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THE PATH OF TRACE ELEMENTS IN A COMBUSTION PROCESS: FROM FEED COAL TO ASH PRODUCTS

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A research report submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in partial fulfillment of the requirements for the degree of Master of Science in Engineering (Metallurgy and Materials) .

Johannesburg, 2010

I declare that this research report is my own, unaided work. It is being submitted for the degree of Master of Science in Engineering (Metallurgy and Materials) in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other University.

Raushaan Mohammed

_____day of _____,

ABSTRACT

Coal is an important component in enabling the worlds energy demands to be met. This is largely due to the fact that coal is a relatively inexpensive fuel when compared to the other options such as oil, gas and nuclear. In 2005 coal fired power generation accounted for 41% of the worlds electricity supply with this figure expected to rise to around 46% by 2030 (Energy Information Administration, 2009). Despite the world's dependence on coal as a means of producing electricity, the combustion of coal in coal fired plants has received international scrutiny due to the pollutants (CO_2, NOx, SOx and trace elements) generated from the combustion of coal in a chain grate boiler. This research focuses on the trace elements released by the combustion of coal and the partitioning behaviour of selected trace elements (As, B, Be, Cd, Pb, Hg, Se, Cr, Ni, Sb, Co, Mn, Ur and Th). These trace elements were selected because they are included in the US Clean Air Act Amendments Law of 1990 which states that they are potentially toxic airborne pollutants and the lowering of their concentrations in the environment is important (Aunela-Tapola *et al.* 1998). There is little or no available literature on trace element partitioning and emissions in South Africa, despite the fact that there are approximately 8000 industrial boilers in this country (personal communication, Falcon February 2010).

Inductively Coupled Plasma-Mass spectroscopy was used to obtain the concentration of the selected trace elements in the four samples being investigated (feed coal, bottom ash, fly ash and stack emission) which were obtained from a chain grate boiler. Proximate analysis and particle size distribution (PSD) were performed to explain certain trends observed with the trace element partitioning and emission results.

The results from the research show that the concentration of most of the trace elements increases throughout the value chain i.e. from feed coal through bottom ash and flyash to stack emission. Furthermore, the presence of highly volatile trace elements such as Hg and Se in the

bottom ash is best explained by the proximate analysis which indicates that unburnt coal is present in the bottom ash. This indicates that the combustion of coal in the chain grate boiler in this research is relatively inefficient. All trace elements were found to be highly enriched in the stack emission which is due to the inefficient capture of particulate and vapour species by the environmental control device/s (in this case, only an ESP). This was verified by the PSD results which showed that particles of up to 17μm were present in the stack emission.

The research concludes that although industrial boilers combust lower amounts of coal than larger pulverized fuel boilers, the trace element emissions from industrial boilers are significant. This may be due to cost reduction practices resulting in the implementation of cheaper, less efficient environmental control devices leading to the escape through the stack of a larger concentration of trace elements adsorbed onto particulate matter.

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CHAPTER 1 - INTRODUCTION

1.1 INTRODUCTION

"Modern life is unimaginable without electricity. It lights up houses, buildings, streets, provides domestic and industrial heat and powers most equipment used in homes, offices and machinery in factories." (World Coal Institute, 2008, p. 20). In addition to this, improving the access to electricity has become a key factor in poverty alleviation both locally and internationally. These trends in the world's dependence on electricity have developed over the several decades and are expected to continue over the next 25 years (Energy Information Administration, 2009).

Over the years a mix of primary fuels has been used to generate electricity worldwide, such as oil and gas. However, although generation from nuclear power as well as natural gas-fired generation has grown rapidly, since power can be generated in a more environmentally friendly manner, coal has continued to be the most widely used fuel. This is largely due to the high prices of oil and natural gas that have allowed for coal to be established as a dominant source of electricity generation, and also the environmental concerns around nuclear waste. In addition to this, coal is economically attractive, especially in countries which are rich in coal resources. In 2005, coal fired power generation accounted for 41% of the worlds electricity supply; and this is projected to rise to 46% by 2030. This is because as the world's population increases, the demands for resources - such as fuel for electricity - are also expected to increase (Energy Information Administration, 2009).

In Africa, the demand for electricity grows at an average annual rate of 3.1% (Energy Information Administration, 2009). In 2005, 47% of the total electricity generation was accounted for by coal fired power plant. However, this figure is expected to drop to 32% by 2030 due to stricter environmental legislation being implemented (Energy Information Administration, 2009). South Africa is Africa's largest electricity generator, producing almost

43% of the continents electric power. Although the country is an important regional supplier (Southern African Development Community), exporting of electricity to other countries such as Zimbabwe and Swaziland has resulted in South Africa's own demand increasing dramatically thereby placing strain on the country's state owned power utility, Eskom. As a result of Eskom's inability to keep with the country's demand, South Africa experienced a number of power cuts in 2008 (Energy Information Administration, 2009).

In South Africa coal is mainly used for power generation (electricity). Around 93% of the regions electricity is derived from coal fired power stations. This electricity requirement was achieved in 2008 by Eskom who utilized 118 Mt of coal. SASOL liquefaction and steam generation industries is the second largest consumer of coal in South Africa with 48 Mt of coal being used in 2008 to supply the country with half of its liquid fuel requirements. In the same year, about 14 Mt of coal was used for domestic and other industries, whilst the metallurgical industry utilized only about 5 Mt of coal, including anthracites and coking coals (personal communication, Pinheiro September 2009). South Africa is also one of the largest exporters (fourth in the world) of coal. In 2008 it exported 64 Mt of coal, with most of the export to the European Union (Bergh 2009). From this it can be seen that coal is important to South Africa, not only in terms of power generation but also as a source for liquid fuels and as means of foreign exchange earnings. In fact coal is the second largest foreign commodity earner in South Africa after gold. Furthermore, coal is important for heat and power generation domestically as well as industrially i.e. for both large scale (Eskom type) and small scale (chain grate) boilers. According to Falcon, there are about 8000 small scale industrial boilers in South Africa (personal communication, February 2010). Small scale boilers include spreader stokers and chain grate stokers. It is this sector and its emissions, and trace element emissions in particular that this research seeks to address.

1.1.1 Coal and the Environment

Despite South Africa's, as well as the worlds', reliance on coal as a means of producing electricity, the use of coal and coal-fired plants have received international scrutiny from environmental organizations. This is largely due to the fact that it is well known that the transformation of fossil fuels, such as coal, results in negative environmental impacts on the environment. This includes the release of pollutants such as the oxides of sulphur (SOx) and nitrogen (NOx) as well as trace elements such as mercury (Hg). The emission of these pollutants not only contributes to global climate change, but also affects living organisms as well as human health (World Coal Institute, 2008).

The release of trace elements has gathered a great amount of interest from researchers and environmental authorities globally. This is due to severe health impacts which have been prevalent as a consequence of exposure to significant levels of certain trace elements. Exposure of trace elements to living organisms occurs via three routes: air, water and soil. Trace elements are released from the combustion of coal into the atmosphere in the vapour phase or as fine particles. All power stations equipped with BACT particulate control systems aim to achieve collection efficiencies of > 99.9 % with efficiencies of up to >99.9%. Due to the high tonnages of coal utilized, the remaining 0.1 % can result in significant amounts of submicron particles passing through these particulate control devices. Due to the relatively large surface areas of these submicron particles, high concentrations of trace elements are adsorbed onto the surface of these particles during cooling, and are subsequently released into the atmosphere. The fact that these trace elements do not undergo decomposition in the environment leads to their accumulation in food chains (bio-accumulation). For this reason the US Clean Air Act Amendments Law of 1990 has identified certain trace elements as potential air toxic trace elements, and the lowering of their emission into the atmosphere is of primary importance. These trace elements are mercury (Hg), selenium (Se), arsenic (As), beryllium (Be), cadmium (Cd), antimony (Sb), chromium (Cr), cobalt (Co), lead (Pb), nickel (Ni) and manganese (Mn) (Aunela-Tapola *et al*. 1998). It is also important to note that although the lowering of these

trace element emissions is essential, the effective disposal of the ash products which are consequently enriched in trace elements is of similar importance due to the possibility of leaching into the aquatic environment (Finkelman 1994; Aunela-Tapola *et al*. 1998; Guo *et al*. 2002).

1.2 AIM

This research project seeks to understand the behaviour and distribution of hazardous air pollutant trace elements in a chain grate boiler, and to compare the findings to data published in literature on pulverized coal boilers

1.3 OBJECTIVES

- To determine the presence and concentrations of trace elements in a selected industrial boiler feed coal in South Africa.
- To identify the trace elements which are volatilized and released to the environment as a consequence of coal combustion in a chain grate boiler.
- To compare the results obtained from the research with data from pulverized fuel boilers, thereby providing an understanding of the environmental effects of the trace elements released during coal combustion from that coal and under conditions applied in that industrial boiler process.
- To compare the relative enrichment and emissions from the research (chain grate stoker) and other studies (pulverized fuel boiler process) thereby determining the environmental impact of the chain grate stoker process relative to some pulverized fuel process studies.

1.4 RESEARCH QUESTIONS

1) **What happens to the trace elements in coal, during the transformation from coal to the ash products as a consequence of coal combustion?**

In order to address this question the research will look at two sub-questions. These are:

- What is the concentration of the trace elements in the feed coal?
- What is the partitioning behaviour of the trace elements; i.e. after combustion, where are the trace elements enriched or depleted?

2) **How accurate are the trace element mass balances?**

3) **What are the possible implications on small scale industrial boilers?**

1.5 HYPOTHESIS

Combustion of coal in chain grate boilers leads to the release of trace elements into the atmosphere via the stack.

1.6 SCOPE OF THE PROJECT

The scope of this project considers the behaviour of trace elements during coal utilization and their potential health impact. This research report investigates the presence and concentrations of trace elements in a selected South African coal product and in the combustion by-products resulting from its use. By drawing on the differences in the presence and concentrations of trace elements in the coal and ash products, conclusions will be reached in terms of which trace elements are released into the environment and which are enriched in the ash products as a

consequence of combustion in a chain grate stoker process. The results obtained from the research can be used to compare the impacts of trace elements from South African coal with other investigated world coals. The research can also provide a starting point for further studies focused on the presence of specific oxidation states of trace elements, and an understanding of trace element release from chain grate boilers. .

CHAPTER 2 - LITERATURE REVIEW

2.1 INTRODUCTION

This chapter provides the theoretical framework for the research. It looks at the use of coal in a combustion process as well as the distribution of trace elements amongst the combustion products (bottom ash fly, stack emission). It also explores the environmental and health impacts associated with exposure to trace elements.

2.2 LOCATION OF SOUTH AFRICAN COAL RESERVES

The major coal resources of South Africa are contained within the main Karoo Basin (approximately 49%). In 1988, 97% of South Africa's saleable production was obtained from the Karoo Basin. The major contributing factor to this was the fact that the coal seams were fairly shallow with 96% of the coal seams lying at depths of less than 200 m. Also, a working thickness of between 1.2 m and 6 m facilitates mining of these coal seams with relative ease (Cadle *et al.* 1993).

The coal in the Karoo Basin is dominated by low grade bituminous coal and only 12% of the reserves have an ash content of less than 20% (Cadle *et al.* 1993). The rank of the coal tends to increase from west to east (i.e. from Witbank through Mpumalanga to KwaZulu Natal) (Cairncross 2001). The 19 coalfields of South Africa are located across the country in the provinces of KwaZulu-Natal, Mpumalanga, Limpopo, Free State, Gauteng, North-West Province and Eastern Cape (Jeffrey 2005a). Figure 2.1 shows the location of the 19 coalfields of South Africa.

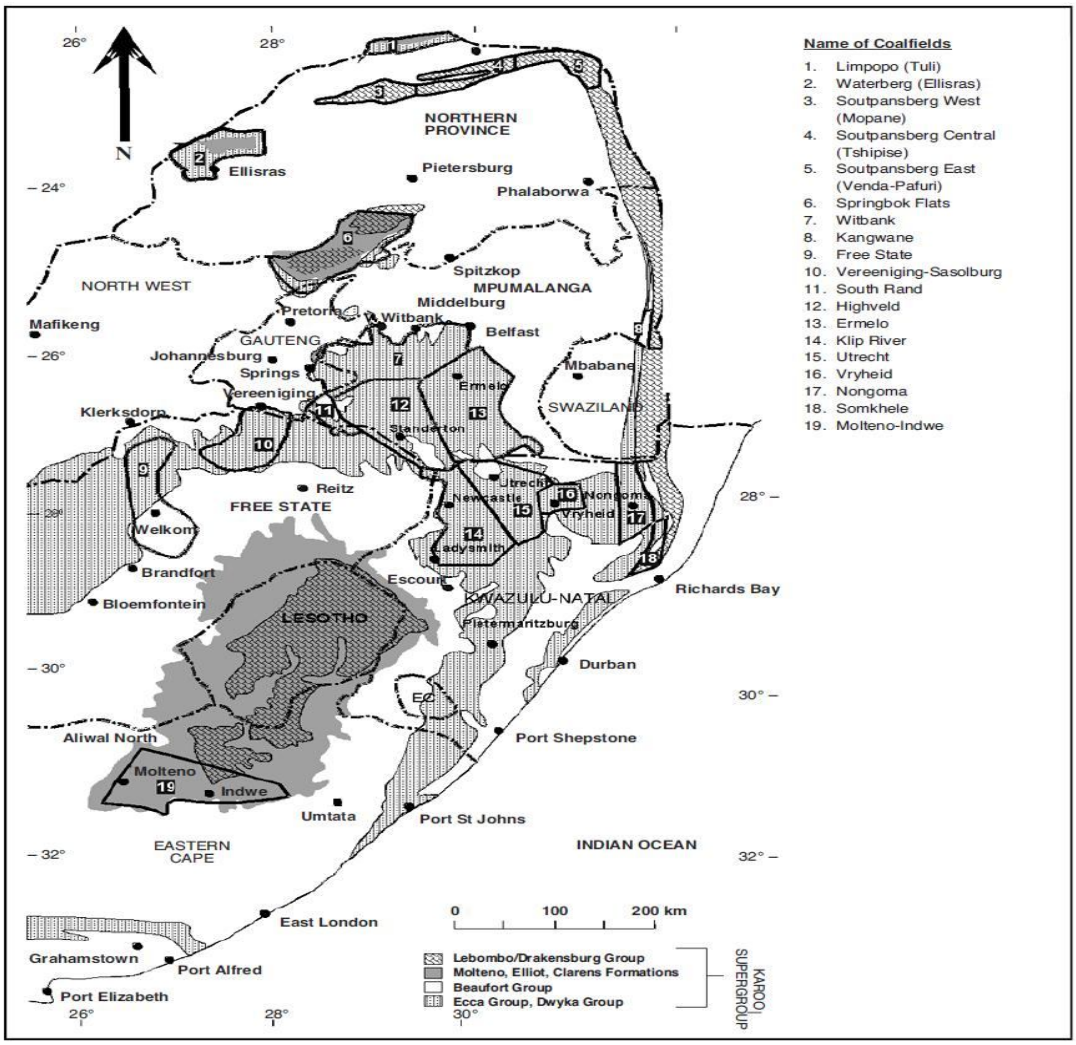


Figure 2.1: Map showing the location of coalfields within South Africa (Jeffrey 2005a)

The majority of the country's coal deposits located in the Highveld, Witbank, and the Northern Province (Jeffrey 2005a; Bergh 2009). According to Bergh (2009), the Highveld and Witbank coalfields accounted for 66% of the remaining coal reserves of the country in 2004. As mentioned previously, these two coalfields are expected to be replaced by the Waterberg coalfields as this area is said to contain a vast majority of the South Africa's *in situ* virgin coal resources (Jeffrey 2005b). This shows that over a fairly short period of time the coal reserves in the Highveld & Witbank coalfields will decline drastically and this is indicative of coal being a

finite resource and that there is a continual increase in the use of coal which further exacerbates the environmental impacts of coal, both presently and in the future.

2.3 ELEMENTS IN COAL

As a natural resource, coal is an important component in enabling the world's future energy demands to be met. This is largely due to the fact that coal reserves are more abundant than other fossil fuels (Grainger & Gibson, 1981; Kurose *et al.* 2004). Coal is a complex organic rock which is made up of a mixture of organic and inorganic materials (Grainger & Gibson, 1981; Vissilev *et al.* 2001; Hu *et al.* 2006;). According to Hu *et al.* (2006), modern analytical techniques have detected up to 86 elements present in coal. These elements can be separated into three groups, depending on the concentrations within which they occur in coal.

Elements that occur in concentrations of more than 1000 ppm fall into the group major elements. These typically include Carbon (C), Hydrogen (H), Oxygen (O), Nitrogen (N) and Sulphur (S). The second group, minor elements, occurs in concentrations of between 100 and 1000 ppm and includes Silicon (Si), Aluminium (Al), Calcium (Ca), Magnesium (Mg), Potassium (K), Sodium (Na), Iron (Fe), Manganese (Mn) and Titanium (Ti). The third and final group, *trace elements*, occur at concentrations of less than 100 ppm; hence the term 'trace'. These elements include Chromium (Cr), Arsenic (As), Lead (Pb), Mercury (Hg) and Cadmium (Cd), amongst others. However, due to the fact that the presence and concentration of trace elements are variable, because of the different coalification processes, the trace elements present in different coals may differ; both qualitatively and quantitatively (Xu *et al.* 2003).

2.4 TRACE ELEMENTS

In the past, the focus of environmental studies has been mainly on the gaseous pollutants released from coal combustion, such as SO_2, CO_2, CO and NO_x. However, trace element

emissions from combustion have recently gathered a great amount of interest from researchers and regulatory authorities due to their toxicities toward living organisms (Karayigit *et al.* 2000; Sandelin & Backman, 2001; Zhang *et al.* 2008).

The concentration of trace elements in fossil fuels is variable, and according to Klika *et al.* (2001) these trace element concentrations are controlled by the coal origin, geological history and the coal rank. Trace elements are present in the coal as impurities in the minerals and macerals in both inorganic and organic forms (Ratafia-Brown 1994). Many studies have been conducted in order to determine the concentration of trace elements in coals from different countries as well as from different coalfields within a country (Cairncross *et al.* 1990; Karayigit *et al.* 2000; Wagner & Hlatshwayo, 2005; Hu *et al.* 2006; Bergh 2009. These studies were not necessarily performed with the intention of determining which trace elements will be emitted or which will remain in the ash products, but rather the presence and modes of occurrence of the trace elements. Knowledge of the modes of occurrence is beneficial as it assists in determining the possibility of a specific trace element being emitted into the atmosphere as well the effectiveness in removing the trace element by beneficiation prior to utilization, thus preventing it from being emitted into the atmosphere. The trace element concentration from a few of these studies is presented in the Table 2.1. It should be noted that they also include results from studies conducted in South Africa on different South African coals and studies worldwide (presented as global averages).

Trace Element (ppm)	Witbank Coalfield 2 Seam (Cairncross *et al.* 1990)	Witbank Coalfield 4 Seam (Bergh, 2009)	Highveld Coalfield 4 Seam (Wagner & Hlatshwayo, 2005)	Global Average range (Swaine, 1994)	Global Average (Zhang *et al.* 2004)
As	4.6	4.7	3.14	0.5 – 80	5
Cd	*	0.3	0.44	0.1 – 3	0.6
Pb	10	15.03	7.51	2 – 80	25
Hg	*	0.3	0.2	0.02 – 1	0.12
Mo	*	2.1	1.18	0.1 – 10	5
Se	0.9	1.2	1.05	0.2 – 10	3
Cr	28	41.4	70.5	0.5 – 60	10
Cu	9.7	16.8	13.2	0.5 – 50	15
Ni	17	27.2	21.1	0.5 – 50	15
V	27	39.2	33.5	2 – 100	25
Sb	0.47	0.5	0.32	0.05 – 10	3
Co	7.9	11.0	6.3	0.5 – 30	5
Mn	*	163.4	19.6	5 – 300	50
Ur	4.0	2.6	*	0.02 – 5.5	3.1
Th	15.0	8.9	*	0.1 – 12.2	1.9

*These trace elements were not determined

Table 2.1 : The concentration of trace elements in different South African coals and also the global averages/range as reported by Zhang et al. (2004) and Swaine (1994), respectively.

The concentration of trace elements can differ from coal to coal and even between coals in the same coalfield. This is highlighted in the table where the trace element concentrations differ between coal seams in the Witbank coalfield. Most trace elements are present in higher concentrations in the Witbank no. 4 seam than the Witbank no. 2 seam, with the exception of Uranium and Thorium. Research conducted by Watling & Watling (1982) on South African coals showed that there is a notable variation in trace element concentrations vertically within South African coalfields.

Table 2.1 also shows that certain trace elements (As, Cd, Pb, Mo, Se, Sb and Ur) in some South African coals are present in lower concentrations than the global average (Zhang *et al.* 2004)

whilst others (Hg, Cr, Cu, Ni, V, Co, Mn and Th) are higher. The Cr concentration in the Highveld no. 4 seam falls out of the global range (0.5 – 60) reported by Swaine (1994).

According to Sandelin & Backman (2001) the Toxic Release Inventory of the U.S. Environmental Protection Agency has been focusing on modelling the trace element emissions from coal- fired power stations. This is because coal combustion is highly responsible for the release of trace elements, amongst other pollutants, into the environment. The main controlling factor leading to the mobilization of trace elements is the chemical affinities of these elements toward others; more specifically towards minerals in the coal (Xu *et al.* 2003; Yiwei *et al.* 2008). Other controlling factors include the concentrations at which the trace elements exist as well as the physical changes and chemical reactions which occur with other volatile components and sulphur in the coal (Querol *et al.* 1995). Another very important controlling factor is the partitioning behaviour of these trace elements in combustion and environmental control systems i.e. different combustion/environmental control systems may yield different results in terms of trace elements emission (Ratafia-Brown, 1994).

2.4.1 Mode of occurrence

There are many different types of minerals present in coal, to which trace elements have varying degrees of affinity. These include silicate, sulphide, carbonate, and chloride minerals (Raask, 1985). Silicate minerals constitute the major part of the total mineral content in most bituminous coals, with alumino-silicates and quartz constituting 60-90% of the mineral matter in these coals (Raask, 1985). According to Hu et al. (2006), through the use of modern analytical methods, 74 trace elements have been detected in coals. Hu *et al.* (2006) further states that many countries have established standards of both water and air quality which limits the concentration of 21 of these trace elements (As, Cl, Pb, Hg, Cd, Se, Mn, Ni, Cu, Zn, F, Cr, Sb, Co, Mo, Be, V, Tl, Th, U and Ag).

The main reason for these elements being regulated and focused upon is the fact that they are harmful to the environment, wildlife, and humans (Hu *et al.* 2006). The U.S. Clean Air Amendment Act of 1990 has identified As, Sb, Cr, Be, Hg, Mn, Se, Ni, Cd, Co, Pb and U as potentially Hazardous Air Pollutants (HAP's). It is for this reason that this paper, as well as previous studies, have focused on the trace element occurrence and concentrations of these elements (Karayigit *et al.* 2000).

When dealing with the trace element released from coal as a consequence of combustion, the modes of occurrence of these trace elements are of utmost importance and will, therefore, be discussed further. A number of researchers have reported on the affinities of different trace elements. These results were collated and combined by Xu *et al.* (2003). Table 2.2 shows the elements which exhibit inorganic affinity. Furthermore, the elements showing inorganic affinity are separated into the specific inorganic minerals to which their affinities lie.

Type of inorganic material	Elements
Clay minerals and feldspars	Al, Ba, Bi, Cr, Cs, Cu, Ga, K, Li, Mg, Na, Ni, P, Pb, Rb, Sn, Ta, Th, Ti, U, V, Y and the REE's (Rare earth elements)
Iron sulphides	As, Cd, Co, Cu, Fe, Hg, Mo, Ni, Pb, S, Sb, Se, Ti, W and Zn
Carbonates	C, Ca, Co and Mn
Sulphates	Ba, Ca, Fe and S
Heavy minerals (Tourmaline)	B

Table 2.2: The elements which have inorganic affinity and the inorganic mineral groups to which they have a specific affinity (Xu et al. 2003).

There are certain elements which have many mineral phases. For example, Co and W can be associated with carbonates and also sulphides; Ni, Cu, Pb can be associated with clay minerals and sulphides; and C and B can have an association with the inorganic material as seen in the table above, but they exhibit association with organic matter as well (Xu *et al.* 2003).

Determining the modes of occurrence is of great importance because once the modes of occurrence is known, the researcher is able to draw conclusions on whether or not specific trace elements will be volatilized and released into the air, enriched in the fly ash, or not readily volatilized and enriched in the slag/bottom ash after the combustion process (Xu *et al*. 2003). Furthermore, the modes of occurrences of the trace elements are responsible for determining the best utilization of the coal.

Many studies aimed at determining the occurrence and concentration of various trace elements in coals as well as the mineral content have been conducted. An example of this is the work conducted by Karayigit *et al.* (2000) on feed coals for coal-fired power stations in Turkey which showed that certain elements increased in concentration with an increase in the ash yields. This observation enabled them to come to a conclusion that the elements (Ba, Bi, Ga, Pb, Gd, Nb, Rb, Sc, Ta, La, Ce, Pr, Nd, Sm and Eu) which showed this positive correlation to the ash yield were elements that have an inorganic affinity in the coals from that power plant.

Furthermore, by the use of scanning electron microscopy (SEM), they were able to determine whether these trace elements were present on the surface or within the minerals. This information is of great use as it could be an indication that the elements on the surface of the minerals would more readily volatilize rather than elements hosted in the minerals. It was also found that in the feed coals, Ba, Bi, Pb, Th and the rare earth elements (REE's) were present within the minerals (Karayigit *et al.* 2000). However, since Karayigit *et al.* (2000) limited their study to the feed coals and not the combustion products (bottom and fly ash), it cannot be shown that the elements hosted in the minerals are not volatilized and that they are retained solely in the ash products.

Affinities toward organic material can also be obtained by drawing a correlation between elements which constitute inorganic minerals and the trace elements present. In the same study by Karayigit *et al.* (2000), results showed that Be exhibited no correlation with Al, K, Ti and ash yields and that this would consequently indicate an organic affinity. However, as mentioned before, the presence and mode of occurrence of trace elements differ from coal to coal and it is therefore essential to ensure that when analyzing these affinities it is important to take into account the coal that is being used (Querol *et al.* 1995)

Recent studies conducted by Hlatshwayo (2008) on South African coal samples yielded results for the modes of occurrence of a variety of trace elements with the focus being on Hg, As and Se. Hlatshwayo (2008) showed that Hg had both organic and inorganic associations. The results presented also show that the distribution of Hg is associated with organic and inorganic fractions in the proportions of 52% and 47% respectively, indicating a more or less equal distribution. As and Se on the other hand, were found to be associated with the mineral matter and by calculation 91% association with inorganic material, within the coal.

A study conducted by Bergh (2009) documented the modes of occurrence of selected trace elements in coal from the Witbank 4 seam. The results can be seen in the following table.

Mineral	Associated element/s
Pyrite	As, Cd, Co, Cu, Hg, Mo, Ni, Pb, Se
Apatite	F,Cl
Clays (kaolinite and illite)	Cr, Mn, V
Monazite	U, Th

Table 2.3: Trace elements association (Bergh, 2009).

The study conducted by Bergh (2009) showed that majority of the trace elements which were determined had strong associations with sulphide species, specifically pyrite. However, the study also showed that As and Hg are associated not only with pyrite, but also with the organic sulphur components of the coal. Xu *et al.* (2003) also reported that As and Hg are predominantly associated with sulphide and organic fractions (Xu *et al.* 2003; Bergh, 2009).

In a review compiled by Yudovich & Ketris (2006), show it is that Se mostly occurs in association with sulphide species and organic fractions. This review reports results which correspond to the findings of Bergh (2009) and in the studies collated by Xu *et al.* (2003), in terms of the pyrite association of As. Huggins *et al.* (2000) conducted a mode of occurrence study of chromium on four coals from the USA and their study showed that Cr was present in the coals in two forms. The major association was with the organic portion (50-90%) of the coal and the minor association with the clay mineral illite (10-50%). The results from this study differs significantly from results obtained from studies conducted by Bergh (2009) and results from various studies collated by Xu *et al.* (2003), which show that the major association of Cr is with clay mineral (illite).

From all the information presented regarding mode of occurrence of trace elements, it is clear that the mode of occurrence of certain trace elements can differ from coal to coal. However, the modes of occurrence of some trace elements like Hg, Se, As and Cd are fairly constant. They are found to be associated with pyrite.

2.4.2 Fate of trace elements in combustion processes

If the trace elements are not removed from the coal by pre-combustion or coal preparation processes (beneficiation), these trace elements are susceptible to being released into the environment as an emission. This is because they are only able to be released from the combustion process by a finite number of pathways; via the ash products (bottom and fly ash) and airborne emissions. The partitioning of the trace elements amongst the different pathways in a specific combustion process is very important as it can indicate the environmental consequences of the trace elements as well as the requirements to minimize the environmental impacts, i.e. ash disposal and environmental control devices (Ratafia-Brown, 1994).

In terms of their release into the environment, the modes of occurrence are the determining factors for trace element release. Other important factors include the design of the combustion system and the operational modes of this combustion system (Ratafia-Brown, 1994; Xu *et al.* 2003). During combustion, certain trace elements are more readily volatilized than others. Studies based on the partitioning of trace elements date back as far as 1975 when Klein *et al.* (1975) reported that trace elements are separated into three groups based on their relative volatility coupled with their partitioning between combustion by-products: slag, fly ash and emission. The following results were obtained from their study:

	Trace elements	**Enrichment**
Group 1	Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Sr, Ta, Th, and Ti	Slag, Slag/fly ash
Group 2	As, Cd, Cu, Ga, Pb, Sb, Se and Zn	Fly ash and poorly in slag
Group 3	Hg, C1, and Br	Emission (gas phase)
Other	Cr, Cs, Na, Ni, U, and V	Variable

Table 2.4: The results from a study conducted by Klein et al. (1975) on the partitioning behavior of trace elements in a coal fired power station

Clarke (1993) conducted a similar study many years later and also reported that trace elements can be separated into three groups depending on their behaviour during combustion and gasification. He also went as far as to include the boiling points of different trace element species. This is important as it will give an indication of the behaviour of that species in the process i.e. whether the trace element will be volatilized based on the temperature it is subjected to as well as in what state it will exist in different temperature zones. Figure 2.2 indicates the groups and the elements, which fall within those groups. Table 2.5 shows the boiling point temperatures of selected trace element species:

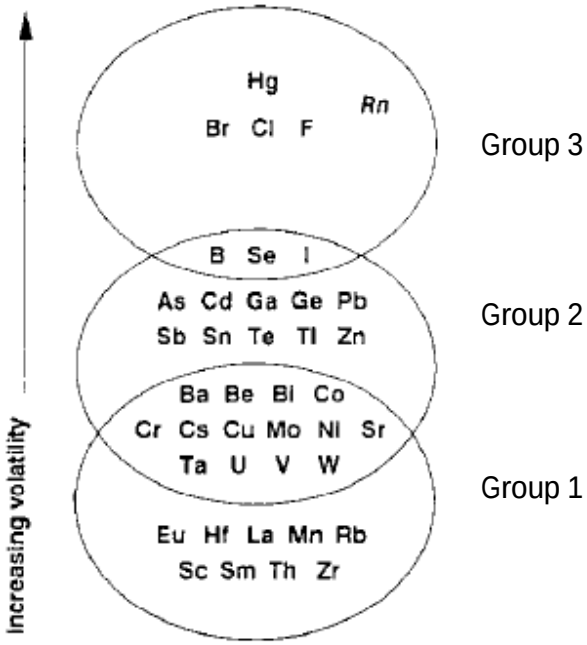


Figure 2.2: Classification of trace elements by their behaviour during combustion and gasification (Clarke, 1993).

Trace element/ Compound	Boiling point (°C)		Trace element/ Compound	Boiling point (°C)
Se	217		B_2O_3	1800
SeO_2	317		CoO	1800
Hg	357		Mn	1960
As_2O_3	465		Cu	2570
As	613		Ni	2730
Zn	907		Co	2870
Sb_2O_3	1155		Cr_2O_3	3000-4000

Table 2.5: The trace elements in free and compound form with their boiling points (Clarke, 1993).

From Figure 2.2, Group 1 elements are believed to be enriched in the coarse residues or equally partitioned between the coarse residues and the fine particles. Group 2 elements are those elements which are volatilized in the combustor or gasifier and condense downstream. The most volatile elements are present in Group 3 and these are the elements which may be present in the gas phase released from the boiler or reactor. It can also be seen that since elements such as Hg, Se, B and the halogens occur in Group 3, they are the elements most likely to be volatilized and released into the environment (Clarke, 1993). This is highly significant as Hg is known to be toxic to humans as will be discussed in section 2.7.1.

Looking at the studies conducted by Clarke (1993) and Klein *et al*. (1975) it can be seen that there are similarities in the results. However, the study conducted by Clarke (1993) accounts for those trace elements which Klein *et al*. (1975) could not assign a group. Furthermore, Clarke (1993) shows that many elements like Se, B, I, Ba, Be, Bi, Co, Cr, Cs, Cu, Mo, Ni, Sr, Ta, U, V and W can be found in more than one group as their mineral associations may differ from coal to coal.

According to a paper by Xu *et al.* (2003), the trace elements that have chemical affinity towards the organic material and the sulphide fractions tend to be volatilized first. Thereafter, during flue gas cooling these elements adsorb with relative ease onto fine particles. Xu *et al.* (2003) also state that the elements showing chemical affinity toward discrete mineral matter are less readily volatilized and therefore remain in the ash products.

Similarly, research conducted by Noda & Ito (2008), showed that under combustion conditions the trace elements Hg and Se tend to be volatilized, and both are somewhat absent at high temperatures in the fly ash. This corresponds with the statement made by Xu *et al*. (2003), that those elements with chemical affinity towards organic and sulphide fractions are the first to be that volatilized, as well as work by other researchers which shows that both Hg and Se are

believed to have chemical affinity toward sulphide fractions, but more specifically iron sulphide (pyrite) (Xu *et al.* 2003; Ohki *et al.* 2005).

On the other hand, Ohki *et al.* (2005) reports that although As and Pb, which are moderately volatile, are less readily released into the gas streams as they become enriched/concentrated in the fly ash. Similarly, based on their research Noda and Ito (2008) have report that when sampled at high temperatures, the B found in fly ash exhibits different properties. Also, the presence of Hg and Se in the fly ash is highly dependent on temperature; with decreases in temperature leading to increases in the capture of these trace elements in the fly ash.

Another study conducted on Spanish coals by Pires *et al.* (1997) yielded results which enabled them to determine the relative volatility of some of the elements present in the coals. These results can be seen in Table 2.6:

Group	Volatility	Enrichment	Elements
I	Very low (20%)	Slag (bottom ash)	Ba, Li, Rb, Sr and Ta
II	High to medium (>20%)	Fine flyash particles	As, B, Cd, Ge, Mo, Sb, Tl and Zn
II a	High to medium	Medium enrichment in flyash fractions	W, U and V
II b	High to medium	Strong enrichment in fly ash	Cr, Co, Cu, Ni and Pb
III	High (~100%)	Vapour	Se, Hg and S

Table 2.6: The relative volatility and the enrichment of some trace elements based on results obtained from the study conducted by Pires et al. (1997).

The results obtained from the research by Pires *et al.* (1997) correlates with that of Ohki *et al.* (2005) as well as Noda & Ito (2008) as all three of them report that Hg and Se are highly

volatilized and are not enriched in the fly ash, but rather released into the air, and that As and Pb are moderately volatile and are enriched in the fly ash and not readily released into the air. Querol *et al*. (1995) conducted a similar but more extensive study on Spanish feed coals from a power station. They found that certain elements showed enrichment within the fly ash - some elements exhibited enrichment in the slag (bottom ash); some showed no fractionation between fly ash and slag, and others showed volatile behaviour.

Several other studies (Meij, 1994; Ratafia-Brown, 1994; Rizeq *et al.* 1994; Swaine, 1994; Martinez-Tarazona & Spears, 1996; Aunela-Tapola *et al.* 1998; Helble, 2000; Sandelin & Backman, 2001; Huang *et al.* 2004; Meij & te Winkel, 2004) have been conducted in different power stations in order of determining the distribution of harmful trace elements in the process of power generation by coal combustion. It is important to note that the results obtained from each of the studies have similarities, but do vary as the power stations differ in operating conditions and configuration, especially in terms of temperature profile throughout the process and the particulate collection systems. The consequence of control systems being different is that several trace elements become enriched in sub-micron fly ash particles and the efficiency of the collection devices (Electrostatic precipitators (ESP) and Fabric bag filters) determines the release of trace element and associated particulate matter into the atmosphere. Also, as mentioned previously, the mode of occurrences of trace elements vary from coal to coal, and this is directly responsible for the distribution of the trace elements in the process (Huang *et al.* 2004).

Helble (2000) reported that certain volatile trace elements, such as Hg and Se, are volatilized at the combustion temperatures, but even when temperatures drop in regions of the air pollution control devices and the stack, these trace elements still remain in the gas phase and are emitted into the atmosphere in the gas phase. Helble also states that other trace elements with a lower volatility than that of Hg and Se tend to vaporize at combustion temperatures, but instead of remaining in the gas phase they condense on the submicron fly ash particles. The reason for this phenomenon is the fact that a decrease in particle size leads to an increase in

surface area thereby facilitating the condensation of the trace elements on the surface of the submicron fly ash particles.

According to Meij (1994), trace elements become enriched in the ash products and the enrichment is dependent on the type of ash as well as the particular trace element. For this reason the term 'relative enrichment' (RE) was introduced. The equation for the relative enrichment is:

$$RE = \frac{\text{Element concentration in ash}}{\text{Element concentration in coal}} * (\%\ \text{ash content in coal})/100 \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Using this equation, trace elements can be classified and put into one of the three classes depending on the RE value obtained. The results from numerous studies in the Netherlands were collated by Meij (1994) thus leading to the classification of the trace elements into the three groups, based on the relative enrichment calculations and their behaviour in the combustion process within the boiler and ducts. Table 2.7 represents the classification system to which the trace elements are assigned based on their relative enrichment factors/ratios.

Class	Bottom ash	Fly ash (ESP)	Fly ash (Flue gas)	Behaviour in installation
I	≈1	≈1	≈1	Not volatile
IIc	<0.7	≈1	1.3<.....≤2	Volatile. Condensation occurs
IIb	<0.7	≈1	2<.....≤4	
IIa	<0.7	≈1	>4	
III	<<1	<1		Very volatile. Limited condensation

Table 2.7: The classification of trace elements based on relative enrichment factors/ratios (Meij 1994).

Class I: Non volatile, do not vaporize

Class II: The elements which fall into this class do vaporize and when the temperature decreases from the combustion temperature of about 1600 ^{o}C to around 160 ^{o}C, the dew points of different chemical compounds will be reached thereby leading to the condensation of these elements onto the surface of fly ash particles. These trace element containing particles can also form by nucleation and the subsequent growth of these particles occur by heterogeneous condensation and coagulation. This class is divided into three groups based on the volatility with an increase in volatility from group IIc to IIa.

Class III: This class is reserved for elements with the highest volatility. The elements in this class are present in elemental or compound forms which have low dew points. This means that they are emitted (completely or at least partially) into the atmosphere in the vapour phase, unless a pollution control device like a Flue Gas De-sulphurisation (FGD) is installed (Meij, 1994).

As mentioned previously, the research conducted in the Netherlands utilized the classification system proposed by Meij (1994) to identify the partitioning behaviour of the trace elements in their study. The results are presented in the Table 2.8:

Class	Elements
I	Al, Ca, Ce, Cs, Eu, Fe, Hf, K, La, Mg, Sc, Sm, Si, Sr, Th and Ti
IIc	Ba, Cr, Mn, Na and Rb
IIb	Be, Co, Cu, Ni, P, U, V and W
IIa	As, Cd, Ge, Mo, Pb, Sb, Tl and Zn
III	B, Br, C, Cl, F, Hg, I, N, S and Se

Table 2.8: The classification of elements based a research conducted in the Netherlands (Meij, 1994).

The study performed by Huang *et al.* (2004) was conducted at a power station equipped with a three field ESP and the efficiency of this ESP was reported to be about 99 %. This study reported enrichment factors as well as the mechanism of adsorption of certain trace elements. An improved RE factor is introduced in this study. The benefit of this RE factor is that it takes both

the ash content of the coal and the combustion products into account. The equation which represents this RE factor is:

$$REs = (C_{in}/C_{ic}) \times [(A_{ad})_c]/[(A_{ad})_n] \,.\, (A_{ad})_n \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

C_{in} : trace element concentration in the combustion product

C_{ic} : trace element concentration in the feed coal

$(A_{ad})_c$: % ash content in the feed coal

$(A_{ad})_n$: % ash content in the combustion product

Using this enrichment factor Huang *et al.* (2004) were able to classify the trace elements.

Group I: very volatile, mainly emitted in the vapour phase - Hg, Se and Cr

Group II: volatilized at high temperatures, condense on fly ash particles and are emitted mostly in the fly ash – Pb, Zn, Cd and Se

Group III: not volatile, retained in the bottom ash – Mn and Cr

Some trace elements like Se and Cr are present in more than one group, and this is as a consequence of different modes of occurrences in the coal. Cr in particular is highly variable as it is classified in group I and Group III. This is due to the fact that Cr can have organic association thus making it more readily volatilized, thereby placing it in to Group I. The association with minerals is the reason for it being placed in Group III. Despite Cr being grouped into these two groups, other studies (Clarke 1993) show that Cr can fall into groups where it is enriched in the fly ash, but also enriched in the bottom ash. From this it is clear that Cr classification is variable.

The study by Huang *et al.* (2004) also shows that trace element enrichment increases as fly ash particle size decreases. This trend was determined by sampling the fly ash at the different fields of the ESP. Particle size deceased as they moved from the 1st field to the 3rd field. Thereafter

the enrichment factors of the trace elements were determined in each sample and plotted on a graph as indicated by Figure 2.3:

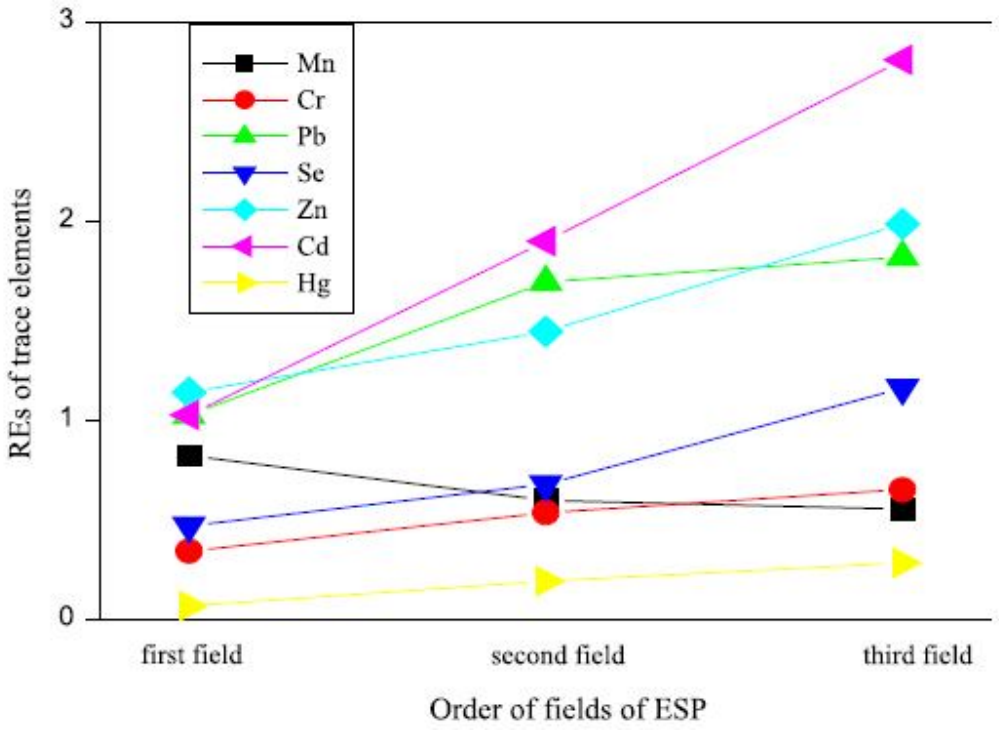


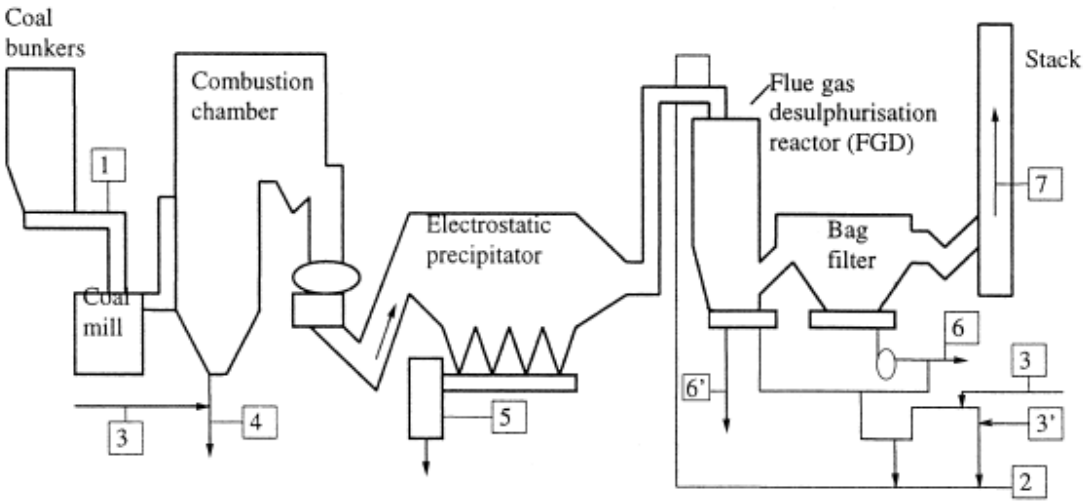
Figure 2.3: The concentration of trace elements relative to the average particle size based on samples collected from the three fields of as ESP (Huang *et al.* 2004).

From the graph it is evident that the enrichment of all the trace elements (except Mn which is not volatilized), increases from the 1st field to the 3rd i.e. This is, trace element enrichment increases as particle size decreases.

Huang *et al.* (2004) report that the volatility of trace elements governs the adsorption mechanism of trace elements onto the fly ash particles. For elements which are less volatile the main adsorption mechanism is a chemical reaction; whereas for volatile trace elements, like Cd, Zn and Se, the dominant adsorption mechanisms are physical processes such as condensation, coagulation and sedimentation.

The study also shows that certain trace elements like Hg, Cr and Zn tend to show an increase in volatilization with an increase in furnace temperature. A reduction in available oxygen leads to Hg and Se being enriched to a greater extent in the fly ash (Huang *et al.* 2004)

The study conducted by Aunela-Tapola *et al.* (1998), in two Finnish power stations equipped with low NOx burners, ESP and a FGD unit (spray-dryer-type reactor and a fabric filter) yielded good results in terms of lowering the trace element emissions. Below is the design of the power stations which indicates all of the components as well as the feed coal and the by-products along the route of the process:



*Incoming mass streams: 1–coal; 2-lime; 3- sea water; 3'-raw water.

Outgoing mass streams: 4-bottom ash; 5-ESP ash ; 6,-end product of FGD; 6'-coarse FGD product and 7-flue gas

Figure 2.4: Schematic representation of the Finnish power station with a numbering system illustrating the incoming and outgoing mass streams (Aunela-Tapola *et al.* 1998).

Sampling of the bottom ash, ESP ash and particulate matter in the flue gas was performed and the enrichment results were presented, as can be seen in the Table 2.9. Also in included in the table, for comparison, is results from a similar study conducted by Meij (1989). The

classification of the trace elements in the three by-products of the combustion process is based on calculation of the enrichment factors proposed by Meij (1989).

	Meij 1989		Plant A	Plant B
Group I	Mn		Mn	Mn
Group II	As, Be, Cd, Co, Cr, Ni, Pb, Tl, V, Zn		As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Se	As, Be, Cd, Cr, Hg, Ni, Pb, Tl, Zn
Group III	Br, Hg, Se			

Table 2.9: The classification of trace elements from a study conducted by Aunela-Tapola et al.(1998) (plant A and B) based on the enrichment factors proposed by Meij (1989).

From Table 2.9 it can be seen that the results obtained from the two studies are similar in terms of classification of the trace elements. The major difference is that Meij (1989) shows Hg and Se to be present mainly in the vapour phase (Group III), but Aunela-Tapola *et al.* (1998) show that Hg and Se do become highly enriched on the submicron fly ash particles.

The results from the study by Aunela-Tapola *et al.* (1998) also shows that the concentration of all trace elements, including the volatile Hg and Se, are very low. This is attributed to the environmental control systems which are present within the power station. Thus, with the correct environmental control systems in place, a significant lowering of trace element emissions can be attained.

2.4.3 Gasification

Thus far the discussion has been on the concentration and partitioning behaviour around coal combustion, but gasification of coal is very important on a global scale. In South Africa SASOL is the second largest consumer of coal. In 2008 they gasified about 48 MT of coal to produce

liquid fuels and chemicals. Therefore trace element behaviour in a gasifier is very important as this process is a possible source of trace element emission into the atmosphere.

Bunt & Waanders (2008) conducted a study on the coals used in the Sasol–Lurgi MK IV FBDB gasifier. Their research showed that the gasification of coal also leads to the volatilization of trace elements. The focus of the study was on the trace elements Hg, As, Se, Cd and Pb which, according to literature, are the most volatile trace elements. Results showed the sequence of volatility between these trace elements is as follows:

As < Pb < Cd < Se < Hg

Wagner *et al.* (2008) conducted research focusing on a Hg mass balance over a plant with pulverized coal combustion and gasification. The results from the research showed that Hg is readily volatilized in a power generation plant and this verifies the volatility of Hg as well as shows that the combustion of coal in power generation leads to the emission of Hg. From the results obtained it is estimated that approximately 1.25 tonnes of Hg is emitted through the stack annually. The Hg mass balance obtained from the study was 100.6%, which translates to all the Hg being accounted for, as indicated in Table 2.10.

	Ave Hg distribution %
Coal	(100)
Bottom ash	2.8
Fly ash	10.91
Stack	86.9
Balance	100.6
Assumptions: Coal and ash values are for a single point in time; flue gas values extracted over an hour of sampling. All boilers are equally represented.	

Table 2.10: The distribution of the Hg in the steam plant (Wagner *et al.* 2008).

Results from the same study showed that the gasification of coal does not contribute to the emission of Hg via the stacks but rather enrichment of the Hg in the ash products and downstream in the gas cooling plant.

From the research reviewed here it can be seen that there are two trace elements, Hg and Se, that are the potential trace elements that will be volatilized and released as airborne pollutants (Pires *et al.* 1997; Ohki *et al.* 2005). Studies conducted on South African coals by Wagner *et al.* (2008), Hlatshwayo (2008), and Bunt & Waanders (2008) also show Hg and Se as being trace elements which are very volatile and therefore a potential airborne pollutant when coal undergoes combustion. However, as mentioned previously, coals differ worldwide as well as within countries and the behaviour of trace elements will vary due to this fact, i.e. difference in modes of occurrence.

2.4.4 Mass balance of trace elements in combustion plants

Thus far the discussion has been on the concentration and partitioning behaviour of certain trace elements in pulverized fuel combustion processes based on relative enrichment factors, but another important section of trace research is calculating the mass balances for the trace elements of interest. Mass balances are the most direct method of determining the partitioning behaviour of trace elements and mass balance closures assist in verifying the authenticity of the results (Ratafia-Brown 1994). In order to calculate these mass balances, the concentration of the trace elements in each stream (coal and combustion products) is needed as well as the flow rates of each of the streams. Studies have been conducted on determining mass balances in both pulverized coal-fired systems (Aunela-Tapola *et al.* 1998) and fluidized bed combustion systems (Klika *et al.* 2001). It should be noted that determining mass balances is very difficult as trace elements occur at concentrations which are generally low and at times can be close to or below the detection limit of instruments used to analyze trace elements. Also, it is a very challenging task to determine the quantity flow rates of each of the streams as flow recorders are not always installed in each of the streams. The mass balance results obtained from a study

conducted by Aunela-Tapola *et al.* (1998) in two Finnish pulverized coal fired power stations will be discussed. The reason for choosing this study is that information is provided on both the concentration of the trace elements in each stream as well as the flow rates of each stream.

The first step in calculating mass balances is to calculate the mass flow rate of each of the trace elements in both the ingoing and outgoing streams using the equation below:

$$Q_{ij} = q_j.c_{ij} \quad \ldots\ldots (3)$$

Q_{ij} – This is the flow rate of trace element i in stream j

q_j – The flow rate of the stream

c_{ij} – The concentration of trace element i in stream j

Thereafter, the sum of the trace element flow rates for the ingoing $(Q_{i,\ in})$ and outgoing $(Q_{i,\ out})$ streams should be calculated. The closure (ratio) of the mass balances is then performed as to determine the success of the mass balances.

$$(Out/In) = (Q_{i,\ out}) / (Q_{i,\ in}) \quad \ldots\ldots (4)$$

A closure value of 1.0 or close to 1.0 is indicative of a successful mass balance. When the value is lower than 1.0 it indicates that there is error in the analysis; that is, the trace element flow in the outgoing streams was detected lower than the true value, or the trace element flow in the ingoing streams was detected higher than the true value. A closure value of higher than 1.0 also indicates errors – trace element flow in the outgoing streams was determined to be higher than the true value, or the trace element flow of the ingoing streams were determined to be lower than the true value.

In the power stations investigated by Aunela-Tapola *et al.* (1998), each was equipped with an ESP and a FGD (Schematic in figure 2.4). The results from their study illustrates that trace element mass balances are susceptible to large degrees of uncertainty. They found that in the one power plant the closure of the element mass balances was within ± 30% for all of the trace elements analyzed, barring Cr. In the same power plant certain element mass balance closures were more accurate, ± 20%. Those elements were As, Be, Cd, Mn, Pb, Tl and Zn. In the other plant it was found that all the trace element mass balance closures were within ± 30% and quite a few trace element mass balance closures (Cd, Co, Cr, Cu, Hg, Mn, Ni and Pb) were shown to be within ± 20%. From this it is clear that accurate mass balance determinations are very difficult, but it is not impossible to obtain mass balances with lower percentage of uncertainty, provided trace element concentration analysis is performed by a reputable laboratory, good sampling technique is practiced and the flow rates throughout the process are accurately determined.

2.5 POWER GENERATION

About 41% of the worlds electricity is derived from coal fired power stations. This is largely due to the fact that coal is the most abundant of all fossil fuels and also because it is a relatively inexpensive resource (Kurose *et al.* 2004; World Coal Institute, 2008). Presently, pulverized or fluidized-bed coal combustion is being employed in coal fired power stations in order to generate electricity (Kurose *et al.* 2004). According to Finkelman & Gross (1999), it is expected that over the next few decades there will be an increase in the consumption of coal in developing countries such as China and India. As a result of coal being an inexpensive energy resource, the economies of these developing countries can be strengthened and their citizens can be afforded higher standards of living (Finkelman & Gross, 1999). In 2005/2006, the World Coal Institute reported that China was the highest coal producer in the world followed by USA and then India (World Coal Institute, 2008). Table 2.11 verifies the statement made by Finkelman & Gross (1999) regarding developing countries becoming more dependent of coal as an energy source as well as a commodity in benefiting their economies and citizens.

County	Quantity in Mt
China	2549
USA	981
India	452
Australia	323
South Africa	244
Russia	241
Indonesia	231
Poland	90
Kazakhstan	83
Colombia	72

Table 2.11: The top 10 hard coal producers in 2007 (World Coal Institute, 2008).

South Africa's most abundant source of energy is coal with over 90% of the regions electricity obtained from coal-fired power stations (World Coal Institute, 2008; Eskom, 2009). According to Moumakwa & Marcus (2005), the mining of coal is cheaper in South Africa than in the rest of the world due to relatively shallow depths of the coal seams. This further facilitates the extensive use of coal in electricity generation. South African coal is generally of a low quality and heat value with a high ash content. This low quality coal affords cheap power generation, which is produced mainly by thermal power stations, and can be found mainly in Gauteng, Mpumalanga and the Free State (Eskom, 2009).

2.6 COMBUSTION

"Combustion is the generation of thermal energy as a result of [the] oxidation of the combustible constituents of coal in the presence of heat" (Falcon & Ham, 1988, p. 146). According to Falcon & Ham (1988) there are many factors responsible for the efficient combustion of coal and these can be divided into inherent/intrinsic factors and external factors. The inherent/intrinsic factors are the organic and inorganic constituents, rank, moisture content, degree of weathering or heat effect, porosity, surface area that is exposed, particle size, oxidation state, initial or ignition temperature, and peak combustion temperature. The

external factors are those factors which influence the combustion process in terms of the operating conditions. These include environmental temperature, temperature, and velocity of the combustion air, both the design and spacing of the burners, residence time, nature of mixing of solids and gas, particle size, and throughput (Falcon & Ham, 1988).

The process of combustion is important in terms of driving the process of power generation. Zhang *et al.* (2008) verify this statement by reporting that about 25% of the world's energy consumption is obtained by coal combustion with the annual global energy consumption expected to be about 10.6 billion tons of coal in 2030 which corresponds with an annual increase of 2-3% per annum. Due to the increase in demand for electricity worldwide, especially in developing countries that depend heavily on coal as a source of this electricity, a greater awareness to the environmental and consequent human impacts from coal burning are being observed. Pollution caused by coal combustion includes sulphur emissions, CO_2 emissions, particulate release, as well as trace element emission (Karayigit *et al.* 2000). The environmental and human impacts associated with these coal combustion pollutants are the result of the mobilization of the toxic organic and inorganic components present in the coal when it is subjected to the combustion process; i.e. elevated temperatures (Finkelman *et al.* 2002).

During the combustion of coal in pulverized coal-fired utilities two ash products are formed. These are fly ash, which accounts for approximately 80% of all ash, and bottom ash which is the remaining larger particles and molten matter (slag or clinker). The opposite is applicable to stoker systems, where 80 % exits the boiler as bottom ash and 20 % is fly ash (Jankowski *et al.* 2006; Depoi *et al.* 2008; Marx & Morin 2008; CIRCA, 2009).

There are three key systems which have proved to be successful in power generation as well as being economically viable: traditional stoker, pulverized and the cyclone firing systems. Each of the systems has been developed to meet specific requirements. However, according to Marx and Morin (2008), pulverized fuel combustion systems are the dominant combustion systems

with stoker systems being the least dominant. Discussion on each of the three systems is discussed further below.

2.6.1 Stoker Firing Systems

The combustion of the fuel (coal/biomass) occurs on, as well as above, a grate within a furnace, thereby affording more stable combustion and much higher combustion capacities. The selection of the grate is based on the fuel that is being burned. There are two main stoker systems which are used presently: spreader stokers and chain grate stokers (Johnson 2002; Marx & Morin 2008). According to Rizeq *et al.* (1994), stoker boilers account for only 1 % of the total boilers in operation, and they are being phased out due to their inefficiencies in both coal combustion and environmental pollution control devices (Johnson 2002). This might be true in terms of other countries, but it has been reported that South Africa has about 8000 small boilers (personal communication, Falcon 2010).

2.6.2 Pulverized Fuel Systems

As mentioned above, pulverized fuel firing systems are the most commonly used systems in the power industry. There are three basic pulverized fuel firing designs: (i) vertical or arch, (ii) wall-fired (most common) and (iii) tangentially- fired pulverized coal boilers (Marx & Morin 2008). The fine pulverized coal is transported by air into the boiler. This mixing of the air with the fine coal affords high temperatures and high combustion efficiencies. Dry or wet bottom ash removal systems are present in pulverized systems. Pulverized dry bottom coal-fired plants are the favoured systems, especially in the US and Netherlands, as they are able to meet NOx emission standards (Rizeq *et al.* 1994).

Below is a diagram of the boiler layout of a thermal power station showing the points at which the bottom ash and fly ash are deposited.

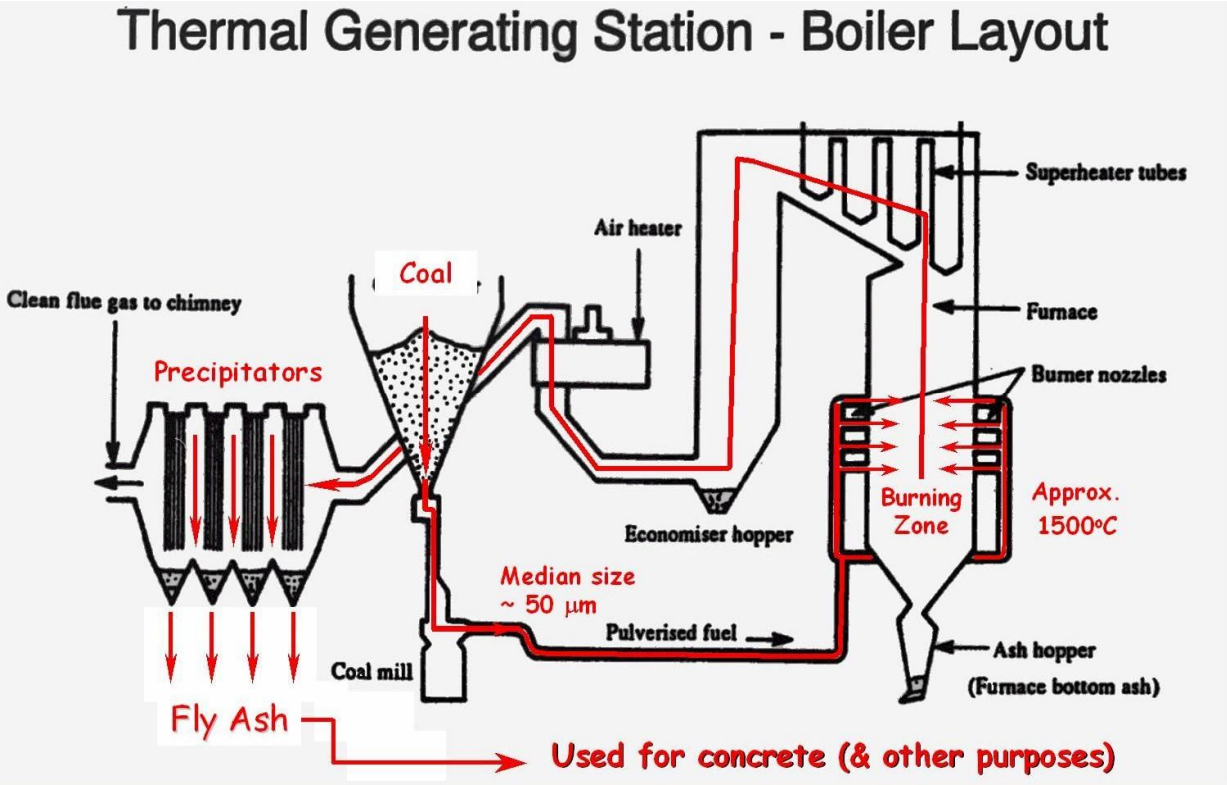


Figure 2.5: Diagram showing the boiler layout in a thermal power station (CIRCA, 2009).

2.6.3 Emission control devices

The emission of trace elements into the atmosphere is highly dependent on the emission control devices installed into the power plants. Furthermore, the efficiency of these devices is responsible for the amount of trace elements which are released into the atmosphere, via the stack. Two environmental control devices will be discussed: Electrostatic precipitators (ESP's) and Fabric filters (baghouses).

Electrostatic Precipitators (ESP's)

ESP's use electrical force to remove particulate matter from a flowing gas stream. The particulate matter is given an electrical charge by forcing them through a carona. Thereafter, electrodes are used to provide a high voltage which forces the particulate matter toward the walls. The particulate matter is then removed from the collector plates into the hopper (Turner *et al.* 1995). There are many types of ESP's, but in this paper only two will be discussed, namely the cold sided ESP and the Hot sided ESP. According to Meij (1994), all pulverized coal-fired power plants in the Netherlands are equipped with cold sided ESP's which are highly efficient. Meij (1994) also reports that these ESP's are able to provide high collection efficiencies for a wide range of particle sizes. However, a significant drop in the collection efficiency is observed for particles between 0.1 and 1 μm. This is due to the electrical resistance of the ash which can be predicted by the composition of the ash. An increase in the collection efficiency will be observed if the following trend is observed: **S >> Na > Fe, K**. However, a negative impact on collection efficiency is likely to occur if this trend is observed: **Ca, Mg > Si, Al**. Hot sided ESP's, on the other hand, are found before the air preheater (flue gas temperature of around 350 ^{o}C). They have a low collection efficiency for trace elements in class III and IIa as these elements are present mainly in the vapour phase at this temperature (Turner *et al.* 1995).

Fabric filters (Baghouses)

With fabric filters, the flowing gas stream passes along the surface of the bags and thereafter radially through the fabric and particles are retained. The collected particulate matter is removed during cleaning of the bags and deposited in the ash hopper (Turner *et al.* 1998). According to Meij (1994), fabric bag filters are capable of removing trace elements like Hg which are in the vapour phase. It achieves this by a mechanism of adsorption onto particulate matter already captured within the bags. Therefore, by using fabric bag filters trace elements in the vapour phase can be removed from the flue gas.

2.7 ENVIRONMENTAL AND HEALTH IMPACTS

Both the airborne and adsorbed trace elements (in fly ash) pose health problems. The presence of trace elements in fly ash can lead to serious environmental impacts and consequently have an impact on the inhabitants of the environment if the disposal of the fly ash is not performed correctly. Pollution from the trace elements would occur by the leaching of these trace elements out of the fly ashes (stockpiles/ash dumps) into the aqueous environment during fly ash-water interaction (Jankowski *et al.* 2006).

Fly ash is a very important secondary material, which can be used in the building industry, the ceramic industry and also in the synthesis of zeolites (Querol *et al.* 1995). However, the presence and the mode of occurrences of trace elements can lead to the fly ash not being utilized as there exists environmental restrictions on trace metals. This is due to the fact that these trace elements can be mobilized and thus lead to pollution of the environment and consequently lead to human health impacts (Querol *et al.* 1995; Font *et al.* 2005). Despite the possibility of leaching of trace metals from the fly ash used in various applications certain countries (Brazil for example) utilize ash products for pozzolanic cement, paving and as landfill. Therefore it is important to understand the properties of the ash products as to determine the feasibility of utilizing them for industrial applications (Levandowski & Kalkreuth, 2009).

As mentioned previously, certain trace elements are released into the environment as an airborne pollutant. These trace elements may occur in the elemental vapour form as well as being adsorbed onto submicron flyash particles (particulate matter). The latter form of the trace element has also gained a lot of attention from an environmental point of view and this is due to many negative aspects associated with these trace elements adsorbed onto these submicron flyash particles and also as majority of trace element emitted from the stack is associated with flyash particles. Due to the small particle size there is a lowered efficiency of capture by the environmental control systems like ESP's thereby allowing their release into the

environment. Furthermore the residence time of these particles in the atmosphere are relatively long which facilitates the transport of these trace elements, via particulate matter, to the source (humans and other living organisms). Once living organisms come into contact with the trace element containing particles, by inhalation or ingestion for bioaccumulated elements, they efficiently enter the pulmonary region of the respiratory tract where they are deposited and are removed slowly from this region. This allows the trace elements and the particulate matter to have enough time to inflict harm to the living organism (Swaine, 1994; Martinez-Tarazona & Spears, 1996).

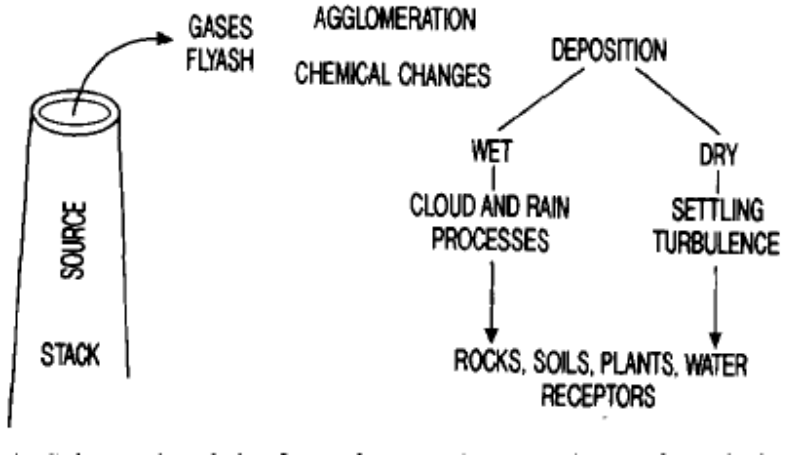


Figure 2.6: Schematic of the fate of trace elements released from the stack (Swaine, 1994).

The schematic in figure 2.6 indicates that trace elements in both, the gaseous and particulate form do not just remain as an airborne pollutant but through agglomeration and chemical changes are deposited into water and soil systems (Swaine, 1994).

Trace elements have varying toxicities toward living organisms and for this reason the trace elements which have shown to have toxic effects towards humans will be discussed. These elements are Hg, As, Se, Cr and other trace elements (Pb, Ni, Cd and Zn).

2.7.1 Mercury (Hg)

There are many sources (natural and anthropogenic) of mercury in our environment and these include: volcanoes, oceans, land exhalation, mining, and the anthropogenic sources like coal combustion that accounts for more than half of the atmospheric mercury generated from anthropogenic sources (Zielonka *et al.* 2005; Hlatshwayo, 2008;). According to the United Nations Environmental Control Programme (UNEP) (2010), the mercury emissions from anthropogenic sources was estimated to be about 1930 metric tons with fossil fuel combustion contributing to 45 % of the total emission.

Due to the fact that mercury is a highly volatile trace element, it is primarily released as an airborne pollutant by the combustion of coal. Studies conducted in Russia show that mercury concentrations in ash products are low with > 1% present in the bottom ash and 5-30 % is present in the collected ESP flyash (Yudovich & Ketris, 2005a). According to Finkelman & Greb (2008), there are many health problems associated with the exposure of mercury to human beings. However, these health problems are not as a consequence of direct exposure to the mercury released from the combustion of coal, but rather the exposure to the methylated form of the mercury coupled with the amplification in concentration as it moves progressively up the food chain.

Mercury can also be deposited into aquatic ecosystems (oceans, seas and lakes) and then speciate as methylmercury in the aquatic system. Mercury in this form can lead to severe toxic effects to humans because it can bioaccumulate in fish and consumption of large amounts of the fish can lead to the person developing neurotoxicity. According to the Pollution Prevention Report (1998), it has been found that mercury concentrations in fish can range between 0.07 and 0.17 μg/g, but far higher concentration have been found in larger ocean dwelling living organisms like dolphins where mercury concentrations of 10 μg/g were present.

The consumption of fish containing high concentrations of methylmercury by pregnant women can lead to fatal consequences for the foetus. Studies conducted by the U.S. Environmental Protection Agency (EPA) have ascertained that neurological disorders in the foetus are a likely consequence of high intake of methylmercury contaminated fish (Pollution Prevention Report, 1998; Finkelman & Greb, 2008). These neurological disorders arise when mercury concentrations are significant thereby reducing the production of selenoproteins in the brain tissue of the foetus, forming mercury selenide. This mercury selenide accumulates in the brain cells and consequently leads to lowered levels of selenium thus causing damage to the brain cells of the foetus. This deficit in the neurodevelopment is termed "Minamata Syndrome" and this is due severe mercury poisoning of babies born in Minamata, Japan. (Sondreal *et al.* 2000; Sondreal *et al.* 2004).

The main human health hazard associated with exposure to mercury, but more specifically methylmercury, is as a consequence of the ingestion of fish contaminated with this harmful form of mercury. The mode of action of this methylmercury is very simple - once it enters the human body, it is effectively absorbed into the blood stream and then transported to the points where it is accumulated (brain, kidneys and liver). Thereafter, the methylmercury inflicts its damage, which is usually irreversible, to areas of the central nervous system that control coordination, sensory, auditory and visual functions (Pollution Prevention Report, 1998; Sondreal *et al.* 2004).

In a study conducted by Horvat *et al.* (2003), it was determined that mercury of concentrations as high as 0.569 ppm were present in rice found in China (Guizhou province). This is due to the deposition of mercury into the soil thereby leading to its presence in the rice. This is highly problematic as rice is consumed in large quantities in the country (being the stable diet). The problem in the Guizhou province is further exacerbated by the fact that mercury in coal used in this region contain mercury concentrations of up to 55 ppm (refer to table 2.1 for typical global values). This shows that mercury can enter the food chain through air, water and soil (Finkelman *et al.* 2002; Yudovich & Ketris, 2005a).

From what has been explained above, it is clear why mercury is a high-priority concern and if this problem is to be circumvented, a joint effort is required by all countries that utilize coal combustion to obtain energy. Due to the long residence time (1-2 years) of atmospheric mercury coupled with effective transport in the global air currents, it is imperative that all countries cooperate as to minimize the amounts of mercury emitted into the atmosphere by coal- fired combustion (Lee *et al.* 2006). Table 2.12 will highlight the need for global cooperation in terms of the residence time and transport distance of the three forms of atmospheric mercury.

Type of mercury	Residence time in the Atmosphere	Transport distance
Hg^{o} (elemental mercury vapor)	One year	Global
Hg_p (mercury adsorbed onto particulate matter	Dependent on particle size – can range from hours to years	Local, regional and global
Hg^{2+} (divalent mercury)	Days	Regional

Table 2.12: The three forms of atmospheric mercury as well as their residence time and transport distance in the atmosphere (Environmental and Occupational Health Report, 2005).

2.7.2 Arsenic

Arsenic occurs in the environment as an arsenic compound rather than in the free form. It has an affinity towards sulphur, oxygen, chlorine, carbon and hydrogen; and depending on which of the elements it bonds to, it forms inorganic or organic arsenic compounds. In coal, arsenic is predominantly present as a sulphide compound (mainly pyrite), but can also be organically bound. Arsenic also tends to form compounds with metals and the most common metal arsenides are those of lead, gold copper and silver. The inorganic form of arsenic is the dominant form in terms of atmospheric arsenic (arsenic compounds adsorb onto particulate

matter) whilst arsenite and arsenate salts are the compounds which are soluble in water (Pollution Prevention Report 1998).

Arsenic has gained much environmental attention as it can be transported through the environment by air as well as water and it has also been determined that arsenic possesses carcinogenic properties. According to Guo *et al.* (2004) and Zielinski *et al.* (2007), both natural and anthropogenic sources of arsenic can have serious impacts on human health, social sustainability and global agriculture.

According to the Pollution Prevention Report (1998), the main route at which arsenic enters the human body is through ingestion, but inhalation of arsenic is also prevalent. Arsenic poisoning can lead to both acute and chronic toxic effects and these include effects on the cardiovascular, respiratory, nervous and hematopoietic systems. This coupled with potential carcinogenic properties make arsenic a serious environmental and occupational hazard. The symptoms associated with arsenic poisoning are: Scaly lesions mainly on the skin of the hands and feet (hyperkeratosis), flushed appearance and freckles (hyperpigmentation), lesions of the skin (Bowen's disease) and squamous cell carcinoma. Below is a picture of a man who suffered from arsenic poisoning (Finkelman & Greb 2008).



Figure 2.7: Photograph showing the evidence of chronic arsenic exposure from residential coal combustion. Hyperkeratosis, the brown, scaly patches covering this man's body and Bowen's disease, the black lesion on the left breast (Finkelman & Greb, 2008).

2.7.3 Selenium

Selenium is a nonmetal which has chemically related analogues namely tellurium and sulphur, with sulphur being the closest analogue. Like most elements, it is useful for certain bodily functions (cell function) and as mentioned previously, if selenium levels drop significantly neurological disorders will arise. However, it should also be noted that excessive amounts of selenium can lead to toxic effects. The human body is able to tolerate the intake of 400 μg of selenium per day, and if this amount is surpassed selenosis is the likely outcome. According to Zheng *et al.* (1992), nearly 500 cases of selenosis were reported in southwest China and the cause of this was the use of carbonaceous shale which contained high concentrations of selenium. There are many symptoms associated with selenosis and these range from minor to severe. These symptoms are: garlic odoured breath, irritability, fatigue, hair loss, sloughing of

nails, gastrointestinal disorders, and neurological damage (Pollution Prevention Report, 1998; Sondreal *et al.* 2004).

2.7.4 Chromium

The dominant form of chromium in coal is trivalent chromium (Cr^{3+}), which is essential in small quantities for certain metabolic processes like glucose, protein and lipid metabolism. However, by the process of oxidation (combustion of coal) more than 50 % of this benign trivalent chromium can be transformed into hexavalent chromium (Cr^{6+}) (Finkelman & Greb, 2008). The hexavalent chromium is not desired as it possesses both toxicological and potent carcinogenic properties. For this reason chromium has been identified as 1 of the 11 potentially hazardous "air toxic" elements in the 1990 Amendments to the US Clean Air Act. According to Huggins *et al.* (2000), the amount of chromium released into the atmosphere each year is in the region of a few tons. Based on the fact that the average concentration of chromium in coals is 20 ppm and that about 95% of chromium is present in the ash products, due to the mode of occurrence and relative volatility. The amount of Cr produced per annum indicates that a large amount of Cr is released due to the huge consumption of coal in combustion processes (Huggins *et al.* 1999; Huggins *et al.* 2000; Narukawa *et al.* 2007).

Many symptoms associated with chronic exposure to chromium have been observed and they include: wheezing, coughing, loss of breath, bronchitis, septum, lowered pulmonary functioning, pneumonia as well as a variety of other respiratory disorders. Also, based on the potent carcinogenic properties, over exposure to chromium, more specifically Cr^{6+}, can lead to cancer (Karar *et al.* 2006).

2.7.5 Other Trace elements

Extensive discussions on the health impacts of trace elements Hg, Se, As and Cr have been presented in this paper thus far, but there are human health impacts associated with over exposure to other elements such as Pb, Ni, Mn, Cd and Zn. Pb poisoning leads to severe negative effects on hemo group syntheses, nervous system and vascular system. According to Karar *et al.* (2006), Cd and Ni can lead to respiratory illness and disorders, and the former is known to have carcinogenic properties. The effects of over exposure to Mn and Zn range from neurological diseases in the case of Mn and deterioration in the case of Zn.

Toxicities pertaining to trace element exposure have been discussed above, but it is important to note that the fine particulate matter released by coal combustion have equally harmful effects on living organisms. Querol *et al.* (1995), has reported that fine fly ash particles have weak mutagenic properties. Also, experiments conducted on experimental animals have yielded results which show that particulate matter containing certain trace elements are carcinogenic and have harmful effects to the respiratory system. Therefore, the determination of the portioning behavior of trace elements in combustion products is essential in studying their toxicities.

CHAPTER 3 – METHODOLOGY

3.1 INTRODUCTION

This chapter is divided into two sections. The first section focuses on the general sample preparation and analytical methods which can used in the determination of trace element concentration in coal and ash by products. The second section is focused on the research methodology: sampling, sample preparation and analytical methods which were employed as to obtain the trace element concentrations, proximate analysis, and particle size distribution (PSD).

3.2 TRACE ELEMENT ANALYSIS TECHNIQUES

3.2.1 Inductively Coupled Plasma-Atomic emission spectroscopy/Mass spectrometer

Both Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP- AES) and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) make use of extremely high temperature (10000 K) argon plasma, which is responsible for the excitation of the elements within the sample. ICP-AES involves the excitation of ions to a higher energy state followed by the ions returning to the ground state leading to the emission of photons which have a wavelength characteristic of a particular ion (element). The detector then converts the radiation into an electronic signal which is later converted to concentration data (Harris 2003; Hlatshwayo 2008). ICP-MS differs slightly from ICP-MS in that the concentration of trace elements present in the sample is determined based on mass rather than emitted light.

The preferred analytical techniques for trace element analysis are ICP-AES/MS. This is due to the low detection limits which are achieved using these instruments (Hlatshwayo, 2008). According to Wagner & Hlatshwayo (2005), ICP-MS is possibly a better tool in the determination of trace element concentration. Several studies (Karayigit et al. 2000; Guo et al. 2002; Hu *et al.* 2006; Depoi *et al.* 2008; Levandowski & Kalkreuth, 2009) have utilized ICP-AES/MS in the determination of trace element content in coal and combustion product samples after the extraction of the trace elements from the solid samples by an acid digestion or dissolution.

3.2.2 Cold Vapour Atomic Absorption Spectrometry

Atomic absorption techniques have been used for chemical analysis since the 1950's (Huggins 2002). Cold Vapour Atomic Absorption Spectroscopy (CVAAS) in particular is the favoured technique in terms of Hg determination due to its sensitivity as well as reduced interferences (Wagner & Hlatshwayo 2005). Similar to ICP-AES/MS, CVAAS requires the extraction of the mercury from the solid sample, via dissolution or digestion, into a liquid solution (Hg^{2+} form). Thereafter the mercury (Hg^{2+}) is reduced by either tin (II) chloride or sodium tetrahydroborate (III) to yield free mercury atoms which are then captured for analysis. The free mercury atoms are captured in a gold or silver amalgam (Wagner & Hlatshwayo, 2005).

Many researchers have utilized CVAAS in the determination of mercury in coal and combustion products due to its reliability and accuracy (Bushell & Williamson, 1996; Huang *et al.* 2004; Wagner & Hlatshwayo 2005; Zielonka *et al.* 2005 and Zhang *et al.* 2008).

3.3 SAMPLE PREPARATION TECHNIQUES

As mentioned previously, the determination of trace elements in coal and combustion products ICP-AES/MS and CVAAS requires the extraction of the trace elements from the solid sample into a solution. This section will focus on microwave digestion as it is a relatively new yet extensively used sample preparation technique. This technique involves the addition of acids to the vessel containing the sample. Thereafter the vessel is sealed and placed into the microwave where the sample in subjected to high pressure and a rapid increase in temperature (Hlatshwayo, 2008).

Microwave digestion is commonly used to extract trace elements from a solid sample as it has many advantages and these include (Wagner & Hlatshwayo, 2005):

- Relatively good precision and repeatability
- 90% lower sample preparation time
- Minimal sample mass is required (maximum of 0.5g for an organic sample such as coal).
- Able to retain volatiles such as mercury, which volatilize at temperatures of around 140 ^{o}C. This is achieved due to the fact that the digestion is performed in a closed vessel.
- Minimum supervision is required as compared to conventional hot plate methods
- Cross-contamination and worker exposure to toxic fumes is eliminated as compared to conventional methods

3.4 SAMPLING AND ANALYTICAL METHODS SELECTED FOR THIS PROJECT

3.4.1 Research Sampling

Coal and ash products were collected from a small industrial boiler (chain grate stoker). The samples which were collected included the feed coal, the bottom (coarse) ash, the fly ash collected by the ESP and the stack emission. The details of the sampling were not supplied at the time of sampling. The schematic below indicates the sampling points:

feed coal	→	bottom ash	→	fly ash	→ stack emission
(1)		(2)		(3)	(4)

Samples were milled to achieve a particle size of >250 µm. The proximate analysis was performed for all of the samples excluding the stack emission (limited sample quantity). Inductively Coupled Plasma – Mass Spectrometry was performed on all of the samples. The particle size distribution was performed only on the stack emission.

3.4.2 Proximate Analysis

The coal and combustion products (bottom ash, fly ash and stack emission) were submitted to UIS Analytical Services where standard methods were employed in the determination of moisture, ash content and volatile matter. Fixed carbon was determined by difference. The standard methods employed in the determination include:

- Moisture: SANS 5925 (2007)
- Ash content: SABS ISO 1171 (1997)
- Volatile matter: SABS ISO 562 (1998)

3.4.3 Sample Preparation (Microwave Digestion) for ICP-MS

The acids for the microwave digestion were pure analytical grade acids from MERCK and SIGMA-ALDRICH.

0.3 g of the sample was weighed out and placed into the microwave digestion vessel. Thereafter, the acids were added using a pipette. The volumes of acid which were added: 10 ml nitric acid (70%), 5 ml hydrofluoric acid (55%) and 1 ml hydrochloric acid (40%) The vessels

were then placed into the microwave for 15 min at approximately 210 ^{o}C and 20.0 atm. Thereafter boric acid was added as to neutralize free fluoride ions in the solution.

3.4.4 Inductively Coupled Plasma-Mass spectroscopy

This analysis was outsourced to UIS Analytical Services. The concentration of the trace elements in all of the samples was determined using the ICP-MS (Perkin Elmer Elan DRC Plus) as ICP-MS has a low detection limit.

CHAPTER 4 - RESULTS AND DISCUSSION

4.1 INTRODUCTION

The results obtained in this research will be presented in a manner which will explain the trends observed in the chain grate combustion process in terms of trace element partitioning and more importantly the emission of trace elements into the environment.

4.2 PROXIMATE ANALYSIS

The proximate analysis was performed as it is a fundamental analysis when performing coal research. For this study, the ash content of the coal as well as the ash products is of utmost importance as it enables one to calculate the relative enrichment factors, which is essential in determining the partitioning behaviour of the trace elements in the combustion products.

Sample	Proximate analysis (% air dry basis)			
	Moisture	Ash	Volatiles	Fixed Carbon
Coal	4.0	15.2	25.2	55.6
Bottom ash	1.2	64.8	1.6	32.4
Fly ash	0.3	75	1.3	23.4
Stack	Insufficient sample			

Table 4.1: Proximate analysis values obtained on an air dry basis for coal, bottom ash and fly ash

The proximate analysis indicates that the combustion of coal is incomplete as the proportion of fixed carbon present in the bottom ash and flyash is high (32.4 and 23.4 respectively) and the ash content is relatively low. The presence of volatiles in the ash products further enhances the

fact that incomplete combustion has occurred in this chain grate stoker. This is indicative of a combustion process which is inefficient and could explain unexpected values which arise in the research.

4.3. TRACE ELEMENTS AND THEIR CONCENTRATIONS IN THE COAL

The first step in a study on trace element distribution is the determination of the trace elements which are present in the coal and their corresponding concentrations. The reason for this is that by determining the original trace element concentrations in the coal, it is possible to identify the extent to which certain trace elements are enriched or depleted in each of the combustion products i.e. Bottom ash, fly ash (ESP) and stack emission. For this study the trace elements which were determined are those which have been identified in the literature as being possible airborne toxic trace elements. The data presented in Table 4.2 is the concentration of trace elements which were analyzed in the feed coal.

Trace element	Concentration (ppm)
As	4.06
B	49.1
Be	2.37
Cd	0.10
Pb	13.7
Hg	0.20
Se	0.82
Cr	43.3
Ni	11.2
Sb	0.29
Co	2.07
Mn	26.1
Ur	3.01
Th	5.50

Table 4.2: The trace elements which were analyzed for in the study and their corresponding concentrations in coal.

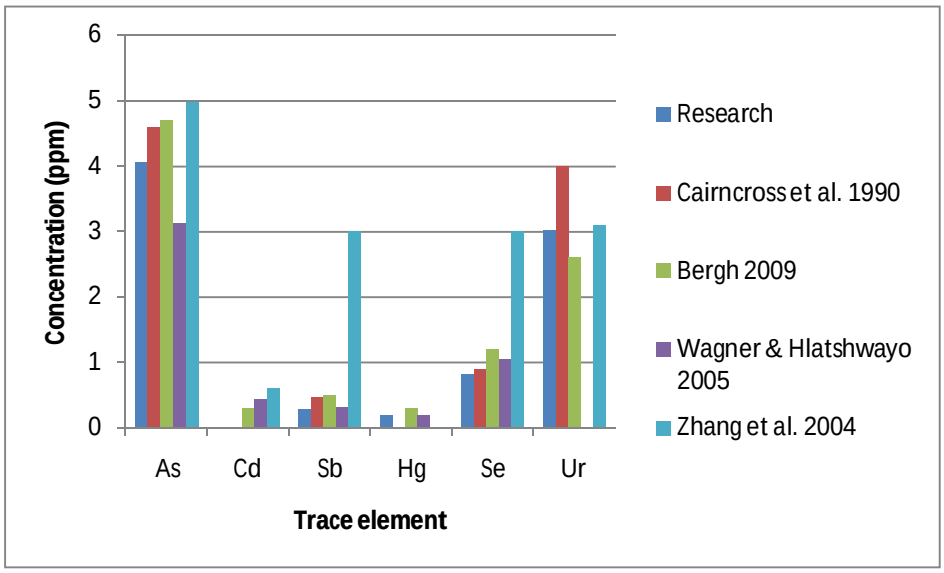
The values from Table 4.2 are then tabulated (see Table 4.3) against other values obtained from previous studies on South African coals. This was done in order to draw a comparison of the trace element concentrations of coals from different studies conducted in South Africa coupled with a global average of a range of other studies conducted. The reason for the comparison is that it gives an indication of the concentration of trace elements in South African coals over a period of approximately 20 years. Furthermore, by comparing these studies, which have been conducted at different times and in different coalfields over a 20 year period, it can be seen whether there is a variation of trace elements in the same coalfield and between coalfields. Also, it allows one to determine whether the coal being utilized presently is more contaminated with trace elements than the coals used in the past.

By comparing the results to the global average presented by Zhang *et al.* (2004), a comparison between results compiled from many studies conducted worldwide and the research results can be obtained. This gives an indication whether South African coals, in particular these research samples, have higher, lower or comparable concentrations of trace elements relative to coals from other countries. This is very important, especially to South Africa, as the country is the fourth largest exporter of coal with an export figure of 64 MT in 2008 (Bergh, 2009). Most of this export coal was to the European Union, which is fully supportive of the environmental lobby as well as the increase in the environmental legislation towards achieving its' goal of so called 'clean coal' (Bergh, 2009). From this it can be seen that determining trace element concentrations in coal is very important in terms of financial cost implications due to export and environmental legislation as well as health impacts.

	Concentration (ppm) of trace elements in research coal sample and selected South African coals				
Trace Element (ppm)	**Research Report Results**	**Witbank Coalfield 2 Seam (Cairncross et al. 1990)**	**Witbank Coalfield 4 Seam (Bergh, 2009)**	**Highveld Coalfield 4 Seam (Wagner & Hlatshwayo, 2005)**	**Global Average (Zhang et al. 2004)**
As	4.06	4.6	4.7	3.14	5
B	49.1	*	*	*	*
Be	2.37	*	*	*	*
Cd	0.10	*	0.3	0.44	0.6
Pb	13.7	10	15.03	7.51	25
Hg	0.20	*	0.3	0.2	0.12
Se	0.82	0.9	1.2	1.05	3
Cr	43.3	28	41.4	70.5	10
Ni	11.2	17	27.2	21.1	15
Sb	0.29	0.47	0.5	0.32	3
Co	2.07	7.9	11.0	6.3	5
Mn	26.1	*	163.4	19.6	50
Ur	3.01	4.0	2.6	*	3.1
Th	5.50	15.0	8.9	*	1.9

*These trace elements were not determined

Table 4.3: The trace element concentrations compared to results obtained from previous studies conducted in South Africa and a global average reported by Zhang et al. (2004)



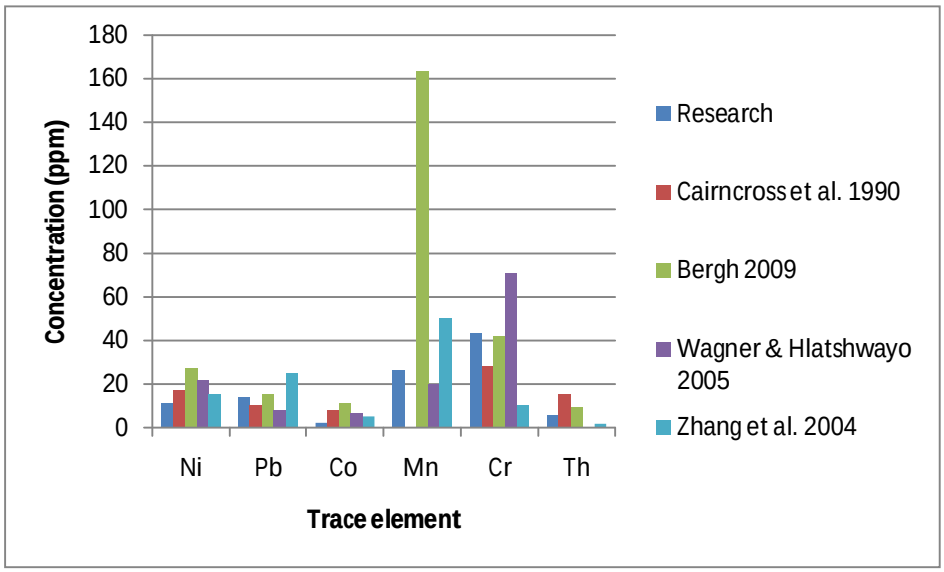


Figure 4.1: (a) & (b) Comparison of research results and other studies including a global average

The concentration of the trace elements present in the coal sample that was analyzed is generally lower than the concentrations determined in other coals from South Africa. Deviations from this can be seen with trace elements such as As, Pb, Cr and Ur. Further discussion on certain trace elements can be seen below. The focus here has been placed on

those trace elements which are found to be higher in concentration when compared to the South African studies as well as those which exceed global averages.

The concentration of As in the coal sample from this research is higher than that determined by Wagner & Hlatshwayo (2005), but lower than the results obtained from studies performed on coals from the Witbank no. 2 and no. 4 seams (Cairncross *et al.* 1990 and Bergh, 2009) as well as 25% lower than the global average (Zhang *et al.* 2004). The Pb concentration is almost double that of what is present in the Highveld coals (Wagner & Hlatshwayo, 2005) and about 4 ppm higher than the concentration which was present in the Witbank no. 2 seams coals (Cairncross *et al.* 1990). However, the Pb concentrations obtained from the research was found to be lower than the Witbank no. 4 seam coals (Bergh, 2009), and more importantly, over 10 ppm lower than the global average (Zhang *et al.* 2004).

Cr is a trace element which occurs in coal with two different oxidation states. The dominant form is the Cr^{3+} species which is said to be benign. Despite this, however, it is in fact essential for certain metabolic processes. The toxic form is Cr with a 6+ oxidation state. It is important to note, that even though the 3+ oxidation state is the minor oxidation state of Cr in coal, during combustion more than 50 % of Cr^{3+} can be oxidized to the carcinogenic Cr^{6+}. Huggins *et al.* (1999) verified this through results obtained from a study conducted at a power station which showed that the concentration of Cr^{6+} present in the fly ash was more than twice the amount present in the original coal. For this reason the Cr concentrations within coal is very important. Unfortunately, the concentration of Cr in the coals from the three South African studies, as well as from the research, is far higher than the global average reported by Zhang *et al.* (2004). The concentration of Cr determined in the research sample is higher than that determined in both the studies conducted on Witbank coals, but is less than the concentration determined by Wagner & Hlatshwayo (2005) in Highveld coals. Despite the relatively high concentration of Cr in South African coals, the enrichment of Cr occurs mainly in the fly ash, so Cr does not pose a serious threat in terms of being an airborne pollutant, but rather due to leaching from the fly

ash into aquatic ecosystems (Meij, 1994; Pires *et al.* 1997; Aunela-Tapola *et al.* 1998; Jankowski *et al.* 2006). Therefore, to ensure that Cr, especially Cr^{6+}, is not leached into aquatic ecosystems, safe and effective disposal of the fly ash should be performed.

There are three other trace elements which occur in concentrations greater than that of the global average. These are Hg, Ni and Th. The Hg concentration determined in the research is identical to the value obtained from the Highveld coals and lower than the concentration determined by Bergh (2009) in Witbank no. 2 seam but higher than the global averages. This is very important as Hg is a highly volatile trace element which is readily released (mainly in the vapour phase) into the environment and can be transported long distances leading to possible toxicity to living organisms in the immediate vicinity and areas within range (Lee *et al.* 2006; Hlatshwayo, 2008). For this reason, coupled with the fact that elemental Hg is able to travel globally by the wind, the concentration of Hg present in South African coal is very important in world pollution context as the concentration of Hg is higher than the global average in this research as well as in the studies conducted in the Witbank and Highveld. The Ni and Th concentrations were found to be much lower than the studies conducted on South African coals, but are found to be considerably higher than the global average.

Other highly toxic volatile trace elements like Cd and Se are present in the research coal sample in concentrations less than that determined in the other South African studies and more importantly, far less than the global average.

In the study conducted by Wagner & Hlatshwayo (2005), an interesting trend was observed whereby the siderophile (Mn, Cr, Co, Ni and V) elements were found to be enriched in the coal relative to the global averages and the chalcophile (As, Cd, Cu, Pb, Sb, Se and Zn) elements were depleted; and in most cases very depleted. This research does not show that correlation, but instead it can be observed that the siderophile elements which were analysed in this study are

depleted relative to the global average reported by Zhang *et al.* (2004), with the exception of Cr, which is highly enriched. In terms of the chalcophile elements, all of them are much depleted.

From the research results and the results from the three other studies conducted on South African coals, it is clear that the coal studied in this research contain comparable, yet lower, trace element contents. This decrease in the concentration of trace elements implies more of a 'clean coal' than the other coals which were studied. What is also promising, is that the concentrations of most of the trace elements, especially the trace elements of major concern, in all four studies, are lower than the global averages reported by Zhang *et al.* (2004) and fall well within the global range presented by Swaine (1994).

4.4. DISTRIBUTION OF TRACE ELEMENTS IN THE STOKER PROCESS

The aim of the research was to determine which trace elements are enriched in the ash products as well as those which are emitted through the stack into the atmosphere from a chain grate stoker. The results obtained from this study were compared with results obtained from large pulverized coal-fired power station. The value of this approach is that there is a lack of literature on trace element partitioning in chain grate stoker combustion processes and the findings in this research could raise awareness with regard to the emission of trace elements from smaller industrial boilers such as a chain grate stoker. However, due to time restrictions (being only a MSc 50/50 research project) as well as the lack of information and restricted access to the chain grate stoker from which the samples were obtained, the results presented are based on assumptions with regard to the flow rates and sampling procedures. Against this background, recommendations will be presented to assist researchers who envisage undertaking a similar study.

Due to these limitations and to the fact that the mass balance calculations cannot be performed accurately, it is not possible to verify the results. Certain assumptions will therefore be made so as to create a situation whereby the results can be understood, to this limited degree.

As presented in the literature review, there are two methods by which trace element partioning behaviour can be classified: Relative enrichment factors and mass balances. In this research the relative enrichment factors will be calculated in order to determine the partitioning behaviour of the trace elements; and this will be indicative of their volatility. The purpose of calculating the mass balances was to verify the results of the trace element concentrations as well as the relative enrichment factors. However, this is not the case as the flow rates are unknown. Therefore the mass balances will still be calculated using flow rates of a fluidized bed system so as to illustrate an understanding of the concept of mass balances. But, the mass balance closure results are likely to be erroneous.

Below is a table containing the concentration of the trace elements which were analyzed in the coal, bottom ash, fly ash (ESP) and stack emission. The table also contains the ash content for the coal and the three combustion products, obtained from the proximate analysis. These concentration and ash content values were used in calculating the relative enrichment factors. Thereafter, the partitioning behaviour of each of the analyzed trace elements was determined. Trace element mass balances were also determined using the concentration values presented in table 4. However, as mentioned previously, in order to calculate mass balances, the flow rates of the ingoing and outgoing streams must be known. In this respect, the research loses some of its value due to the lack of this information which is needed for calculating the mass balances. For this reason the information from a study conducted on a fluidized boiler combustion process was used. The only flow rates which were known is that of a fluidized combustion process and a pulverized coal-fired combustion process as discussed in the literature review. The flow rate from the fluidized bed combustion process was selected for use here because the pulverized combustion system contained a flue gas desulphurization (FGD)

unit as well as an electrostatic precipitator (ESP) which would have biased the example. Another reason for using the flow rates from the fluidized bed process is that the combustion temperature of the chain grate process is expected to be closer to the fluidized temperature of 850 ^{o}C than the pulverized coal-fired process of approximately 1400 ^{o}C.

	Coal	Bottom ash	Fly ash (ESP)	Stack emission
% Ash	15.2	64.8	75.0	
	(mg/kg)	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**
Trace element				
As	4.06	2.30	26.8	163
B	49.1	103	215	1033
Be	2.37	8.34	14.0	18.2
Cd	0.10	0.29	0.64	1.25
Co	2.07	6.36	15.2	32.0
Cr	43.3	155	265	312
Hg	0.20	0.27	0.46	1.55
Mn	26.1	102	155	528
Ni	11.2	53.1	63.4	145
Pb	13.7	7.7	149	611
Sb	0.29	0.34	2.59	8.57
Se	0.82	1.10	3.02	33.1
Th	5.5	14.4	21.0	53.2
U	3.01	11.1	19.8	20.9

Table 4.4: The concentration (in mg/kg or also can be reported as ppm) of trace elements in the coal and combustion products

From table 4.4, it can be seen that apart from volatile trace elements such as As and Pb, most of the trace elements increase in concentration from the coal to the stack emission. As and Pb show a decrease in concentration in the bottom ash followed by an increase in the fly ash and a huge increase in the stack emission. It is surprising that the more volatile trace elements such as Hg and Se do not show the same trend exhibited by As and Pb, i.e. where their concentration

in the bottom ash is lower than their concentration in the coal. Hg, in particular, is not expected to be present in the bottom ash due to its high volatility, but the presence of Hg in the bottom ash is probably due to the lowered efficiency of the chain grate stoker boiler. This can be seen from the proximate analysis (see table 4.1) which shows that the percentage fixed carbon present in the bottom ash is fairly high (32.4%) relative to the value present in the coal (55.6%). Also, the relatively low ash value of the bottom ash coupled with the detection of volatile matter enhances the fact that there is unburned coal in the bottom ash. This is a possible reason for Hg being present in the bottom ash. Furthermore, many of the other trace elements are enriched in the bottom ash to a higher degree compared to studies conducted in pulverized coal-fired power stations. This is also due to the combustion inefficiency within the chain grate stoker. Another possible reason for the moderate volatile species being present in the bottom ash is that the combustion temperature of the chain grate stoker could much lower than that of a pulverized coal-fired boiler. This, however, cannot be confirmed as no information pertaining to the chain grate stoker is known.

4.4.1 Partitioning behaviour of trace elements based on relative enrichment (RE) factors

The partitioning behaviour of trace elements in the chain grate stoker process was determined based on the classification system proposed by Meij (1994) which is based on RE factors. When calculating the RE factors for the bottom ash and the fly ash, the improved RE factor equation was used (Huang *et al.* 2004). However, the RE factor for the stack emission was determined using the standard equation proposed by Meij (1994). The reason for this is that there was not sufficient stack emission sample to do the proximate analysis. These RE values are tabulated in Table 4.5.

Trace element			
	Relative Enrichment Factors		
	Bottom Ash	Fly Ash	Stack Emission
As	0.133	1.338	6.102
B	0.492	0.887	3.198
Be	0.825	1.197	1.167
Cd	0.680	1.297	1.900
Co	0.721	1.488	2.350
Cr	0.840	1.240	1.095
Hg	0.317	0.466	1.178
Mn	0.917	1.204	3.075
Ni	1.112	1.147	1.968
Pb	0.132	2.205	6.780
Sb	0.275	1.810	4.492
Se	0.315	0.746	6.136
Th	0.614	0.774	1.470
U	0.865	1.333	1.055

Table 4.5: Trace element RE factors in the three combustion products

From Table 4.5 it can be seen that apart from three trace elements i.e. Be, Cr and U, the RE factors of most of the trace elements increase from the bottom ash to the stack emission. Using the information presented in Table 4.5, the trace elements from the study can be classified according to the classification proposed by Meij (1994). The results from this classification system can be seen in Table 4.6. Table 4.6 also contains the results from a study conducted in the Netherlands on a pulverized coal-fired power station (Meij 1994). This was done as to compare the partitioning behaviour in two different combustion systems i.e. the large pulverized coal-fired power station and the significantly smaller industrial chain grate stoker.

Class	Meij 1994		Research Results Elements
I	Th		Possibly Cr and U
IIc	Cr and Mn		Be, Cd, Cr, Ni, U and Th
IIb	Be, Co, Ni and U		Co, Mn
IIa	As, Cd, Pb and Sb		As, Pb, Sb,
III	B, Hg, and Se		B, Hg, Se

Table 4.6: Trace elements classified based on the classification system proposed by Meij (1994)

The classification system proposed by Meij (1994) was used successfully in determining the partitioning behaviour of most of the trace elements based on their RE factors. It should be noted that the placement of certain trace elements into class II was slightly problematic as the classification system illustrates that for a trace element to be placed in this class the RE factor of the trace element in the bottom ash should be a value of less than 0.7. This is not seen with trace elements like Be, Cr, Mn, Ni and U. This is probably due to the inefficient combustion of the coal in the chain grate stoker process, as mentioned previously, which is illustrated by the proximate analysis presented in Table 4.1. Therefore, these trace elements were placed in the class to which their RE factors match closest. Be for example is enriched by factor of 0.825 in the bottom ash which makes it higher and not lower than the 0.7 which is needed to classify it as a class II element, but, due to the fact that it is closer to 0.7 than 1, it falls into class II rather than class I. Also, the RE factor in the stack emission is 1.167 where as the classification for a class IIc element is 1.3 <…..≤ 2 and a value of approximately 1 illustrates a class I element. Based on this it was determined that Be is a class IIc element rather than a class I element as both the RE values lie closer to the classification values associated with a class IIc element.

The classification of Cr is slightly more challenging as its RE in the bottom ash is 0.840, which also closer to 0.7 rather than 1. The problem arises due to the fact that the RE in the stack

emission (1.095) is closer to 1 rather than the range of 1.3<.....≤2 which is required for the element to be classified as a class IIc element. For this reason the classification of Cr into either class I or IIc is difficult and therefore Cr has been classified as one of those trace elements which are able to fall within two classes. Due to the fact that the combustion in the chain grate process was inefficient, as well as the RE being higher than it should be, Cr is classified as being a class IIc element. The partitioning behaviour of U is similar to Cr in that it has simila r RE factors to Cr and therefore was placed in class IIc. Mn and Ni also possess RE factors in the bottom ash which place them in class I, but due to their relatively high RE in the stack emission they have been classified as being present in class IIb and IIc respectively.

Nevertheless, despite the slight difficulty in assigning a few of the trace elements from the study to the classes proposed by Meij (1994), the partitioning behaviour based on the classification was determined successfully.

Comparing the two sets of results, there are clear similarities and differences. Both studies show that B, Hg and Se are classified as class III elements. This shows that even though there are differences between the two processes, the most volatile elements like B, Hg and Se, are highly volatilized in the boiler. Thus they remain in the vapour phase throughout both processes and condense on submicron particles along the process with majority of the condensation taking place in the stack. It should also be noted that the enrichment of B and Se in the stack emission are much higher than that of Hg. For this study there are two possible reasons to explain this phenomenon. The first is that the particulate matter (fly ash) which passed through the ESP and enters the stack, contains high concentrations of B and Se. The second is that Hg is present in a vapour form and the collection of the vapour species was performed simultaneously with the particulate matter. Therefore, instead of the Hg vapour condensing onto the collected particulate matter it condensed on the walls of the stack or on the walls of the sampling container. Other similarities between the two processes are observed with the trace elements: Cr, Co, As, Pb and Sb.

The major difference between the two studies is that in the study conducted on the pulverized coal-fired power station samples, Th was classified as a class I element, which means that their RE results showed Th as being non volatile. This is not the case in this research where it was found that Th is volatilized to a certain degree and is a class IIc element. The other differences are seen in the classification of the trace elements between the different groups within class II. In the study conducted in the Netherlands (Meij 1994), Cd was shown to have a higher volatility (class IIa), but in this research it was found that Cd is less volatile in the chain grate boiler and is a class IIc element. This is probably due to the lowered combustion temperature which is expected in the chain grate combustion process, but this statement cannot be supported as the combustion temperature is unknown. The majority of the difference in the two studies is observed between class IIc and IIb. The research results obtained from the chain grate stoker shows that trace elements Be, Ni and U are more volatile than those determined in the pulverized coal-fired power station from Netherlands study. Mn also exhibits higher volatility in the chain grate stoker.

The results from these RE factors do not only indicate the partitioning behaviour of the trace elements in the process, but also the relative volatility of the trace elements within the process. Therefore, the arrangement of the trace elements, in order of increasing volatility, can be seen below. The volatility was determined by using the classification of the trace elements in the research and the ratio of stack emission/bottom ash was used to determine the relative volatility of the trace elements within classes.

U < C r < Be < Ni < Th < Cd < Co < Mn <Sb < As < Pb < Hg < B <Se

The relative volatility sequence obtained from the study is the similar as that which was expected. The main difference can be seen with Mn, which is one of those trace elements which was expected to occur lower in the sequence (lower volatility). This is because many studies conducted report than Mn is a relatively non volatile trace element and is expected to

reside mainly in the bottom ash (Klein *et al.* 1975; Clark, 1993; Meij, 1989; Aunela-Tapola *et al.* 1998).

A trace element volatility sequence, in the Sasol–Lurgi MK IV FBDB gasifier, was reported by Bunt & Waanders (2008). The sequence is seen below:

As < Pb < Cd < Se < Hg

By comparing the two sequences it can be seen that the volatility in both processes are similar except for Se which was determined to be more volatile than Hg in the chain grate stoker process. This difference can be attributed to differing operational conditions, quality of sampling as well as lowered combustion efficiency.

4.4.2. Trace element concentration along the path of the stoker process (RE vs Particle size)

Several studies have reported that trace element concentration increases with particle size. This is due to the fact that in combustion processes trace elements are volatilized in the boiler, where the temperature is extremely high. As they move through the process and enter regions where the temperature drops, they condense onto the surface of submicron fly ash particles (Meij, 1994; Helble, 2000; Huang *et al.* 2004).

From Table 4.5 it can be seen that most of the trace elements in the chain grate stoker process increase in concentration from the bottom ash (largest particle size) to the stack emission (smallest particle size). This is fairly consistent with results from a study by Huang *et al.* (2004) whereby he reported that most of the trace elements (Cr, Pb, Se, Zn, Cd and Hg), analyzed in his study, increased in concentration with a decrease in particle size. The only element which did

not follow this trend was Mn. However, in this study, Mn increased in concentration from the larger particles in the bottom ash to the smaller particles in the stack emission. Be, Cr and U, however, did not follow this trend whereby a decrease in particle size leads to an increase in concentration (RE).

The increase in concentration with a decrease in the particle size (bottom ash to stack emission) of certain trace elements was more evident in certain trace elements than others. Below is a graph (Figure 4.2) which illustrates the general relationship between particle size and certain trace elements.

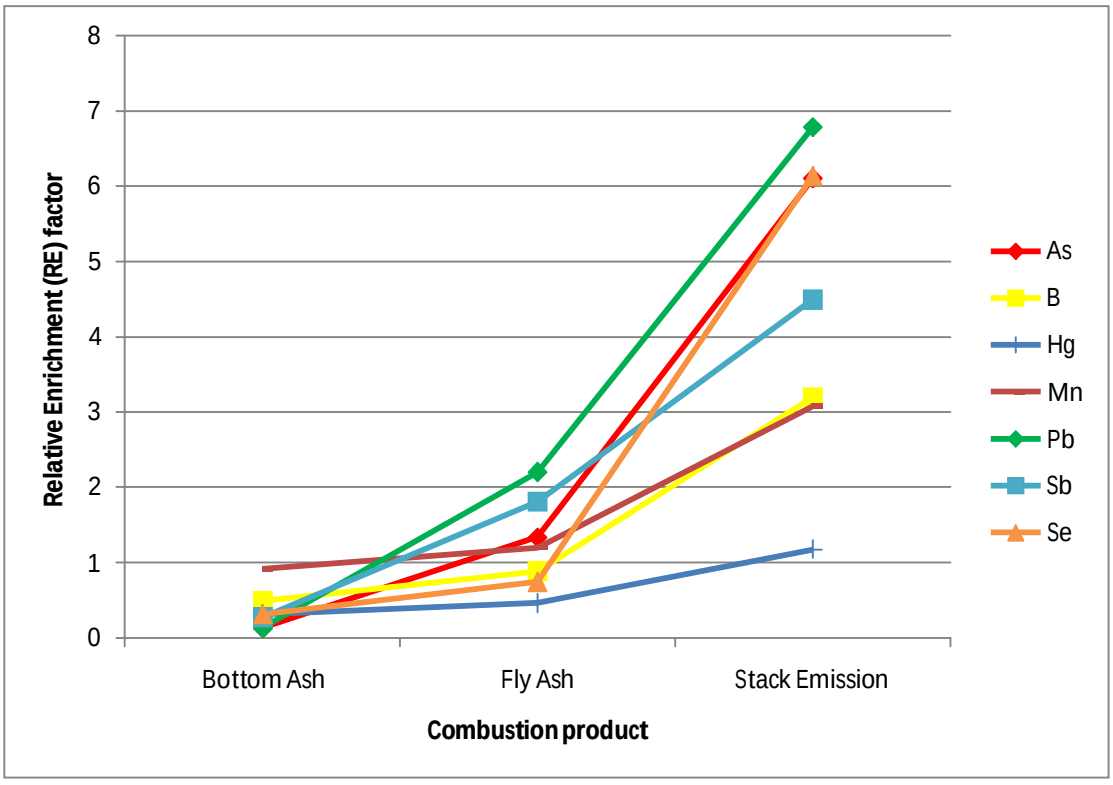


Figure 4.2: The relationship between particle size (based on combustion product) and trace element concentration (in terms of RE)

4.4.3. Mass balances

As mentioned previously, the determination of mass balances is important in determining the accuracy of the concentration results obtained from the analysis of the coal and combustion products. It is also very useful in verifying whether the partitioning of the trace elements was determined correctly. Unfortunately, there is no information (most importantly, flow rates) pertaining to the coal and combustion products which has been analyzed in this research. Therefore, the flow rates of a study conducted by Klika *et al.* (2001), in a fluidized bed power utility will be used merely to illustrate the concept of mass balance on the results from this research. There are several discrepancies which are likely to result in the trace elements mass balances not being successful (mass balances and closure ratios will be erroneous as mentioned above). Firstly, the process involved in this research is a chain grate stoker process and not a fluidized bed process. Secondly, the efficiency of the environmental control devices is likely to be different. This is because based on the results obtained in this study it was found that the efficiency of the ESP in the chain grate process was low. This was verified by the particle size distribution (PSD) which showed that particulate matter of sizes up to 17 μm were allowed to pass through the ESP into the stack (See appendix 1 for the tables containing the PSD results).

The reason for using the flow rates from another study is that the flow rates of the process under investigation are unknown; and due to proprietary issues they cannot be obtained. Also, no literature could be found on the flow rates in a chain grate stoker process. The flow rates to be used in the mass balance calculations for this study are extracted from the study conducted by Klika *et al. (*2001) and listed in the Table 4.7 below.

Mass stream	Flow rate (kg/h)
Coal	19368
Bottom ash	6327
Fly ash (ESP)	512
Stack emission	2.0

Table 4.7: The flow rates to be used in calculating the mass balances in this study

The trace element balances for each of the trace elements over the whole process were determined using the concentration values from Table 4.3 and the flow rates from table 4.7. These trace element balance values were obtained by using the equation: $Q_{ij} = q_j.c_{ij}$. Table 4.8 contains the trace element balances in all the mass streams in the process.

	Coal (mg/h)	Bottom ash (mg/h)	Fly ash (ESP) (mg/h)	Stack Emission (mg/h)	Total input (g/h)	Total output (g/h)	Closure Ratio Out/In (%)
As	78634.08	14552.1	13721.6	326	78634	28600	36
B	950968.8	651681	110080	2066	950969	763827	80
Be	45902.16	52767.18	7168	36.4	45902	59972	131
Cd	1936.8	1834.83	327.68	2.5	1937	2165	112
Co	40091.76	40239.72	7782.4	64.0	40092	48086	120
Cr	838634.4	980685	135680	624	838634	1116989	133
Hg	3873.6	1708.29	235.52	3.1	3874	1947	50
Mn	505504.8	645354	79360	1056	505505	725770	144
Ni	216921.6	335963.7	32460.8	290	216922	368715	170
Pb	265341.6	48717.9	76288	1222	265342	126228	48
Sb	5616.72	2151.18	1326.08	17.14	5617	3494	62
Se	15881.76	6959.7	1546.24	66.2	15882	8572	54
Th	106524	91108.8	10752	106.4	106524	101967	96
U	58297.68	70229.7	10137.6	41.8	58298	80410	138

Table 4.8: Element balances across the whole chain grate stoker process including totals of the ingoing streams, outgoing streams and closure ratio.

Based on the results obtained from the mass balances it can be seen that the closure ratios are completely erroneous. Due to the processes being different and the flow rates unlikely to be same, this was expected. Nevertheless, the results from Table 4.8 will be explained assuming that they were determined using the flow rates from the process in the study.

Certain trace element balances were determined with relatively good accuracy (≤20% error). These elements are: B, Cd, Co and Th. The Th mass balance was in fact determined with an accuracy of 96%,. The mass balances of the most volatile elements like As, Hg, Pb and Se were unsuccessfully determined. Their element balance closures were ≤50% with Se being the slight exception with an element balance closure of 54%. The trace element balance of Sb was also determined to be far less than 100% and showed a closure ratio of 62 %. In general, the trace elements which were determined to be most volatile were determined to have mass balance closures of far less than 100%, barring B (80%). The likely reason for this is that due to the volatility of the above mentioned trace elements, the capturing of the vapour species of Hg and Se, in particular, was not successful. Also, as mentioned previously, the vapour species collected condensed on the sides of the sampling container and not onto the particulate matter which was captured from the stack. In terms of explaining why the closure ratios of As and Pb are so low, the possible condensation of these trace elements within the ESP is a plausible reason.

Certain trace elements were determined to be much higher in the outgoing streams than the incoming streams and this is reflected by a percentage of much greater than 100%. These elements include: Be, Cr, Mn, Ni and U. A possible reason for this occurring is that coal is not the only ingoing stream. In many combustion processes lime is added to act as a desulphurization material and this lime can contain trace elements (Klika *et al.* 2001). Another possible reason is that in the ESP, these elements may have condensed within the device and when the sampling was performed the excess trace elements passed through into the ash hopper thereby raising their concentration in that ESP fly ash sample.

From the results and subsequent explanations, it is clear that mass balances are useful in determining the validity of results pertaining to trace element distribution, but they are susceptible to high degrees of error (Ratafia-Brown, 1994). In order of obtaining mass balance results which are of an acceptable standard, the concentration of the trace elements must be determined accurately, mass flow rates should be determined throughout the process and knowledge of all the incoming and outgoing streams should be known.

4.4.4. Trace element emission into the environment

Based on the results presented in Table 4.4 it is clear that the chain grate stoker process involved in this research is responsible for the release of a large concentration of trace elements into the atmosphere. Certain trace elements such as As, B, Cr, Mn, Ni and Pb are released into the environment at concentrations of greater than 100 ppm. This changes the classification (reported by Xu *et al.* 2003) of these elements, from trace elements (elements occurring in concentrations of less than 100 ppm) to minor elements (elements occurring in concentrations of between 100 ppm and 1000 ppm). It also explains for B moving further away from its classification as a trace element to a major element as it is released into the environment at a concentration of 1033 ppm. This is indicative of the severe environmental pollution associated with the combustion of coal in the chain grate process.

Owing to the lack of information on sampling, the relatively low Hg content, as compared with other volatile trace elements like B and Se, in the stack emission sample cannot be explained with total conviction. Furthermore, not knowing the flow rates of the mass streams do not enable us to determine whether the Hg mass balance is correct. Most, if not all, literature presents Hg as being the most volatile of trace elements present in coal. It is, therefore, expected that Hg should be emitted in relatively large quantities when compared to its original concentration in the coal. The probable reason for the Hg concentration in the stack emission

being low relative to a so called 'non volatile element' such as Mn is that the sampling technique used in the stack emission sampling was not successful in capturing volatile Hg vapour completely. Also, the vapour Hg could have condensed onto submicron fly ash particles which subsequently condensed on the walls of the stack. This could explain why the Hg concentration in the stack is relatively lower than expected.

Due to the inefficiency of the ESP in the chain grate process, all the trace elements studied in this research are released into the environment via the stack with varying concentrations. According to the classification system proposed by Huang *et al.* (2004), class II trace elements are enriched mainly in the fly ash, but due to the inefficiency of the ESP most of these trace elements are enriched in the stack to a greater extent than in the fly ash collected by the ESP. Furthermore, the type (cold side or hot side) of ESP installed in the plant is unknown, and based on the results it could be assumed that the ESP present in the plant is a hot side ESP. This would explain the high enrichment of class IIa elements in the stack emission. Due to hot side ESP's having a temperature of approximately 350 ^{o}C, the elements which fall into class IIa are to large extent in the vapour form at this temperature (Meij, 1994), thereby explaining their relatively high enrichment in the stack emission (they condense on particulate matter in the stack). Therefore, the combustion of coal in small industrial boilers like the chain grate stoker is responsible for emitting large amounts of toxic trace elements (belonging to all the classes) into the atmosphere. However, these emissions can be significantly decreased with the implementation of efficient environmental control devices. .

CHAPTER 5 – CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

5.1.1 Trace elements in coal

The concentration of the trace elements in the feed coal shows that most elements are present in concentrations similar to that of other South African coals. Trace element concentrations are within the global average with the exception of Hg, Cr and Th. Hg is of specific concern as it is probably the most toxic trace element.

5.1.2 Trace elements in coal to ash

The results from the research show that most of the trace elements analysed increase in concentration from the coal to the stack emission. Volatile trace elements are expected to be depleted in the bottom ash relative to the feed coal. This is observed with the trace elements, Pb and As. However, Hg and Se, which are reported as being more volatile, are present in the bottom ash at higher concentration than the feed coal. The proximate analysis gives a possible reason for this occurrence as it shows that the bottom ash contains a high percentage of fixed carbon (32.4%) as well as a small percentage of volatiles (1.6%). This indicates that unburned coal still exists in the chain grate ash indicating that this specific combustion process as studied in this research is inefficient. Therefore, large percentage of Hg and Se is present in the unburned coal in the bottom ash and at relatively high concentrations.

5.1.3 Trace element partitioning behaviour

Trace element partitioning behaviour determined in this study is similar to the results obtained in a study conducted by Meij (1994) on a pulverized fuel boiler with a few variations (See table 4.6). Furthermore, the research results indicate that all trace elements are highly enriched in the stack emission. This infers that relatively large concentrations of trace elements are released into the atmosphere from the combustion of coal in this chain grate boiler.

5.1.4 Environmental impact of trace elements

In conclusion, the results from this research indicates that the combustion of coal in smaller boiler operations such as a chain grate stoker can contribute significantly to the emission of hazardous trace elements into the environment. This occurs in particulate form and vapour form. In the current set of circumstances, this is due to the relatively inefficient environmental control devices employed in the boiler under investigation. The PSD results verify this statement by showing that particles of up to 17 μm were present in the stack emission sample which had passed through the ESP. It would appear that older industrial boilers such as the chain grate boiler studied in this research may well be emitting large concentrations of most trace elements in the ash products and therefore into the atmosphere. These trace elements are also capable of leaching into the aquatic environment from the ash dumps if the capturing, handling and disposal of the ash products is not performed correctly. Further work is therefore required to verify and address this observation.

Given that industrial boilers (chain grate) account for about 1% of the coal fired power generation worldwide, the results presented in this paper indicate that these systems release a large amount of trace elements, especially those adsorbed onto submicron fly ash particles, into the environment. Furthermore, in a South African context, it has been reported that there are more than 8000 industrial boilers in the country therefore indicating that power generation

from industrial boilers is prominent in South Africa. This indicates that environmental and health problems arising from burning of coal in industrial boilers is very significant in the country. The reason for this is that stoker boilers have a lower efficiency as compared with the pulverized fuel boilers which have replaced stoker boilers for this very reason (Johnson 2002). Furthermore, these systems are probably fitted with more primitive environmental control devices therefore only affording the capture of larger sized particulate matter with the smaller, submicron, particles passing through the stack into the atmosphere. This statement was confirmed by the PSD results obtained for the fly ash from the stack emission which show that the ESP is not efficient as particles of greater than 10 μm are present. The obvious consequence of this is that large concentrations of trace elements are emitted from the industrial boilers despite the relatively small amounts of trace elements in the feed coal coupled with smaller quantities of coal combusted as compared with pulverized fuel boilers in power stations. Therefore, it is clear that there is a need for further research of trace element distribution in industrial boiler processes as to determine the manner in which the trace elements enter the environment i.e. adsorbed onto particulate matter or vapour phase.

5.2 Recommendations and Future work

Research on industrial boiler processes such as the chain grate stoker is very important due to the environmental and health impacts associated with the release of trace elements into the environment from these boilers. Focus on the environmental impacts of industrial boilers has been very limited and this is highlighted by the serious lack of literature published on trace element distribution in industrial boilers. This is probably due to the fact that quantities of coal combusted in pulverized fuel boilers by far outweigh the quantities combusted in industrial boilers. Industrial boilers are a means of generating low cost energy so it is also safe to assume that the environmental control systems in place are not as advanced/effective as those implemented into large pulverized fuel power stations. This is evident in the results from this research which shows that most of the trace elements are highly enriched in the stack emission

relative to their concentration in the feed coal. It is therefore recommended that the following research be undertaken in future.

5.2.1 In terms of efficiency and environmental impact:-

Extensive research must be done on the distribution of trace elements in industrial processes, especially in terms of the emission of trace elements. For these types of researches to be successful, many of the uncertainties exhibited in this research need to be eliminated.

1. Firstly, an understanding of the industrial boiler process on which the study will be based on is very important.
2. The efficient combustion and burn-out of coal feedstock must be ensured.
3. The combustion temperature should be monitored and controlled as different trace elements volatilize at certain temperatures depending upon their mode of occurrence.
4. The exit temperature of the boiler which impacts on the form of the trace elements i.e. whether they remain in the vapour phase or condense onto submicron fly ash particles needs to be investigated (e.g. Hg).
5. The temperature in the stack is also very important as it can explain the enrichment of certain trace elements on particulate matter as well as the enrichment or depletion of certain trace elements in the vapour phase i.e. lower stack temperatures should lead to trace elements in the vapour phase condensing onto particulate matter.

5.2.2 In terms of the methodology, the following steps are recommended:

1. Sampling and accurate trace element analysis is the most important factor of a study on trace element partitioning and emission. Sampling of coal and combustion products should be done over a longer period of time as to lower the possible error.

2. The samples should be taken with objects which do not lead to the contamination of the samples and furthermore these samples need to be stored in suitable containers.
3. Simultaneous sampling of coal and combustion products should be performed to obtain samples which are representative of each other and that specific burning process. Sampling of the coal and combustion products should be performed over a few days with sampling undertaken more than once on each of the days in order to obtain representative samples from the process. This will give a more accurate indication of the behaviour of trace elements in the combustion process of interest.
4. It would also be ideal if sampling could be undertaken in the flowing streams rather than a stock or bunker as this would give a more representative indication of the process being studied. The most important point to remember when conducting sampling is that the sampling method employed should be representative of the burning process of interest.
5. Due to the presence of the trace elements being very low, often in the parts per million (ppm) and parts per trillion (ppt) range, the trace element concentrations in the coal and ash products need to be analyzed by certified/accredited laboratories.
6. Another important focus in terms of future research should be on the form of the specific trace elements as certain forms are toxic to living organisms whilst others are slightly toxic or benign. An example is chromium which is highly carcinogenic when in the Cr^{6+} oxidation state, but benign when present in the Cr^{3+} oxidation state.

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APPENDIX

Appendix A: Particle Size Distribution (PSD) Results

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.010	0.00	0.080	0.00	0.634	7.20	5.053	48.05	40.244	100.00	320.535	100.00
0.011	0.00	0.090	0.00	0.717	8.45	5.709	53.36	45.469	100.00	362.148	100.00
0.013	0.00	0.102	0.00	0.810	9.69	6.450	59.06	51.371	100.00	409.163	100.00
0.014	0.00	0.115	0.00	0.915	10.93	7.287	65.08	58.041	100.00	462.281	100.00
0.016	0.00	0.130	0.00	1.034	12.18	8.233	71.29	65.575	100.00	522.296	100.00
0.018	0.00	0.147	0.00	1.168	13.47	9.302	77.51	74.089	100.00	590.102	100.00
0.021	0.00	0.166	0.00	1.320	14.85	10.510	83.49	83.707	100.00	666.711	100.00
0.024	0.00	0.187	0.00	1.491	16.35	11.874	88.95	94.574	100.00	753.265	100.00
0.027	0.00	0.211	0.10	1.684	18.05	13.416	93.60	106.852	100.00	851.056	100.00
0.030	0.00	0.239	0.32	1.903	19.99	15.157	97.11	120.724	100.00	961.542	100.00
0.034	0.00	0.270	0.66	2.150	22.22	17.125	99.49	136.397	100.00	1086.372	100.00
0.038	0.00	0.305	1.14	2.429	24.78	19.348	100.00	154.104	100.00	1227.408	100.00
0.043	0.00	0.345	1.79	2.745	27.69	21.860	100.00	174.110	100.00	1386.753	100.00
0.049	0.00	0.389	2.63	3.101	30.97	24.698	100.00	196.714	100.00	1566.785	100.00
0.055	0.00	0.440	3.63	3.503	34.63	27.904	100.00	222.251	100.00	1770.189	100.00
0.062	0.00	0.497	4.76	3.958	38.69	31.527	100.00	251.105	100.00	2000.000	100.00
0.070	0.00	0.561	5.96	4.472	43.16	35.620	100.00	283.704	100.00		

The PSD results (determined by Tsebo Molapo) presented above show that particles of 17.125 µm were present in the stack emission sample.