2	5.1	5.9	47.8	15.6	18.4
Quartz	23.5	64.6	75.0	22.4	64.8	46.7
Siderite/FeOxide	1.5	3.6	2.4	0.8	0.6	0.4
Rutile	0.7	0.2	0.3	1.1	0.4	0.5
Coal	1.2	1.4	2.9	16.0	1.6	6.7

The diagonal line drawn through 0 represents the line along which the points would fall if the proportions of the relevant mineral estimated from the VAC CQA prediction data were exactly equal to those determined directly by QEMSCAN chemical analysis. For a perfect correlation, all points would plot along this line, and the correlation equation parameters would be: a=1, b =0, and R^2 =1.0. Other similar graphs for strong correlations were obtained for pyrite, quartz and k-bearing minerals, with high R^2 values, low values for b, and with values for a close to 1(See APPENDIX D). The added advantage of this way comparing results is that it not only enables the analyst to compare the actual accuracy of the instruments but the analyst is also able to compare between the instrument as an “honesty check”.

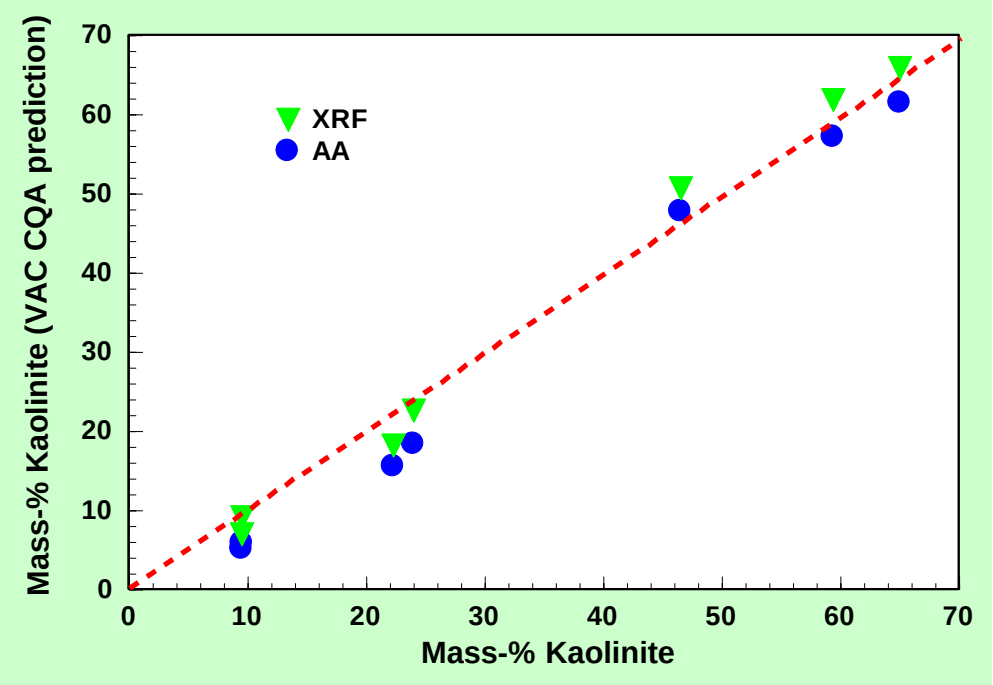

Figure 4.7: Mass-% Kaolinite - QEMSCAN, VAC CQA based on XRF and AA

Overall, it appears that the mineral predictions based on XRF compare more favourably to QEMSCAN than the AA based predictions. QEMSCAN has identified K-alteration phases. The VAC CQA predicted siderite, calcite and dolomite is due to Ca, Mg and Fe not associated with these phases in these rock fragments, but with other phases such as K-alteration and muscovite/illite.

4.2.2.5 Non-coal rock fragments minerals effect on slagging and clinker formation

In this section mineral matter that were characterized in the non-coal rock are brought into context as to how they contribute to slagging or clinker formation. The major minerals in the non-coal rock fragments were found to be quartz, kaolinite and minor minerals are muscovite/illite and microcline.

Extraneous quartz grains have been suspected to react to form glass, especially above the quartz melting point of 1710˚C, but can also persist as essentially unreacted particles throughout the different stages of a coal conversion process[23].

Kaolinite, pyrite, muscovite and carbonates have been identified by Matjie *et al*[12] as the major minerals that initiate the first stage of clinker formation (in gasifiers). The dehydration of kaolinite and muscovite/illite together with the devolitilisation of coarse pyrite and carbonates contribute significantly to the formation of a melt. On cooling (of which rock fragments are suspected to play a significant role), some coal minerals will crystallise out and the non-coal minerals will stick to those minerals to form a clinker. But because these are coal minerals, they will behave differently to kaolinite, pyrite, and muscovite in non-coal rock fragments.

Mineral associations is one of the factors not included in the current study, but will play a crucial role into how the minerals in non-coal rock fragments will behave under certain coal conversion processes. An example of this is kaolinite which can be associated with fluxing minerals. Kaolinite will behave differently in gasification and combustion units. The temperatures at which a melt (hence slag/clinker) is formed can be affected to some degree[23].

Chapter 5: SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

The main objective of the study was to determine the chemical and mineralogical properties of mainly rock fragments whereas coal and ash clinkers were also characterised in order to gain a broader understanding of these properties in relation to coal and the formation of ash clinkers.

5.1 Summary and Conclusions

Non-coal rock fragments as well as a coal from the Highveld coalfield and ash clinker sample from a commercial gasifier were characterised using different analytical methods namely XRF, PXRD, QEMSCAN and normative methods. Commercial Rietveld-based methods SIROQUANT and TOPAS, and freely available software program MAUD were used for quantitative analysis. SIROQUANT was more accurate owing to the fact that an internal standard was used for quantifying non-crystalline material. Both the methods can be used for quantitative analysis as long as the non-crystalline mineral matter is also quantified.

QEMSCAN can also be used as very good tool for the discrimination of mineral and as a tool for confirming XRF and normative analysis results. The combination QEMSCAN and VAC CQA prediction provides a powerful technique for determining the mineralogy of the sample, total mineral matter, ash-% and elemental proportions.

The major minerals determined in all samples analysed were quartz, kaolinite, muscovite/illite and minor minerals of feldspar in form of microcline. The most abundant mineral overall was quartz.

5.2 Recommendation and Future work

Due to time constrains on the project (this is a research report), certain essential analysis were not completed and should be included in future work:

- The chemistry and mineral interaction should be understood in order to determine the suitability of including non-coal rock fragments for gasification and combustion purposes. This would support or disapprove the use of stone in certain coal conversion processes.

- The study of mineral phase transformation during coal conversion processes i.e at high temperatures
- Quantification of amorphous material in the non-rock rock fragments
- Mineral associations in non-coal rock fragment should be investigated

Over and above this, the study is intended to be pioneering work on understanding the minerals in both coal seams and included non-coal (inter-seam strata, roof and floor) such that better technologies can be better developed to suit the South African coals. This will enable the South African coal consumers to be able to make the most out of the declining coal qualities and for coal conversion facilities to predict clinkering and slagging behaviour.

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APPENDIX A: AA Results

ASH ANALYSIS(AA)

Sample	Solid 2	Solid 3	Solid 4	Solid 5	Solid 6	Solid 7
SiO_2	88.70	76.60	66.80	83.40	64.70	65.50
Al_2O_3	4.28	14.70	30.00	7.62	30.50	28.60
Fe_2O_3	4.35	3.10	0.83	4.51	1.25	1.88
P2O5	0.03	0.12	0.04	0.02	0.03	0.05
TiO_2	0.29	0.60	1.21	0.21	0.80	1.44
CaO	0.55	0.33	0.10	0.41	0.24	0.36
MgO	0.03	0.22	0.31	0.51	0.36	0.34
K_2O	0.95	3.10	0.89	2.48	2.12	1.64
Na_2O	0.07	0.22	0.23	0.23	0.28	0.31
SO_3	0.43	0.23	0.07	0.48	0.17	0.18

APPENDIX B: Quantitative profile outputs for MAUD and TOPAS

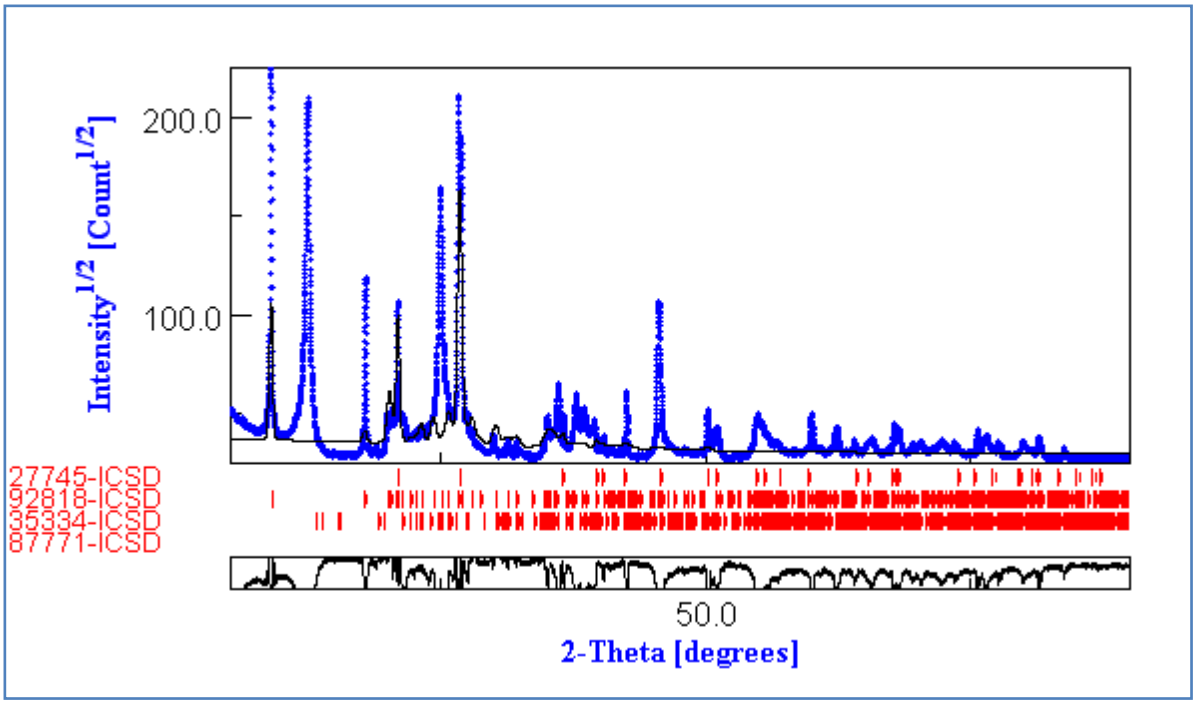

Figure B1: MAUD quantitative output profile for solid 2

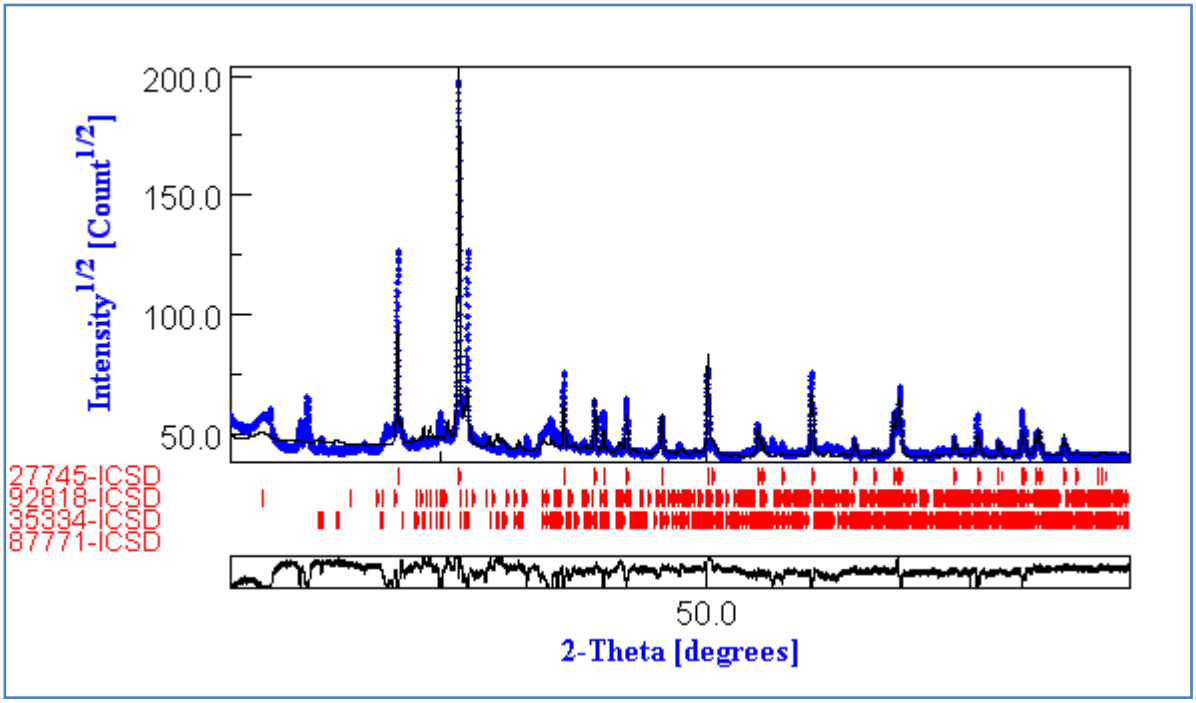

Figure B2: MAUD quantitative output profile for solid 3

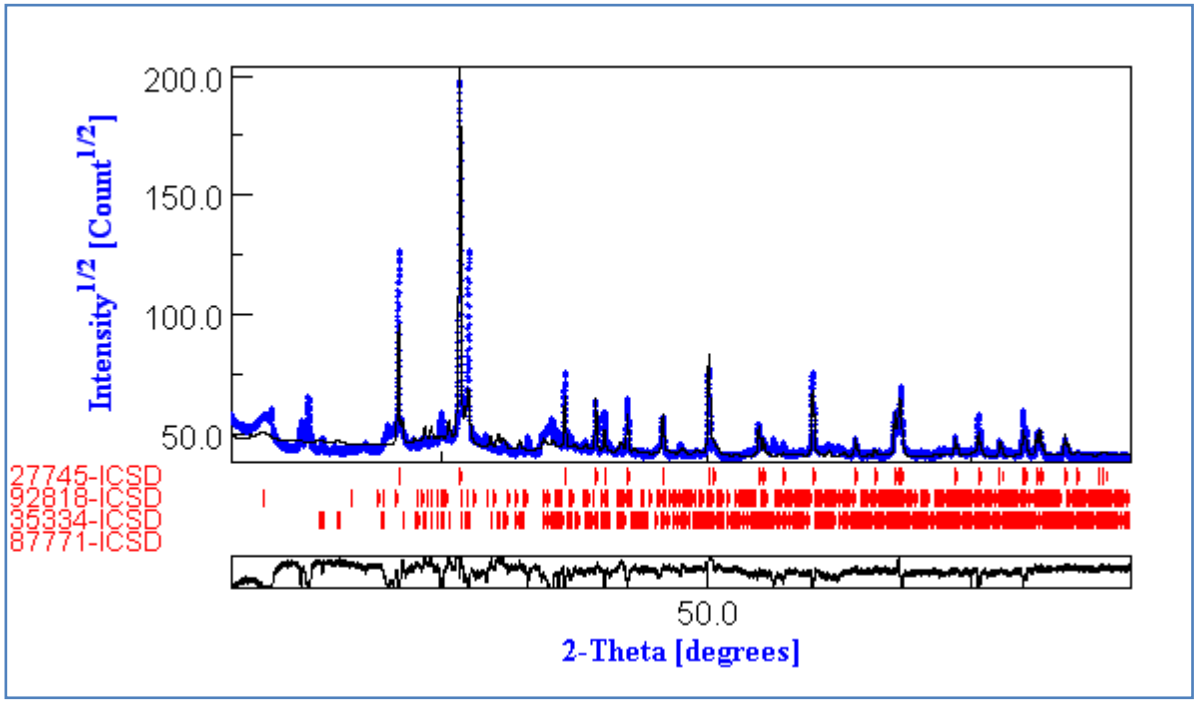

Figure B3: MAUD quantitative output profile for solid 4

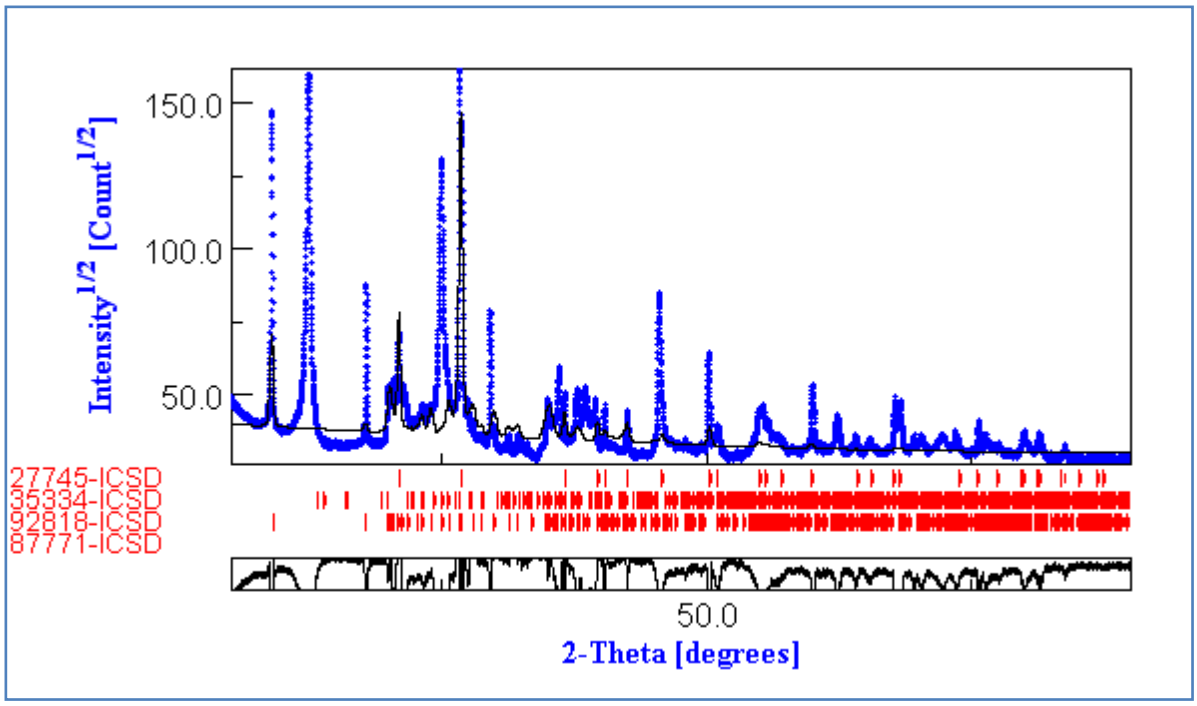

Figure B4: MAUD quantitative output profile for solid 5

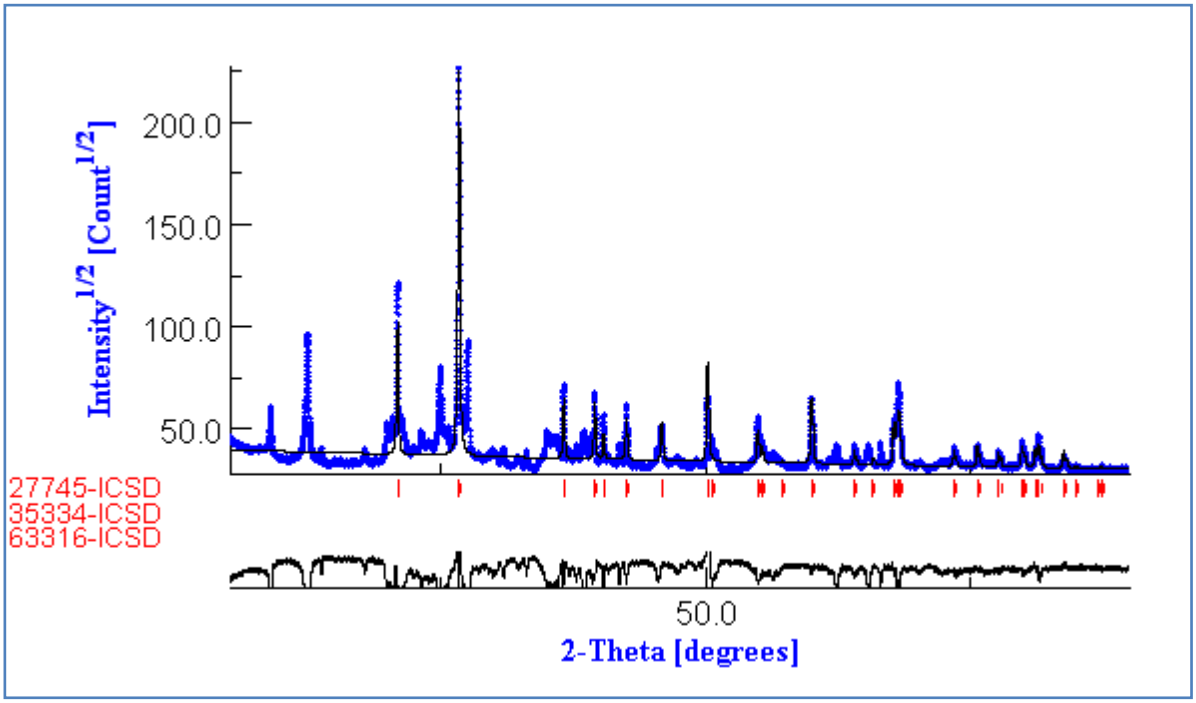

Figure B5: MAUD quantitative output profile for solid 6

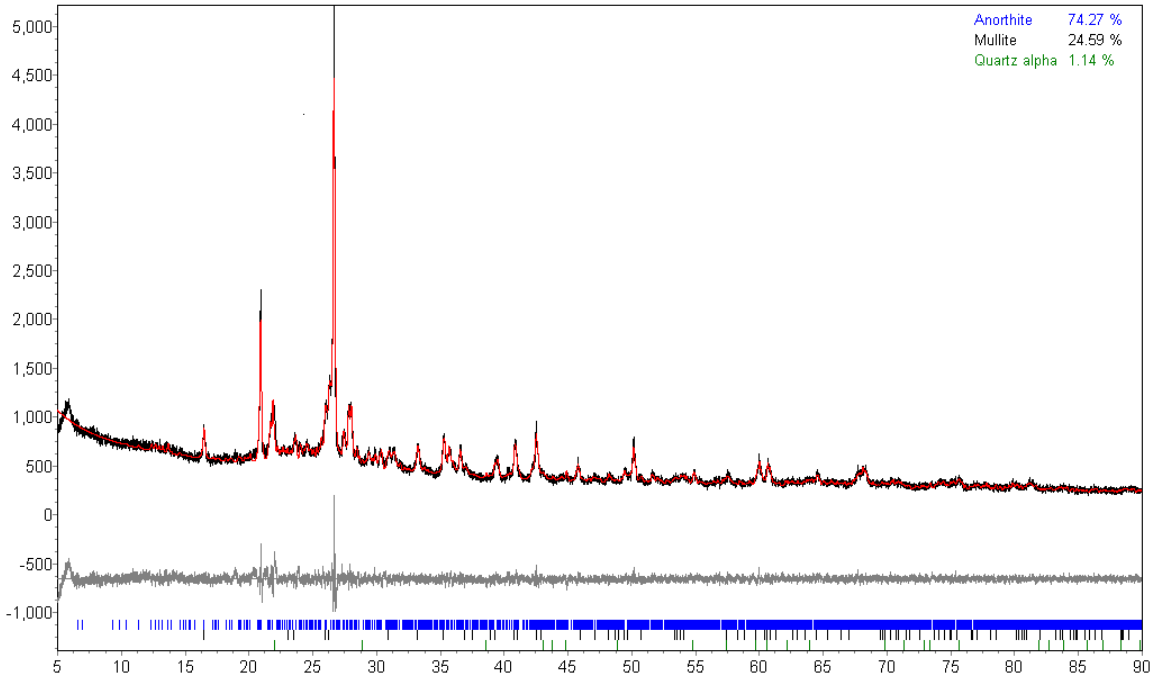

Figure B6: A figure showing the phase quantification output profile for ash

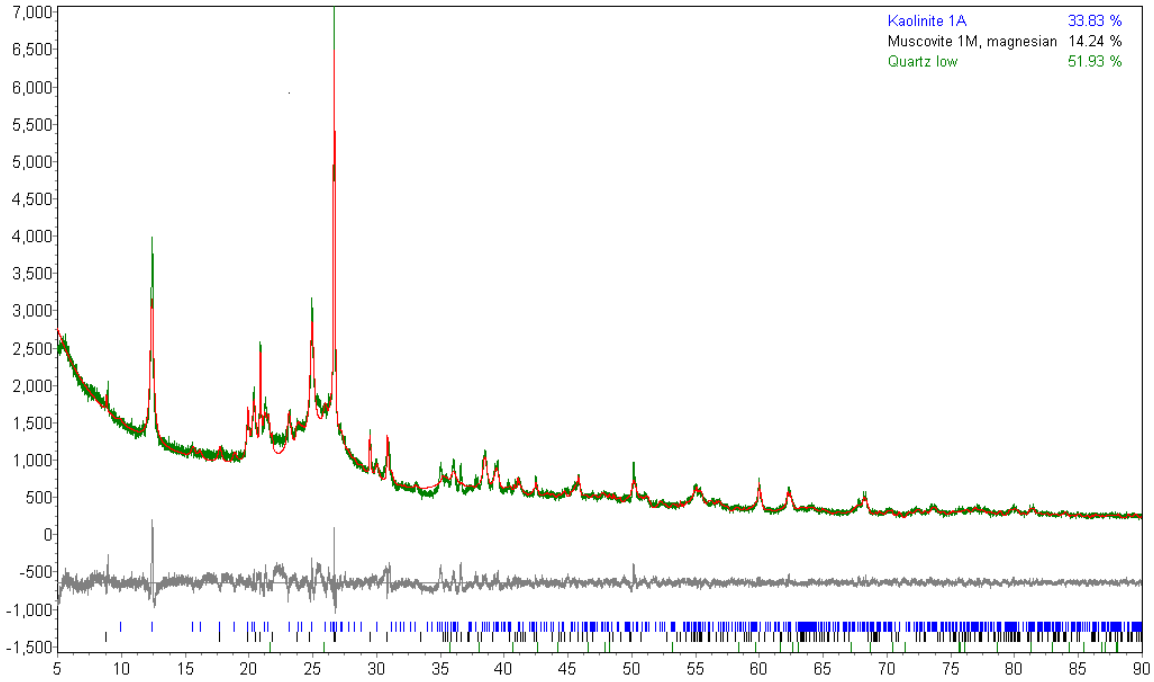

Figure B7: A figure showing the phase quantification output profile for coal

APPENDIX C: TOPAS phase quantification text output

Ash\gash.raw"

Range Number : 1

R-Values

Rexp : 4.49	Rwp : 6.37	Rp : 4.89	GOF : 1.42
Rexp`: 8.65	Rwp`: 12.28	Rp` : 9.79	DW : 1.06

Quantitative Analysis - Rietveld

Phase 1 : Anorthite	74.269 %
Phase 2 : Mullite	24.590 %
Phase 3 : "Quartz alpha"	1.141 %

Background

One on X		3197.314
Chebychev polynomial, Coefficient	0	239.7912
	1	-191.3514

Instrument

Primary radius (mm)	217.5
Secondary radius (mm)	217.5
Receiving slit width (mm)	0.2281897
Divergence angle (°)	1.169651

Corrections

Zero Error	0.04346322
Cylindrical sample I correction uR	0.0932287
LP Factor	56.20592

Structure 1

Phase name	Anorthite
R-Bragg	0.830
Spacegroup	P-1
Scale	4.50769581e-005
Cell Mass	3085.713
Cell Volume (Å^3)	1474.74023
Wt% - Rietveld	74.269
Crystallite Size	
Cry Size Lorentzian (nm)	86.9
Crystal Linear Absorption Coeff. (1/cm)	157.001
Crystal Density (g/cm^3)	3.474
Preferred Orientation Spherical Harmonics	
Order	4
y00	1
y20	0.001070839
y21m	-0.0004192785
y21p	-0.0004456307
y22m	-8.597826e-005
y22p	0.0006793703
y40	0.0008611642
y41m	5.69321e-005
y41p	-0.001879788

y42m	-0.0003726486
y42p	-0.0007601658
y43m	-0.001890196
y43p	-0.0005855382
y44m	2.108444e-005
y44p	-0.001448858
Lattice parameters	
a (Å)	8.6344207
b (Å)	12.7651467
c (Å)	14.8284362
alpha (°)	92.19147
beta (°)	115.2373
gamma (°)	92.11422

Site	Np	x	y	z	Atom	Occ	Beq
Ca1	2	0.26435	0.98410	0.05381	Ca+2	0.5775	5.541
Na1	2	0.13963	0.91980	0.14506	Na+1	1.054	18.36
Ca2	2	0.06390	0.07713	0.09706	Ca+2	0.4337	-4.153
Na2	2	-0.09379	-0.34179	0.03264	Na+1	0.3928	-6.856
Ca3	2	0.35732	0.07433	0.61696	Ca+2	1.136	13.51
Na3	2	0.68268	0.21163	0.57471	Na+1	0.2396	-9.881
Ca4	2	0.31462	0.01490	0.49428	Ca+2	0.6542	11.31
Na4	2	0.07713	-0.02851	0.59823	Na+1	1.018	-3.644
Si1	2	0.04574	0.13008	0.14303	Si+4	0.3276	-8.299
Al1	2	0.10515	0.10769	0.64563	Al+3	0.7141	-0.6949
Al2	2	0.17109	0.27990	0.90621	Al+3	1.523	20
Si2	2	0.91180	0.15756	0.39421	Si+4	0.6411	-6.988
Al3	2	0.69140	0.09393	0.14930	Al+3	0.9873	-4.031
Si3	2	0.71059	0.06937	0.60401	Si+4	0.6716	-4.387
Si4	2	0.27393	0.14043	0.78884	Si+4	0.402	-9.683
Al4	2	0.35090	0.09277	0.31952	Al+3	0.7474	-5.406
O1	2	0.05801	0.14057	0.99417	O-2	0.9929	-9.775
O2	2	0.95926	0.14970	0.46403	O-2	0.5699	-10
O3	2	0.61787	0.94921	0.14924	O-2	1.782	-4.982
O4	2	0.56540	1.02025	0.61507	O-2	0.6744	-7.186
O5	2	0.86450	0.11027	0.13055	O-2	1.469	10.43
O6	2	0.89963	0.03552	0.65209	O-2	0.6131	-10
O7	2	0.92633	0.86641	0.13016	O-2	1.868	4.02
O8	2	0.90968	0.85938	0.59929	O-2	1.669	7.072
O9	2	0.07254	0.22707	0.08639	O-2	1.827	7.113
O10	2	-0.02880	0.33269	0.63637	O-2	1.788	13.4
O11	2	0.03916	0.63408	0.10167	O-2	1.572	-0.6741
O12	2	0.09866	0.73096	0.61966	O-2	2.511	3.907
O13	2	0.20298	0.10499	0.21953	O-2	2.077	-5.639
O14	2	0.29943	0.09199	0.72191	O-2	1.175	-5.771
O15	2	0.18613	0.89670	0.27315	O-2	0.9012	1.445
O16	2	0.26570	0.83820	0.75909	O-2	0.7424	2.252
Ca5	2	0.84916	0.50864	0.59567	Ca+2	0.5563	-2.873
Na5	2	0.72776	0.58018	0.58789	Na+1	0.7911	-7.973
Ca6	2	0.75369	0.56252	0.50573	Ca+2	0.3145	-9.167
Na6	2	0.86054	0.74201	0.37302	Na+1	0.5541	-4.167
Ca7	2	0.84493	0.55484	0.11269	Ca+2	0.5289	-6.173
Na7	2	0.86524	0.72404	0.24544	Na+1	0.2857	-9.621
Ca8	2	0.91122	0.43309	0.13709	Ca+2	0.4681	2.251
Na8	2	0.33848	0.74459	0.09224	Na+1	0.7261	-8.255
Si5	2	0.48433	0.37423	0.39207	Si+4	1.178	0.4036
Al5	2	0.56167	0.34910	0.88540	Al+3	1.838	2.585

Al6	2	0.62490	0.30823	0.67514	Al+3	2.319	15.62
Si6	2	0.60288	0.30258	0.09195	Si+4	0.4998	-8.618
Al7	2	0.92254	0.37090	0.32885	Al+3	2.066	20
Si7	2	0.82570	0.40281	0.85636	Si+4	0.3855	-2.435
Si8	2	0.15111	0.37163	0.66716	Si+4	0.7556	-7.615
Al8	2	0.22043	0.35819	0.17374	Al+3	2.293	20
O17	2	0.55603	0.68009	0.56927	O-2	0.6578	-9.354
O18	2	0.46704	0.70268	1.03996	O-2	0.8984	-8.611
O19	2	0.07664	0.48979	0.61657	O-2	0.8269	-8.815
O20	2	0.07110	0.46890	0.12959	O-2	1.394	-3.457
O21	2	0.33613	0.54678	0.55983	O-2	0.7243	-7.716
O22	2	0.42557	0.50775	0.06811	O-2	2.105	18.48
O23	2	0.29553	0.36002	0.64847	O-2	2.969	20
O24	2	0.42083	0.40987	0.16297	O-2	0.6227	-9.587
O25	2	0.53182	0.78278	0.62980	O-2	2.607	13.9
O26	2	0.49318	0.85735	0.12907	O-2	2.686	7.446
O27	2	0.59800	0.17021	0.61370	O-2	2.07	-2.03
O28	2	0.53326	0.18184	0.12682	O-2	2.527	6.644
O29	2	0.67198	0.63935	0.66244	O-2	1.488	0.5085
O30	2	0.82470	0.47030	0.25049	O-2	0.3163	-10
O31	2	0.69980	0.43078	0.64924	O-2	1.617	2.556
O32	2	0.64128	0.43345	0.15812	O-2	2.125	20

Structure 2

Phase name	Mullite
R-Bragg	0.429
Spacegroup	Pbam
Scale	0.000650365786
Cell Mass	620.926
Cell Volume (Å^3)	168.18115
Wt% - Rietveld	24.590
Crystallite Size	
Cry Size Lorentzian (nm)	53.5
Crystal Linear Absorption Coeff. (1/cm)	246.751
Crystal Density (g/cm^3)	6.131
Preferred Orientation Spherical Harmonics	
Order	4
y00	1
y20	-0.00177295
y22p	0.005820201
y40	-0.0185808
y42p	-0.1049104
y44p	0.00929407
Lattice parameters	
a (Å)	7.5543878
b (Å)	7.7087107
c (Å)	2.8879941

Site	Np	x	y	z	Atom	Occ	Beq
Al1	6	0.00000	0.00000	0.00000	Al+3	0.4328	20
Cr1	6	0.00000	0.00000	0.00000	Cr+3	0.08651	20
Al2	8	0.12632	0.33977	0.23102	Al+3	0.4536	6.858
Si1	8	0.13262	0.33156	0.28454	Si+4	0.317	7.966
Al3	8	0.07084	0.05998	0.26244	Al+3	0.1553	-5.261
O1	8	0.30510	0.37864	0.92379	O-2	0.8149	-3.929
O2	8	0.16433	0.21949	-0.23057	O-2	1.086	11.02

O3	8	0.34932	0.10758	0.45650	O-2	0.4111	20
O4	8	0.44378	-0.02776	0.49247	O-2	0.1972	-8.133

Structure 3

Phase name	Quartz alpha
R-Bragg	5.265
Spacegroup	P3121
Scale	7.22624257e-005
Cell Mass	481.019
Cell Volume (Å^3)	90.67396
Wt% - Rietveld	1.141
Crystallite Size	
Cry Size Lorentzian (nm)	130.8
Crystal Linear Absorption Coeff. (1/cm)	424.975
Crystal Density (g/cm^3)	8.809
Lattice parameters	
a (Å)	4.6637680
c (Å)	4.8136896

Site	Np	x	y	z	Atom	Occ	Beq
Si1	6	0.50000	0.00000	0.00000	Si+4	1	1
O1	6	0.41680	0.23800	0.14080	O-2	0.5	1
Si1	6	0.44500	0.00000	0.33330	Si+4	1	1
O1	6	0.39470	0.30900	0.24470	O-2	1	1

APPENDIX D: VAC CQA plots

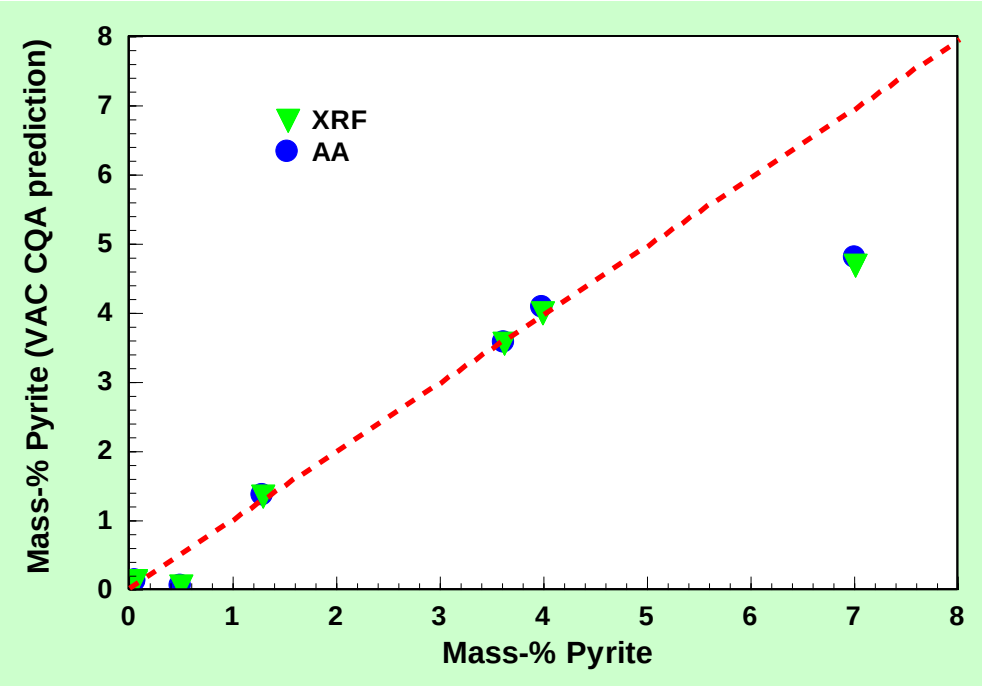

Figure D1: Mass-% Quartz - QEMSCAN, VAC CQA based on XRF and AA

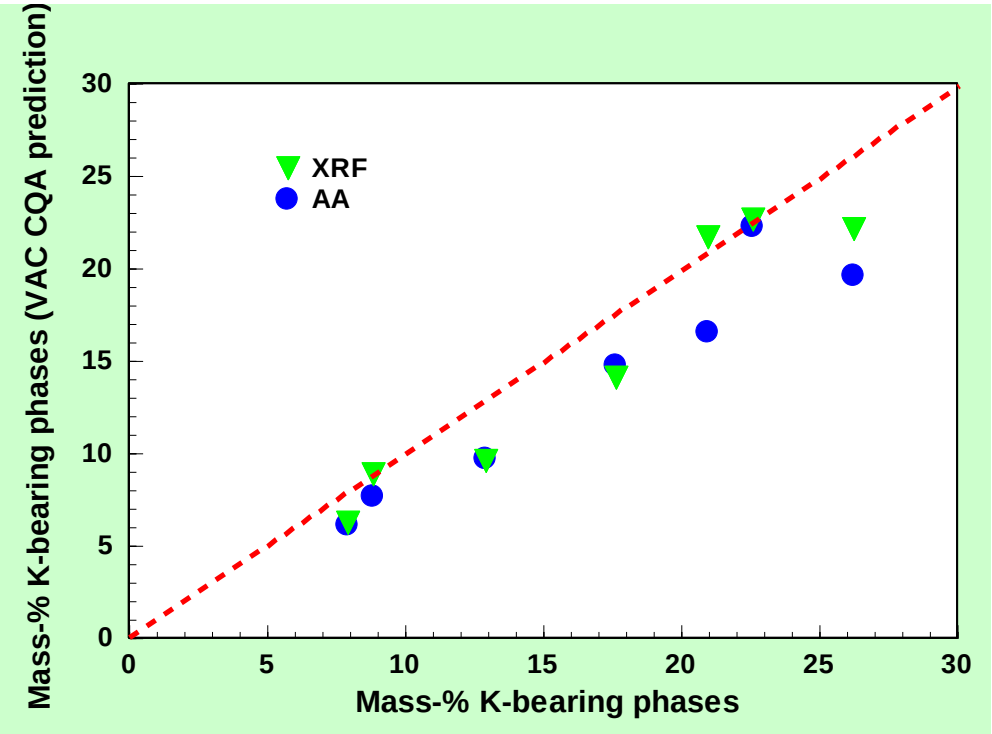

Figure D2: Mass-% Quartz - QEMSCAN, VAC CQA based on XRF and AA

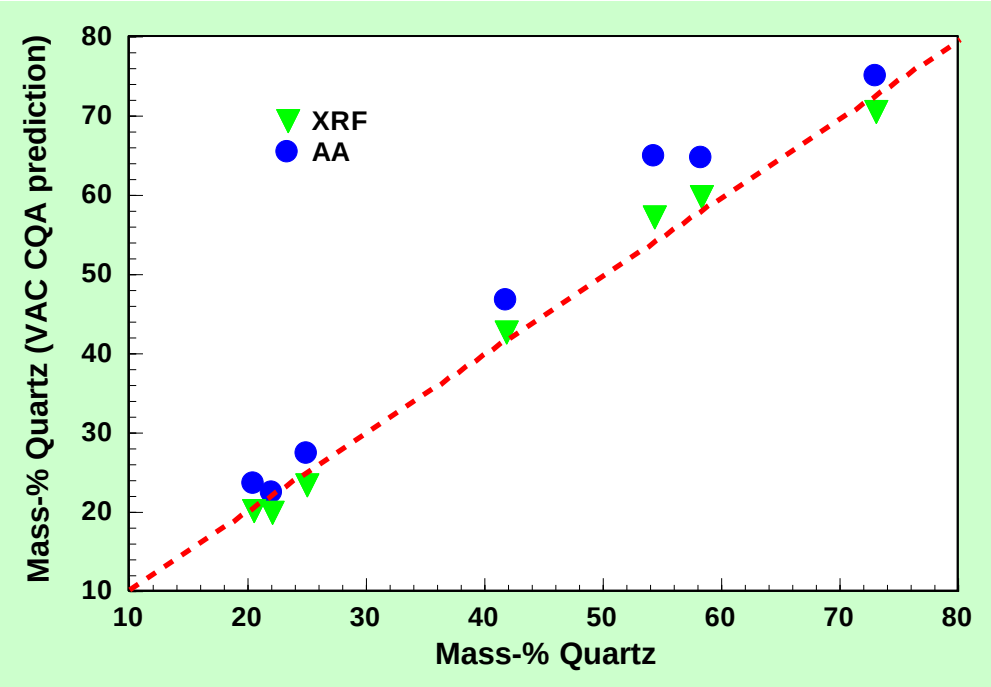

Figure D3: Mass-% Quartz - QEMSCAN, VAC CQA based on XRF and AA