

# Detailed Characterisation of Sasol Ashes

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## ABSTRACT

Sasol utilises coal based gasification and combustion processes to produce synthesis gas and steam. Coal ashes (gasification ash and steam station ash) are the by-products of these processes. The conversion of Sasol ashes into viable products is an on-going research interest. In support of this research initiative, a need was identified to better understand the chemical, physical and mineralogical attributes of the various ash types produced at Sasol. To fulfil this requirement, representative samples of gasification ash (GA), clinker fragments (bottom ash) and fly ash from the steam station from Sasol Infracem (Sasolburg); and samples of gasification ash and fly ash from Secunda were submitted for various physical, chemical and mineralogical analyses. This paper outlines the application of analytical techniques to qualify and quantify the remaining coal minerals, glass phases, metal oxides present in both gasification ash and fly ash. In this study the mobility of selected water-extractable ion species in the ash samples was determined.

The preliminary results indicate that CCSEM and XRD are able to identify and describe the minerals and phase proportions in gasification ash, fly ash and clinker samples. The majority of the alumina (>85%) in the gasification ash and clinker samples is associated with anorthite, amorphous glass and metakaolinite. The majority of the remaining 15% of the alumina is associated with mullite, silicon-rich alumino-silicate and potassium-bearing alumino-silicates with the rock fragments. The distribution of SiO<sub>2</sub> in the gasification ash varies between 23% to 42% in alumino-silicate, 27% to 39% in interstitial/matrix glass and between 12% to 22% in quartz. In contrast the SiO<sub>2</sub> distribution in fly ash ranges from 51% to 54% in alumino-silicate, 25% to 27% in quartz; and 8% to 10% in interstitial/matrix glass. The Inductively Coupled Plasma Mass Spectrometry (ICP MS); and Inductively Coupled Plasma optical emission Spectrometry (ICP-OES) analyses of the ash leachates showed that none of the analysed leachates exceeded the US EPA regulatory limits for As, Ag, Ba, Cd, Cr, Pb, Hg and Se. As such, these ashes could not be classified as hazardous materials.

## INTRODUCTION

Sasol utilises a low rank bituminous coal in gasification and combustion processes to produce synthesis gas (also referred to as syngas) and steam respectively. Approximately 28 million tons of coal (70 % of the coarse coal feedstock) is consumed annually by the gasification process at Sasol Synfuels in Secunda which results in the production of about 7 million tons of gasification ash. Sasol Infrachem in Sasolburg gasifies approximately 6 million tons of coal annually and produces about 1.5 million tons of ash. The remaining 30 % of the coal utilised, a finer coal fraction, is combusted to produce steam and electric power. Coal ashes (gasification ash and fly ash) are by-products of these processes.

In the past Sasol coal ashes were only characterised by X-ray diffraction (XRD) for mineral phase identification and X-ray fluorescence spectrophotometry (XRF) for elemental analyses. Inductively Coupled Plasma (ICP) and Atomic Absorption Spectrometry (AAS) analyses on leachates were conducted to evaluate potential environmental impacts associated with the disposal and/or re-use of ash residues. The purpose of this study was to undertake a detailed physical, chemical and mineralogical characterisation of the different Sasol ash types using the latest available analytical techniques.

The objectives of this study were as follows:

- Qualify and quantify the minerals, glasses and elements present in Sasol coal ashes.
- Determine the  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  distributions relative to the respective ash phases.
- Describe the characteristics of the char (carbon loss) in the ash samples.
- Determine the mobility of selected trace element species in the coal ash samples by conducting the Toxicity Characteristic Leaching Procedure (TCLP) and water soluble ion species using the German DIN 38414-T4 water leach test.

The available concentration and mineral form of Al and Si are of particular interest should these ashes be used for construction and waste stabilisation purposes and, therefore, need to be characterised in detail. In this study, XRD, XRF, computer controlled scanning electron microscopy (CCSEM), scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS) techniques were used. The CCSEM was also used to determine the mineralogy of the gasification ash, bottom ash and fly ash samples, the proportion of glass phases in these samples, the distribution of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  and also to help describe the characteristics of the char particles (Details of CCSEM method are described in Appendix A). The elemental analyses were conducted using ICP

(leachates), XRF, proximate (moisture content, ash, volatile matter, fixed carbon, total sulphur) and ultimate (C, H, N, S and oxygen) analytical techniques.

Although the field leaching behaviour of elements present in coal ashes cannot be accurately simulated with laboratory leaching tests, the leachability of the trace element species from coal ashes to be placed in the environment can be estimated. The most commonly used laboratory leaching test to evaluate the potential impact of coal ashes and other waste solid materials on the environment is the US Environmental Protection Agency (EPA<sup>1</sup>) Toxicity Characteristic Leaching Procedure (TCLP). According to Danny and Valsaraj<sup>2</sup>, the US EPA requires that the TCLP leachates should be analyzed for eight elements which include: arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg), selenium (Se) and silver (Ag). The results of leachate analyses are then also compared to the South African Department of Water Affairs and Forestry (DWA<sup>3</sup>) standards which are given in the Minimum Requirements document for waste handling and disposal. The distilled water extractable cations and anions were evaluated using the German standard DIN 38414-T4 leaching test.

## METHODOLOGY

The following sample preparation procedures were used in this study to obtain representative samples for chemical and mineralogical analyses:

Sample details and preparation:

Gasification ash

In order to evaluate the chemical and mineral characteristics of minerals, glasses and elements present in the coarse gasification ash, a representative sample of gasification ash was required. Coarse gasification ash was sampled from each gasifier at regular three hour intervals. The sampling program lasted for a week. At the end of the week, the entire composite sample (approximately 1 ton) was crushed and milled to 100% passing 1mm. A representative sample of this crushed gasification ash was submitted for analysis.

The gasification ash details are as follows:

- Sasol Infracem gasification ash
- Sasol Synfuels gasification ash phase 1 (Gasifiers 25, 29, 34, 38, 41 and 46 situated on the West Area (Phase1))
- Sasol Synfuels gasification ash phase 2 ( Gasifier 2, 5, 9, 13 and 17 on the East Area (Phase 2) )

## Bottom ash

The breather pipe from the boiler precipitator hoppers was opened to allow bottom ash to fall onto a sampling sheet. After washing and cooling, 5 kg of clinker fragments were hand picked from the bottom ash. Bottom ash was crushed and milled to 100% passing 1mm.

## Fly ash

A total of 5 kg sample of fly ash was also collected every hour for a period of 5 days from the hoppers at the various Steam Stations. To obtain a 1kg representative fraction, the bulk fly ash sample was coned, quartered and riffled.

The details of the fly ash samples are as follows:

- ◆ Sasol Infrachem Steam Station 1 fly ash
- ◆ Sasol Infrachem Steam Station 2 fly ash
- ◆ Sasol Infrachem Steam Station 2 bottom ash
- ◆ Sasol Synfuels Steam Station fly ash.

Analytical methods used during the characterisation of Sasol coal ashes

The analytical methods used in this study are briefly described in this section:

- CCSEM analysis

Each fly ash sample was physically screened into +75, -75+38 and -38  $\mu\text{m}$  size fractions by Moruo Mineralogical Services (formerly Anglovaal Mining Limited Mineralogical Laboratory).

A representative fraction of the crushed gasification ash, crushed bottom ash and screened fly ash was placed in a 30 mm mould to which iodoform ( $\text{CHI}_3$ ) doped epoxy resin was added. After thoroughly mixing the epoxy resin and sample the epoxy resin was allowed to cure for 12 hours. The hardened sections were ground and polished exposing the individual particles in the sample. To ensure good sample conductivity and image quality (under the SEM) the polished sections were carbon coated.

The unique feature of the polished section preparation method described above was the use of iodoform doped epoxy resin. Iodoform ( $\text{CHI}_3$ ), raised the atomic

mass of the epoxy resin, which enables the CCSEM to discriminate organic (carbon rich) or char particles from the epoxy resin.

In order to derive the elemental distributions selected clinker fragments were set in epoxy resin. These clinker fragments and the +75  $\mu\text{m}$  fly ash fractions were submitted to Moruo Mineralogical Services to quantify the elemental proportion of selected phases using SEM based energy dispersive X-ray spectrometry (SEM-EDS).

- XRF analysis using fusion method (for all solid samples)

An XRF spectrometer (ARL9800XP (SIM-SEQ)) at Set Point Laboratories was used to investigate the characteristic spectra of elements present in the solid sample. For quantification analysis, the intensity of characteristic line of the element analysed was measured.

The procedure employed for the analysis of Fe, Mn, V, Ti, Ca, K, P, Si, Al, Mg, Na, Cl and S in solid samples by XRF using monochromators and goniometers is as follows:

The coarse solid sample of coal ash was initially ground to a particle size of 100 % < 200  $\mu\text{m}$ . The powdered sample was calcined at 850°C for 4 hr in order to remove all organic compounds and water contained in the sample. The calcined sample was converted into a solid solution by fusion with lithium tetra borate ( $\text{Li}_2\text{B}_4\text{O}_7$ ). The prepared solid solution and standard (NIMN from Mintek) were placed in the sample holders and placed in the sample compartment of the XRF spectrometer. The intensity of a characteristic line of the element to be determined was measured. The concentration of the element in the sample was calculated from the intensity measured.

- XRD analysis (for solid samples)

All the samples were received as dry, fine powder. A mass of approximately 4 g of each sample, were further ground and homogenised by hand in an agate mortar.

The additional grinding, as required for a quantitative XRD analysis, was done using the agate segments in a McCrone micronising mill over 10 minutes. This fine grinding, followed by spiking the samples with 10 mass%  $\text{CaF}_2$  as an internal standard, was required to conduct the quantitative XRD analyses at the Materials Characterisation laboratory.

Approximately 0.5 g of the ground sample was placed in a stainless steel sample holder and exposed to the X-ray beam to generate the sample's diffraction pattern.

The following experimental parameters were used during the analysis of Sasol coal ashes:

XRD Instrument:	the PANalytical (Philips) X'pert Pro XRD System
Goniometer:	PW3050/60 (Theta/Theta configuration)
X-ray Detector:	X'Celerator (Solid state, RTMS)
X-ray Tube:	Cobalt target, ceramic, LFF-type ( $\lambda$ Co $K\alpha$ =
1.7889Å:	
Voltage	40 KV
Amperage:	40 mA
Fixed. Divergence Slit:	1.0 °
Anti-scatter slit:	2.0 °
Scan from:	5 ° 2 $\theta$
Scan to:	145 °2 $\theta$
Soller Slits:	0.04 °
Scanning:	Continuous
Duration of scan:	3hrs & 14 hrs

- Water leach test and Toxicity Characteristic Leaching Procedure (TCLP)

The DIN 38414-T4 water leaching test involved mixing 100g of ash with 1000ml of distilled water in a conical flask. The flask was shaken in a rotary shaker for 24 hrs. The solid material was separated from the liquid by filtration. The filtrate was then analysed for pH, EC, TDS, alkalinity, major cations, major anions and trace elements.

The TCLP test defined in EPA Method 1311 was used to evaluate the mobility of inorganic compounds present in ash. Ash samples were crushed to obtain a desired particle size and extracted with an acetic acid solution. A liquid-to-solid ratio of 20:1 was used to extract metal species from the ash for a period of 18hr. The mixture was then filtered through a 0.6  $\mu$ m to 0.8  $\mu$ m glass fiber filter prior to conducting chemical analyses. The TCLP leachates were then analyzed for selected elements (Cd, Hg, V, Al, As, Co, Cu, Mn, Ni, Pb, Se, Ti, Zn, Ag, Ba, Cr and Fe) using the Inductively Coupled Plasma Mass Spectrometry (ICP MS) and Inductively Coupled Plasma optical emission Spectroscopy (ICP-OES) analytical techniques. In this study, the ash TCLP results from three different laboratories were compared namely:

- Sasol Infrachem Laboratory,
- Talbot and Talbot Laboratory
- Mineral Waste Characterisation and Classification Centre (UCT)

## RESULTS AND DISCUSSION

The results obtained during the characterisation of Sasol low rank bituminous coal ashes by different analytical techniques are presented in this section.

### Particle size distribution

The particle size distribution (PSD) of the fly ashes was determined by physically screening the samples using 30 cm diameter wire mesh screens (**Table 2**). Screens used had aperture of 75  $\mu\text{m}$  and 38  $\mu\text{m}$ .

**Table 2: Mass-% particle size distribution**

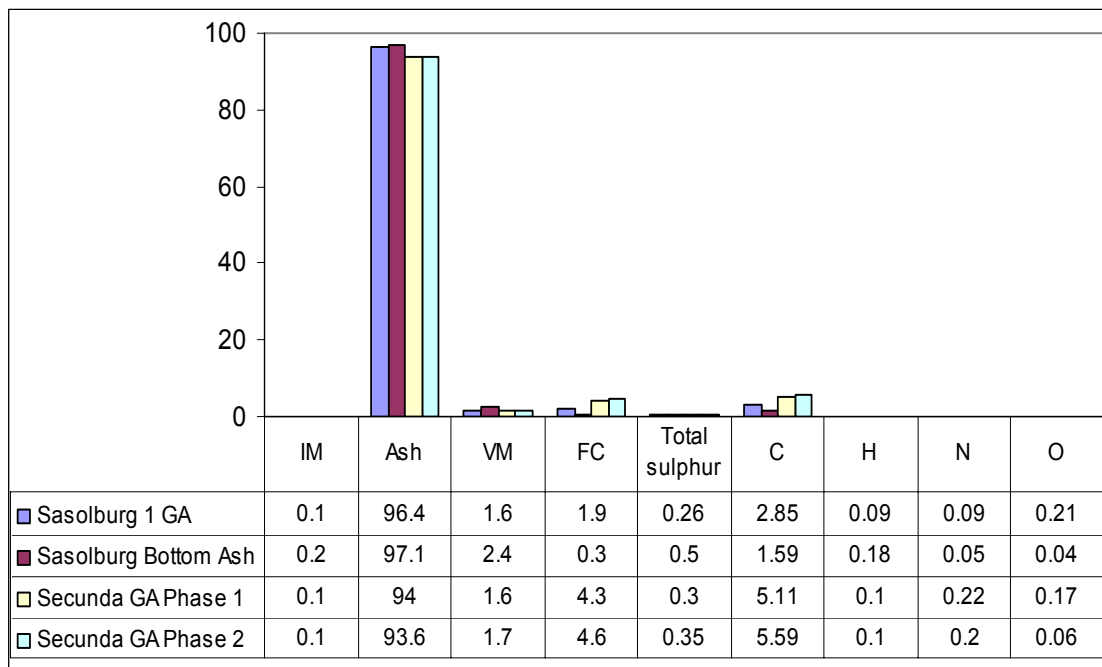
Synfuels Fly Ash (Secunda)	84.5	15.5	69.4	15.1
Sasol Infrachem Steam Station 1 FA (Sasolburg)	67.5	32.5	56.7	10.7
Sasol Infrachem Steam Station 2 FA (Sasolburg)	73.6	26.4	63.6	10.0

The average particle size of the Sasol Infrachem (Sasolburg) steam station fly ash is significantly coarser than the Secunda fly ash. The potential impact of a coarse pulverized fuel particle size distribution will be discussed later on in this report.

### Proximate, ultimate and XRF analyses

#### Gasification ash and bottom ash

The ultimate and proximate results obtained from Coal and Mineral Technologies (CMT) are summarized in **Figure 1** and the XRF elemental results from Set Point Laboratories in **Figure 2**. A notable feature of the ultimate and proximate analyses (**Figure 1**) is the low ash-% and corresponding high carbon content of the Secunda gasification ash compared to Sasolburg gasification ash and bottom ash.



**Note:** VM=Volatile matter, FC=Fixed carbon, IM =Inherent moisture,

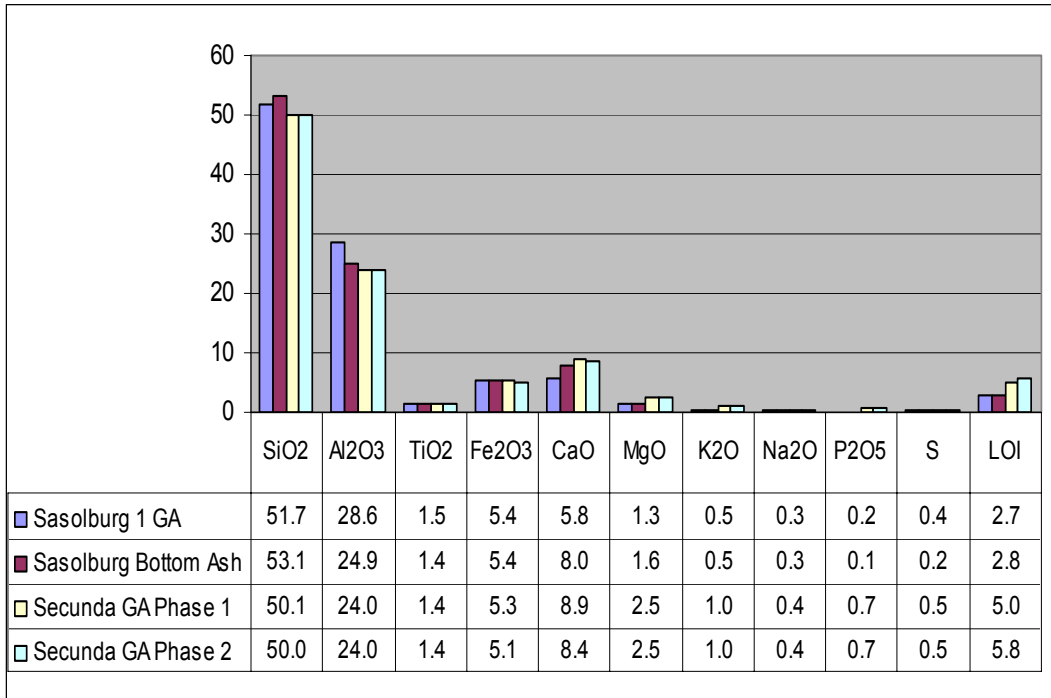
**Sasolburg GA= Sasol Infrachem gasification ash, Sasolburg bottom ash= Sasol Infrachem bottom ash, Secunda GA Phase 1 and Phase 2= Sasol Synfuels gasification ash**

**Figure 1: Proximate and ultimate analyses of Sasol Infrachem and Secunda ash, gasification ash and bottom ash**

The higher L.O.I. (>5%) of the Synfuels gasification ash supports the lower ash and higher carbon content (**Figure 2**). The Synfuels gasification ash sampled for this investigation has a higher carbon loss than the Sasol Infrachem gasification ash. This is based on the uncombusted carbon content exceeding 5% in the Synfuels gasification ash compared to 2.8% in the Sasol infrachem gasification ash.

Based on the ash elemental proportions, the Sasol Infrachem gasification ash differs slightly from the Synfuels gasification ash. The main differences are the lower CaO and MgO content and the higher SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> content. Excluding the proportion of SiO<sub>2</sub> and MgO, the Sasolburg Infrachem power station bottom ash is similar to Secunda Synfuels gasification ash.



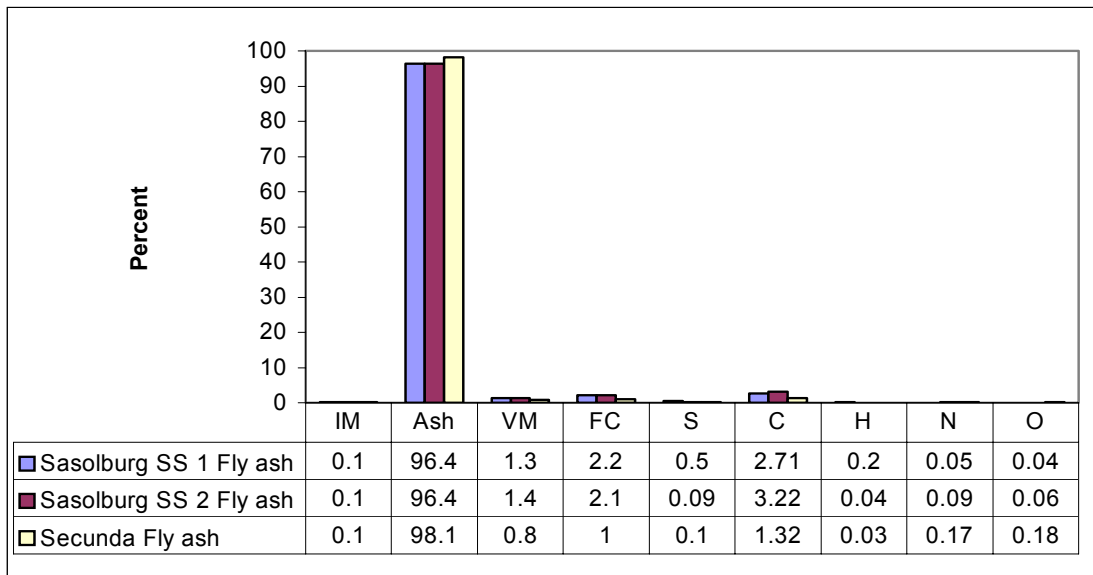


**Sasolburg GA= Sasol Infrachem gasification ash, Sasolburg bottom ash= Sasol Infrachem bottom ash, Secunda GA Phase 1 and Phase 2= Sasol Synfuels gasification ash, L.O.I= Loss on ignition**

**Figure 2: XRF ash elemental analyses on Sasolburg Infrachem and Secunda Synfuels gasification ash and bottom ashes**

#### Fly ash samples

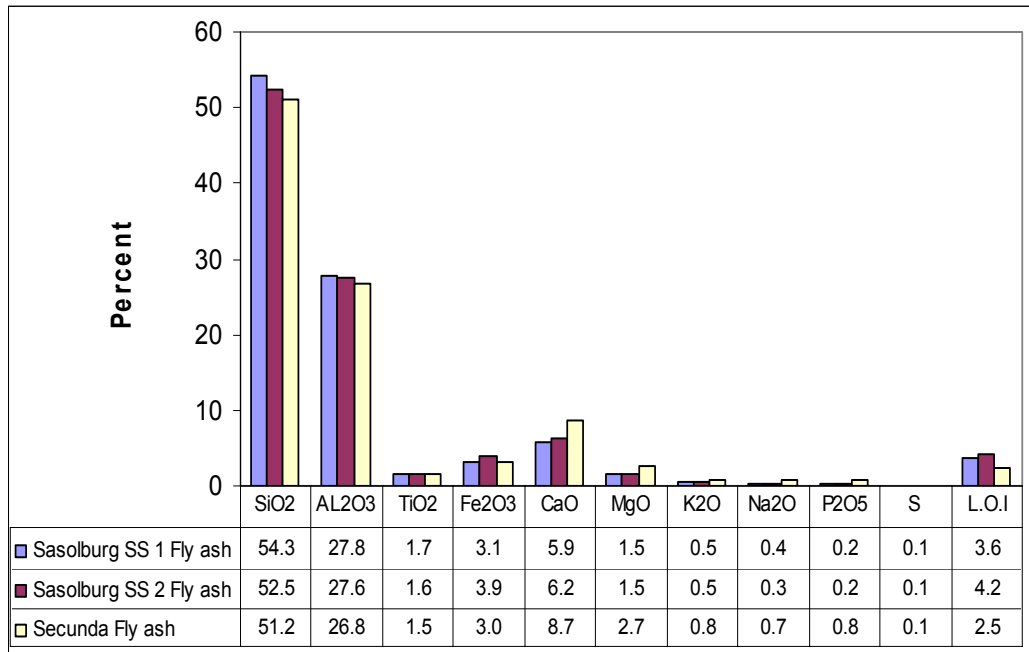
The calculated total proximate and ultimate analyses and XRF fly ash elemental analyses are presented in **Figures 3 and 4**, respectively. The total elemental proportion is the weighted average of the individual size fractions using the particle size distribution (**Table 2**) as the weighting factor. The proximate, ultimate and XRF elemental results for the individual size fractions are summarised in Appendix A.



**Note: VM=Volatile matter, FC=Fixed carbon, IM =Inherent moisture, Sasol 1 fly ash= Infracchem Steam Station 1 fly ash, Sasol 2 fly ash= Infracchem Steam Station 2 fly ash, Secunda fly ash= Synfuel fly ash**

**Figure 3: Figure 3: Proximate and ultimate analysis of Sasolburg steam station (SS) 1, Sasolburg steam station (SS) 2 and Secunda steam station fly ash**

The proportion of carbon loss in Synfuels fly ash is lower compared to Sasol Infracchem fly ash. Carbon loss in the ash is a function of operation efficiency and intrinsic properties of the coal feedstock.



**Note: Sasol 1 fly ash= Infrachem Steam Station 1 fly ash, Sasol 2 fly ash= Infrachem Steam Station 2 fly ash, Secunda fly ash= Synfuel fly ash**

**Figure 4: Figure 4: XRF ash elemental analysis of Sasolburg steam station (SS) 1, Sasolburg steam station (SS) 2 and Secunda steam station fly ash**

Generally, gasification ash contains higher Na, S and Fe proportions and L.O.I compared to fly ash (see Synfuels results in **Figure 2 and Figure 4**). These differences are attributed to the differences in particle size distribution of coal feedstock and difference in the operating conditions within a boiler and gasifier.

#### CCSEM results

Describing the mineralogy of the gasification ash, bottom ash and fly ash is made difficult by the occurrence of glass or amorphous phases in these sample types. Amorphous glass is by definition, a phase with no fixed elemental proportions and has no ordered crystalline structure. To overcome this problem, a unique nomenclature scheme based on elemental proportions was developed for gasification ash, bottom ash and clinkers. This scheme was described in detail in a previous study on CCSEM technique in Appendix A.

The nomenclature used is based on the elements present and the likely coal mineral source of the elements. For instance, the ash phase kaolinite (pyrite, carbonate), describes an Al-silicate with minor concentrations of Fe, Ca and Mg. It is presumed that the Al and Si are derived from kaolinite, Fe from pyrite and siderite and Ca/Mg from the carbonates (calcite and dolomite).

Since there is no major coal mineral with the same elemental composition, this phase must have formed in the gasifier during the gasification of coal.

The individual phases can be classified further into five broad groups. These groups are:

- ◆ Interstitial and matrix glass – This glass is principally an aluminio-silicate glass with varying proportions of the fluxing elements such as Ca, Fe, Mg, K, P and Ti. It is perceived that this glass is principally derived from included minerals associated with “coal”.
- ◆ Rock fragment glass – this is the K-bearing aluminio-silicate glass found in the rock fragments. This phase is derived from microcline and muscovite, which are common constituents of sub-arkosic/arkosic sandstone, siltstone and mudstone rock fragments.
- ◆ Laths in glass matrix (crystallites) – these are elongated (laths) crystals in glass matrix. It is perceived that these phases crystallised during the cooling of the molten glass.
- ◆ Rock fragments minerals – These represent the original minerals found in rock fragments. Typical minerals are unaltered quartz grains and the transformation products of kaolinite (aluminio-silicate).
- ◆ Extraneous “pyrite” and “carbonates” – These are the high temperature transformation products of the large extraneous pyrite and carbonate particles in the coal feedstock. On entering the gasifier, extraneous pyrite transforms to pyrrhotite, Fe-S-O and finally to Fe-oxide and extraneous carbonates to Ca-oxide and Ca-Mg-oxide.
- ◆ Char – uncombusted “coal”.

Gasification or combustion operating conditions

The chemical and physical attributes of the fly ash and gasification ash are in part influenced by the conditions within the boiler and gasifier. These operating conditions are:

- ◆ **Ash residence time** - the residence time of ash in a boiler is significantly shorter than ash in a gasifier. An increase in the residence time promotes high temperature mineral transformation and crystallisation of anorthite from molten slag. It is for this reason that the gasification ash and bottom ash should have a higher proportion of anorthite and mullite.
- ◆ **Feedstock particle size** - the coal feedstock to the gasifier is significantly coarser than the pulverised fuel supplying the power station boilers. Due to the fine nature of the pulverised fuel (feedstock to the boiler), there is a lower proportion of fluxing minerals (pyrite and carbonates) in direct contact with included kaolinite and quartz in a carbon matrix (“coal”). This will have an impact on the formation of glass phases as the probability of fluxing minerals interacting with other minerals is reduced. Glass formation in fly ash is

controlled by association characteristics of the minerals in pulverised fuel coal particles and by the physical and chemical interaction of fly ash phases within the combustion zone of the boiler.

- ◆ **Sample selectivity** - in a gasifier, the coarse coal feedstock is fed from the top and slowly gravitates to the bottom of the gasifier. The mineral matter (“ash”) entering the gasifier will eventually exit the bottom of the gasifier as coarse/gasification ash. In contrast, the mineral matter “ash” entering the pulverised fuel boiler will exit the boiler either as fly ash or as bottom ash. There is a natural size and density segregation within a pulverised fuel boiler. Invariably the coarse and dense minerals, slag fragments, ash eyebrows fragments and slag deposits will gravitate to the ash hopper and form the bottom ash. The fly ash will mainly consist of fine ash particles and smaller slag fragments and will exit via the top of the boiler.

Irrespective of the differences in the fly ash formation process within a boiler and the clinker formation process in a gasifier, the same phase nomenclature and classification scheme adopted for gasification ashes is applicable for the fly ash.

The detailed mineral characteristics of gasification ash have been described in detail in the previous CCSEM report Van Alphen and Matjie<sup>4</sup>. For a comprehensive description, the reader should refer to this report.

#### Percent mineral proportions – gasification ash and bottom ash

Macroscopically, the coarse ash and clinkers consist of rock fragments (“stone”) in a matrix of “glass” (**Figure 5**). In this context, “glass” consists of amorphous glass and crystalline phases, which have crystallised out of the molten glass during cooling.



**Figure 5: Clinker fragments highlighting rock fragments (light colour) in a matrix of “glass” (black).**

The mineralogy of the rock fragment in a clinker sample is controlled by the original source. The major rock fragments are fine-grained siltstone/mudstone and fine to coarse-grained sub-arkosic or arkosic sandstone.

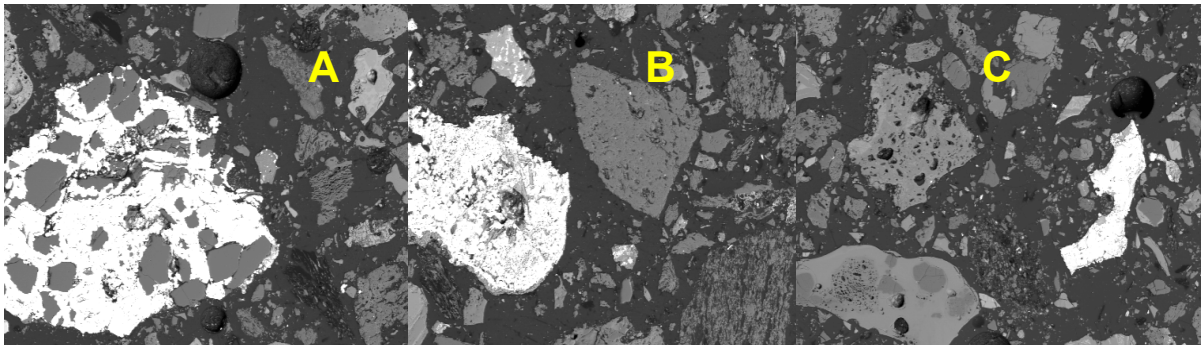
The mass-% mineral and phase abundance of the Sasol Infrachem gasification ash, Secunda gasification ash and Sasol bottom ash are summarised in **Table 3**. The classification/nomenclature scheme used for this report is described in detail in the previous CCSEM report Van Alphen and Matjie<sup>4</sup>. For comparative purposes previously reported mass-% phase proportions for the Secunda gasification ash (GA9) and clinker sample is included. A detailed description of each phase is summarised in Appendix C.

**Table 3: Mass percent mineral and phase distribution (Refer to appendix C for detail phase description).**

Kaolinite(pyrite) (Fe-aluminio-silicate glass)	4.1	2.3	1.8	2.3	2.2	2.2
Kaolinite(carbonate, pyrite)(Ca-Fe- aluminio-silicate glass)	7.6	6.7	7.9	11.7	12.2	11.5
Kaolinite(carbonate) (Ca-aluminio-silicate glass)	10.1	23.4	18.3	14.9	21.5	14.3
Quartz(carbonate, pyrite)	1.4	0.4	1.2	1.3	1.4	2.3
Quartz(carbonate)	2.9	6.3	1.7	1.7	3.3	4.3
<b>Total</b>	<b>26.0</b>	<b>39.0</b>	<b>30.9</b>	<b>32.0</b>	<b>40.6</b>	<b>34.5</b>
Microcline glass	1.9	0.3	2.0	2.1	2.4	3.1
Muscovite glass	1.8	0.2	1.2	1.4	1.8	2.0
<b>Total</b>	<b>3.7</b>	<b>0.5</b>	<b>3.2</b>	<b>3.5</b>	<b>4.2</b>	<b>5.1</b>
Anorthite	4.2	12.7	8.7	6.3	10.1	19.0
Mullite	2.6	1.0	2.8	0.6	1.5	0.7
<b>Total</b>	<b>6.9</b>	<b>13.7</b>	<b>11.6</b>	<b>6.9</b>	<b>11.6</b>	<b>19.7</b>
Quartz	6.6	10.8	11.7	9.1	9.2	9.6
Aluminio-silicate (originally kaolinite )	42.0	24.4	27.0	25.5	21.9	19.2
Qtz60Kao40	4.4	3.6	4.6	0.9	4.5	4.6
Qtz80Kao20	1.4	0.9	1.9	0.1	2.0	2.2
<b>Total</b>	<b>54.3</b>	<b>39.8</b>	<b>45.2</b>	<b>35.7</b>	<b>37.6</b>	<b>35.4</b>
Pyrrhotite/Fe-S-O/ Fe-oxide	5.5	3.8	3.5	12.5	2.2	1.4
Carbonate/CaMgOxi de	1.8	1.4	1.4	1.3	2.1	2.6
<b>Total</b>	<b>7.3</b>	<b>5.2</b>	<b>4.9</b>	<b>13.8</b>	<b>4.3</b>	<b>4.2</b>
Char	0.6	1.2	3.2	6.8	1.5	1.0
Other	1.3	0.5	1.0	1.3	0.1	0.1

Based on **Table 3** there are a number of notable differences:

- ◆ Sasol gasification ash has a higher proportion of alumino-silicate and corresponding lower proportion of interstitial/matrix glass than the Secunda gasification ash (GA9 and current samples). The Sasol gasifier ash has a relatively high  $\text{Al}_2\text{O}_3$  content (**Figure 2**), which supports the observed alumino-silicate trend. The Sasol Infrachem power station boiler bottom ash has similar phase proportions as the Secunda gasification ash. The XRF ash elemental analysis (**Figures 1 and 2**) in general supports this surprising trend.
- ◆ Secunda phase 2 gasification ash is characterised by a high proportion of “extraneous” Fe-oxide particles. Some prominent examples of extraneous “Fe-oxide” particles are illustrated in **Figure 6**. This trend is not reflected in the  $\text{Fe}_2\text{O}_3$  variations (**Figure 2**). Fe-oxide is a transformation product of pyrite.
- ◆ On average the proportion of “char” in the Secunda gasification ash is higher than Sasol gasification ash. This is supported by the L.O.I. and carbon trends illustrated in **Figures 1 and 2**, respectively. The majority of the char occurs as discrete particles and are not attached to or included in glass or rock fragments. It is common for these char particles to have kaolinite, quartz, carbonates and pyrite inclusions.



**Figure 6: Numerous extraneous “Fe-oxide” (originally pyrite) particles (white) in Secunda phase 2 gasification ash. Particle A is predominately pyrrhotite/Fe-S-Oxide particle with quartz (dark grey) inclusions. Particles B and C are predominately Fe-oxide particles with minor Fe-S-oxide. (Width of each image is approximately 900  $\mu\text{m}$ )**

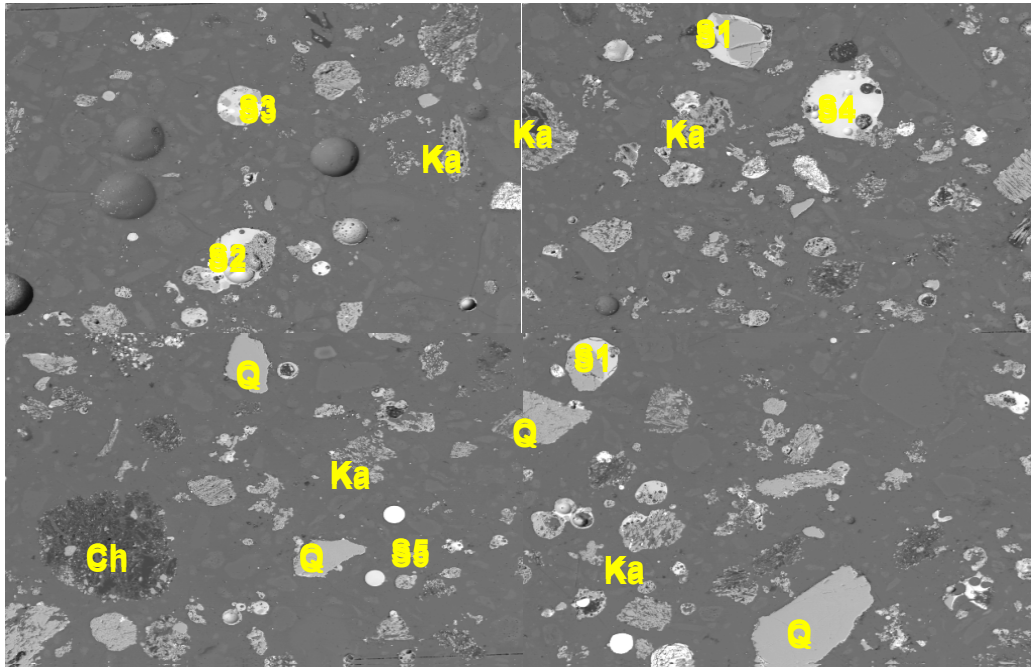


## Percent mineral proportions - fly ash

The impact of the fly ash formation process and the operating conditions of a boiler described above has on the fly ash physical and chemical attributes that are highlighted in **Figures 7 and 8**. The main differences are:

- Attachment and chemistry of the glass phases – the elemental composition of the glass phase in fly ash is similar to the interstitial/matrix glass phase present in the gasification ash. These glass phases can be described as aluminosilicate with varying concentrations of typical fluxing elements (Ca, Mg, Fe, K and Na). In fly ash, these glass phases typically occur as discrete spherical particles or as coated or partially coated unaltered quartz and kaolinite. In a gasification ash, the glass phase is closely associated with the large rock fragments (**Figure 5**).
- The occurrence of crystalline anorthite laths in a glass matrix is not visible in the glass fly ash particles. Anorthite and mullite can occur as sub-micron crystallites on the surface of fly ash particles.

Although significantly smaller, extraneous Al-silicate (originally kaolinite), quartz, “Fe-oxide” (originally pyrite), “CaOxide/CaMgOxide” (originally carbonates) and char particles are common constituents of fly ash **Figure 7** (fly ash) and **Figure 8** (gasification ash).



**Figure 7: Typical fly ash particles – +75  $\mu\text{m}$  fraction Sasol 2 fly ash. (Width of the image is approximately 1800  $\mu\text{m}$ )**

Particle descriptions:

Q – Extraneous quartz particles

Ka – predominately “honeycomb” alumino-silicate particles. Can have small quartz inclusions

Ch – predominately char particle (black) with quartz and alumino-silicate inclusions (grey)

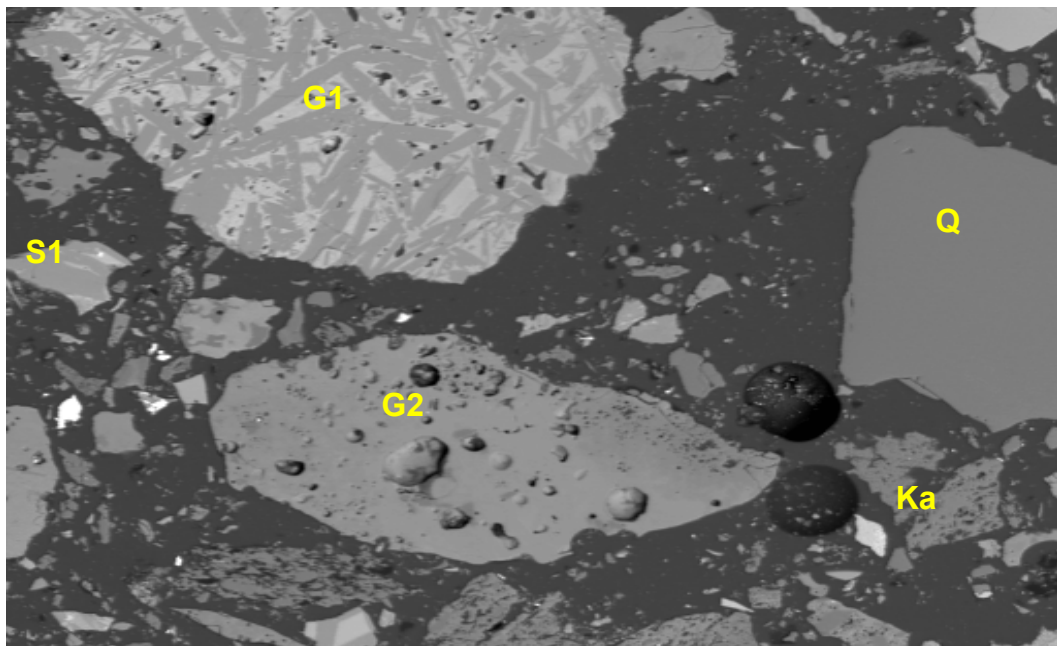
S1 – Quartz particle (grey) partially surrounded by Ca-Mg-Fe bearing alumino-silicate glass

S2 – Alumino-silicate (dark grey) surrounded by Ca-Mg-Fe bearing alumino-silicate glass

S3 – predominantly Ca-Mg-Fe-silica rich glass with minor quartz inclusions.

S4 – spherical Ca-Mg-Fe-alumino-silicate fly ash particle

S5 – small (white) spherical Fe-bearing alumino-silicate particle.



**Figure 8: Typical gasification ash particles – Secunda 1 gasification ash  
(Width of the image is approximately 900 µm)**

Particle description:

Q – Large extraneous quartz grain

G1 – “Anorthite” laths (grey) in matrix of glass

Ka – predominately alumino-silicate

G2 – predominantly Ca-Mg-Fe-bearing alumino-silicate glass with quartz inclusions (dark grey)

The “total” calculated mass-% phase proportions for the individual fly ash particles are tabulated in **Table 4**. The “total” mass phase proportion is the weighted average of the individual size fractions using the particle size distribution (**Table 2**) as the weighting factor. The mass-% phase distributions for the individual size fractions are summarised in **Appendix D**.

**Table 4: Calculated mass-% phase proportions – Fly ash samples**

Fly ash phases	Sasol power Station1 FA	Sasol power station 2 FA	Secunda FA
	<b>Alumino-silicate glass (particles S1 to S4, figure 7)*</b>		
Kaolinite(pyrite)(Fe-alumino-silicate glass)	0.5	0.7	0.5
Kaolinite(carbonate, pyrite) (Ca-Fe-alumino-silicate glass)	1.4	1.5	0.7
Kaolinite(carbonate)(Ca-alumino-silicate glass)	8.9	9.2	8.8
Quartz glass	0.7	0.8	0.6
<b>Total</b>	<b>11.5</b>	<b>12.2</b>	<b>10.5</b>
<b>K-bearing phases</b>			
Orthoclase glass	0.4	0.4	1.3
Muscovite glass	0.5	0.7	1.2
<b>Total</b>	<b>0.9</b>	<b>1.1</b>	<b>2.5</b>
<b>Crystallites</b>			
Anorthite <sup>#</sup>	Refer to note		
Mullite	2.1	1.7	2.7
<b>Total</b>	<b>2.1</b>	<b>1.7</b>	<b>2.7</b>
<b>Rock fragments</b>			
Quartz	14.5	15.1	14.0
Alumino-silicate(originally kaolinite)	58.4	56.8	56.0
Qtz60Kao40	3.5	3.3	3.0
Qtz80Kao20	1.1	1.1	0.9
Ti-oxide	0.3	0.1	0.0
<b>Total</b>	<b>77.8</b>	<b>76.3</b>	<b>73.9</b>
<b>Extraneous</b>			
Pyrrhotite/Fe-S-O/Fe-oxide	1.0	1.9	1.4
Carbonate/CaMgOxide	2.1	1.6	4.3
<b>Total</b>	<b>3.1</b>	<b>3.5</b>	<b>5.7</b>
<b>Char and other</b>			
Char	4.3	5.0	4.2
Other	0.3	0.1	0.5
<b>Total</b>	<b>4.6</b>	<b>5.1</b>	<b>4.7</b>

\* Alumino-silicate glass is equivalent to “interstitial and matrix glass” (**Table 4**).

# Discernable anorthite laths prominent in the gasification ash were not detected in fly ash

Based on the details in **Table 4** the following trends are noted:

- ◆ The fly ashes are characterised by a high proportion of alumino-silicate (>55 mass- %) and corresponding low proportion of alumino-silicate glass phases (<12 mass-%). In the gasification ash, the proportion of alumino-silicate glass (interstitial and matrix glass) is significantly higher (>26 mass-%)
- ◆ The fly ashes are similar in composition. Secunda fly ash has marginally higher orthoclase/muscovite glass and carbonate/CaMg-oxide proportions. The marginally higher K<sub>2</sub>O and CaO/MgO proportions (**Figure 4**) support this trend.
- ◆ The proportion of char is similar for all three fly ashes analysed. The char tends to concentrate in the +75 µm size fraction (**Appendix D**). There was no direct relationship between the coarse grind (**Table 2**) and the proportion of char in the fly ash. Excluding char, the fly ash phases have a similar distribution to the particle size distribution (**Table 2**).
- ◆ Anorthite laths, which are prominent in gasification ash, were not detected in the fly ash. It is plausible, that anorthite is present and occurs and sub-micron laths that are smaller than the scanning electron beam resolution. The short residence times within the boiler will not promote crystallisation of anorthite laths from molten slag. In contrast, the longer residence times in the gasifier will favour the crystallisation of anorthite.
- ◆ Mullite in fly ash describes a phase with Al/Si ratio similar to mullite Al/Si ratio. It is plausible that a proportion of “mullite” is actually Al-rich silicate glass, which has been misidentified. CCSEM mineral identification is based entirely on elemental proportions and is thus unable to distinguish minerals based on its degree of crystallinity.

#### Elemental distribution

A purpose of this investigation is to determine the distribution of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. The Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> content can be calculated from the Al and Si X-ray counts for each analytical point analysed. The algorithms used are summarised in **Appendix E**.

To calculate the elemental distribution for the individual ash and fly ash phases, selected samples of clinkers were analysed by SEM-EDS X-ray spectrometry.

The SEM-EDS analysis concentrated on the elemental proportions of the glass phases and anorthite. The elemental composition are summarised in **Appendix F**. The average elemental compositions are summarised in **Table 5**.

**Table 5: Average elemental composition based on SEM-EDS analysis**

Na <sub>2</sub> O	0.82	0.36	0.26
MgO		1.97	1.61
Al <sub>2</sub> O <sub>3</sub>	36.93	24.76	25.06
SiO <sub>2</sub>	42.28	54.57	48.86
K <sub>2</sub> O		0.93	0.37
CaO	18.86	7.27	6.94
Fe <sub>2</sub> O <sub>3</sub>		7.65	13.57
TiO <sub>2</sub>		2.50	3.33
Total	98.89	100.00	100.00

The SEM-EDS analysis confirms that the crystalline laths common (**Figure 8**) in the gasification ash has the same elemental proportions as the mineral, anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>). Anorthite contained on average 0.8% Na<sub>2</sub>O. The gasification ash interstitial glass is similar in composition to the fly ash aluminosilicate glass. The only notable difference is the lower SiO<sub>2</sub> and higher Fe<sub>2</sub>O<sub>3</sub> proportion of fly ash glass. These observations are based on a few analyses and should be interpreted in this context.

In order to calculate the Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> distribution by phase it is necessary to derive the average elemental proportion of each phase and the mass percent proportion of each phase. The mass-% phase proportions of the individual phases are tabulated in **Table 3** for the gasification ash and **Table 4** for the fly ash. The average elemental compositions of the individual phases are based on the average SEM-EDS analysis (**Table 5**) and the CCSEM derived elemental analysis using the algorithms described in **Appendix E**.

The calculated Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> contents for the individual samples compared to the XRF ash elemental proportions is summarised in **Table 6**. Since the elemental distributions are based on average phase proportions, the agreement between the CCSEM derived and XRF ash elemental analysis is acceptable for the purpose of calculating the elemental distribution for each phase. The Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> distribution across size fractions for the fly ashes are summarised in **Appendix G**.

**Table 6: Comparative Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> contents.**

Sasol Infrachem1 GA	26.2	26.1	55.0	55.6
Sasol Infrachem bottom ash	29.2	29.0	52.0	54.1
Secunda Phase1 GA	27.7	25.3	55.2	52.9
Secunda Phase 2 GA	24.4	25.5	48.8	53.0
Sasol Infrachem steam station1 Fly ash	31.5	29.2	56.8	57.0
Sasol Infrachem steam station2 Fly ash	30.9	29.3	56.9	55.7
Secunda Fly Ash	31.0	27.8	55.1	53.2

The average Al<sub>2</sub>O<sub>3</sub> distribution is summarised in **Table 7** and the SiO<sub>2</sub> distributions in **Table 8**. Based on **Tables 7 and 8** the following trends are noted:

- ◆ Al<sub>2</sub>O<sub>3</sub> is predominately present in alumino-silicate in the gasification ash and bottom ash. The proportion of Al<sub>2</sub>O<sub>3</sub> associated with alumino-silicate ranges from 36% (Sasol bottom ash) to 58% (Sasol Infrachem gasification ash). In contrast, the proportion of Al<sub>2</sub>O<sub>3</sub> associated with alumino-silicate in the fly ashes ranges from 75% to 79%.
- ◆ After alumino-silicate, the interstitial/matrix glass is a major Al-bearing phase. The proportion of Al<sub>2</sub>O<sub>3</sub> associated with interstitial/matrix glass ranges from 22% to 37% in the gasification

and bottom ashes. The proportion associated with interstitial/matrix glass in fly ash is significantly lower ranging from 8% to 10%.

- ◆ Anorthite and mullite are also major sources of Al<sub>2</sub>O<sub>3</sub>. The total proportion of Al<sub>2</sub>O<sub>3</sub> associated with anorthite and mullite ranges from 10% to 21% in the gasification ashes. In the fly ashes the proportion of Al<sub>2</sub>O<sub>3</sub> associated with mullite ranges from 1% to 3%.
- ◆ The proportion of Al<sub>2</sub>O<sub>3</sub> associated with the remaining phases is less than 12% in the gasification ash and 8% in the fly ashes.
- ◆ The distribution of SiO<sub>2</sub> in the gasification ash varies between 23% to 42% in alumino-silicate, 27% to 39% in interstitial/matrix glass and between 12% to 22% in quartz. In contrast the SiO<sub>2</sub> distribution in fly ash is similar to gasification ash except that the proportion in alumino-silicate ranges from 51% to 54%, 25% to 27% in quartz and 8% to 10% in interstitial/matrix glass.
- ◆ The proportion of SiO<sub>2</sub> associated with the remaining phases is less than 15% in the gasification ash and 12% in the fly ashes.
- ◆ In terms of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> distribution, the Sasol gasification ash is distinct from the Secunda gasification ash and from the Sasol Infracchem bottom ash.

**Table 7: Percent Al<sub>2</sub>O<sub>3</sub> distribution**

Glass Matrix	22.1	36.8	27.6	32.5	9.1	9.9	8.8	
Orthoclase glass	1.5	0.2	1.3	1.6	0.2	0.3	0.2	
Muscovite	1.8	0.3	1.7	2.2	0.3	0.4	1.1	
Anorthite	5.4	17.9	11.6	9.6	0.5	0.7	1.2	
Mullite	5.9	2.7	7.2	1.6	4.9	4.1	6.4	
Quartz	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Alumino-silicate (originally kaolinite)	57.4	36.9	42.1	45.0	78.4	77.8	75.9	
Qtz60Kao40	3.5	3.2	4.1	0.9	2.3	2.2	2.0	
Qtz80Kao20	0.7	0.5	1.0	0.1	0.5	0.5	0.4	
Pyrrhotite/Fe-S-O/ Fe-oxide	0.6	0.4	0.3	1.4	0.1	0.2	0.1	
Carbonate/CaMgOxide	0.4	0.0	0.6	0.4	0.2	0.2	0.5	
Char	0.2	0.7	1.9	3.4	3.2	3.8	3.3	
Other	0.6	0.4	0.7	1.3	0.2	0.1	0.0	
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	

**Table 8: Percent SiO<sub>2</sub> distribution**

Glass Matrix	27.3	38.7	30.6	35.8	8.6	9.1	8.2	
Orthoclase glass	2.0	0.3	2.3	2.8	0.9	1.1	0.8	
Muscovite	1.6	0.2	1.1	1.3	0.4	0.4	1.3	
Anorthite	3.4	9.8	6.7	5.5	0.4	0.6	1.0	
Mullite	1.4	0.5	1.3	0.2	0.9	0.7	1.2	
Quartz	12.4	19.6	21.1	18.6	25.3	26.1	25.1	
Alumino-silicate (originally kaolinite)	42.1	23.4	25.2	27.3	53.4	51.7	52.8	
Qtz60Kao40	5.9	4.6	6.0	1.3	4.6	4.4	4.1	
Qtz80Kao20	2.2	1.4	2.9	0.2	1.6	1.6	1.4	
Pyrrhotite/Fe-S-O/ Fe-oxide	0.4	0.4	0.2	1.1	0.1	0.2	0.1	
Carbonate/CaMgOxide	0.1	0.0	0.1	0.1	0.4	0.3	0.7	
Char	0.2	0.7	2.0	4.9	3.2	3.8	3.2	
Other	0.9	0.4	0.6	0.8	0.2	0.1	0.0	
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	

### XRD analysis results

It is clear from the results summarised in **Table 9** that the ash samples from Sasol Infrachem steam stations One and Two are of a similar mineralogical composition, where mullite and  $\alpha$ -quartz are the major crystalline phases, while quick-lime, the iron oxides (magnetite, hematite and maghemite) and anhydrite are the minor phases. From the recent work done by Sobiecki<sup>5</sup>, anorthite and other Ca and/or Mg silicates were not found to be present in both Sasol Infrachem FA samples. The XRD analysis of Secunda GA phase 1 and 2 samples shows that the anorthite was found to be the major mineral present (likewise mullite and alpha-quartz) and diopside, gehlenite and indialite were identified in small concentrations. It is interesting to notice, that the Infrachem GA sample contains more mullite and less anorthite (although the same glass content), than the Secunda GA samples. From the results given in **Table 9** it is clear that all Sasol fly ashes analysed contain quicklime (CaO) while in the gasification ashes lime arising from dolomite and calcite reacted with free aluminium silicate to form calcium alumino-silicates. The gasification ashes contained cristobalite, high temperature polymorph of alpha-quartz but not detected in the FA samples. The XRD results reveal that all analysed coal ash samples from the gasification and combustion plants contain a large quantity (45% to 73 mass%) of amorphous non-crystalline phases.



**Table 9: Crystalline phases identified and quantified in Sasol coal ashes by XRD**

MINERALS IDENTIFIED	Infrachem SS1 FA (%)	Infrachem SS 2 FA (%)	Synfuels Phase 1 GA (%)	Synfuels phase 2 GA (%)	Synfuels FA (%)	Infrachem GA (%)
Mullite – $\text{Al}_6\text{Si}_2\text{O}_{13}$ [15-0776]	28.0	18.9	14.6	12.6	13.9	25.6
$\alpha$ -Quartz - $\alpha$ - $\text{SiO}_2$ [46-1045]	19.9	14.7	13.9	15.1	9.9	11.0
Cristobalite – $\beta$ - $\text{SiO}_2$ [27-605]			0.9	0.5		2.4
Magnetite – $\text{FeFe}_2\text{O}_4$ [19-0629]	0.6	0.3	0.8	0.2		
Maghemite - $\gamma$ - $\text{Fe}_2\text{O}_3$ [39-1346]	1.3	0.6			0.3	1.3
Hematite - $\alpha$ - $\text{Fe}_2\text{O}_3$ [33-0664]	1.2	1.3	0.8	0.6	1.2	
Quicklime – $\text{CaO}$ [37-1497]	2.2	1.4		0.3	1.8	
Rutile - $\text{TiO}_2$ [21-1276]		0.9				
Anhydrite – $\text{CaSO}_4$ [37-1496]	0.6	0.5	0.6			
(*)Anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ [41-1486]			17.9	14.6		9.2
Diopside $\text{Ca}(\text{Mg,Al})(\text{Si,Al})_2\text{O}_6$ [25-1217]			2.9	1.3		
Gehlenite $\text{Ca}_2\text{Al}_2\text{SiO}_7$ [35-0755]			1.4	0.2		
Indialite– $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ [48-1600]			0.3	0.4		
Noncrystalline content (glass)	46.2	61.3	45.9	54.2	73.0	50.4

(\*)The chemical formula of anorthite, as reported, is a general one for this type of calcium/ aluminium silicate. However, it is more likely, that sodium does partially displace calcium, in a larger or smaller degree, forming a solid solution (e.g., anorthite, sodian –  $(\text{Ca, Na})(\text{Si, Al})_4\text{O}_8$ ).

## Water leach (DIN 38414-T4) results

The water leach test is used to measure the concentration of water extractable ions in the ash. The results of the leachable salts from the ash samples used in this study are given in **Table 10**.

**Table 10:** Leachate analyses results from the water leach tests (DIN 38414-T4)

Substance	Infracem GA	Infracem Bottom Ash	Secunda phase 1 GA	Secunda phase 2 GA	Infracem SS1 FA	Infracem SS2 FA	Secunda FA
pH	11.7	10.9	11.6	11.6	12.7	12.7	12.6
EC ( $\mu$ S/cm)	1591	2110	1044	1078	9688	9494	9137
TDS (mg/L)	866	1160	561	579	5930	5800	5570
F (mg/L)	0.5	1.7	0.7	0.8	1.1	1.4	0.9
NO <sub>2</sub> (mg/L)	0.3	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
NO <sub>3</sub> (mg/L)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Cl (mg/L)	1.6	85	1.7	1.7	0.6	0.6	4
SO <sub>4</sub> (mg/L)	130	896	133	147	106	110	71
PO <sub>4</sub> (mg/L)	0.3	0.4	0.4	0.4	0.4	0.4	0.4
P ALk (mg/L)	303	39	102	154	2287	2221	2392
M ALK (mg/L)	348	73	225	237	2475	2471	2495
NH <sub>3</sub> (mg/L)	0.4	0.2	0.2	0.3	1.8	2.0	0.3
CO <sub>3</sub> (mg/L)	90	68	204	166	376	500	206
HCO <sub>3</sub> (mg/L)	0	0	21	0	0	0	0
Mg (mg/L)	<1	<1	<1	<1	<1	<1	<1
Ca (mg/L)	307	268	142	128	687	853	884
K (mg/L)	1	49	6	7	1	1	10
Na (mg/L)	5	180	10	10	3	2	9
Al (mg/L)	6	1	12	13	0.2	0.08	0.09
As (ppb)	<4.3	<4.3	<4.3	<4.3	<4.3	<4.3	<4.3
Cd (ppb)	<2.5	<2.5	<2.5	<2.5	4	4	7
Co (ppb)	<1.0	<1.0	1	<1.0	6	2	<1.0
Cr (ppb)	4	4	6	5	397	1377	736
Cu (ppb)	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1
Fe (ppb)	12	12	17	19	30	18	19
Mn (ppb)	<0.34	0.6	<0.34	<0.34	<0.34	0.6	0.7
Mo (ppb)	<7.0	<7.0	<7.0	<7.0	<7.0	<7.0	<7.0
Ni (ppb)	<6.1	8	<6.1	<6.1	<6.1	<6.1	<6.1
Si (ppb)	3	3	2	2	1	<1	<1
Pb (ppb)	<23	<23	<23	<23	<23	<23	<23
V (ppb)	20	26	17	20	<1.3	1	82
Zn (ppb)	130	166	128	139	244	297	398

As to be expected, the pH values for all the leachates from gasification and steam station ashes were high (i.e. pH > 10). Fly ash leachates had slightly higher pH values (average pH of 12.7) compared to the gasification ash leachates which had an average pH value of 11.7. The observed leachate pH values are probably due to the presence of OH<sup>-</sup> ions which are produced on the

hydrolysis CaO. The ash leachate pH will probably remain alkaline as long as the free CaO is present in the ash. Relatively high leachate electrical conductivities (EC values) were observed from the fly ash leachates. The EC values in fly ash leachates were approximately 5 times greater than for gasification ash leachates. This implies that ash samples, especially fly ash is not only very alkaline in nature but is also saline. The EC results were in good agreement with the total dissolved solids (TDS) results which also showed that fly ash leachates had TDS values 6 times greater than the gasification ash leachates TDS values.

The results given in **Table 10** indicate that the predominant ions in the leachates are  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and  $\text{Ca}^{2+}$  with minor amounts of  $\text{Cl}^-$ , Na and  $\text{K}^+$ . Of these ions, the more problematic ones to the environment are  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cl}^-$  ions. This is because some of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cl}^-$  in ash occur in the form of soluble amorphous glasses attached to surfaces of glass particles. There are no known ways to control the concentration of these ions in solution. It must, however, be pointed out that the major portion of these species in the ash is expected to be readily flushed out on the first contact of the ash with rain water. As a result, the subsequent leachates are expected to be of better quality with respect to these ions. The other divalent ions such as sulphate, calcium, carbonate and magnesium have a range of possible mechanisms that control their leachability from the ash. It is speculated that the formation of gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is the main mechanism that controls the concentration of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  in the leachates. Generally, the water leachable proportion of trace elements was significantly low (**Table 10**) except for Cr and Zn which were relatively higher.

#### TCLP results

TCLP analyses are commonly used to indicate whether a waste should be classified as a hazardous (waste) material. At best, the TCLP provides some indication of the mobility of specific contaminants for leaching. In South Africa, the Department of Water Affairs Minimum Requirements (DWAf MR) document for waste handling and disposal stipulates that industrial wastes such as coal ash are not exempted from the hazardous wastes rules. As a result, the TCLP leachate concentrations of the selected contaminants in these wastes should be compared with the specified regulatory levels. In this report, the U.S EPA TCLP regulatory limits and the DWAf Allowable risk limits (ARL) were used as a reference. **Table 11** gives the average TCLP data compared with the U.S EPA and the DWAf allowable risk levels for Ag, As, Ba, Cd, Cr, Pb, Hg and Se. The EPA and DWAf risk levels should serve as a reference for subsequent data presented in **Tables 12, 13** and **14**. Other constituents in coal ash that provides an assessment of environmental performance include Al, Co, Cu, Fe, Mn, Ni, V and Zn.

Acidic leaching (in this case dilute acetic acid) is used to assess the mobility of trace metals, as they are generally more mobile under acidic conditions.

According to Campbell<sup>6</sup> under basic conditions, metals tend to form insoluble hydroxides (OH) or oxy-hydroxides (OOH). The average leachate results from the three laboratories (**Table 11**) of the ash samples tested in this study confirm that none of the leachates generated from the steam station and gasification ashes exceeded the USEPA and the DWAF regulatory limits. As such, these ashes would not be classified as hazardous waste materials.

From the results given in **Table 11**, it can be seen that the leachable concentrations of the US EPA regulated elements are significantly lower than the EPA limits.

Ag: Silver is present in coal ash in extremely low concentrations which does not pose any threat to the receiving environment.

As: Arsenic is found in coal ash at low to somewhat high concentrations. The most probable arsenic species present in the ash is As (V) which has a relatively low toxicity compared to arsenic (III) species.

Ba: Barium occurs in coal ash leachates at concentrations below regulatory standards. In the presence of sulphate ions (as in the case of coal ash), barium forms an insoluble BaSO<sub>4</sub>.

Cd: Cadmium is another regulated element and is present in low concentrations in ash. Available laboratory data indicate that very low concentrations of Cd can be found in ash leachates. Cadmium levels in ash leachates are usually comparable to that from naturally occurring soil leachates.

Cr: Chromium in the ash occurs in two oxidation states Cr(III) and Cr(VI). The dominant valence state of Cr in coal ash according to Hansen et al<sup>7</sup>. is expected to be Cr(III) not Cr(VI) since it principally associated with a ferromagnetic fraction.

Hg: Mercury is a US EPA regulated element which is present in extremely low concentrations in the ash. Previous studies have shown that the leaching and migration of Hg from the ash into the environment is not likely to occur. Therefore, Hg in coal ash is unlikely to pose a risk to the environment from landfills and impoundments where the ash is disposed.

Pb: Lead is present in the ash in solid phase compounds that have very low dissolution and leaching potentials.

Se: Low concentrations of selenium can leach from coal combustion ashes. The leaching potential for Se is somewhat higher under alkaline conditions (pH greater than 10) such as existing in the ash. The environmental chemistry of Se is complex because Se in ash is present in two valence states i.e. Se (IV) and Se (VI).

**Table 11: Averaged TCLP leachate results for the power station and the gasification ashes**

Sample name	Ag (ppb)	As (ppb)	Ba (ppb)	Cd (ppb)	Cr (ppb)	Hg (ppb)	Pb (ppb)	Se (ppb)
Sasol Infrachem gasification ash	9	14	786	4	46	8	8	44
Sasol Infrachem steam station 2 bottom ash	25	7	909	7	44	7	10	17
Sasol Infrachem steam station 1 fly ash	29	15	1143	12	774	17	8	46
Sasol Infrachem steam station 2 fly ash	26	12	1044	10	657	14	6	41
Secunda phase 1 gasification ash	12	8	835	10	60	8	7	17
Secunda phase 2 gasification ash	6	19	836	8	13	8	8	33
Secunda steam station fly ash	19	89	756	7	1430	21	4	77
<b>TCLP regulatory level</b>	<b>5000</b>	<b>5000</b>	<b>100000</b>	<b>1000</b>	<b>5000</b>	<b>200</b>	<b>5000</b>	<b>1000</b>
<b>DWAF allowable risk level</b>	<b>2000</b>	<b>430</b>	<b>7800</b>	<b>31</b>	<b>4700</b>	<b>22</b>	<b>100</b>	<b>260</b>

In this study, three different laboratories (Sasol Infrachem Laboratory, Talbot and Talbot Laboratory and the Mineral Waste Characterisation and Classification Centre (UCT)) were used. The main reason for using three different laboratories was to assess the reproducibility of the TCLP test and also to evaluate the accuracy of the various analytical techniques being used by the different laboratories.

When comparing the results of trace elements extracted by the three laboratories (**Table 12, 13 and 14**), it is observed that Ag, As, Ba, Cd, Pb, Se did not dissolve in the water leachate in concentrations that exceeded the US EPA and DWAF limits. Only Hg in the Sasolburg Infrachem Steam Station 1 fly ash and the Secunda Synfuels power station fly ash leachates exceeded DWAF Allowable risk levels in the Sasol Infrachem Laboratories results. Mercury is associated with pyrite and could be arising from the unburnt carbonaceous matter in coal. The Hg concentrations in the fly ash leachates were in the range of 29 to 49 ppb according to the Sasol Infrachem Laboratories. While the other leachate analyses results for Hg from this laboratory are consistent with those from Talbot and Talbot Laboratories, the elevated fly ash leachate results that were reported seem to be a consequence of analytical error. The Mineral Waste Characterisation and Classification Centre at the University of Cape Town reported the lowest Hg concentrations in all the ash leachates compared to the other two laboratories. The differences in the results reported by the three laboratories are attributed mainly to the different analytical techniques used as Talbot and Talbot and the Mineral Waste Characterisation and Classification Centre used ICP-MS while Sasol Infrachem Laboratories used the ICP-OES technique.

Barium, arsenic, silver, cadmium, lead, chromium and selenium concentrations in the leachates were several orders of magnitude below both the EPA and DWAF regulatory limits. This is due to the fact that these elements are present in low concentrations in coal ash. As a result, the leaching of these elements from the ash does not pose an environmental threat.

**Table 12: TCLP leachate results for the power station and the gasification ashes from Sasol Infrachem Laboratories**

Sample name	Ag (ppb)	As (ppb)	Ba (ppb)	Cd (ppb)	Cr (ppb)	Hg (ppb)	Pb (ppb)	Se (ppb)
Sasol Infrachem gasification ash	1	10	393	1	32	14	2	73
Sasol Infrachem steam station 2 bottom ash	5	5	700	10	5	10	10	20
Sasol Infrachem steam station 1 fly ash	1	11	700	20	753		5	88
Sasol Infrachem steam station 2 fly ash	1	10	563	15	620	22	3	79
Secunda phase 1 gasification ash	1	1	641	20	72	14	4	16
Secunda phase 2 gasification ash	1	26	637	14	18	14	3	55
Secunda steam station fly ash	1	1	408	11	1000		3	122
<b>TCLP regulatory level</b>	<b>5000</b>	<b>5000</b>	<b>100000</b>	<b>1000</b>	<b>5000</b>	<b>200</b>	<b>5000</b>	<b>1000</b>
<b>DWAF allowable risk level</b>	<b>2000</b>	<b>430</b>	<b>7800</b>	<b>31</b>	<b>4700</b>		<b>100</b>	<b>260</b>

**Table 13: TCLP leachate results for the power station and the gasification ashes from Talbot and Talbot Laboratories**

Sample name	Ag (ppb)	As (ppb)	Ba (ppb)	Cd (ppb)	Cr (ppb)	Hg (ppb)	Pb (ppb)	Se (ppb)
Sasol Infrachem gasification ash	10	10	1170	10	20	10	10	50
Sasol Infrachem steam station 2 bottom ash	10	10	880	10	10	10	10	30
Sasol Infrachem steam station 1 fly ash	10	20	1400	10	780	10	10	30
Sasol Infrachem steam station 2 fly ash	8	15	1325	12	730	11	9	28
Secunda phase 1 gasification ash	10	10	1040	10	10	10	10	30
Secunda phase 2 gasification ash	10	10	1070	10	10	10	10	40
Secunda steam station fly ash	10	130	1300	10	1950	10	10	70
<b>TCLP regulatory level</b>	<b>5000</b>	<b>5000</b>	<b>100000</b>	<b>1000</b>	<b>5000</b>	<b>200</b>	<b>5000</b>	<b>1000</b>
<b>DWAF allowable risk level</b>	<b>2000</b>	<b>430</b>	<b>7800</b>	<b>31</b>	<b>4700</b>	<b>22</b>	<b>100</b>	<b>260</b>



**Table 14: TCLP leachate results for the power station and the gasification ashes from the Mineral Waste Characterisation and classification centre**

Sample name	Ag (ppb)	As (ppb)	Ba (ppb)	Cd (ppb)	Cr (ppb)	Hg (ppb)	Pb (ppb)	Se (ppb)
Sasol Infrachem gasification ash	16	23	795	1	86	1	13	8
Sasol Infrachem steam station 2 bottom ash	61	7	1148	2		2	11	2
Sasol Infrachem steam station 1 fly ash	76	13	1329	5	790	11	8	21
Sasol Infrachem steam station 2 fly ash	70	12	1243	4	621	8	5	18
Secunda phase 1 gasification ash	25	14	825	1	99	1	6	5
Secunda phase 2 gasification ash	8	20	800	1	10	1	12	3
Secunda steam station fly ash	46	135	560	0.4	60	5	0.3	38
<b>TCLP regulatory level</b>	<b>5000</b>	<b>5000</b>	<b>100000</b>	<b>1000</b>		<b>200</b>	<b>5000</b>	<b>1000</b>
<b>DWAF allowable risk level</b>	<b>2000</b>	<b>430</b>	<b>7800</b>	<b>31</b>		<b>22</b>	<b>100</b>	<b>260</b>

## Discussion of the additional leachate results

Aluminium is not one of the US EPA regulated metals. The ash leachate results given in **Table 15** shows that the Al concentration in all the ash leachates (except Synfuels FA) exceeded the DWAF Allowable Risk Level. This suggests that Sasol ashes have a high content of leachable aluminium species present in the glassy phase which can leach into the receiving environment. In a highly alkaline environment pH above 10 (as prevalent in fly ash), increased aluminium concentrations in the leachates can be expected due to an increase in Al solubility at high pH conditions. However, this reactive form of aluminium in coal ashes usually reacts with silicate glasses to form insoluble solid phase hydrous aluminosilicates. From the work reported by Benson<sup>8</sup> the formation of aluminosilicates will significantly reduce the amount of aluminium leaching from the ash

Iron is another non US EPA regulated element. The ash leachate results in Table 15 reports Fe concentrations that exceeded the DWAF limits in the Synfuels gasification ash. Iron species in coal ash is found in partially oxidised pyrite and aluminosilicate glasses. At high pH, the concentration of leachable Fe is likely to decrease as Fe precipitates in the form of iron hydroxide. The leachate results for cobalt, copper, nickel and zinc show that the leachable concentrations were several orders of magnitude below their respective DWAF limits. All these elements could form insoluble hydroxide precipitates at pH levels above 6.

Manganese concentration in all the ash leachates exceeded the DWAF limit. However, manganese will decrease in solubility at pH values greater than 6 as it will readily form the insoluble  $MnO_2$ . Secunda Steam Station ash is the only sample that produced leachates with V concentration exceeding the DWAF limit. According to Pickett<sup>9</sup>, Vanadium in the ash is mainly bound to the oxides in the aluminium-silicate matrix (85 %). The mobility of V in a highly alkaline environment found in coal ash is expected to increase. This implies that in the case of Secunda fly ash there is a chance for vanadium to leach from the Secunda fly ash to the environment when the ash has a direct contact with the receiving environment.

**Table 15:** Aqueous concentrations of additional metal species in the leachate produced during TCLP steam station and gasification ashes

Sample Name	Laboratory	Al	Fe	Co	Cu	Ni	V	Zn
Infrachem gasification ash	Sas Infra	1100	6000	1	49	88	10	247
	T&T	6570	1620	20	10	20	10	160
	MWCCC		1523	25	95	235	97	194
Infrachem steam station 1bottom ash	Sas Infra	250	600	10	10	70	10	30
	T&T	260	750	10	10	80	10	40
	MWCCC		5330	13	82	132	9	169
Infrachem steam station 1 fly ash	Sas Infra		1000	28	34	71	80	475
	T&T		1730	20	60	90	100	230
	MWCCC		1020	15	99	97	97	299
Infrachem steam station 2 fly ash	Sas Infra		957	22	41	65	58	321
	T&T		1698	15	55	88	95	227
	MWCCC		1000	10	84	64	63	173
Synfuel phase 1 gasification ash	Sas Infra			1	49	146	25	446
	T&T	550	780	30	10	130	10	130
	MWCCC			37	61	182	36	116
Synfuel phase 2 gasification ash	Sas Infra	9000	9000	84	12	100	16	241
	T&T	260	810	20	10	110	10	110
	MWCCC		810	35	45	174	44	106
Synfuel steam station fly ash	Sas Infra	24	6	49	1	165	10	131
	T&T	20	1700	10	10	100		30
	MWCCC	18	60	8	4	98		17
<b>DWAF Allowable risk levels</b>		<b>10000</b>	<b>9000</b>	<b>6900</b>	<b>100</b>	<b>1140</b>	<b>100</b>	<b>700</b>

Note: Sas Infra : Sasolburg Infrachem laboratory.

T&T: Talbot and Talbot laboratory.

MWCCC: Mineral Waste Characterisation and Classification centre.

Concentrations of the leached elements are expressed as ppb.

## CONCLUSIONS

Converting Sasol gasification and power generation by-products (gasification ash, fly ash and bottom ash) into useful commodities are areas of interest at Sasol Technology Research and Development. In addition, the mineral matter in coal is a principle source of clinkers in gasifiers and slag/fouling deposits in power station boilers. Understanding clinker formation in gasifiers and slagging/fouling in power stations will be beneficial and should assist in reducing the incidents of gasifier and boiler outage. It is for these reasons that the mineralogical attributes (physical and chemical) of gasification ashes, fly ashes and the clinker (bottom ash) were identified and quantified using CCSEM (Computer Controlled Scanning Electron Microscopy), XRF, ICP, XRD, proximate and ultimate analyses.

From a mineralogical perspective, the gasification ash, bottom ash and fly ash are the by products of gasification and steam generation processes. Mineralogically, these samples can be described as a complex association of alumino-silicate glasses, extraneous rock fragments (stone), alteration products of extraneous pyrite and carbonate particles and the high temperature alteration products of kaolinite, quartz, microcline and muscovite. The mineralogical differences between gasification ash and fly ash are attributed to particle size of the coal feedstock and differences in the operating conditions of a gasifier and boiler. The alumino-silicate glass in fly ash predominately occurs as spherical ash particles and/or coating quartz and kaolinite ash particles. In a gasification ash, the glass phase is closely associated with large rock fragments. Crystalline anorthite laths in a glass matrix is a common feature of the gasification ash and bottom ash, but not common in fly ash. The mass% phase proportions of the ash analysed is summarised in **Table 16**.

**Table16: Percentage of phases present in ash**

Phase							
Interstitial/matrix (alumino-silicate) glass with Ca,Mg,Fe and Ti	26.0	39.0	30.9	32.0	11.5	12.2	10.5
K-bearing glass (transformation products of microcline and muscovite)	3.6	0.5	3.2	3.5	0.9	1.1	2.5
Anorthite (CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> ).	4.2	12.7	8.7	6.3	0.0	0.0	0.0
Mullite (Al <sub>6</sub> Si <sub>2</sub> O <sub>13</sub> )	2.6	1.0	2.8	0.6	2.1	1.7	2.7
Quartz	6.6	10.8	11.7	9.1	14.5	15.1	14.0
Alumino-silicate (transformation products of kaolinite)	42.0	24.4	27.0	25.5	58.4	56.8	56.0
Pyrrhotite/Fe-S-O/ Fe-oxide (transformation of extraneous pyrite)	5.5	3.8	3.5	12.5	1.0	1.9	1.4
Carbonate/ CaMgOxide (transformation of extraneous carbonates)	1.8	1.4	1.4	1.3	2.1	1.6	4.3
Char	0.6	1.2	3.2	6.8	4.3	5.0	4.2
Other	7.0	5.1	7.5	2.4	5.2	4.6	4.5
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Fly ash is characterised by a higher proportion of alumino-silicate (>55 mass %), lower proportion of interstitial/matrix (alumino-silicate) glass (<12 mass %) and absence of anorthite. Higher proportion of alumino-silicate and lower proportion of glass is attributed to limited interaction between fluxing minerals (calcite, dolomite and pyrite) and kaolinite to form glass phase. The extreme fine particle size distribution of power station pulverised fuel (feed to boiler) and conditions within the boiler will reduce the probability of fluxing elements interacting with kaolinite. In comparison, since the gasifier feed is coarse, the proportion of fluxing minerals in

close proximity to “kaolinite” increases as the coal and ash gravitates to the bottom of the gasifier.

The Sasol Infracem (Sasolburg) gasification ash analysed in this study is notably different from the Sasol Synfuels (Secunda) gasification ash. The Sasol Infracem power station bottom ash is similar to the Synfuels gasification ash. This similarity suggests that there is a degree of commonality between the slag formation process in a power station boiler and clinker formation in a gasifier. If further investigation into clinker formation in gasifiers is to be undertaken, this trend could be useful in developing a clinkering formation model.

In general, the Secunda fly ash is significantly finer (85% passing 75  $\mu\text{m}$ ) than the Sasolburg fly ash (71% passing 75  $\mu\text{m}$ ). The difference in fly ash particle size distributions could account for the on average higher carbon loss in Sasol Infracem fly ashes. In general, it is widely recognised that a coarse pulverised fuel particles would take longer to burn. Longer burnout times will increase the proportion of char (carbon) reporting to the fly ash. A significant proportion of the fly ash char occurs in the +75  $\mu\text{m}$  size fraction.

Based on the samples analysed, the Sasolburg gasification ash had a lower carbon (char) loss than the Secunda gasification ash. In general, char in the gasification ash occurs as discrete particles not attached to the alumino-silicate glass and rock fragments. It is common to have kaolinite, quartz, pyrite and carbonates inclusions in these char particles.

Quantitative Scanning Electron Microscopy Energy Dispersive (SEM-EDS) analysis of the prominent laths in gasifier glass confirms that the mineral is anorthite.

Based on CCSEM mass-% phase proportions and the elemental composition of the different phases the proportion of  $\text{Al}_2\text{O}_3$  associated with alumino-silicate varies from 36% to 58%, with interstitial/matrix glass from 22% to 37% and with anorthite/mullite between 10% to 21%. In the fly ash, 75% to 79% of  $\text{Al}_2\text{O}_3$  is associated with alumino-silicate, 8% to 10% with alumino-silicate glass and 1% to 3% with mullite.

The distribution of  $\text{SiO}_2$  in the gasification ash varies between 23% to 42% in alumino-silicate, 27% to 39% in interstitial/matrix glass and between 12% to 22% in quartz. In contrast the  $\text{SiO}_2$  distribution in fly ash ranges from 51% to 54% in alumino-silicate, 25% to 27% in quartz and 8 to 10% in interstitial/matrix glass.

The mineralogical data presented in this investigation is a simplified description of samples with a complex mineralogy. It is conceivable that further investigation might result in extending the categories or simplifying them further. This is a continuous and dynamic process.

The potential of CCSEM as well as XRD mineralogical data can be used to resolve a number of research and operational issues. These include:

- ◆ Suitable techniques for extracting Al from ash – by understanding the mineralogical compositions of the different phases and the proportion of  $\text{Al}_2\text{O}_3$  it becomes possible to select suitable samples and different extraction techniques. It is conceivable that extracting Al from the different ash phases will depend on the attributes of that phase.
- ◆ Formation of clinker brick – developing a brick, which will conform to the required specifications, needs some understanding of the nature of the raw materials used to create the brick. It is conceivable that the different ash phases could react differently with the Portland cement, producing bricks of variable quality. A mineralogical understanding of the raw material could assist in explaining the differences in the brick qualities observed.
- ◆ Since a high proportion of the char appear as discrete particles it might be economically feasible to recover char from ash.

The XRD results indicate that Sasol ashes (gasification ash, bottom ash and fly ash) contain the major crystalline phases such as mullite, quartz and anorthite and minor crystalline phases such as iron oxides (magnetite, hematite and maghemite) and anhydrite. All of the Sasol fly ashes contain lime while in the gasification of coal quick-lime reacted with reactive aluminium silicates and sulphur oxides to form calcium aluminium silicates and calcium sulphate respectively. The XRD analysis of all Sasol ashes analysed shows that coal ashes contain a large amount (45% to 70 wt %) of the non-crystalline, molten alumino-silicates.

Leachate characteristics of Sasol gasification and fly ashes were tested according to the DIN 38414-T4 leach test and the US EPA Toxicity Characteristic Leaching Procedure (TCLP). The ash leachate results substantiate that none of the leachates generated from the Sasol gasification and fly ashes exceeded the US EPA regulatory limits for As, Ag, Ba, Cd, Cr, Pb, Hg and Se. As such, these ashes would not be classified as hazardous.

The leaching results of the other elements that are not regulated by the US EPA but have been listed as elements of concern in the DWAF Minimum Requirements document, Al exceeded the allowable risk levels. However, when the ash hydrates, the aluminium species react with the silicates to form insoluble alumino-silicate precipitates. The net result of these reactions is that the risk posed by the leaching of Al to the surrounding water bodies and soils will be reduced significantly.

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## REFERENCES

- 1.Environmental Protection Agency (EPA). 1986. Federal register, page 1750-1758.
- 2.Danny, D and Valsaraj, K. 1999. TCLP characterization of exploration and production wastes in Louisiana. Final report to Louisiana department of natural resources.
- 3.Department of Water Affairs and Forestry. 1998. Minimum Requirements for the Handling, Classification and Disposal of Hazardous Waste. Second Edition.
- 4.Van Alphen C, Matjie, R.H. January 2004. Characterisation of Secunda GASIFIER9, Feedstock and gasification ash. VAC and Sasol Technology R&D: Technical report
- 5.Sobiecki, A. March 2004. Characterisation of various Sasol ashes by X-ray Diffraction. Sasol Technology R&D: Analytical report.
6. Campbell, A. 1999. TCLP and modified leaching assessment of RBI Grade 81 natural stabilizer and its effect on the environment. Road building international (RBI) internal report.
7. Hansen, L.D., Silberman, D., Fisher, G.L and Eatough, D.J. 1984. Chemical speciation of elements in stack-collected, respirable size, coal fly ash. Environmental Science & Technology 18, 181-186.
- 8.Benson, S. 1993. Ash formation and behaviour in utility boilers. Microbeam, Volume 1, issue 2, page 2.
- 9.Pickett, J. 2002. First delisting petition approval by the US EPA for a vitrified mixed waste. WSRC-MS-00576.



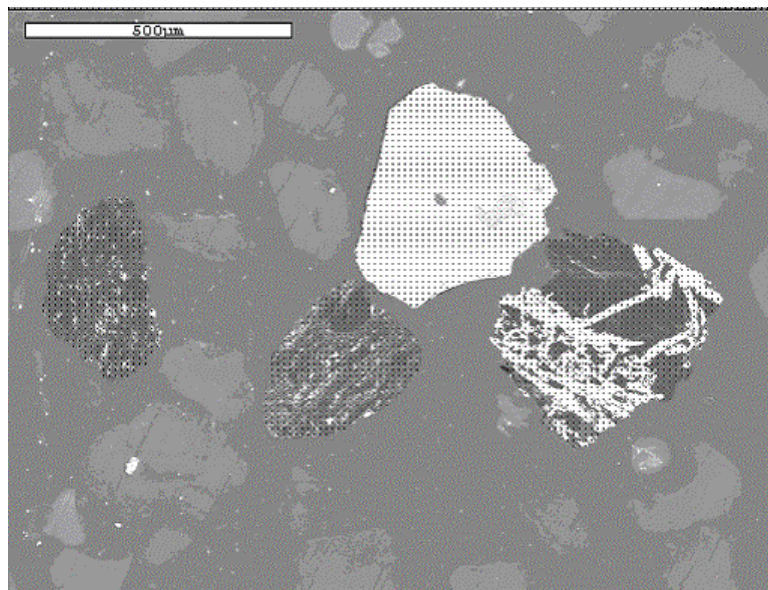
**APPENDIX A**  
**CCSEM: ANALYTICAL METHODOLOGY**  
**(COAL CHARACTERISATION SCANNING ELECTRON MICROSCOPE)**

CCSEM, at TSI is a scanning electron microscope (SEM) configured to automatically and rapidly determine the minerals in coal and phases in fly ash and slag deposits.

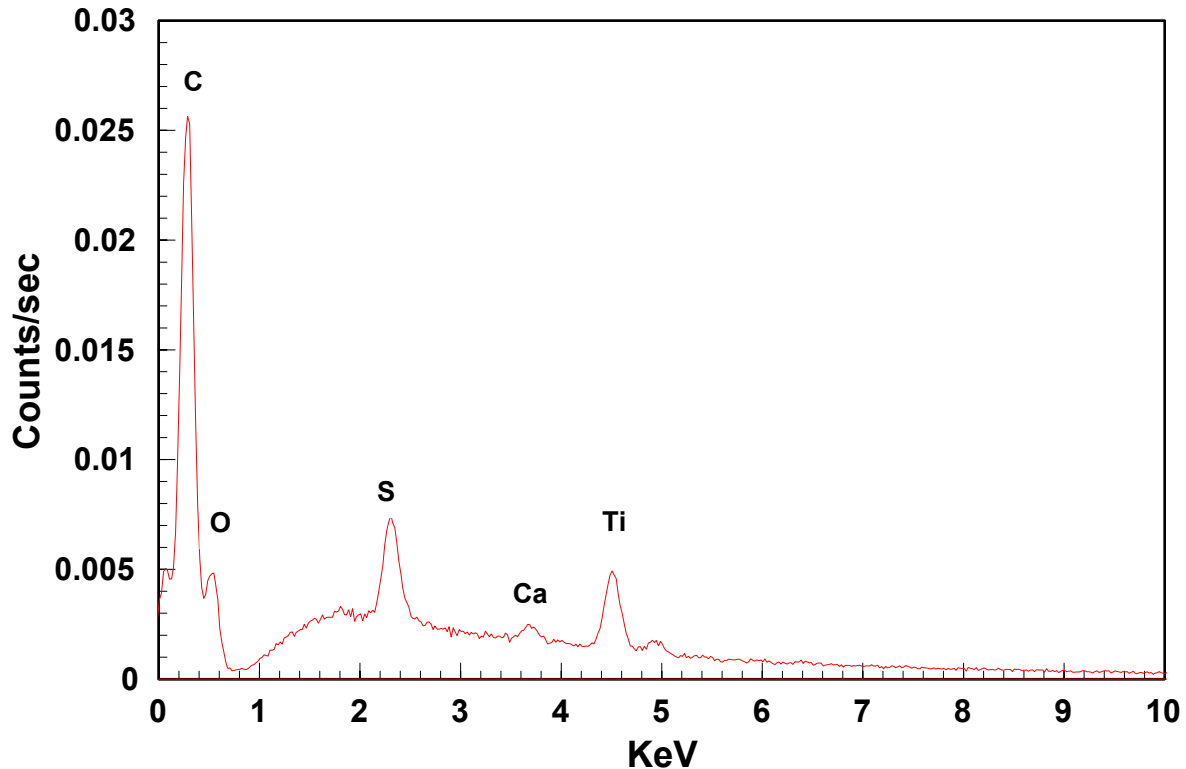
Samples of pulverised fuel or fly ash are mixed with iodinated epoxy resin and allowed to cure. The cured 30 mm mount is polished exposing individual particles in cross-section.

The CCSEM analytical procedure is as follows:

- ◆ Select appropriate magnification (based on particle sizes). Divide the polished section into regularly spaced analytical fields of view or frames.
- ◆ Position the sample at the first field of view and acquired a backscattered electron image (BSI). BSI (Figure A.1) is an atomic mass contrast image and ensures that coal and minerals can be identified by image processing routines.
- ◆ Process the image and establish the regular grid of analytical points for each field of view
- ◆ Position the electron beam at each analytical point and acquire a 100 msec X-ray spectrum (Figure A.2). Relative elemental composition of the phase is derived from the X-ray spectrum.
- ◆ Position the sample at the next field of view and repeat the process until all the fields of view have being analysed.



**Figure A.1: Processed backscatter electron image of pulverised fuel with the regular grid of analytical points superimposed (black dots). The scale bar represents 50  $\mu\text{m}$  and the estimated point spacing is 11.21  $\mu\text{m}$ . In this image, coal is black, epoxy resin is grey and mineral matter is white.**



**Figure A.2: Typical X-ray spectrum of coal.**

The development of mineral identification rules based on the principles of fuzzy logic is crucial for CCSEM analysis. The rules are listed in an ASCII file (\*.sui) and are developed by examining the polished section and identifying the minerals present prior to undertaking an automated CCSEM analysis. The file developed is unique and can be used for subsequent CCSEM analysis.

Mineral nomenclature for pulverised coal is based on the typical minerals found in pulverised fuel. In context of pulverised coal, the CCSEM mineral “coal” describes a C-rich phase (Figure A.2) and describes the organic rich fraction of pulverised fuel. Coarse ash and clinker phase identification is based on the elemental composition and nomenclature is based on the perceived coal mineral source.

The major outputs from CCSEM analyses are:

- ◆ Mass % mineral or phase proportions in pulverised fuel or fly ash, respectively. Mineral proportions (volume-%) are determined by dividing the number of analytical points for each phase by the total

number of analysed points. The mass-% can be calculated by multiplying the volume-% by the density of the phase.

- ◆ The oxide elemental composition can be calculated from the mass-% mineral proportions.
- ◆ Association characteristics of minerals in coal and phases in fly ash.
- ◆ Size variation of the different minerals
- ◆ Proportion of included minerals compared to proportion of extraneous minerals. From a slagging perspective, mineral transformation of included minerals will be exposed to higher temperatures and reducing conditions compared to extraneous mineral particles. This difference in localised environment has an impact on mineral transformations.

## APPENDIX B

### Sasol Fly Ash - Proximate, ultimate and ash elemental analysis

**Table B.1: Proximate, ultimate analysis – Infrachem SS1 Fly ash**

	Proximate analysis			
Inherent moisture (%)				0.1
Ash (%)				96.4
Volatile matter (%)				1.3
Fixed carbon (%)				2.2
Total sulphur (%)				0.5
Carbon (%)				2.71
Hydrogen (%)				0.2
Nitrogen (%)				0.05
Oxygen (%)				0.04
SiO <sub>2</sub>	51.9	56.1	55.4	54.34
Al <sub>2</sub> O <sub>3</sub>	26.4	27.6	28.6	27.78
TiO <sub>2</sub>	1.42	1.65	1.8	1.66
Fe <sub>2</sub> O <sub>3</sub>	2.98	3.41	3.12	3.11
CaO	5.9	6.15	5.78	5.86
MgO	1.2	1.5	1.6	1.46
K <sub>2</sub> O	0.42	0.5	0.46	0.45
Na <sub>2</sub> O	0.3	0.3	0.4	0.36
P <sub>2</sub> O <sub>5</sub>	0.17	0.21	0.27	0.23
MnO	0.01	0.01	0.01	0.01
Cr <sub>2</sub> O <sub>3</sub>	0.02	0.02	0.02	0.02
V <sub>2</sub> O <sub>5</sub>	0.02	0.02	0.02	0.02
Cl	0	0	0	0.00
S	0.1	0.01	0.07	0.07
L.O.I.#	8.37	1.19	1.29	3.58
Total	99.21	98.67	98.84	98.94
	32.53	10.74	56.73	100.0

\*Calculated total: Weighted average using particle size distribution (PSD) as weighting factor

#L.O.I: Loss on ignition

**Table B.2: Proximate, ultimate analysis – Infracem SS 2 Fly ash**

	Proximate analysis			
Inherent moisture (%)				0.1
Ash (%)				96.4
Volatile matter (%)				1.4
Fixed carbon (%)				2.1
Total sulphur (%)				0.09
Carbon (%)				3.22
Hydrogen (%)				0.04
Nitrogen (%)				0.09
Oxygen (%)				0.06
SiO <sub>2</sub>	49.90	53.70	53.40	52.51
Al <sub>2</sub> O <sub>3</sub>	24.20	26.70	29.10	27.57
TiO <sub>2</sub>	1.31	1.48	1.74	1.60
Fe <sub>2</sub> O <sub>3</sub>	4.73	3.86	3.58	3.91
CaO	6.72	6.38	5.99	6.22
MgO	1.20	1.30	1.60	1.46
K <sub>2</sub> O	0.39	0.39	0.50	0.46
Na <sub>2</sub> O	0.20	0.20	0.30	0.26
P <sub>2</sub> O <sub>5</sub>	0.16	0.16	0.24	0.21
MnO	0.02	0.01	0.01	0.01
Cr <sub>2</sub> O <sub>3</sub>	0.02	0.02	0.02	0.02
V <sub>2</sub> O <sub>5</sub>	0.02	0.02	0.02	0.02
Cl	0.00	0.00	0.00	0.00
S	0.30	0.07	0.06	0.12
L.O.I#	9.98	4.21	1.76	4.18
Total	99.15	98.50	98.32	98.56
	26.41	10.00	63.59	100.0

\*Calculated total: Weighted average using particle size distribution (PSD) as weighting factor

#L.O.I: Loss on ignition

**Table B.3: Proximate, ultimate analysis – Secunda Fly Ash**

	Proximate analysis			
Inherent moisture (%)				0.1
Ash (%)				98.1
Volatile matter (%)				0.8
Fixed carbon (%)				1
Total sulphur (%)				0.1
Carbon (%)				1.32
Hydrogen (%)				0.03
Nitrogen (%)				0.17
Oxygen (%)				0.18
SiO <sub>2</sub>	51.90	50.90	51.10	51.19
Al <sub>2</sub> O <sub>3</sub>	21.30	25.70	28.20	26.75
TiO <sub>2</sub>	1.05	1.34	1.63	1.50
Fe <sub>2</sub> O <sub>3</sub>	3.42	3.92	2.74	3.02
CaO	11.00	9.89	7.87	8.66
MgO	2.30	2.80	2.70	2.65
K <sub>2</sub> O	0.86	0.77	0.85	0.84
Na <sub>2</sub> O	0.40	0.50	0.80	0.69
P <sub>2</sub> O <sub>5</sub>	0.46	0.57	0.94	0.81
MnO	0.04	0.05	0.04	0.04
Cr <sub>2</sub> O <sub>3</sub>	0.01	0.02	0.02	0.02
V <sub>2</sub> O <sub>5</sub>	0.02	0.02	0.03	0.03
Cl	0.00	0.00	0.00	0.00
S	0.20	0.08	0.10	0.11
L.O.I#	6.08	2.13	1.72	2.46
Total	99.04	98.69	98.74	98.78
	15.54	15.08	69.39	100.0

\*Calculated total: Weighted average using particle size distribution (PSD) as weighting factor

#L.O.I: Loss on ignition

## APPENDIX C

### Detailed description and elemental composition of the phases in gasifier ash, bottom ash and fly ash

The nomenclature and resultant classification of ash phases is based on the elemental composition and potential coal mineral source of these minerals. This classification is unique.

**Table C 1: Non crystalline phases present in gasification ash.**

Phase name	
Kaolinite(pyrite) (Fe-alumino-silicate glass)	Al-silicate with variable proportions of Fe, Ti and K
Kaolinite(carbonate,pyrite) (Ca-Fe-alumino-silicate glass)	Al-silicate with variable proportions of Ca, Mg, Fe, Ti and K
Kaolinite(carbonate) (Ca-alumino-silicate glass)	Al-silicate with variable proportions of Ca, K and Ti
Quartz(carbonate, pyrite)	Si-rich glass with minor Ca, Fe and Al
Quartz(carbonate)	Si-rich glass with minor Ca and Mg
Microcline glass	K-bearing Al-silicate glass. Al/Si ratio similar to microcline
Muscovite glass	K-bearing Al-silicate glass. Al/Si ratio similar to muscovite
Anorthite	Anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ )
Mullite	$\text{Al}_4\text{Si}_2\text{O}_{10}$
Quartz	Unaltered quartz grains
"Metakaolinite"	"Honeycomb" kaolinite Al-silicate with trace K and Fe. (Transformation product of kaolinite)
Qtz60Kao40	Si-rich Al-silicate. Al and Si proportion is assuming a fine mixture of 60% quartz and 40% "metakaolinite". Trace proportions of K and Fe can be present.
Qtz80Kao20	Si-rich Al-silicate. Al and Si proportion is assuming a fine mixture of 80% quartz and 20% "metakaolinite". Trace proportions of K and Fe can be present
Pyrrhotite/Fe-S-O/Fe-oxide	Transformation product of extraneous pyrite
Carbonate/CaMgOxide	Transformation product of extraneous carbonates and associated with char
<b>Carbon</b>	
Char	Uncombusted carbon

## APPENDIX D

### Mass-% and percent phase proportions – fly ash

**Table D.1: Mass-% phase proportions – Infrachem SS 1 fly ash**

	+75			
Kaolinite(pyrite)	0.8	0.6	0.4	0.5
Kaolinite(carbonate,pyrite)	1.1	1.4	1.6	1.4
Kaolinite(carbonate)	7.1	10.1	9.7	8.9
Quartz_glass	1.0	0.1	0.6	0.7
<b>Total</b>	<b>10.0</b>	<b>12.2</b>	<b>12.2</b>	<b>11.5</b>
Orthoclase glass	0.3	0.7	0.4	0.4
Muscovite glass	0.3	0.4	0.7	0.5
<b>Total</b>	<b>0.5</b>	<b>1.1</b>	<b>1.1</b>	<b>0.9</b>
Anorthite				
Mullite	2.9	3.8	1.4	2.1
<b>Total</b>	<b>2.9</b>	<b>3.8</b>	<b>1.4</b>	<b>2.1</b>
Quartz	13.8	14.4	14.9	14.5
Metakaolinite	56.8	52.8	60.4	58.4
Qtz60Kao40	4.5	4.2	2.8	3.5
Qtz80Kao20	1.6	1.6	0.7	1.1
Ti-oxide	0.4	0.0	0.4	0.3
<b>Total</b>	<b>77.0</b>	<b>73.0</b>	<b>79.1</b>	<b>77.8</b>
Pyrrhotite/Fe-S-O/Fe-oxide	0.9	0.4	1.2	1.0
Carbonate/CaMgOxide	2.4	4.6	1.5	2.1
<b>Total</b>	<b>3.2</b>	<b>4.9</b>	<b>2.7</b>	<b>3.1</b>
Char	6.1	3.3	3.5	4.3
Other	0.2	1.6	0.1	0.3
<b>Total</b>	<b>6.3</b>	<b>4.9</b>	<b>3.6</b>	<b>4.6</b>



**Table D.2: Percent phase proportions – Infrachem SS 1 fly ash**

Alumino-silicate glass	28.3	11.4	60.2
Glass-rock fragments	19.0	13.2	67.6
Crystallites	44.3	19.4	36.4
Rock fragments	32.2	10.1	57.7
Extraneous	33.6	16.9	49.5
Char	46.1	8.2	45.9
Particle size distribution	32.5	10.7	56.7

**Table D.3: Mass-% phase proportions – Infracem SS 2 fly ash**

	<b>+75</b>			
Kaolinite(pyrite)	1.0	1.0	0.6	0.7
Kaolinite(carbonate,pyrite)	1.6	1.2	1.5	1.5
Kaolinite(carbonate)	8.3	10.7	9.3	9.2
Quartz_glass	1.1	0.2	0.7	0.8
<b>Total</b>	12.0	13.1	12.2	12.2
Orthoclase glass	0.4	0.4	0.4	0.4
Muscovite glass	0.6	0.6	0.8	0.7
<b>Total</b>	1.0	1.0	1.2	1.1
Anorthite				
Mullite	3.2	2.6	1.0	1.7
<b>Total</b>	3.2	2.6	1.0	1.7
Quartz	12.7	14.1	16.2	15.1
Metakaolinite	50.9	53.1	59.7	56.8
Qtz60Kao40	3.6	4.2	3.1	3.3
Qtz80Kao20	1.5	2.7	0.6	1.1
Ti-oxide	0.1	0.2	0.0	0.1
<b>Total</b>	68.8	74.3	79.6	76.3
Pyrrhotite/Fe-S-O/Fe-oxide	1.4	2.9	1.9	1.9
Carbonate/CaMgOxide	2.4	2.7	1.2	1.6
<b>Total</b>	3.8	5.6	3.1	3.5
Char	11.0	3.2	2.9	5.0
Other	0.2	0.2	0.1	0.1
<b>Total</b>	11.2	4.4	3.0	5.1

**Table D.4: Percent phase proportions – Infracem SS 1 fly ash**

Alumino-silicate glass	26.0	10.7	63.2
Glass-rock fragments	24.1	8.6	67.2
Crystallites	48.4	15.0	37.6
Rock fragments	23.8	9.7	66.3
Extraneous	28.3	15.9	55.8
Char	58.2	6.5	36.7
Particle size distribution	26.4	10.0	63.6

**Table D.5: Mass-% phase proportions – Synfuels fly ash**

	<b>+75</b>			
Kaolinite(pyrite)	0.8	1.0	0.4	0.5
Kaolinite(carbonate,pyrite)	0.8	0.6	0.6	0.7
Kaolinite(carbonate)	11.1	12.4	7.5	8.8
Quartz_glass	0.9	0.7	0.4	0.6
<b>Total</b>	<b>13.7</b>	<b>14.7</b>	<b>8.9</b>	<b>10.5</b>
Orthoclase glass	1.4	1.7	1.1	1.3
Muscovite glass	0.7	1.5	1.2	1.2
<b>Total</b>	<b>2.1</b>	<b>3.2</b>	<b>2.4</b>	<b>2.5</b>
Anorthite				
Mullite	3.3	4.2	2.2	2.7
<b>Total</b>	<b>3.3</b>	<b>4.2</b>	<b>2.2</b>	<b>2.7</b>
Quartz	20.9	13.4	12.6	14.0
Metakaolinite	37.1	49.6	61.5	56.0
Qtz60Kao40	2.8	3.5	3.0	3.0
Qtz80Kao20	1.1	1.2	0.8	0.9
Ti-oxide	0.1	0.1	0.0	0.0
<b>Total</b>	<b>61.9</b>	<b>67.7</b>	<b>77.9</b>	<b>73.9</b>
Pyrrhotite/Fe-S-O/Fe-oxide	2.7	1.9	1.0	1.4
Carbonate/CaMgOxide	6.6	3.8	3.9	4.3
<b>Total</b>	<b>9.3</b>	<b>5.7</b>	<b>4.9</b>	<b>5.7</b>
Char	9.4	3.8	3.1	4.2
Other	0.2	0.6	0.6	0.5
<b>Total</b>	<b>9.6</b>	<b>4.4</b>	<b>3.7</b>	<b>4.7</b>

**Table D.6: Percent phase proportions – Synfuels fly ash**

Alumino-silicate glass	20.2	21.1	58.8
Glass-rock fragments	13.4	19.6	66.9
Crystallites	18.9	23.7	57.4
Rock fragments	13.0	13.8	73.1
Extraneous	25.4	15.2	59.7
Char	35.3	13.8	51.5
Particle size distribution	15.5	15.1	69.4

APPENDIX E  
ALGORITHM USED TO ESTIMATE  $\text{Al}_2\text{O}_3$  AND  $\text{SiO}_2$  CONTENT

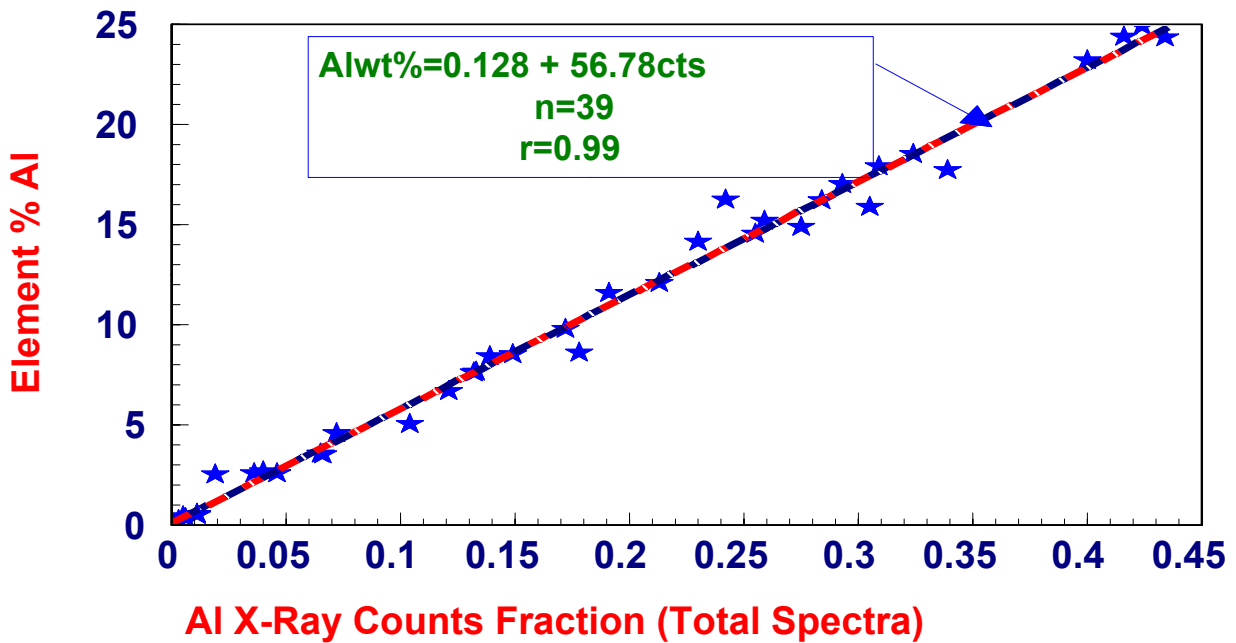


Figure E.1: Algorithm used to calculate  $\text{Al}_2\text{O}_3$  content form Al-X-ray counts

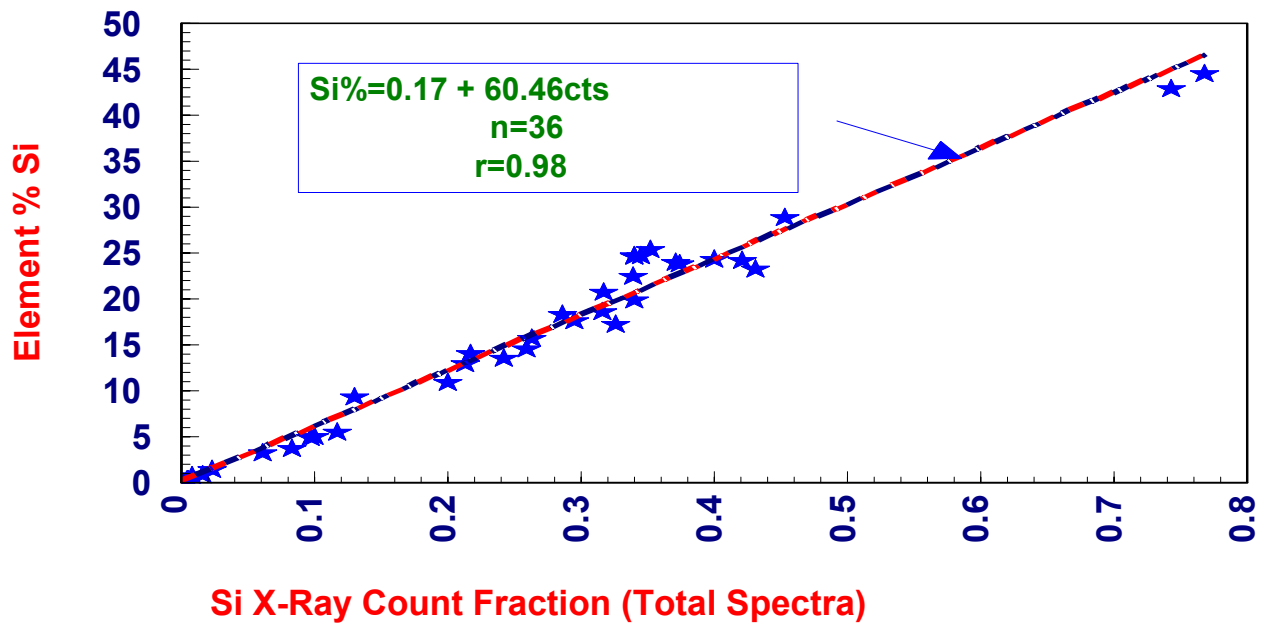


Figure E.2: Algorithm used to calculate  $\text{SiO}_2$  content form Si-X-ray counts

## APPENDIX F

### Average phase elemental analysis

Energy dispersive X-ray analysis is based on acquiring EDS X-ray spectrum of selected points. The X-ray counts for the individual elements were standardised against mineral standards of known and precise compositions. The analytical conditions of Scanning Electron Microscope (SEM) were 15kV acceleration voltage, 1nA beam current and count time of 200 seconds.

**Table F.1: Anorthite composition – gasification ash**

<b>Min</b>	0.21	36.20	41.32	17.71	98.41
<b>Max</b>	1.09	37.88	43.44	19.67	99.12
<b>Average</b>	0.82	36.93	42.28	18.86	98.89

**Table F.2: Interstitial glass and matrix glass – gasification ash**

<b>Min</b>	0.22	0.60	17.77	44.83	0.23	3.20	0.38	0.92	100.00
<b>Max</b>	0.52	6.87	36.56	65.52	1.81	11.74	20.63	4.59	100.00
<b>Average</b>	0.36	1.97	24.76	54.57	0.93	7.27	7.65	2.50	100.00

**Table F.3: Alumino-silicate glass – fly ash**

					<b>K<sub>2</sub>O</b>				
<b>Min</b>	0.00	0.33	10.24	30.93	0.00	1.78	1.10	0.62	100.00
<b>Max</b>	0.56	4.74	36.15	82.04	0.86	18.82	42.20	5.43	100.01
<b>Average</b>	0.26	1.61	25.06	48.86	0.37	6.94	13.57	3.33	100.00

## APPENDIX G

### Percent Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> distribution – fly ash

**Table G.1: Percent Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> distribution – Infracem SS1 fly ash**

Glass Matrix	2.5	1.1	5.6	9.1
Orthoclase glass	0.1	0.0	0.1	0.2
Muscovite	0.1	0.1	0.2	0.3
Anorthite	0.1	0.0	0.4	0.5
Mullite	2.2	1.0	1.8	4.9
Quartz	0.0	0.0	0.0	0.0
Metakaolinite	24.8	7.6	46.0	78.5
Qtz60Kao40	1.0	0.3	1.0	2.3
Qtz80Kao20	0.2	0.1	0.2	0.5
Pyrrhotite/Fe-S-O/Fe-oxide	0.0	0.0	0.1	0.1
Carbonate/CaMgOxide	0.1	0.1	0.1	0.2
Char	1.5	0.3	1.4	3.2
Other	0.0	0.0	0.0	0.0
<b>Total Al<sub>2</sub>O<sub>3</sub></b>	<b>32.7</b>	<b>10.5</b>	<b>56.9</b>	<b>100.0</b>
			<b>-38</b>	
Glass Matrix	2.3	1.0	5.3	8.6
Orthoclase glass	0.5	0.0	0.5	0.9
Muscovite	0.1	0.1	0.2	0.4
Anorthite	0.1	0.0	0.3	0.4
Mullite	0.4	0.2	0.3	0.9
Quartz	7.8	2.7	14.8	25.3
Metakaolinite	16.9	5.2	31.3	53.4
Qtz60Kao40	1.9	0.6	2.1	4.6
Qtz80Kao20	0.8	0.3	0.6	1.6
Pyrrhotite/Fe-S-O/Fe-oxide	0.0	0.0	0.1	0.1
Carbonate/CaMgOxide	0.1	0.1	0.1	0.4
Char	1.5	0.3	1.5	3.2
Other	0.0	0.0	0.0	0.0
<b>Total SiO<sub>2</sub></b>	<b>32.6</b>	<b>10.4</b>	<b>57.0</b>	<b>100.0</b>

**Table G.2: Percent Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> distribution – Infracem SS2 fly ash**

Glass Matrix	2.5	1.1	6.3	9.9
Orthoclase glass	0.1	0.0	0.2	0.3
Muscovite	0.1	0.0	0.2	0.4
Anorthite	0.1	0.1	0.5	0.7
Mullite	2.0	0.6	1.5	4.1
Quartz	0.0	0.0	0.0	0.0
Metakaolinite	18.4	7.3	52.1	77.8
Qtz60Kao40	0.6	0.3	1.3	2.2
Qtz80Kao20	0.2	0.1	0.2	0.5
Pyrrhotite/Fe-S-O/Fe-oxide	0.0	0.0	0.1	0.2
Carbonate/CaMgOxide	0.1	0.0	0.1	0.2
Char	2.2	0.2	1.4	3.8
Other	0.0	0.0	0.0	0.0
<b>Total Al<sub>2</sub>O<sub>3</sub></b>	<b>26.4</b>	<b>9.8</b>	<b>63.8</b>	<b>100.0</b>
Glass Matrix	2.3	1.0	5.8	9.1
Orthoclase glass	0.4	0.0	0.6	1.1
Muscovite	0.1	0.0	0.3	0.4
Anorthite	0.1	0.0	0.4	0.6
Mullite	0.3	0.1	0.3	0.7
Quartz	5.8	2.5	17.9	26.2
Metakaolinite	12.3	4.8	34.6	51.7
Qtz60Kao40	1.2	0.6	2.6	4.4
Qtz80Kao20	0.6	0.4	0.6	1.6
Pyrrhotite/Fe-S-O/Fe-oxide	0.0	0.0	0.1	0.2
Carbonate/CaMgOxide	0.1	0.0	0.1	0.3
Char	2.1	0.2	1.3	3.7
Other	0.0	0.0	0.0	0.0
<b>Total SiO<sub>2</sub></b>	<b>25.6</b>	<b>9.8</b>	<b>64.6</b>	<b>100.0</b>

**Table G.3: Percent Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> distribution – Synfuel fly ash**

Glass Matrix	1.7	1.8	5.1	8.6
Orthoclase glass	0.1	0.0	0.1	0.2
Muscovite	0.2	0.2	0.7	1.1
Anorthite	0.1	0.2	0.8	1.2
Mullite	1.2	1.5	3.6	6.3
Quartz	0.0	0.0	0.0	0.0
Metakaolinite	7.9	10.2	58.4	76.5
Qtz60Kao40	0.3	0.3	1.4	2.0
Qtz80Kao20	0.1	0.1	0.2	0.4
Pyrrhotite/Fe-S-O/Fe-oxide	0.0	0.0	0.1	0.1
Carbonate/CaMgOxide	0.1	0.1	0.3	0.5
Char	1.1	0.4	1.6	3.1
Other	0.0	0.0	0.0	0.0
<b>Total Al<sub>2</sub>O<sub>3</sub></b>	<b>12.8</b>	<b>15.0</b>	<b>72.3</b>	<b>100.0</b>
Glass Matrix	1.6	1.7	4.8	8.2
Orthoclase glass	0.2	0.2	0.4	0.8
Muscovite	0.2	0.3	0.8	1.3
Anorthite	0.1	0.2	0.7	1.0
Mullite	0.2	0.3	0.7	1.2
Quartz	5.8	3.6	15.7	25.2
Metakaolinite	5.4	7.0	40.3	52.7
Qtz60Kao40	0.6	0.7	2.8	4.1
Qtz80Kao20	0.3	0.3	0.8	1.4
Pyrrhotite/Fe-S-O/Fe-oxide	0.0	0.0	0.1	0.1
Carbonate/CaMgOxide	0.2	0.1	0.5	0.7
Char	1.1	0.4	1.6	3.2
Other	0.0	0.0	0.0	0.0
<b>Total SiO<sub>2</sub></b>	<b>15.9</b>	<b>14.9</b>	<b>69.3</b>	<b>100.0</b>