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EXTRACTION OF URANIUM ASSOCIATED WITH SPRINGBOK FLATS COAL SAMPLES

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A dissertation submitted to the Faculty Engineering and the Built Environment, University of the Witwatersrand, in fulfillment of the requirements for the degree of Master of Science

June 4, 2015

DECLARATION

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

_____

(Signature of Candidate)

_____Day of_____2015

ABSTRACT

The presence of coal in the Springbok Flats Coalfield (SFC) has been known since the beginning of the 1900's. The SFC has not been mined to any degree of economic profit, in part because of the presence of uranium (U) present in the coal. The motivation behind this study is the limited research on the amount of U that is associated with coal, as well as the quality of coal that is associated with the U. Concurrently, there is limited research focusing on the leaching of U from southern African coals in separating the two commodities.

Five boreholes (BH) were drilled in the SFC (BH1 to BH5); BH5 had two coal zones, an upper coal zone (UCZ) and a lower coal zone coal (LCZ). Coal samples were collected, selected and characterized. The U content in the coal samples was determined using Inductively Coupled Plasma Mass Spectrometry, Instrumental Neutron Activation Analysis, and X-Ray Fluorescence. Thereafter, coals with U content greater than 10 mg kg^{-1} were selected, and an extraction/leaching process was applied using sulfuric acid.

Coal samples from BH1, the UCZ in BH5, and the LCZ in BH5 has an ash content over 50% average. These boreholes samples were considered to be primarily carbonaceous mudstones. BH2 resembled a typical South African bituminous coal, recording a carbon content ranging from 27.88% to 65.28%, averaging 44.6%; volatile matter and calorific values averaged 24.3% and 18.2 MJ/kg respectively. BH3 and BH4 had horizons with relatively good quality coal, where the carbon content and volatile matter averaged 38% / 39.7% and 22.4% / 15.1% respectively. BH3 had the highest U content average of all the borehole coal zones, registering 33 mg kg^{-1}, followed by BH2 (26 mg kg^{-1}) and BH1 (14 mg kg^{-1}). BH4, the UCZ in BH5, and the LCZ in BH5 all had U content averages less than 10 mg kg^{-1}. 11 samples containing U content higher than 10 mg kg^{-1} were selected for leaching. The samples were successfully leached with U content ranging from 4 μg L^{-1} to 1789 μg L^{-1} obtained in the leachates. Three samples with a U content higher than 50 mg kg^{-1} were selected to be leached under optimal conditions; U extraction increased under optimal conditions. The highest increase in U content was 106% from 1186 μg L^{-1} to 2438 μg L^{-1} leached into solution. Cake results displayed the U was successfully extracted using sulfuric acid, reaching a maximum of 50.7%, when leached at 5 M, and a 67.3% maximum when sample were leached at 10 M.

DEDICATION

For you my loving father, brother and fiancé

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TABLE OF ABBREVIATIONS

Abbreviation	Meaning	Abbreviation	Meaning
ASTM	American Society for Testing and Materials	ICP-MS	Inductively Coupled Plasma Mass Spectrometry
BA	Bottom Ash	INAA	Instrumental Neutron Activation Analysis
BH	Borehole	IRP	Integrated Resource Plan
C	Carbon	ISO	International Organization for Standardization
CGS	Council For Geoscience	LCZ	Lower coal zone
CO_2	Carbon dioxide	LOI	Mass lost on ignition
CSIR	Council for Scientific and Industrial Research	$MgClO_4$	Magnesium perchlorate
CV	Calorific Value	N	Elemental nitrogen
DMR	Department of Mineral Resources	NaoH	Sodium hydroxide
DOE	Department of Energy	NCV	Net calorific value
FA	Fly ash	NECSA	Nuclear Energy Corporation of South Africa
FC	Feed Coal	NMR	Nuclear magnetic resonance
GCV	Gross calorific value	NO_x	Nitrogen oxides
H	Elemental hydrogen	O	Elemental oxygen
H_2O	Water	Penn State	Pennsylvania State University
HNO_3	Nitric acid	PWR	Pressurized water reactor
HCl	Hydrochloric acid	RF	Radio Frequency
HF	Hydrofluoric acid	SA	South Africa

SABS	South African Bureau of Standards	UCZ	Upper Coal Zone
SAPA	South African Press Association	UJ	University of Johannesburg
SAPP	Southern African Power Pool	U	Uranium
SFC	Springbok Flats Coalfield	USGS	United States Geological Survey
SO_2	Sulfur dioxide	USEIA	United States Energy Information Administration
SRM	Standard reference material	WITS	University of the Witwatersrand
SX	Solvent extraction	XRD	X-Ray Diffraction
TC	Thermal conductivity	XRF	X-Ray Fluorescence
TGA	Thermogravimetric analysis		

CHAPTER ONE: INTRODUCTION

1.1 PROJECT BACKROUND AND OVERVIEW

The Springbok Flats Coalfield (SFC) is situated in the Limpopo Province, approximately 30 km north of Pretoria overlapping the districts of Waterberg and Polokwane. Figure 1.1 displays the uppermost part of the Hammanskraal Formation that consists of interbedded carbonaceous shale and coal, reported here as the coal zone (Sanderson, 1997). The coal seams in the SFC have thicknesses of 5 – 8 m, and can go up to 12 m. For the most part, the coal is comprised of bright coal with low ash content, which is a good coking coal for export as well as local metallurgical industries (Christie, 1989).

The coal zones in the central and the north-eastern parts of the basin have significant uranium (U) content. The U is hosted in the coal in the Late Permian, uppermost part of the Hammanskraal Formation within the SFC basin (Cole, 1998). The U in the SFC is disseminated throughout the coal and the carbonaceous shale, with U phases having grain sizes of less than 20 microns (Cole, 2009).There is limited research pertaining to the amount of U that is associated with coal. At the same time there is limited research focusing on the leaching of U from coal, which is important in determining the characteristics of the coal and U resources in the coalfield, and in determining the extent to which the two commodities could potentially be separated from each other.

Effective separation of U from the coal in the SFC using leaching methods could be considered as a beneficiation method for both coal and U when the two commodities are in association. The Department of Mineral Resources (DMR) has seen a need for South African coal researchers and metallurgists to conduct research for cleaner coal processing and energy production, and have thus created intervention strategies for the optimal beneficiation of coal (DMR Beneficiation Strategy, 2011), which, amongst numerous other objectives, seeks to invest in metallurgical research to disentangle U and coal in the SFC, in an effort to increase the country's reserve base of coal and U.

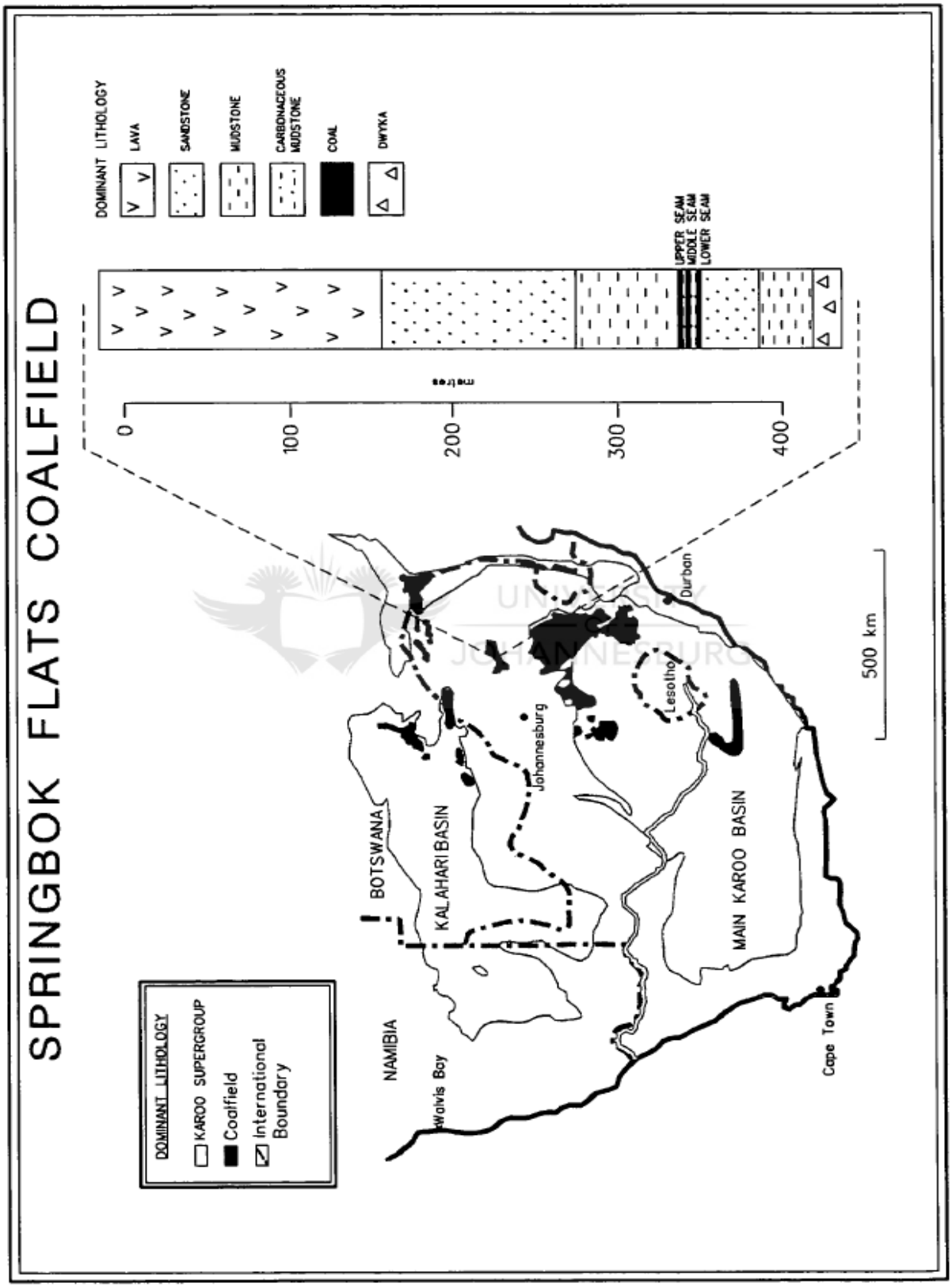


Figure 1. 1: Stratigraphic column of the Springbok Flats Coalfield (Sanderson, 1997)

The aim in this study was to assess the chemical and mineralogical characteristics of selected borehole core samples from the SFC coal zones, and to determine the possibility of using sulfuric acid for economic extraction of U from the SFC coal samples. The chemical characteristics of the coal samples were studied by proximate and ultimate analyses, which are the basic accepted characterization techniques used to determine coal quality. The mineralogical characteristics of the SFC samples were studied by X-Ray Fluorescence (XRF) to determine the inorganic component of the coal, and X-Ray Diffraction (XRD) analysis was used to determine the mineral phases present in the coal samples. XRF and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) were used to quantify the U that is hosted in the coal zone. Instrumental Neutron Activation Analysis (INAA) was used to determine the U isotope, and to confirm U content results from ICP-MS and XRF. Thereafter, coals with high amounts of U were selected and an extraction/leaching process was applied using an acid medium,

Success of this project could increase the coal and /or U resources that South Africa has for future utilization, and may assist in the economic growth of the country. Currently the energy industry does not have an extraction method for U in coal. U could be utilized for nuclear power generation (produces less greenhouse gases than fossil fuel power generation), and the coal could be exported (providing valuable revenue), or used in energy sector (thus extending South Africa's coal reserves).

1.2 COAL FORMATION

Coal is a combustible fuel credited with being the largest source of energy worldwide. South Africa's coal based processes produce 90% of the domestic primary energy and the country is one of the largest coal producers in the world (Kalenga, 2011; Koper, 2004). The United States Energy Information Administration (USEIA) loosely defines coal as a readily combustible, black or brownish-black rock whose composition, including inherent moisture, consists of more than 50% by weight carbon and more than 70% by volume of carbonaceous material (Index Mundi, 2014)

Coal is formed from plants, grown in swampy environments tens of millions of years ago. The presence of water hindered the supply of oxygen and allowed thermal and bacterial decomposition of plant material to take place, inhibiting the completion of the carbon cycle (Limanto, 2014). Under these conditions of anaerobic decay, in the biochemical stage of coal formation, a carbon-rich material called peat formed, which became pressed and compacted through pressure and time (Limanto, 2014). When one compares coals on a global context, southern African coals have been found to be rich in minerals, relatively hard to beneficiate and differ greatly in rank and organic matter composition (Falcon and Ham, 1988). Differences between northern hemisphere (Laurasian) and the southern hemisphere (Gondwana) coals are due to conditions reigning at the time the coal was formed, and to the geological events that took place in each region (Falcon and Ham, 1988). Gondwana land conditions led to mineral-rich peat, which formed relatively thick coal seams with time. The shallowness of burial during these times have resulted in southern African coals being close to the surface when compared to their Laurasian counterparts (De Wit *et al.*, 1988; Scotese, 1990)

The degree of coalification undergone by a coal, as it matures from peat to anthracite, is referred to as the 'rank' of the coal. Table 1.1 gives the coal rank in terms of carbon and moisture content. Low rank coals, are characterized by high moisture levels and a low carbon content, and hence a low energy content. Higher rank coals are accompanied by a rise in the carbon and energy content and a decrease in the moisture content of the coal.

Table1. 1: Coal rank classification (Limanto, 2014)

Rank:	Lignite	Subbituminous	Bituminous	Anthracite
% Carbon:	65-72	72-76	76-90	90-95
%Water:	70-30	30-10	10-5	~5

1.3 COAL IN SOUTH AFRICA

An in-depth look at the coal deposits of South Africa is beyond the scope of this project, Herbert Kynaston effectively began research on coal deposits in South Africa in 1906, when research was conducted in the Komatipoort coalfield (Cairncross, 2001). Since then many rigorous studies have been conducted into the Karoo basin coals to properly characterize and quantify the coal reserves and resources of the country (Cadle *et al.,* 1993; Cairncross, 1989; Cairncross, 1987; Christie, 1989; Falcon and Ham, 1988; Falcon and Snyman, 1986; Snyman and Botha, 1993; Snyman *et al.,* 1984). This section deals mostly with coal production in South Africa, particularly the relative production figures of the country compared to the world. The section also gives insight into the supply of energy as well as energy requirements of the country, looking particularly at the current energy generated from coal, and the nuclear sector. Finally, the section introduces the study area for this project.

1.3.1 COAL PRODUCTION AND EXPORT IN SOUTH AFRICA

South Africa is at the forefront of coal production in the world, and plays a significant role in global coal markets. However, South Africa is not the biggest role player when it comes to coal; China, USA, and India are much larger producers and consumers of coal (Eberhard, 2011). In previous years, South Africa has slipped in terms of hard coal production, and now sits sixth behind China, USA, India, Australia and Indonesia (Eberhard, 2011). South Africa has the world's biggest coal export terminal, the Richards Bay coal terminal, and is conveniently positioned between the Atlantic and Pacific coal markets.

One of the biggest problems hindering the growth of the coal industry is the lack of planning and investment coordination between the privately owned mines, state owned rail infrastructure, and port capacity (Pooe and Mathu, 2011). Tables 1.2 and 1.3 show the largest coal producers and exporters in the world.

Table1. 2: Global hard coal production (Eberhard, 2011)

Producers	Million tonnes coal equivalent/annum
China	2 971
USA	919
India	526
Australia	335
Indonesia	263
South Africa	**247**
Russia	229
Kazakhstan	96
Poland	78
Columbia	73
Rest of the world	**253**
World Total	**5990**

Table1. 3: Global hard coal exports (Eberhard, 2011)

Producers	Million tonnes coal equivalent/annum
Australia	2262
Indonesia	230
Russia	116
Columbia	70
South Africa	**67**
USA	53
Canada	28
Vietnam	26
China	23
Kazakhstan	23
Rest of the world	**47**
World Total	**944**

South Africa has between 15-55 billion tonnes of economically recoverable coal reserves; 96% is bituminous coal; metallurgical coal accounts for 2% and anthracite accounts for another 2% (Bredell, 1987; De Jager, 1982; Petric Commission, 1975). The exact estimate differs based on the estimation procedure, BP statistical review of world energy (2014) reported that coal reserves in the country are at 30.2 billion tonnes, and Hartnady (2010) estimated 15 billion tonnes remaining.

Around 80% of sellable coal in South Africa is supplied by mines under the five largest mining groups, namely: BHP Billiton, Exxaro, Sasol, Anglo Thermal Coal, and Xstrata, with the rest of the pie taken by smaller black empowerment miners (Pooe and Mathu, 2011). DMR reported almost 75% of the coal produced in South Africa is used domestically, for electricity generation by ESKOM power plants, and for liquid fuels by Sasol, the rest is exported (Pooe and Mathu, 2011).

Over the past years, ESKOM has not increased its spending on coal based power production appreciably and as such, the country continues to experience power outages (Jacks, 2015; Pooe and Mathu, 2011; SAPA, 2015). Lok (2009) theorized that in the next decade, while South Africa will increase coal production by 75 Mt, the coal production will be sluggish, and the energy supplier (ESKOM) will not be able to meet energy requirements. Table 1.4 shows the coal consumption by ESKOM; over 5 years, ESKOM only increased consumption by 16.48 Mt, lower than the value estimated by Lok (2009), and the effects of this lack of production increase has been felt by many South Africans (Jacks, 2015), with the rand even taking a tumble due to the power cuts experienced (Brownlee, 2015). Hartnady (2010) claimed that the lack of reinvestment by involved parties will lead to most mines closing down or being depleted by 2020.

Table1. 4: ESKOM Coal consumption (Pooe and Mathu, 2011)

Year	Million Tonnes (Mt)
2005	106.3
2006	108.75
2007	112.17
2008	125.30
2009	121.16
2010	122.78

1.3.2 ENERGY SUPPLY IN SOUTH AFRICA

Electricity consumption in South Africa has been rising since 1980. The total installed power generating capacity in the Southern African Power Pool (SAPP, includes SA.) countries is 54.7 GWe, of which around 80% is South African (SAPP statistics, 2008). ESKOM supplies around 95% of the country's electricity, 90% from coal based processes and 5% from nuclear energy: the balance is hydroelectricity (Integrated Electricity Resource Plan (IRP), 2011). South Africa has one nuclear plant at Koeberg, close to Cape Town, built in part due to inefficiencies of transporting coal from Mpumalanga over long distances. The nuclear plant, commissioned in 1984-1985, is made up of twin pressurized water reactors (PWRs), that have a 970 MWe and 940 MWe gross capacities (World Nuclear Association, 2014). The government proposed to expand Koeberg's life of operation from 30 to 40 years, by including six new steam generators, to be installed at the plant in 2017-2018 (World Nuclear Association, 2014).

The Department of Energy (DOE) released its IRP for 2010-2030, which details that South Africa's power breakdown by 2030 should include: 48% coal, 13.4% nuclear, 6.5% hydro, 11% open cycle gas turbines, and 14.5% other renewables (IRP, 2011). Since then, South Africa has signed agreements with Russia, France, China, and South Africa's Standard Bank group for various reasons, including financing new nuclear plants, access to technologies and infrastructures, and building bi-lateral relationships for future collaborations between countries (World Nuclear Association, 2014).

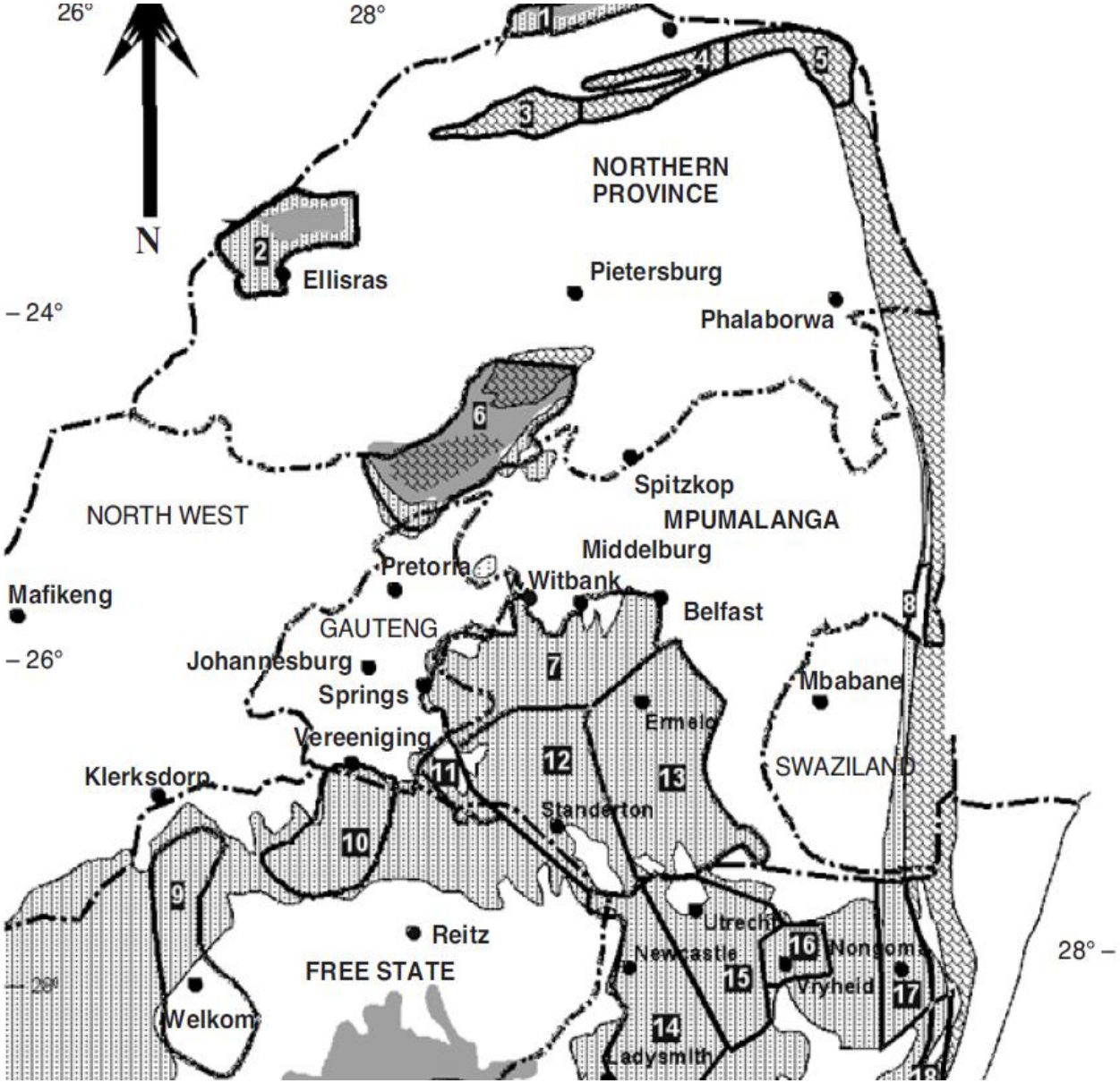
Presently, due to the country's increasingly focus on industrialization, and electricity being placed in more homes since democracy (from 50% of population in 1994 to 86% in 2011), electricity consumption in the country has inevitably risen. This in turn, has placed pressure on ESKOM to build more power stations to deal with the demand (SA News, 2014). As it stands, ESKOM has to enforce load shedding (a process where electricity supply is interrupted to avoid excessive load on the generating plant), for numerous reasons; in some cases, coal quality and plant availability have decreased, impacting plant performance and requiring additional maintenance, and shut off of an already overburdened system. Other factors have included prolonged rain causing wet coal and logistical disruptions such as a delay in fuel supply to power stations (Matona, 2014).

1.3.3 STUDY AREA: THE SPRINGBOK FLATS COALFIELD

Coal in South Africa is found in 19 coalfields located in the northern part of the country (Figure 1.2). The main coal mining areas in the country presently are in the Witbank-Middleburg, Ermelo and Standerton-Secunda areas of Mpumalanga. The Sasolburg-Vereeniging area in the Free State/Gauteng, and northern Kwa-Zulu Natal are other areas in the country where smaller coal utilization processes are found. The SFC is one of the coal areas present in the country. According to Roberts (1992),the SFC is assigned to the Turfan and Warmbad Formations, where the Turfan Formation consists mostly of high ash coal of no major economic value, contrasted to the 12 m thick Warmbad Formation which can be targeted for economic interest.

The presence of coal in the SFC has been known since the beginning of the 1900's with extensive drilling in the basin having taken place between 1952 and 1970's (Christie, 1989). The first coordinated exploration programme was conducted by the Council for Geosciences (CGS), between 1952 and 1957 where 27 boreholes were drilled in the north eastern portion of the coalfield, by Visser and Van der Merwe (1959). The results of the exploration were regarded mainly as unpromising in terms of low coal quality. Further exploration by the CGS between 1970- 1972 in the western and south-central portions of the coalfield, resulted in trace U detection in the upper Ecca coal zone (Christie, 1989).

The SFC coal seams are hosted in Permian aged rocks of the Karoo Supergroup, formed as part of the Beaufort group (Cairncross, 1987). In terms of the tectonic framework, during this age, Gondwana was part of Pangea when relative movements between Gondwana and Laurasia led to the ultimate breakup of Pangea and Gondwana (De Wit *et al.,* 1988; Scotese, 1990). Permian Gondwana coal types have been very different from the carbonaceous Laurasian coals, due primarily to the post glacial climatic setting under which Permian coals originated (Cairncross, 2001; Crowell and Frakes, 1975) and to some extent, due to the premature peat exposure to oxidation resulting in non-reactive inertinite found in Gondwana coals (Falcon and Snyman, 1986; Hunt and Smyth, 1989)



Name of Coalfields

1. Limpopo (Tuli)
2. Waterberg (Ellisras)
3. Soutpansberg West (Mopane)
4. Soutpansberg Central (Tshipise)
5. Soutpansberg East (Venda-Pafuri)
6. Springbok Flats
7. Witbank
8. Kangwane
9. Free State
10. Vereeniging-Sasolburg
11. South Rand
12. Highveld
13. Ermelo
14. Klip River
15. Utrecht
16. Vryheid
17. Nongoma
18. Somkhele
19. Molteno-Indwe

Figure 1. 2: Coalfields in South Africa (Jeffrey, 2005)

Due to the presence of significant quantities of coal and U present, the geology of the SFC has been characterized by numerous studies (Christie, 1989; Du Toit, 1954; Johnson *et al.,* 2006; Nel, 2012; Roberts, 1992; Visser and Van Der Merve, 1959). The basement of the SFC is composed of granites and felsites as well as older metasedimentary rocks of the Transvaal Supergroup. In some areas, the Dwyka group forms part of the basal part of the Karoo Supergroup with the Ecca group deposited directly onto the Dwyka lithologies (Hancox and Gotz, 2014)

The Ecca Group was initially subdivided into three lithological units known as the Lower Coal Bearing Unit, the Middle Ecca "Coal Measures" unit, and the Upper Coal Bearing unit (Du Toit, 1954). However, with time; researchers have chosen to split them into the Turfpann, Warmbad and Merinovlakte Formations. Johnson *et al.* (2006) chose to group all formations into one formation which he termed the Hammanskraal Formation recognizing the Upper Coal Zone (UCZ) and Lower Coal Zone (LCZ). According to Roberts (1992), the coal zones consist of alternating bands of vitrain and carbonaceous mudrock on a millimeter scale. Individual seams hardly exceed 1 m in thickness, and the coal zone thickness ranges from 0 to 12 m, containing a typical coal content of around 30-40%. In the north and north-west parts of the basin, the coal zone is uniformly thin or absent compared to the southwest, which has a succession that is relatively thin and more consistent (Roberts, 1992).

From the bottom upwards, coal seams have been termed the Lower Seam, Middle Seam and Upper seam (Hancox and Gotz, 2014). The lower seam is generally poorly developed, and is of little economic interest. The middle seam, which lies just above the lower seam, is the primary coal resource target, divided into the Lower Middle Seam and Upper Middle Seam by carbonaceous shale parting intercalated with coal bands (Hancox and Gotz, 2014). In some places, specifically the northern and western parts of the Tuinplaats region, the parting is thin and the entire Middle Seam is potentially mineable (Hancox and Gotz, 2014).

1.4 URANIUM OCCURRENCE IN COAL IN THE SFC

Coal, similar to most materials in nature, contains small quantities of naturally occurring prehistoric radionuclides such as ^{40}K, ^{238}U, ^{232}Th, and their decay products (Papastefanou, 2010). In the SFC the upper part of the coal zone occurs where overlaying sediments of the Molteno stage are coarser grained and permeable (Nel, 2012). Linning *et al.* (1983) drew a correlation between pebble grain size and mineralization of U by reporting that U mineralization tended to be highest in places where maximum pebble sizes of the Molteno sediments were encountered. The report also noted that areas of the Beaufort series where U grade was highest coincided with areas that had maximum pebble size of the Molteno Stage. In all probability, Linning *et al.* (1983) reports that U was derived from granite rocks decomposition and then transported in solution during the Molteno stage to areas where the coal had been deposited into what was still peat forming environments.

According to Nel (2012), Breger (1974) theorized that U in coal cannot be attributed to the inherent initial U content in plants; Nel (2012) proposed three hypotheses for the origin of U in coal as follows:

1. U was deposited from surface water by living organisms or other organic matter at the same time as the carbonaceous debris from which the lignite was formed;
2. U was deposited with other detrital minerals in sediments form, which later leached and precipitated from solution;
3. U is epigenetic, after being extracted from ground water by lignite after coalification, it is said that U was derived from outside the peat depository

Nel (2012) concluded that the epigenetic origin of U (U was deposited later than the surrounding or underlying rock formation) is widely accepted as the mechanism in which U was deposited into the coal, as supported by numerous other researchers (Breger *et al*., 1955; Hambleton-Jones, 1976; Nekrasova, 1958). During epigenetic introduction of U solutions into coal beds, U was readily adsorbed if the pH was slightly acidic (Nel, 2012). The natural laws which govern the deposition of U onto coal and other organic rich sediments are caused by humic acid content. Nel (2012) stipulated that humic extracts and indigenous humic matter played an independent major role in

the deposition and precipitation of U into coal. The same sentiments are found in Boyle (1982).

1.5 PROBLEM STATEMENT

The SFC has not been mined to any degree of economic profit, in part because of the presence of U in the coal. There is limited public domain information about the amount of U that is associated with coal, as well as the quality of coal that is associated with the U. Concurrently, there is limited research focusing on the leaching of U from southern African coals in an effort to separate the two commodities and potentially pursue one or both energy creators.

1.6 AIMS AND OBJECTIVES

1.6.1 AIM

The general aim in the project is to assess the feasibility of extracting U from selected SFC coal samples using acid leaching.

1.6.2 OBJECTIVES

The following specific objectives were set for the project

- Obtain 5 freshly drilled SFC borehole cores
- Characterize the coal samples using chemical techniques
- Quantify U present in coal samples using ICP-MS, XRF, and INAA and Identify the type of U isotope by INAA
- Employ an acid medium to leach U and quantify U content post leaching in leachates
- Determine the effect leaching time, temperature and pH has on U extracted into solution and determine the viability of using sulfuric acid to leach U in the coal samples

CHAPTER TWO: LITERATURE REVIEW

In this chapter, the techniques used to evaluate coal properties, the various elements in coal, the significance of these elements in coal combustion, and the effects of coal compounds and combustion products on the environment are given. It also includes the techniques used to evaluate U content in coals, the different isotopes of U detectable, and leaching of U from coals and coal ashes. Each subsection is concluded by mentioning studies conducted (preferably in the SFC) on that subject.

2.1 TECHNIQUES USED TO EVALUATE COAL PROPERTIES

The properties of a specific coal determine its utilization potential. These properties include chemical, physical, plastic, and specialized properties, determined using various testing methods. The chemical properties of coal can be ascertained using proximate analysis and ultimate analysis. Physical properties are found through the determination of the specific heat, specific gravity, petrographic data, and angle of repose, porosity, density, and the hard grove grindability index. Plastic properties include the free swelling index of coal, the Gray-King Low temperature essay and the caking index (Mishra, 2009) with the latter properties relevant specifically in the metallurgical industry.

2.1.1 CHEMICAL PROPERTIES OF COAL

Understanding the chemical properties of coal is important for researchers since the determination of coal quality is controlled by the moisture, volatile matter and carbon content of the coal (Sciazko, 2013). Samples are studied either as received, or after removing the inherent moisture by drying the samples at 100^{o}C-105^{o}C, and recording the mass loss. In most cases, low rank coals are studied on an as received basis, since free air drying of low rank samples may promote oxidation responsible for self-heating and spontaneous combustion, while also emitting harmful greenhouse gasses (Mishra, 2009; Wang *et al.*, 2003).

2.1.1.1 PROXIMATE ANALYSIS

Proximate analysis is an analytical technique used to determine the moisture, volatile matter, ash, and fixed carbon content present in coal. The moisture content is represented by the loss in weight of the sample after it had been heated to 110^{0}C for approximately 4 hours (Penn State, 1992). The moisture is an undesirable component of coal as it reduces the heating value, because water doesn't burn and its weight adds to the transportation costs of coal. The volatile matter content accounts for hydrocarbons, methane, hydrogen and carbon monoxide present in coals. In furnaces and small industrial appliances, coals containing large amounts of volatile matter are easy to ignite, but such coals tend to burn out quickly (Penn State, 1992).

Ash is the non-combustible residue originating from the mineral constituents of the coal. It is important to understand the impacts of ash content in the design of the furnace grate, combustion volume, pollution control equipment and ash handling systems of a furnace. Coals with high ash content are highly undesired, because ash storage and disposal is problematic for companies, due to the toxic elements present in coal ashes such as arsenic, lead, barium, cadmium, mercury and nickel (Gottlieb *et al.,* 2010*)*

Numerous studies have been conducted on the quality of coal in SFC. De Jager (1983) assumed 25-30% ash in raw bituminous coal and between 40-35% ash content in in-situ mineable coals. The Petric Commission (1975) estimated a 30-35% ash content in raw in-situ mineable similar to De Jager (1983). It was also estimated that the ash content should decrease to 22-30% after beneficiation providing a saleable reserve that is 22-30% ash (Petric Commission, 1975).

Proximate analysis data from Nel (2012) showed that the coal in the SFC Tuinplaats region contained 2.1% H_2O, 27.8% ash and 30.2 % volatile matter. The ash content is low and the volatile matter is high enough to meet the requirements of a coal used in South Africa for electricity generation (Pinhiero, 1999).

The CGS has data from over 16000 boreholes with analytical data in its database. The database covers almost the entire basin; there are however gaps in information of some areas in the basin. Three of the five boreholes (Roodevlakte 558 KS, Kroomdraai 626 KR and Wolfhuiskraal 626 JR) studied in this research has analytical data present in the database. Table 2.1 gives the average moisture, volatile matter, fixed carbon and ash content of coal samples present in the CGS database.

Table 2. 1: Proximate analysis data for samples from SFC farms (CGS database)

	H_20	Ash%	Volatiles	Fixed carbon
Roodevlakte	2.3	45.7	23.3	28.6
Kroomdraai 626 KR	2.1	42.6	23.6	31.7
Wolfhuiskraal 626 JR	4.6	39.5	21.0	34.9

Proximate results were also reported by Linning *et al.* (1983); an average moisture content of 2.05% for samples in Tuinplaats 678 KR was reported, the ash content was low (29.1%), the fixed carbon content was high at 40.15%, and the volatile matter content was relatively high (28.7%).

Table 2. 2: Proximate analysis of samples reported in Linning et al., (1983)

	H_2O (%)	Ash (%)	Vol matter (%)	Fixed carbon (%)
Tuinplaats 678 KR	2.05	29.1	28.7	40.15
Kalkbult 139 JR	2.4	35.1	26.6	35.9

Samples obtained from Kalkbult 139 JR recorded slightly higher moisture and ash content than samples from the Tuinplaats 678 KR farm. The volatile matter and fixed carbon content were slightly lower than those reported for samples from Tuinplaats 678 KR. Thus, based on the proximate analysis, it could have been concluded that the coals in Kalkbult 139 JR were probably of poorer quality when compared to the ones from Tuinplaats 678 KR.

2.1.1.2 ULTIMATE ANALYSIS

The ultimate analysis of coal concentrates on determining by weight percentage, the composition of coal, in terms of carbon, sulfur, nitrogen, hydrogen, and oxygen. This is an important coal quality determination technique, as it provides the carbon content, which is by far the principal source of heat, releasing around 33,727 kilojoules per kilogram (Hong and Slatick, 1994). The carbon found in coal represents organic carbon as well as any carbon present as mineral carbonate. It also gives an indication of the carbon dioxide that will be produced during combustion when a carbon atom reacts with two oxygen atoms according to reactions 1 and 2

$2C + O_2 \rightarrow 2CO$ ……..eq1

$2CO + O_2 \rightarrow 2CO_2$ ……..eq2

The hydrogen content represents the hydrogen observed as organic material, as well as all the hydrogen associated with the water compounds present in the coal. Although hydrogen is known to produce more energy than carbon (144,212 kJ/kg for hydrogen compared to 33,727 kJ/kg for carbon), hydrogen accounts for only 5% or less of the coal content, and not all the hydrogen is available for heat generation, as some of it will combine with oxygen and form water vapor (Hong and Slatick, 1994) .

The sulfur content is a combination of the different forms of sulfur found in coal, these being inorganic sulfides such as pyrite and marcasite, organic sulfur compounds, and inorganic sulfates such as Na_2SO_4 and $CaSO_4$. The sulfur content also indicates the pollutant level that will occur during the combustion process as SO_2. Since SO_2 is the single dominant oxide formed during combustion (eq3), it can be predicted with reasonable accuracy from the coal properties, the extent to which the coal will contribute towards emission of SO_2 and the inevitable contribution towards acid rain (Moretti & Jones, 2012). For this reason, understanding sulfur content is crucial to utilization companies, as emission penalties are imposed by most governments.

$S + O_2 \rightarrow SO_2$ ……eq3

The total sulfur content in coals varies from 0.3 up to 15% by weight according to the rank and the origin of coal (Kalenga 2011). The average sulfur content in South African coals is less or equal to 1% by weight (Gonenc *et al.*, 1990). World coals have been reported (Hsieh and Wert, 1985) to range from 0.59-9.45% in sulfur content, with South African coals having a total sulfur value of 0.4-1.29% (Wagner and Hlatshwayo, 2005) and 1.47% (Roberts, 2008)

The most detrimental effect that comes from nitrogen bound within coal is in the emission of NO_2 during combustion. Once in the atmosphere, the NO_2 is involved in a series of reactions that form secondary pollutants. The NO_2 can react with sunlight and hydrocarbons to produce ground level ozone/photochemical (urban) smog, acid rain constituents, and particulate matter (Moretti & Jones, 2012). NO_2 is associated with respiratory disorders, corrosion of materials and damage to vegetation. It seems logical to assume that the nitrogen content in coal, and the way in which it is bound into the coal structure, would affect the amount and distribution of nitrogen oxide emissions.

Nel (2012) conducted ultimate analysis on samples from the northern, southern and Tuinplaats regions in the SFC. Table 2.3 shows the results acquired.

Table 2. 3: Ultimate analysis on SFC (Nel, 2012)

Coal resource	Sample name	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen
Northern	Raw	50.70	3.60	0.83	1.93	8.06
Southern	Raw	50.00	3.50	0.98	2.42	6.88
Tuinplaats	Raw	51.00	3.60	1.00	2.69	6.92

The sulfur content is the only ultimate analysis constituent that is provided in the CGS database. Table 2.4 gives the average values of sulfur from the available farms. The sulfur content is comparable from the farms to be studied, the highest being in the Kroomdraai farm and the lowest from the Wolfhuiskraal farm, but the difference is minimal.

Table 2. 4: Sulfur content of samples in CGS database from SFC farms

Farm name	Average sulfur content (%)
Roodevlakte 558 KS	2.82
Kroomdraai 626 KR	2.83
Wolfhuiskraal 626 JR	2.18

Linning *et al*. (1983) conducted studies of the SFC included a few hundred boreholes, with two of the five farms studied in this research involved (Tuinplaats 678 KR and Kalkbult 139 KR). Table 2.5 gives the analytical data found in the report from these two farms. Samples from the Tuinplaats 678 KR farm had a 2.82% sulfur average similar to samples from the Roodevlakte 558 KS, and samples from the Kroomdraai 626 KR farm recorded in the CGS database. Samples from the Kalkbult 139 JR farm recorded 2.43% average sulfur content closer to the results reported for the Wolfhuiskraal 626 JR farm; however all the results from the 5 farms did not exhibit sulfur content higher than 2.9%.

Table 2. 5 Sulfur content of samples reported in Linning et al., (1983)

Farm name	Average sulfur content (%)
Tuinplaats 678 KR	2.82
Kalkbult 139 JR	2.43

2.1.2 PHYSICAL PROPERTIES OF COAL

A detailed investigation into the physical factors such as the density, specific gravity, porosity, angle of repose, coal petrography, and the hard grove index are beyond the scope of this project; however these subjects have been well covered in literature (Bai *et al*., 2013; Chelgani *et al.,* 2008; Hefta *et al.,* 1986; Hower and Calder, 1997; Hower *et al.,* 2012; Kasperczyk, 1974; Lopez-Peinado *et al*., 1989; Malumbazo *et al.,* 2011; Mastalerz *et al*., 2012; Van Niekerk *et al.,* 2009; Wang *et al.,* 2010,). Calorific value will be discussed in some detail.

2.1.2.1 CALORIFIC VALUE (CV) OF COAL

The CV of coal is the amount of heat released during the combustion of a specified amount of coal. The CV is uniquely characteristic for each substance. It is measured in units of energy per unit of the substance, usually mass, such as MJ/kg. Heating value is commonly determined by use of a bomb calorimeter. The CGS database has Cv data for boreholes drilled in three of the five farms studied in this research:Roodevlakte (22.84 MJ/kg), Kroomdraai 626 KR (18.52 MJ/kg) and Wolfhuiskraal 626 JR (17.32 MJ/kg). Linning *et al.*, (1983) reported CVs for two farms included in this research; Tuinplaats 678 KR (23.2 MJ/kg) and Kalkbult 139 JR (20.8 MJ/kg). Nel (2012) reported a CV of 23.5 MJ/kg for the Tuinplaats region.

De Jager (1983) estimated that raw in-situ mineable coal in the SFC would have a CV of 22 Mj/kg, and that the CV of coal would increase after beneficiation with a 50% yield to 25.6 Mj/kg. A final saleable reserve estimate of 1700 Mt was estimated by De Jager (1983) with a 25.6 Mj/kg calorific value. Christie (1989) studied 11 samples of coal from all throughout the SFC, and found that the CVs varied from 13.2 MJ/kg to 31.2 MJ/kg with an average of 22.2 MJ/kg. The study included looking at the relationship between the ash% and the CV's. An inverse relationship between ash% and CVs is seen in Figure 2.1; the calorific value is highest when the ash content is lowest, not surprising because as stated earlier, ash does not burn and thus samples with a high ash content produce less energy.

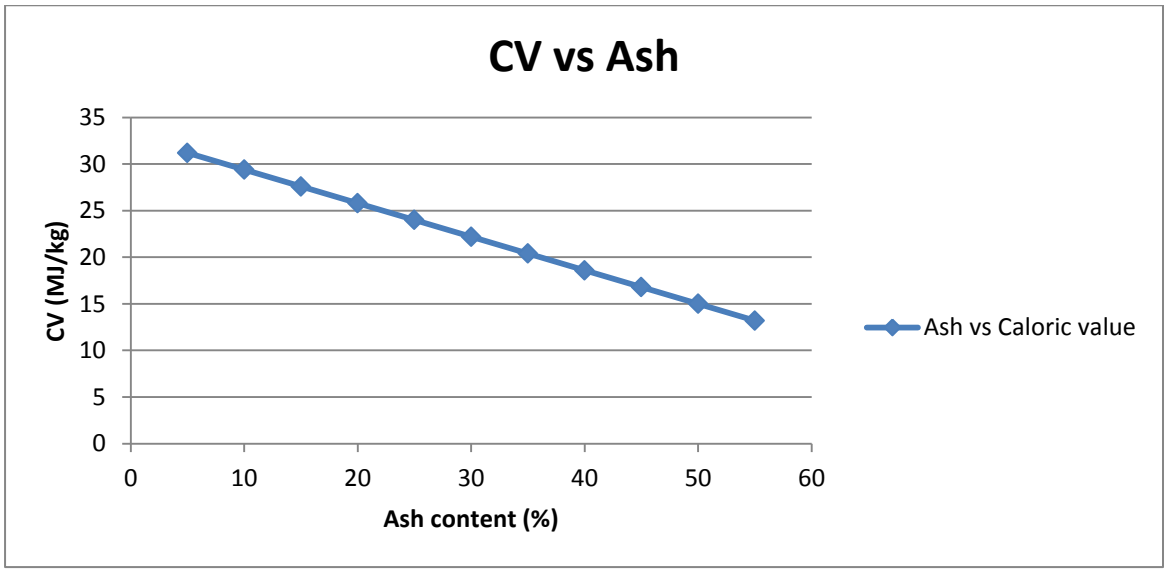


Figure2. 1: Ash vs. CV of SFC coal samples (Christie, 1989)

2.2 URANIUM DETECTION TECHNIQUES IN COAL

Various testing equipment have been used since the turn of the 20th century to determine the radioactivity of geological substances (Hunter, 2006). Electroscopes and spinthariscopes were one of the earliest instruments used for analysis; they became instruments which, although not very useful in precise quantitative analysis, are useful in determining whether an area does in fact possess radioactive material, by recording abnormal radioactivity values (Hunter, 2006). In recent studies, Electroscopes and spinthariscopes have been regarded as precursors for more accurate tests (Zavodska *et al.*, 2009).

Quantifying the U content in coal is vital as U in coal combustion products, even in trace amounts, can be detrimental to the environment. Several studies have displayed how these naturally occurring radionuclides in coal combustion products increase toxic elements in the atmosphere, and overall environment, in some cases becoming health hazards to humans and animals (Agrawal *et al*., 1993; Bencko and Symon, 1977; Sahoo *et a.l*, 2010; Zhang *et al*., 2004; Zheng *et al*., 1999)

Zheng *et al*., (1999) studied the distribution of potentially hazardous trace elements in coals from the Shanxi province, China. One hundred and ten coal and peat samples were studied; the results showed that tertiary brown coals contained an average of 8.2 mg kg^{-1} U, early Permian coals contained 2.7 mg kg^{-1} U. Late Carboniferous coals contained 5.7 mg kg^{-1}, and anthracite reportedly contained 7.7 mg kg^{-1} U.

Numerous studies have been conducted to quantify U content in coals and coal combustion by products using different techniques. This research will use XRF, ICP-MS and INAA; however numerous techniques have been used recording U in coal and the surrounding coal plant environment (Alvarez and Garzon, 1989; Bem *et al.,* 2002; Fardy *et al*., 1989; Font *et al.,* 1993; Hayumbu *et al.,* 1995; McBride *et al*., 1978; Nakaoka *et al*., 1984; Papastefanou and Charalambous, 1979).

2.2.1 X-RAY FLOURESCENCE

X-Ray Fluorescence (XRF) is an analytical technique that uses the interaction of x-rays with a material's electrons to determine its elemental composition. During analysis, energy from an emitted x-ray is produced, characteristic of the elemental atom being analysed, thereby providing data to determine which element was encountered in the material. The energy of the emitted X-ray is independent of material chemistry and bonding structures within the material, thus sodium obtained from NaO, $NaCO_3$ and $NaCl_2$ would be in exactly the same spectral position for all three materials (Horiba Scientific, 2014; Kuhn *et al.*, 1975)

XRF is used to determine the bulk elemental chemistry of a specimen, presented to the instrument as either a fused glass disc or a pressed powder pellet (Boyd, 2004). XRF analysis can be used for both trace element quantity determination and for mineralogical data. Studies have been conducted using XRF analysis on whole coal samples with some success (Mills and Turner, 1980) however, due to the light matrix of coal, and a lack of reliable coal standards (Evans *et al.*, 2001), XRF is considered by some organisations (USGS being one of them) as an analysis that gives low precision results (Palmer and Klizas, 2001). Typically the range of the U content in coals is 0.5-10 mg kg^{-1}, with an average 2 mg kg^{-1} (Swaine, 1990).

Studer (2008) determined the U content in two profile seams from the Swiss Molasse Basin (Riedhof and Mühlebach) (Figure 2.2), and found that for the Riedhof profile, the overlying sandstone, the marl, clay layers, and the freshwater limestone displayed U content of around 10 to 30 mg kg^{-1}. In contrast to that, the upper and lower coal seam displayed U content ranging from a minimum of 107 mg kg^{-1} to a maximum of 611 mg kg^{-1}, averaging 330 mg kg^{-1}.

The Mühlebach profile displayed a similar trend: the sandstone and the marl showed U content of around 10 to 20 mg kg^{-1}, and U in coal varied from a minimum of 80 mg kg^{-1} to a maximum of 655 mg kg^{-1}, averaging 380 mg kg^{-1}. The coaly sandstone below the coal seam in this profile displayed some U enrichment with 260 mg kg^{-1} maximum; however the average was lower than the U content within the coal. Shown in Figure 2.2 are both profiles.

Numerous other researchers have employed XRF analysis to determine the U content in whole coals (Boyd, 2004; Gluskoter *et al*., 1977; Johnson *et al.,* 1989; Mills and Turner, 1980; Swaine, 1994).

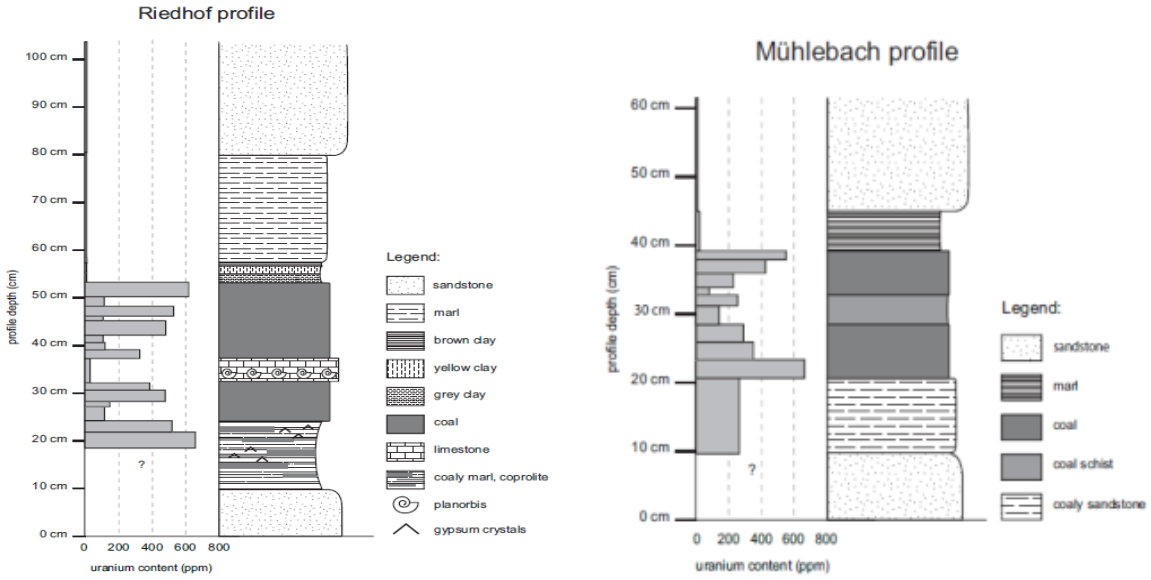


Figure 2. 2: Riedhof profile and Mühlebach profile, (Studer, 2008) (U determined by XRF)

Literature that includes XRF used to analyze whole coal samples in the SFC is limited to say the least; Nel (2012) quantified elemental U content of samples using XRF spectrometry. In Table 2.6, the U_3O_8 content in material from SFC samples is displayed. Coaly shale registered the lowest U and the sandstone had the most U content. Figure 2.3 shows the sites that were drilled; Samples from Berlin 643 KR had U content ranging from 20 mg kg^{-1} to 83 mg kg^{-1}, samples from Hannover 642 KR had between 40 mg kg^{-1} to 11610 mg kg^{-1}, and those from Chester666 KR had between 20 mg kg^{-1} and 2350 mg kg^{-1}. Nel (2012) reported that U mineralization in the SFC occurs in the uppermost coal layer, irrespective of the lithological thickness of such a layer. Figures 2.4 to 2.6 show the results provided by Nel (2012) obtained with XRF analyses.

Table 2. 6: U content in samples studied by Nel, (2012)

	Samples	U_3O_8 (mg kg^{-1})
Set 1	Coaly shale	76
	Sandstone of pale grey	126
	Sandstone of light brown	242
Set 2	Shaly coal	130

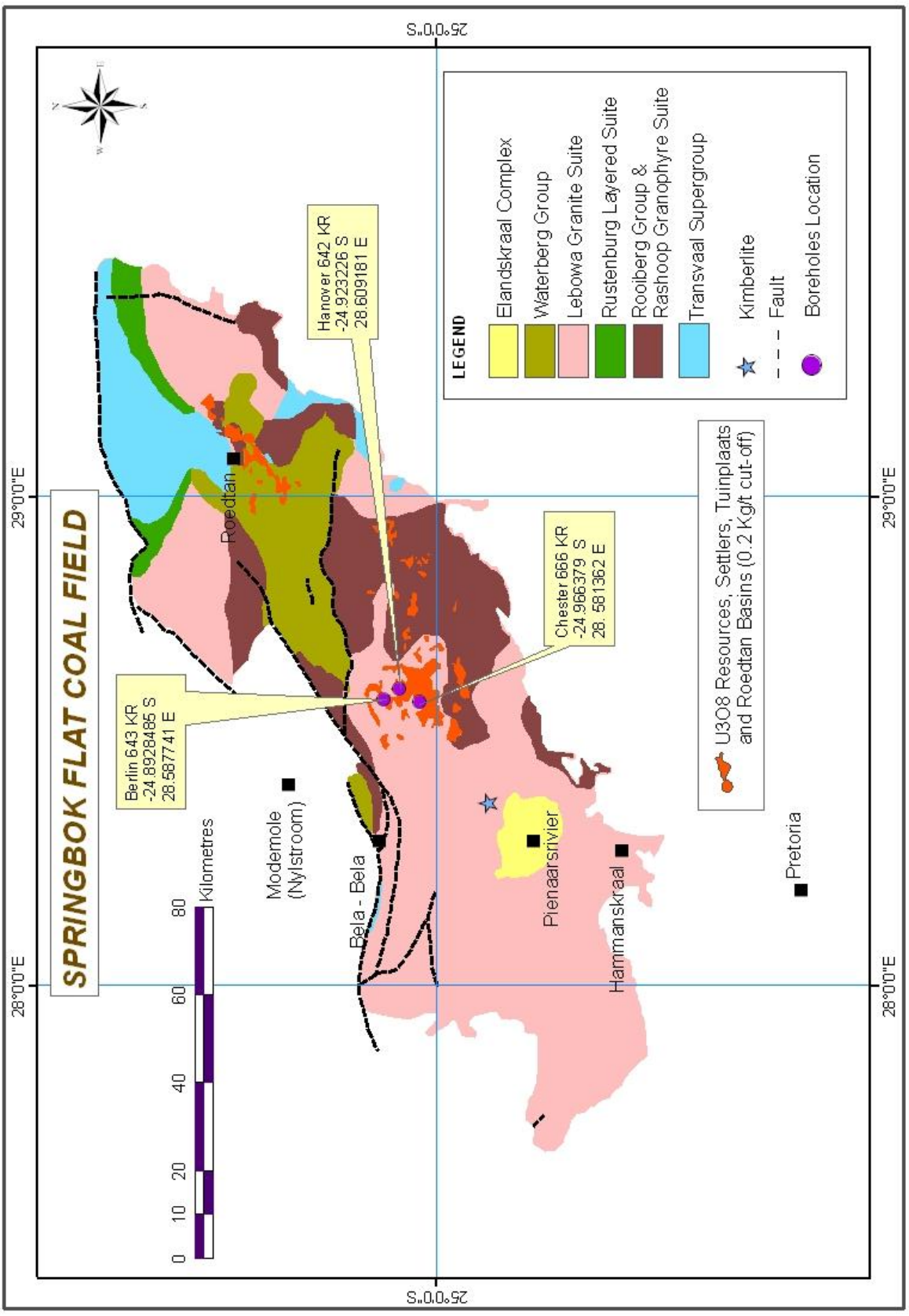


Figure 2. 3: Borehole sites drilled in SFC (Nel, 2012)

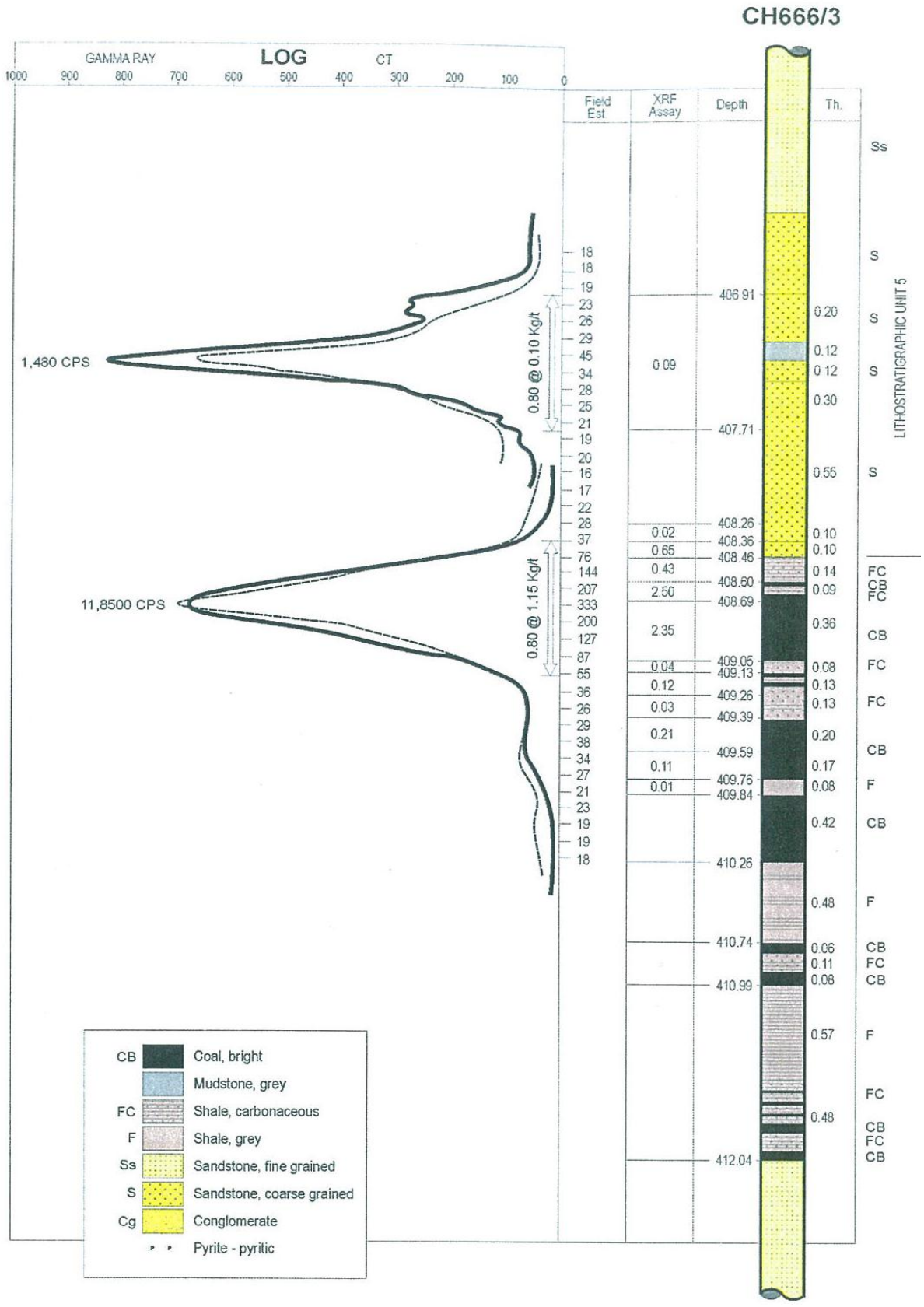


Figure 2. 4: Chester 666/3 U content (Nel, 2012)

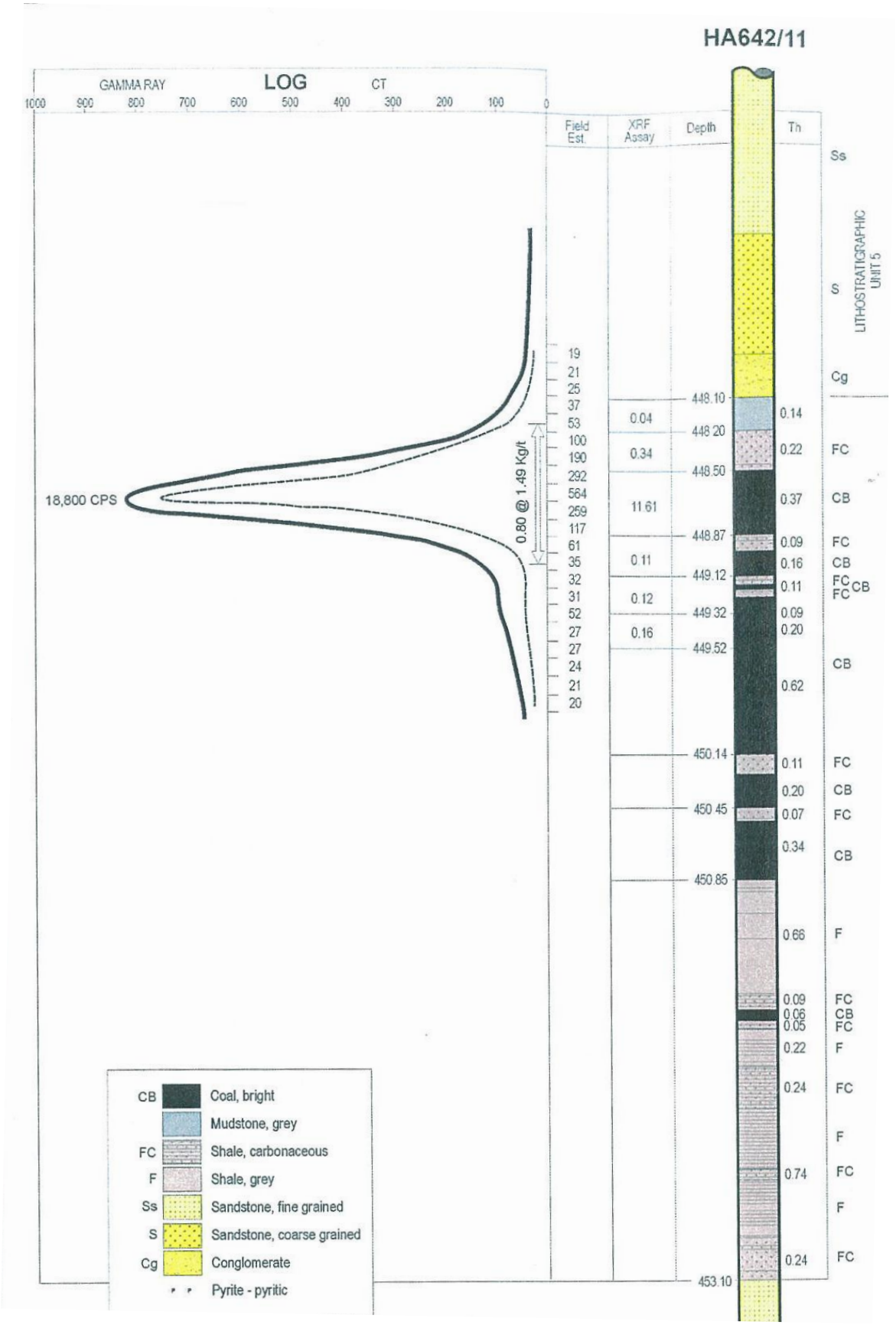


Figure 2. 5: Hanover 642/11 U content (Nel, 2012)

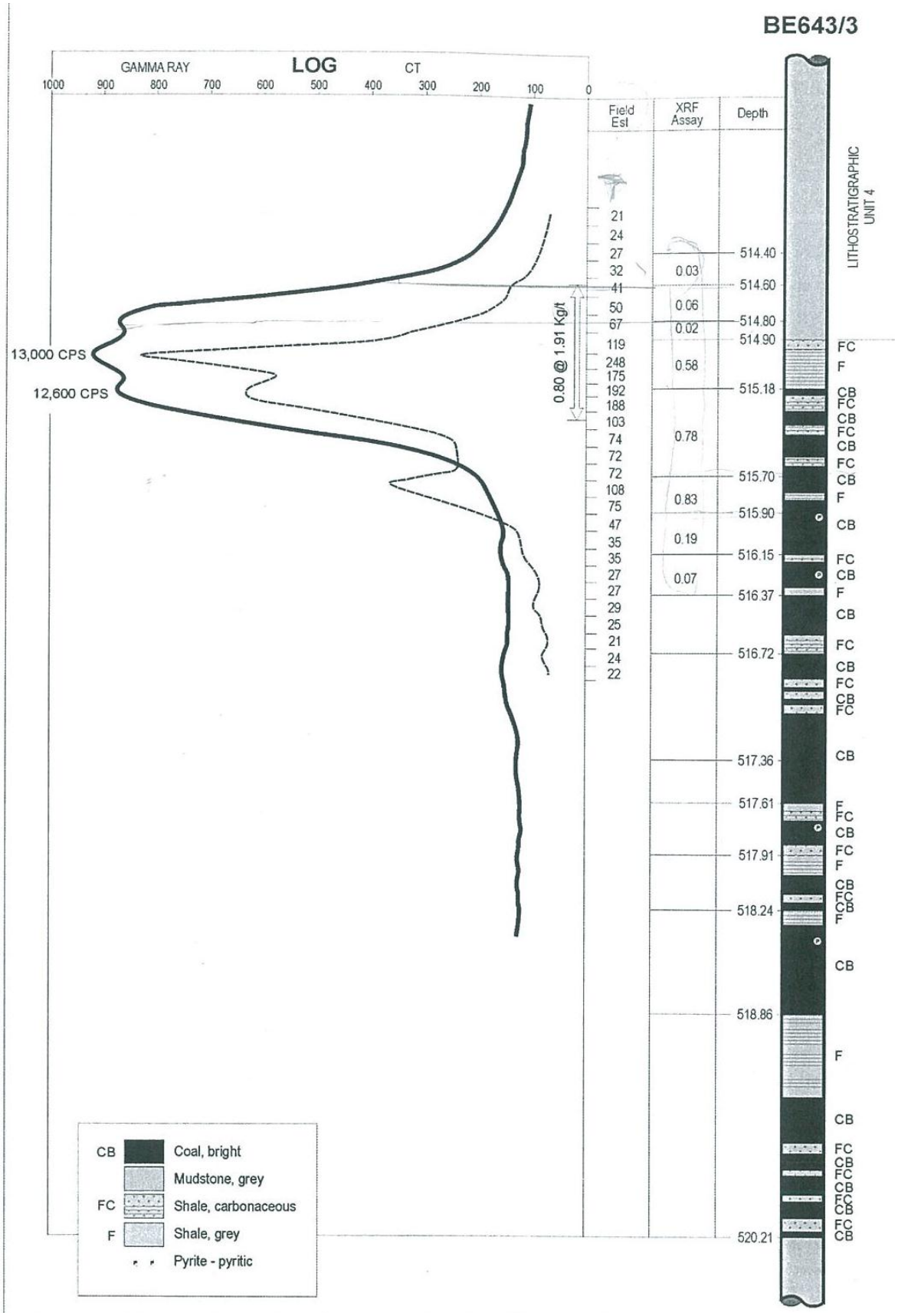


Figure 2. 6: Berlin 643/3 U content (Nel, 2012)

2.2.2 INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

Instrumental Neutron Activation Analysis (INAA) is a sensitive analytical technique, useful for performing both qualitative and quantitative multi-element analysis of major, minor, and trace elements, in samples from almost every conceivable field of scientific interest (Boyd, 2004). According to Swaine (1990), INAA is a well suited analytical method for whole coal determination of trace elements. In numerous cases, INAA is chosen due to the minimal simple preparation it requires; samples are analyzed as is, although rock samples are usually analyzed as powders to ensure representative sampling, resulting in the reduction of contamination and loss of sample. The technique is non-destructive and requires very little sample quantity (Boyd, 2004).

The analysis was first employed in 1936 when Hevesy and Levi found samples containing rare earth elements were highly radioactive after being exposed to a source of neutrons (Zeisler *et al.,* 2003). INAA has the ability to induce radioactivity, quantify and identify the elemental isotope of U present in samples (Heimann and Barron, 2014). The analysis works on the concept of detecting radioactive gamma rays by bombarding the sample with neutrons. When a neutron collides with a target nucleus, a compound nucleus forms in an excited state; the compound nucleus almost always instantly de-excites to a more stable configuration by emitting either one or more gamma ray named prompt gamma rays. In most cases, this newly configured compound nucleus becomes radioactive in nature, and emits gamma rays (Glascock, 2004).

Steinnes (1976) conducted INAA on 25 samples of coal and fly ash. The analysis was run to test the accuracy of the instrument in determining trace elements in coals and coal combustion products. In the investigation values of a known Standard Reference Material (SRM) 1633, were compared with results obtained by previous researchers who had used different analytical techniques. The study found a 12.7 mg kg^{-1} U content, compared to 12.0±0.5 reported by Ondov *et al.* (1975). Klein *et al.* (1975) reported 11.8 mg kg^{-1}, and Millard and Swanson (1975) reported 11.7 mg kg^{-1} content from the same SRM 1633. From these results, Steinnes (1976) concluded that neutron activation is an accurate method of determining trace elements, U in particular, in whole coals and coal ash.

An investigation of Greek coals using INAA conducted by Perricos (1969) found that samples contained U content ranging from 150 mg kg^{-1} to 370 mg kg^{-1}; Table 2.7 shows the results from the investigation, isotope U^{238} was detected in the study. The original U content in the coals was low, yet the content increased at least fivefold in the coal ash.

Table 2. 7: The U content in uraniferous coal as obtained by INAA with values given in mg kg^{-1} (Perricos, 1969)

Sample	U in ash	U in coal sample
U1	2000	370
U2	1400	370
U3	2400	360
U4	900	120
U5	1000	170
U6	800	150

A similar study was done by Sheibley (1973), where U^{238} was detected in Ohio coals; the U content varied from 0.68% to 1.5%. Table 2.8 gives the maximum, mean, and minimum values of U in the coal and ash samples analyzed using INAA.

Table 2. 8: U content in coals and ashes by INAA (Sheibley, 1973)

Samples	Min value (%)	Max value (%)	Average (%)
Coals	0.68	1.5	0.98667
Ashes	3.7	4.9	4.43333

Similar to the results obtained by Perricos (1969), the ash had a higher U content than the coal samples. Numerous other studies (Decat and Van Zanten, 1963; Fardy and McOrist, 1994; Gluskoter *et al.*, 1977; Tiwari *et al.,* 2007) show that INAA is useful in calculating trace amounts of U content in coals and other materials with accuracy and precision. Unfortunately, there is no public domain information available on the use of INAA in the SFC for U determination on coal.

2.2.3 INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is an analytical technique used for elemental determination. The technique was commercially introduced in 1983, and has gained general acceptance in many laboratories (Wolf, 2005). This method has several advantages, such as short duration of the analysis, low detection limits (ng per dm^3), ability to analyse multiple elements at the same time, low sample consumption and minimum spectral interferences (Himri *et al*., 2000).

The process requires that the samples be in solution; while this is fine for liquid samples, it is a clear disadvantage when the sample is a solid sample such as coal. The sample has to be digested in a $HF/HCl/HNO_3$ mixture whilst being heated in a microwave oven. A quadruple mass spectrometer analyses the samples thereafter (Boyd, 2004). This digestion of solid sample into solution is probably the one disadvantage about the analysis as it runs the risk of losing volatile material and the acids add to the expense of the analysis. However, due its highly repeatable and accurate results, especially for liquids, the USGS regards ICP-MS as a high precision procedure (Palmer and Klizas, 2001)

Sahoo *et al.* (2010) conducted research to determine U content and activity ratios from coal and fly ash from Philippine coal fired plant samples using ICP-MS. Feed coal samples ranged from 0.211 mg kg^{-1} to 1.11 mg kg^{-1} U content, averaging 0.51 mg kg^{-1}. Bottom ash samples ranged from 2.45 mg kg^{-1} to 8.12 mg kg^{-1} in U content, and fly ash samples ranged from 6.74 mg kg^{-1} to 21 mg kg^{-1}; as with studies by Perricos (1969) and Sheibley (1973), the ash had higher U content.

Other studies involving trace element determination from coals and coal by products using ICP-MS have been conducted (Querol *et al.,* 1994; Lachas *et al.*, 1999; Fadda *et al.,* 1995), and all show that ICP-MS can be trusted when it comes to accurate results of trace elements in coals and coal combustion products. Similar to INAA, no public domain information was found on the use of ICP-MS in the SFC for U determination on coal.

2.3 LEACHING AND FILTRATION OF URANIFEROUS COALS AND ASHES

Leaching is a hydrometallurgical technique that uses aqueous media to extract valuable metals from ores. In the recovery of U from uraniferous coals, two main techniques are used for leaching, namely: acidic leaching (predominately using sulfuric acid), and alkaline leaching (using a mixture of sodium carbonate and bicarbonate). Alkaline leaching is used when the host rock contains significant amounts of acid consuming components; for example, a material with high carbonate content would exclude acid leaching and in effect require alkaline leaching (Laxen, 1973; Merritt, 1971)

Traditionally, the commonly encountered U processing flowsheet is made up of mining, followed by comminution, acid leaching, solid/liquid separation, solvent extraction (SX) and finally precipitation and recovery. Figure 2.7 displays the process (Lunt *et al.,* 2007)

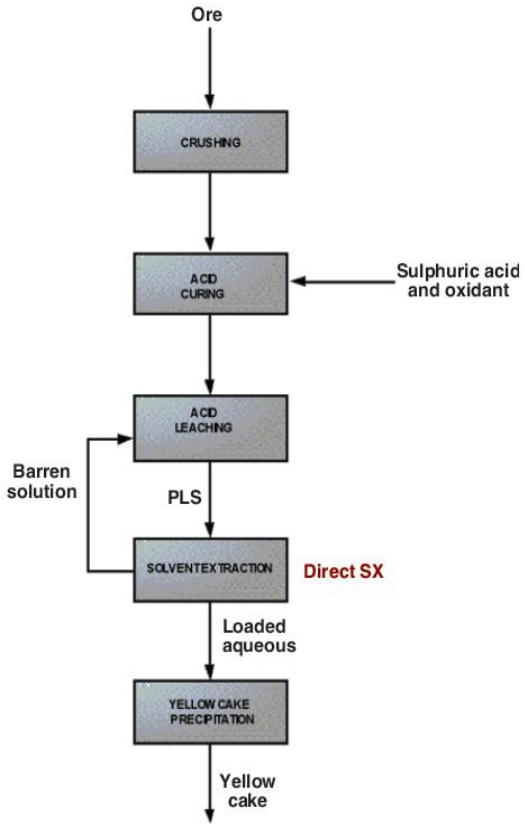


Figure 2. 7: U process flow sheet (Lunt et al., 2007)

Acid leaching is the predominant process used for U extraction and in most cases, sulfuric acid is used because of it's relatively low cost and ease of availability (Edwards and Oliver, 2000). Hydrochloric acid and nitric acid are alternatives to sulfuric acid however they are more costly and cause more serious environmental pollution than sulfuric acid. During leaching, U needs to be oxidized into its hexavalent state (U(VI)) before it can be dissolved by the sulfuric acid (Edwards and Oliver, 2000). The dissolution of hexavalent U in a sulfuric acid leaching system follows equations 4 to 6.

$UO_2^{2+} + SO_4^{2-} \rightarrow UO_2SO_4$ ……eq 4

$UO_2SO_4 + SO_4^{2-} \rightarrow [UO_2(SO_4)_2]^{2-}$ ……eq 5

$[UO_2(SO_4)_2]^{2-} + SO_4^{2-} \rightarrow [UO_2(SO_4)_3]^{4-}$ ……eq 6

Wang *et al.* (2008) leached feed coal, fly ash, and bottom ash samples using sulfuric acid from a Shizuishan coal fired power plant in China, and discovered that time plays a critical role in leaching of trace elements from coal and combustion residues. Experiments were run for 0-4 h, 4-12 h, 12-28 h, and 28-60 hours. The pH was varied and experiments run at pH=2, pH=4 and pH=5.6. Table 2.9 gives the results from the study where FC is the feed coal, BA is the bottom ash, and FA is the fly ash.

When the pH was kept at 2.0, the peak of extraction was after 60 hours. The U content in solution ranged from 0.081 mg L^{-1} to 0.119 mg L^{-1} when leaching feed coal. Feed coal recorded higher extraction rates than both bottom ash and fly ash. When the pH was increased to 4 and 5.6, a general downward trend was observed in terms of U concentration leachable over time. The highest U content leached into solution was achieved during the first 4 hours of the experiments (for pH=4 and pH=5.6), and thereafter, the U contnent in the solution decreased. Table 2.9 also shows the trends experienced by each sample relative to variation in time. Each sample behaved differently when leaching time was varied from 4 hours to 60 hours.

Table 2. 9: The U content of leachates given in mg L^{-1} (Wang et al., 2008)

Element	Sample number	0-4 hours.	4-12 hours	12-28 hours	28-60 hours
		pH= 2.0	**(mg L^{-1})**		
U	FC	0,10546	0,011319	0,080885	0,119229
	BA	0,00776	0,000788	0,003107	0,03712
	FA	0,007731	0,000124	0,008295	0,020359
		pH=4.0	**(mg L^{-1})**		
U	FC	0,091177	0,001224	0,000125	0,000016
	BA	0,000331	0,00022	0,000271	0
	FA	0.000738	0.000402	0.000214	0.000021
		pH=5.6	**(mg L^{-1})**		
U	FC	0,081556	0,006598	0,000236	0,000078
	BA	0,002277	0,000809	0,000286	0,000016
	FA	0,005788	0,0018	0,000194	0,00012

Slivinik *et al*. (1985) assessed U recovery by using Instrumental Gamma Activation Analysis (IGAA) on coal samples from Zirovski, Yugoslavia; various leaching parameters such as pH, temperature and time were studied. The solids content in the slurry were kept at 30% in the slurry at various pH, temp and time. In Table 2.10, U recoveries using acid leaching ranged between 10-20%, of the U present in the coal before leaching. Thus the efficiency of leaching U from raw coal samples was very low. The temperature was kept between 70-95 ^{0}C, using external heating. Slivnik *et al.* (1985) did not provide the actual U content that was leached into solution, only the percentage of U that was leached. Slivnik *et al.* (1985) found that filtering the resulting acid coal slurry gave relatively poor filtration rates especially under gravity filtration. As a result, filtration was not done using gravity filtration, but rather a wash water circuit was required to filter the slurry

Table 2. 10: U leaching (Slivnik et al., 1985)

Solvent	Temperature (C)	pH	Time (h)	U recovery (%)	reagent consumption (kg/t)
H_2SO_4	70-95	0.5-1.2	6-22	10-20	160-180

Maslov *et al.* (2010) conducted a study where U was leached out of Mongolian coal ash dumps; temperature, time, and U recovery were studied, and the results are summarized in Table 2.11. U recoveries were low when the coal ash was treated using water only at T=20^{0}C and t =24 hours compared to the 45.4% recovered when the ashes were treated with 45% sulfuric acid, at T=90^{o}C and t = 2 hours. The study showed the impact sulfuric acid has on leaching of U from Mongolian coal ash samples. A few other studies have been done to extract U from coals and coal ashes (Hurst, 1981; Paul *et al.*, 2006; Wang *et al.*, 1998); however no case studies were found in the public domain on leaching done on coal samples from the SFC, studying U recovery.

Table 2. 11: Results of U leaching Maslov et al. (2010)

Solvent	Temperature	Time	U recovery (%)
H_2O	20	24	1.1
H_2SO_4 (45%)	90	2	45.4

CHAPTER SUMMARY

Numerous studies show that proximate analysis and ultimate analysis can determine the chemical properties of coal. The physical properties of coal can be ascertained using specific heat data. XRF, ICP-MS and INAA are fully capable of determining trace elements in coal, coal ashes, cakes and leachates. Considering that the SFC has been extensively drilled, one is inclined to believe that tests have been made to assess the viability of separating U from coal samples found in the SFC; however due to the limited accessible data, no scope appears to have been given for the application of U recovery from coals in South Africa. The only exception in economic U recoveries in South Africa is the recovery of uranium oxide as by-product from gold ores using concentrated sulfuric acid (Forstner and Wittmann, 1976).

CHAPTER THREE: EXPERIMENTAL PROCEDURE

This chapter presents the methods used to achieve the aims and objectives set out for the project, from drilling right through to leaching and filtration. The equipment used for each analysis as well as the ISO procedures used are discussed here.

The identification of mineral phases in the coal samples did not form part of the aims and objectives of the project; however, in addition, XRD was used to identify the mineral phases present in several selected coal samples that were of interest due to high sulfur and U content. The analysis was conducted with the idea of correlating mineral content to U content. A petrographic microscope was used to identify the pyrite cleats in a few selected coal samples.

3.1 DRILLING OF CORES

The drilling of five boreholes (sponsored by the CGS) in the SFC began on the 28th May 2013, and was completed in September 2013. The names of the farms where the borehole sites were located are included in Table 3.1 and Figure 3.1. Boreholes were drilled at each of the five farms up to 450 m, recovering a 4cm cylindrical core. Table 3.1 also shows the intercepted coal zone depth. The drilling was done by Geosphere™ drilling company. Once the cores were recovered, they were placed in 1.5 m long core trays, and transported to the Donkerhoek Core Shed facility, owned by the CGS, to be logged by a PhD student who is conducting geological studies on the SFC (Ms. Valerie Nxumalo).

Sampling of coal zones for the five drilled boreholes was conducted at Donkerhoek for the purpose of preparing the samples for characterization, U analysis, and subsequent leaching and optimization tests on selected samples.

3.2 SAMPLING AND STORAGE OF THE CORE

The heterogeneous nature of coal offers many challenges to researchers who need to ensure that a sample under investigation is representative of the entire coal (Speight, 2005). This variability in coal composition is taxing as one collects a relatively small portion of sample with the aim of obtaining a sample that is accurately representative of the entire coal region being studied. Thus, researchers are always extra careful when sampling coal; always aiming at collecting samples that reduce bias as much as possible.

The coal zone cores were cut using a Lenox 320 cutter, housed at the Donkerhoek facility of the CGS, into 4 equal parts. Sampling of the coal zone was conducted by placing a 1/4 of the coal zone from the core trays into sample bags. Observing the coal with the naked eye, one could clearly see that the coal zone was not made purely of coal, but other unidentifiable minerals were also inter-bedded in the coal seen clearly in figures 3.2 to 3.7.The remaining ¾ of the core was retained by the CGS for a PhD project and for storage.

Table 3. 1: Farms drilled and intercepted depth of coal in each of the farms.

Farm name	Borehole No	Coordinates	Intercepted coal zone depths (m)
Roodevlakte	1	24°32'28.2"S 29°10'46.2"E	277 – 309.6
Kroomdraai	2	24°50'36.6"S, 28°57'54.4"E	251.3 – 258.0
Tuinplaats	3	24°56'12.01"S, 28°42'21.70"E	341.5 – 345.1
Kalkbult	4	25°2'43.60"S, 28°33'45.85"E	387.8 – 393.7
Wolfhuiskraal	5	25°9'23.90"S, 28°11'25.66"E	UCZ 143.9 – 155.27 LCZ 344.6 – 350.6

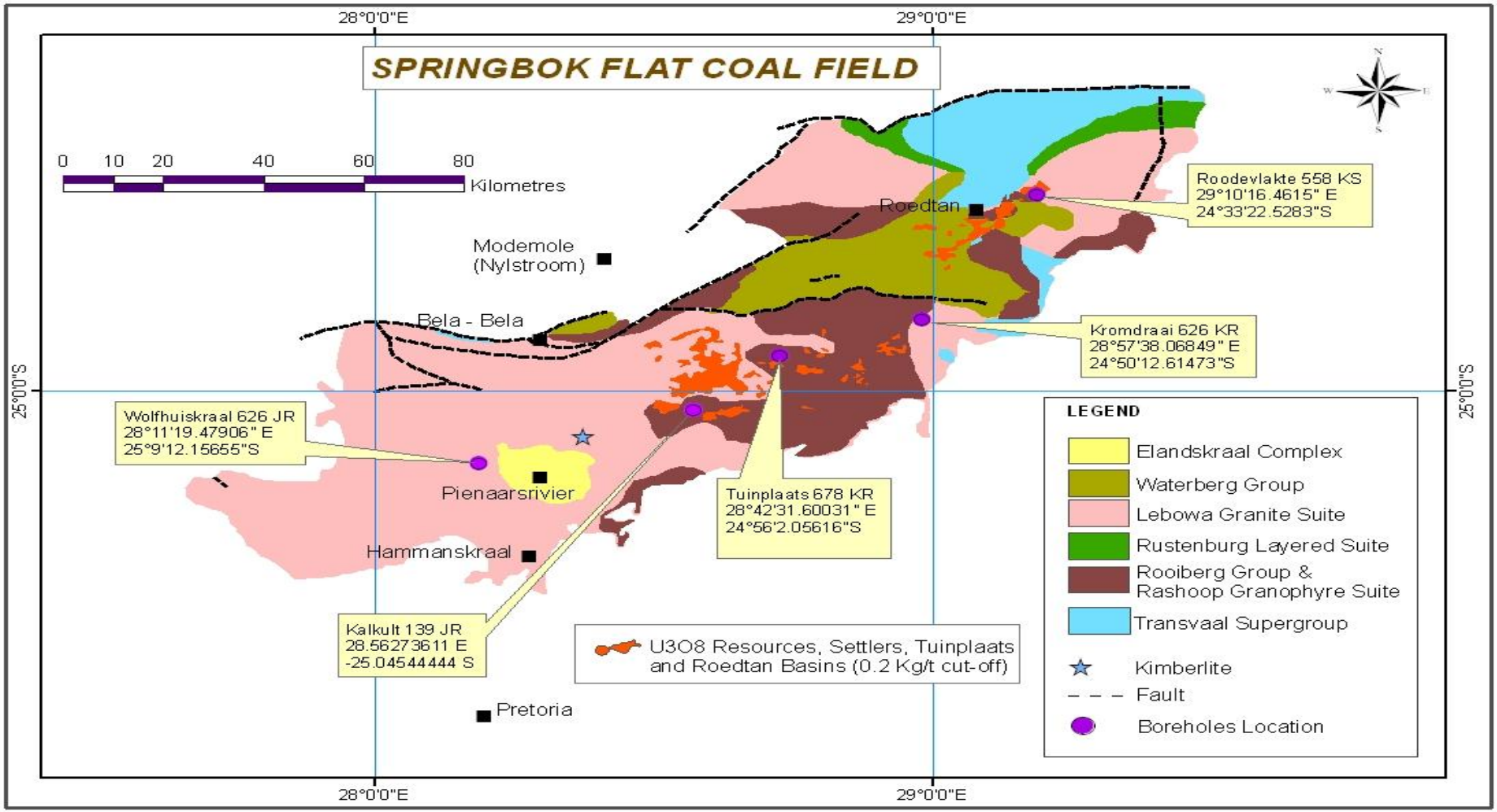


Figure 3. 1: Farm names and location of the boreholes being drilled in the SFC. (CGS database)

Figures 3.2- 3.7 are pictures of the borehole core from BH1 to the UCZ in BH5. Each core tray is 1.5 m in length from end to end. The darker horizons in the boreholes represent the coal zones, made up of interbedded coal and carbonaceous shale. Figure 3.2 shows that BH1 was dominated by carbonaceous mudstones (blue arrows) with very few visible bright coal bands.



Figure 3. 2: BH1: Roodevlakte 558 KS (Courtesy of Ms. Valerie Nxumalo)

Figure 3.3 shows that BH2 had significantly higher bright coal bands compared to BH1. The coal zone was made up predominately of bright coal (red arrows) interbedded with carbonaceous mudstones (blue arrows). Calcite cleats (green arrow) were visible in some areas in the coal zone.



Figure 3. 3: BH2: Kroomdraai 626 KR (Courtesy of Ms. Valerie Nxumalo)

Figure 3.4 shows that BH3 had a coal zone made up of bright coal (red arrows) clustered at the top of the coal zone, the bright bands of coal diminished and carbonaceous mudstones (blue arrows) dominated further down the coal zone.



Figure 3. 4: BH3: Tuinplaats 678 KR (Courtesy of Ms. Valerie Nxumalo)

Figure 3.5 shows BH4 had very few bright bands of coal. Carbonaceous shale dominated the top of the coal zone, bright coal bands were found with regularity, a little further down, towards the middle of the coal zone, and diminished yet again towards the bottom of the coal zone.



Figure 3. 5: BH4: Kalkbult 139 JR (Courtesy of Ms. Valerie Nxumalo)

Figure 3.6 shows that the UCZ in BH5 had very few bright bands of coal with large areas of the coal showing no bright bands of coal at all. Carbonaceous shale (blue arrows) dominated the entire coal zone. The UCZ had another prematurely grown coal zone seen at the top of the image, with the rest seen towards the bottom of the figure.



Figure 3. 6: BH5 UCZ: Wolfhuiskraal 626 JR (Courtesy of Ms. Valerie Nxumalo)

Figure 3.7 shows that the LCZ in BH5 also had very few bright bands of coal and carbonaceous shale (blue arrows) dominated the entire coal zone



Figure 3. 7: BH5 LCZ: Wolfhuiskraal 626 JR (Courtesy of Ms. Valerie Nxumalo)

Samples were taken at different depths along the coal zones and given sample numbers; Tables 3.2 to 3.6 display the depths as well as sample names.

Table 3. 2: Sample numbers and corresponding intercepted depth of coal in BH1

BH1	Roodevlakte 558 KS
Sample name	**Depth (m)**
1436	277.0 -277.9
1437	278.0 -278.78
1438	278.78 -279.37
1439	279.37 - 280.0
1440	280.0 -280.5
1441	308.73-309.1
1442	309.1-309.6

Table 3. 3: Sample numbers and corresponding intercepted depth of coal in BH2

BH2	Kroomdraai 626 KR
Sample name	**Depth (m)**
1426	251.34 - 251.46
1427	252.30 - 252.75
1428	252.75-253.0
1429	253.12 - 253.72
1430	253.72 - 254.18
1431	254.14- 254.25
1432	254.6 - 255.5
1433	255.5-255.93
1434	256.33- 256.70
1435	257.78 - 258.00

Table 3. 4: Sample numbers and corresponding intercepted depth of coal in BH3

BH3	***Tuinplaats 678 KR***
Sample name	**Depth (m)**
1421	341.52- 342.04
1422	342.1.0- 342.7
1423	342.7 – 343.08
1424	343.56 – 344.0
1425	344.0-344.3

Table 3. 5: Sample numbers and corresponding intercepted depth of coal in BH4

BH4	**Kalkbult 139 KR**
Sample name	**Depth (m)**
1443	387.81 -389.13
1444	389.1 -390.0
1445	390.0 - 391.0
1446	391.0 -391.7
1447	391.7 -392.13
1449	393.0 -393.7

Table 3. 6: Sample numbers and corresponding intercepted depth of coal in BH5

	BH5 (UCZ)	**Wolfhuiskraal 626 JR**	**BH5 (LCZ)**
Sample name	**Depth**	**Sample name**	**Depth**
1401	143.90-144.45	1411	344.67 – 345.10
1402	144.5- 145.0	1412	345.10 345.54
1403	151.6-152.10	1413	345.54-345.89
1404	152.10-152.72	1414	345.89- 346.25
1405	152.72- 153.23	1415	346.25-347.10
1406	153.23-153.70	1416	347.10-347.86
1407	153.7-154.1	1417	347.86-348.28
1408	154.1-154.51	1418	348.28-349.05
1409	154.51-154.9	1419	349.05-349.86
1410	154.9-155.27	1420	349.86-350.67

3.3 SAMPLE PREPARATION: CRUSHING AND MILLING

Coal preparation is regarded as both a science and an art; it involves the processing of a coal sample to yield products and waste by means that do not destroy the physical and chemical integrity of the coal (Alberecht, 1979). Crushing and milling were conducted at the Department of Material Science, University of Johannesburg (UJ), Dooronfontein campus and at the School of Chemical and Metallurgical Engineering, University of the Witwatersrand (Wits). The procedure for crushing, milling of coal samples, and splitting that was followed is highlighted as follows:

- Core samples were crushed to -4 mm using a cone crusher.
- The crushed samples were split; half of the sample was retained for further usage and the other half was stored.
- The samples were then milled to -1 mm using a Reutsch mill.
- The remaining sample was milled to -212 µm for proximate, ultimate, XRF and ICP-MS analyses.

3.4 SPLITTING

A MACSALAB Design Rotary Cascade Splitter was used to split the samples; this was conducted at Wits University. This type of splitter had an adjustable feed cone hopper with a trough and electromagnetic vibratory feeder. The splitter ccould handle up to 25 mm particle size before the hopper clogged up. Samples were poured into the rotating containers or tubes, and taken from the tubes and divided into sample bags. The -250 micron split was obtained for proximate, ultimate, XRF and ICP MS analyses.

The rotary splitter was used to produce representative sample quantities of the crushed and milled coal samples. Rotary splitters provide the best possible sample reducing technique available today with high representative accuracy (Haver and Boecker, 2014)

3.5 PROXIMATE ANALYSIS OF COAL

Thermogravimetric analysis (TGA) provided the proximate data on the coal samples. Volatile matter, moisture, carbon, and ash content in coal were determined. The analysis was used to give the ratio of combustible to non-combustible constituents present in the coal (Elder, 1983). Traditionally, combustion and pyrolysis can be conducted using furnaces and prescribed procedures such as ASTM D 7582; many researchers have considered TGA to be a logical alternative for proximate analysis (Fyans, 1977).

The Leco 701 TGA equipment, consisting of a multi stage furnace heater and an electronic microbalance, was utilized for the proximate analysis. The TGA is situated at Mintek. The equipment allowed for continuous monitoring of sample mass as a function of time, and temperature in a sequence of heating steps (Elder, 1983). The equipment rapidly heated up the coal to 107^{o}C, where it was held isothermally, in an inert oxygen free environment. The weight loss at this point was representative of the moisture content present in the coal. Thereafter, the equipment heated up to 950^{o}C, where it was again held isothermally. The mass lost at this stage represented the volatile matter of the coal. At this point, the inert gas was replaced by oxygen. The sample then burnt, losing weight. This was continued until the mass lost was negligible; the mass lost after this step gave a measure of the fixed carbon present in the coal. The inorganic content of individual coals (expressed as weight % ash i.e. ash content) represented the residue left after the organic constituents had been completely oxidized by heating in the presence of oxygen. The procedure follows ASTM D5142.

Figure 3.8 represents the system profile of how the equipment measured the relative portions of moisture, volatiles, fixed carbon and ash content. The equations parameters used to calculate the moisture, volatile, ash and fixed carbon are given as follows:

Moisture

$$((M_1 - M_2) / M_1) * 100 = M_m \qquad \text{.....eq.7}$$

Where M_1 is Initial Mass

M_2 is mass after heating to 107^{o}C

M_m is moisture mass percentage

Volatiles

$((M_2 - M_3) / M_1) * 100 = M_v$ eq.8

Where M_1 is Initial Mass

M_2 is mass after heating to 107^oC

M_3 is after heating to 950^oC

M_v is the volatiles mass percentage

Ash

$(M_4 / M_1) * 100 = M_a$ eq.9

Where M_1 is Initial Mass

M_4 is mass after oxidation

M_a is the ash mass percentage

Fixed carbon

$M_{fc} = M_T - M_a - M_v - M_m$

Where M_T is the total mass of sample

M_a is the mass of ash in the sample

M_v is the mass of the volatiles in the sample

M_m is the mass of the moisture in the sample

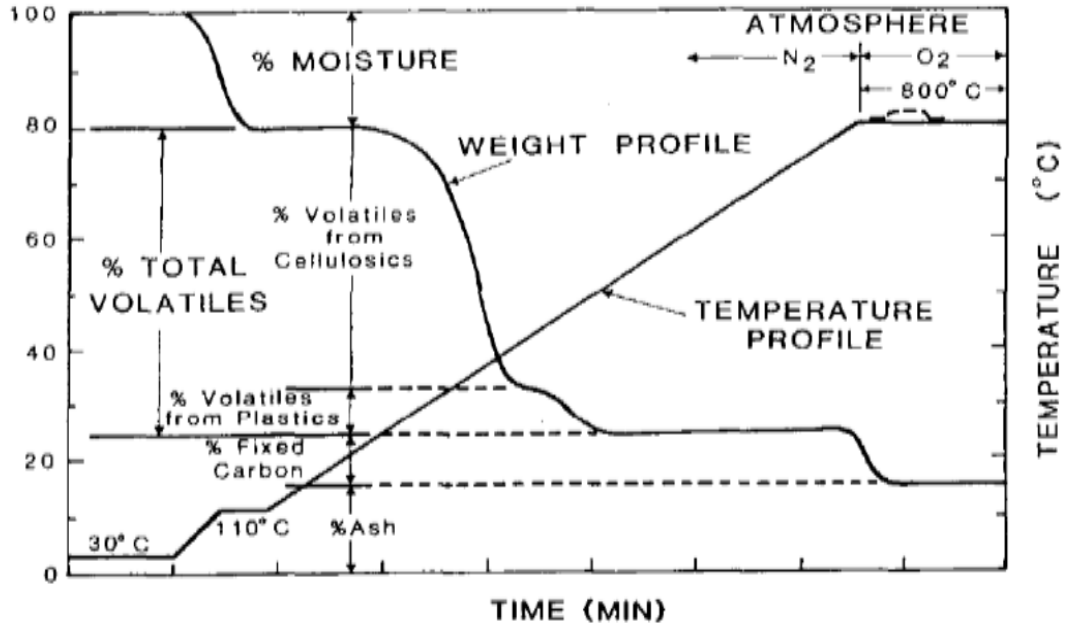


Figure 3. 8: Leco 710 TGA System profile

3.6 ULTIMATE ANALYSES (CHNS)

The Leco CHN628 equipment housed at the CGS coal lab, used for the determination of the C,H,N and S content of coal samples, is made up primarily of two parts: a combustion unit and an adsorption unit. The combustion unit is made up of two separate heated furnaces (combustion furnace and afterburner furnace) and a combustion tube. The required operating temperature for the combustion furnace was 950^{o}C and 850^{o}C for the afterburner furnace. The adsorption unit is composed of a cylinder packed with an anhydrous magnesium perchlorite ($MgClO_4$) as water absorbent. (Sodium hydroxide) NaOH was used as the carbon dioxide absorber. The procedure used follows ASTM D5373.

During analysis, 0.1g of coal sample was placed in silica foil and inserted into the combustion tube under the first furnace where the sample was completely combusted in oxygen (oxidation). C, H and N present in the sample oxidized to carbon CO_2, H_2O and NOx gasses and are swept by the O_2 into the afterburner furnace where further oxidation and particulate removal occurs. The gasses passed through a thermoelectric cooler to remove water vapor.

The combustion gasses were then collected into a vessel known as ballast for equilibration. The gasses were homogenized and sent to a 10cc aliquot loop. Here non-dispersive infrared cells were used to detect H_2O and CO_2; He was used as the carrier gas. The combusted gasses then passed through the anhydrone ($MgClO_4$) to remove CO_2 and H_2O generated during the CO_2 trapping process and onto a thermal conductivity cell (TC), used to detect N_2. NOx gasses travelled through a reduction tube filled with copper to reduce the gasses to N and remove any excess O_2 acquired from the combustion process. The final results were then interpreted by a software that provided the percentage C,H,N. Sulfur was determined by placing a crucible into a 628S machine and during combustion, SO_2 was detected and the sulfur was presented as elemental sulfur.

3.7 CALORIFIC VALUE (CV)

The calorific value of coal gives a measure of heat or energy produced during combustion and it is measured as either gross calorific value or net calorific value (Bureau of Energy Efficiency, 2006). The difference is determined by the latent heat of condensation of the water vapor produced during the combustion process. For the gross calorific value (GCV), all vapors produced during the combustion process were considered as fully condensed, whereas for the net calorific value (NCV), it was assumed that the water left with the combustion products without being fully condensed.

In this study, NCV was used as the measure of CV. It should be noted, however, that conversion to the GCV is possible when the moisture content of the samples is known. A Parr 3600 bomb calorimeter, housed at the South African Bureau of Standards (SABS), in the Council for Scientific and Industrial Research (CSIR) laboratory was used. A known mass of the sample of coal was burned in oxygen in a bomb calorimeter under standard conditions. A high-speed microprocessor performed the temperature measurements of the bomb and calculated the CV from the individual measurements taken. Test results were verified by using a known control sample and plotting the results on a control chart. Predetermined upper and lower control limits were used to identify results that were outliers. ISO 928: solid mineral fuels was used for the determination of the GCV and the calculation of NCV

3.8 XRD

XRD was used to identify mineral phases present in coal samples that were high in sulfur (above 2.5%). The milled and homogenized samples were placed in crucibles and inserted in a Bruker D8 equipment housed at the CGS. XRD equipment consisted of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays were generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target, and bombarding the target material with electrons. A detector then recorded and processed the X-ray signal and converted it to a count rate which was read by the computer

3.9 XRF

XRF is useful in the determination of a material's elemental composition. For major element analysis, the milled sample (<212 µ fraction) was roasted at 1000 °C, for 3 hours to oxidize the Fe^{2+} and S, and to determine the loss of ignition (L.O.I.). Glass disks were prepared by fusing 0.5g roasted sample, and 10 g flux consisting of 70.7% $Li_2B_4O_7$, 19.8% $LiBO_2$ and 0.5% LiI at 950 °C. Quality control/Quality assurance was done by using an in-house amphibolite reference material (sample 12/76). Also 1 in every 10 samples was duplicated during sample preparation.

For trace element analysis, 12g milled sample of the same size fraction as mentioned above, was mixed with 3g Leco wax and pressed into a powder briquette by a hydraulic press, at an applied pressure of 25 ton. The glass disks and wax pellets were analyzed by a PANalytical wavelength dispersive Axios X-ray fluorescence spectrometer, equipped with a 4 kW Rh tube, based in the CGS, XRF laboratory.

3.10 INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS)

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is an analytical technique used for elemental determinations (USGS documents); The analysis was conducted at Wits using a Bruker 500 MHz NMR spectrometer. The instrument combines a high temperature Inductively Coupled Plasma (ICP) source with a mass spectrometer (MS). The ICP source converts the atoms of the elements in the sample to ions. These ions are then separated and detected by the mass spectrometer.

Argon gas flows inside the concentric channels of the ICP torch. The radio-frequency (RF) load coil is connected to a RF generator. As power is supplied to the load coil from the generator, oscillating electric and magnetic fields are established at the end of the torch. When a spark is applied to the argon flowing through the ICP torch, electrons are stripped off of the argon atoms, forming argon ions. These ions are caught in the

oscillating fields and collide with other argon atoms, forming an argon discharge or plasma.

The sample is typically introduced into the ICP plasma as an aerosol, either by aspirating a liquid or dissolved solid sample into a nebulizer or using a laser to directly convert solid samples into an aerosol. Once the sample aerosol is introduced into the ICP torch, it is completely dissolved and the elements in the aerosol are converted first into gaseous atoms and then ionized towards the end of the plasma.

Pulverized coal samples (49) were submitted on 29/01 and 11/02 2014 for total U analysis. The samples were digested in a microwave system (Multiwave 3000, Anton Paar) using concentrated acids following the program presented in Table 3.7 to obtain a liquid sample.

Table 3. 7: Microwave programme for sample extraction

Phase	Power (W)	Ramp (min)	Hold (min)	Fan
1	800	10:00	50:00	1
2	0	0:00	15:00	3

For microwave digestion the following procedure was applied: Sample weight: 0.25g was mixed together with a regent of composition: HNO_3 (4 ml); H_2O_2 (2 ml); HF (2 ml); H_3BO_3 (12 ml). Boric acid (H_3BO_3) was also added to neutralize the HF acid since HF is known to dissolve glass. A ratio of 1:6 was used for HF: H_3BO. This ratio is for complete neutralization of HF. Blank samples, together with a certified reference material (CRM) of coal (SARM 20, SABS), were also prepared for quality control using the same procedure as for the actual samples. Samples were analyzed for U238 isotope using an ICP-MS 7700. The calibration obtained on the day of analysis for U is presented in Figure 3.9

Blanks were used to detect if the machine was working properly and that no contamination existed in the matching prior to analysis. The obtained digests were diluted with de-ionized water and stored in a fridge at ±4°C until analysis. The method detection limit, which was calculated as three times the standard deviation of three blanks measurements, was 0.009 µg U L^{-1}

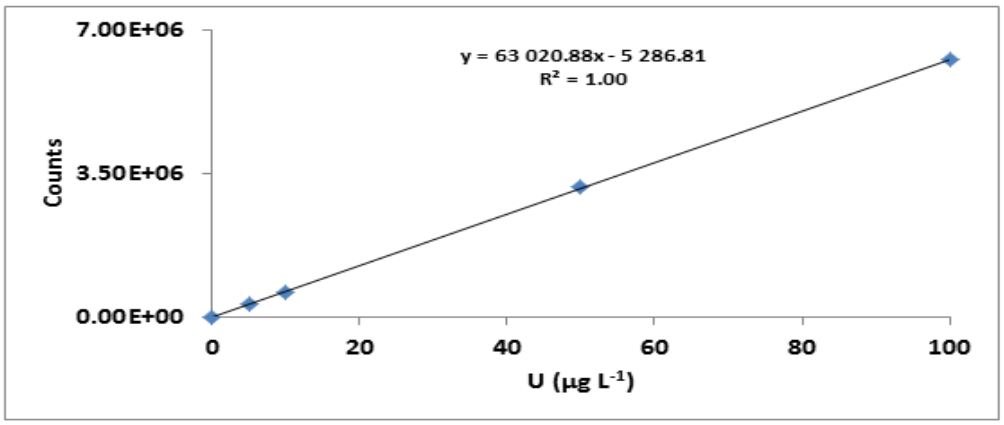


Figure 3. 9: ICP-MS calibration curve for U238 analysis obtained on the 20/02/2014 (Bruker 500 MHz NMR spectrometer)

3.11 INAA

Instrumental Neutron Activation Analysis (INAA) is a sensitive analytical technique that uses radioactive energy detection to perform qualitative and quantitative analysis of U present in the coal samples. During analysis, a neutron collides with a target nucleus, a compound nucleus forms in an excited state. The compound nucleus almost always instantly de-excite to a more stable configuration by emitting either one or more gamma ray named prompt gamma rays. In most cases, this newly configured compound nucleus becomes radioactive in nature (Glascock, 2004). Radioactive decay occurs where one or more characteristic delayed gamma rays are emitted. Depending on the particular radioactive species, the delayed gamma ray will be released at a much slower rate than the prompt gamma ray counterpart according to the half-life of the radioactive nucleus (Glascock, 2004).

The technique was used for 11 samples, with a high U content (10 mg kg^{-1} cut-off), selected from XRF results. A Standard Reference Material (SRM) 3164 from the National Institute for Science and Technology was used, and has a standard U solution with a certified value close to 10 mg/mL. The U was dissolved in about 10 % nitric acid with an associated uncertainty of less than 0.02 mg/mL. Aliquots of this working standard were used to determine U in samples during analysis. The instrument is housed at the Nuclear Energy Corporation of South Africa (NECSA).

3.12 ACID LEACHING AND FILTRATION

Direct acid leaching is the most powerful method to reduce the metal content of coals, as the low pH destabilizes many inorganic parts; for this reason low pH is generally favorable for metal ion solubilization (Seferinoglu *et al.,* 2003). In order to extract U from coal samples, sulfuric acid was used on samples from different boreholes coal zones drilled in the SFC. A cut off point of 10 mg kg^{-1} U was set, with all samples containing 10 mg kg^{-1}, and higher, selected for leaching tests.

500 ml of deionized water was poured into a 600 ml glass beaker. H_2SO_4 (18.4 M) stock solution was slowly added into the glass beaker to reach required pH values of 0.5, 1, 1.5; the pH was continuously monitored and the stock solution added to maintain acidity. 10g of coal sample was poured into a 300 ml flask. 100 ml of the different pH solutions was poured onto the coal samples to maintain a liquid to solid ratio of 1:10, and stirred. Different variables were tested, namely: The effect of time, the effect of temperature, and the effect of pH.

3.12.1 EFFECT OF TIME

Samples were leached for 4, 8 and 24 hours to determine the effect of time on leaching, and to determine when metal equilibrium would be reached in the solution. During leaching, pH and temperature were kept at 0.5 and 25^{O}C respectively.

3.12.2 EFFECT OF TEMPERATURE

To study the effect of temperature, the leaching time was kept constant at 4 hours, pH =1, and the temperature was varied between 25^{o}C and 65^{o}C in increments of 20^{o}C. Thus leaching tests were run at 25^{o}C, 45^{o}C and 65^{o}C. A water bath was used control temperature.

3.12.3 EFFECT OF PH

To study the effect of pH, the leaching time was kept constant at 4 hours and the temperature was kept at 25^{o}C, the pH was varied from pH= 0.5, pH= 1 and pH= 1.5. Leaching was conducted at the CGS chemistry labs, protective including, safety goggles,

gloves and face shield masks were on at all times. The complete Material Safety Data Sheet (MSDS) form is included in the references

Filtration was performed using nitrate cellulose membranes. The mass of the cake was measured by subtracting the known mass of the membrane from the total mass of the cake and membrane defined in equation 10

$M_c = M_{c+m} - M_m$ ……eq.10

Where M_c is the mass of the cake post leaching, M_{c+m} is the mass of the cake and membrane and $M_{m\ is}$ the known mass of the membrane. The filtrate was submitted for ICP-MS, and XRF analysis to determine the content of the metals in the filtrate, specifically U. INAA analysis was performed on both filtrate and cake post-leaching products. Figure 3.10 shows a summary flow sheet of the activities undertaken during this project

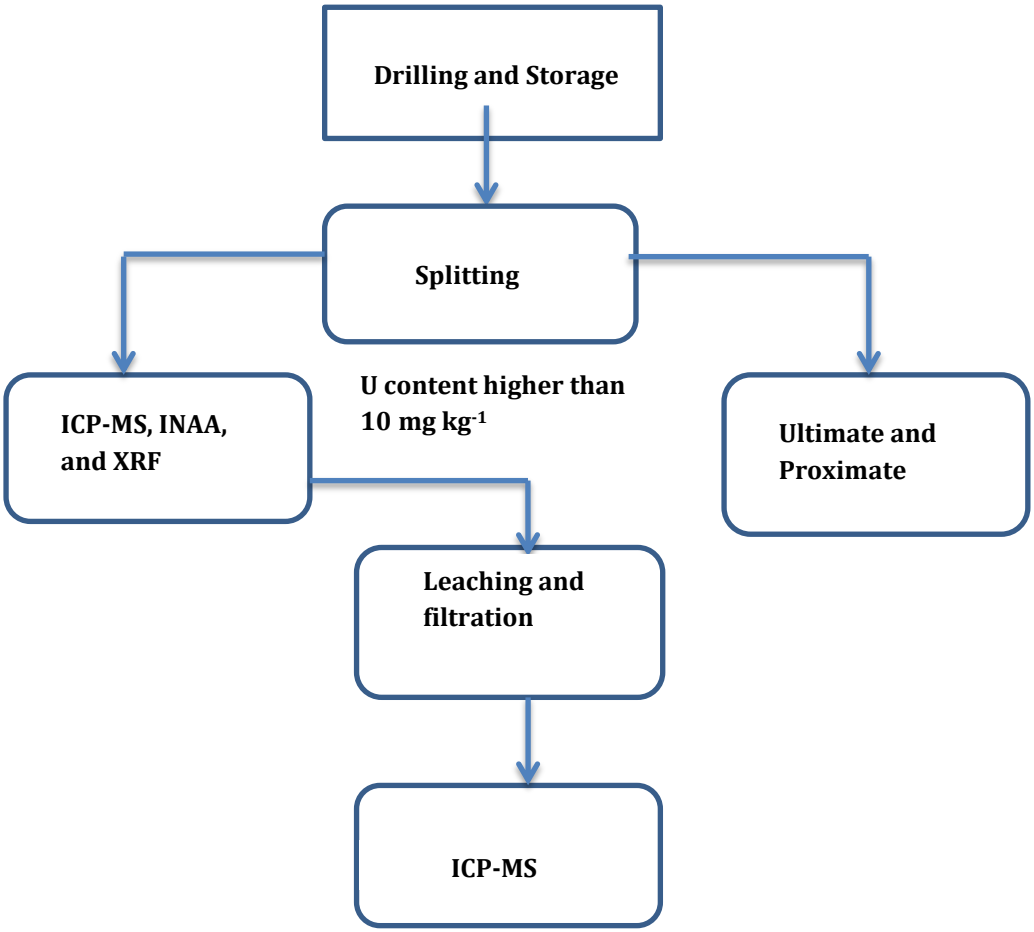


Figure 3. 10: Flow sheet of methodology used in the project

CHAPTER FOUR: RESULTS AND DISCUSSION

In this chapter the results obtained on both coal quality and U occurrence in the borehole coal zones are discussed. The results obtained from leaching the samples are discussed. At the end of each section (coal quality, U quantity, and leaching) a summary of the results is provided. All raw data is given in Appendices A- C. All results reported are on an as received basis.

4.1 PROXIMATE ANALYSIS RESULTS

Splits of samples from 5 borehole coal cores from the SFC underwent proximate analysis, totaling 49 samples. The samples were crushed to -212µ, and analyzed for volatile matter, moisture, ash, and fixed carbon content by TGA. The results from each borehole are discussed.

4.1.1 BH1 (ROODEVLAKTE 558 KS)

The coal zone in BH1 was intersected from 277 m to 309 m, resulting in a 32 m thick coal zone. The proximate results for BH1 are illustrated in Figure 4.1. The fixed carbon content reached a maximum 19.75%, at approximately 310 m in depth. The volatile matter varied from 5.61% to 10.59%, averaging 7.81%. This coal zone has relatively low volatile matter content compared to the samples in the CGS database, which have an average of 24.8% volatile matter in the Roodevlakte area.

The moisture content in BH1 averaged 4.63%, a little higher than the 2.3% H_2O content recorded in the CGS database. A high ash content was observed with a maximum of 88.41% and an average of 79.16%. The ash content is far greater than the 40.3% recorded in the CGS database, and higher than the 30-55% estimated by De Jager (1983), while also being higher than the 30-35% inferred ash by Petric Commission (1975). The proximate analysis of BH1 resembles a proximate analysis of carbonaceous shale, as illustrated by Martins *et al.* (2010). One might conclude that the total coal zone sampled is primarily carbonaceous shale instead of coal.

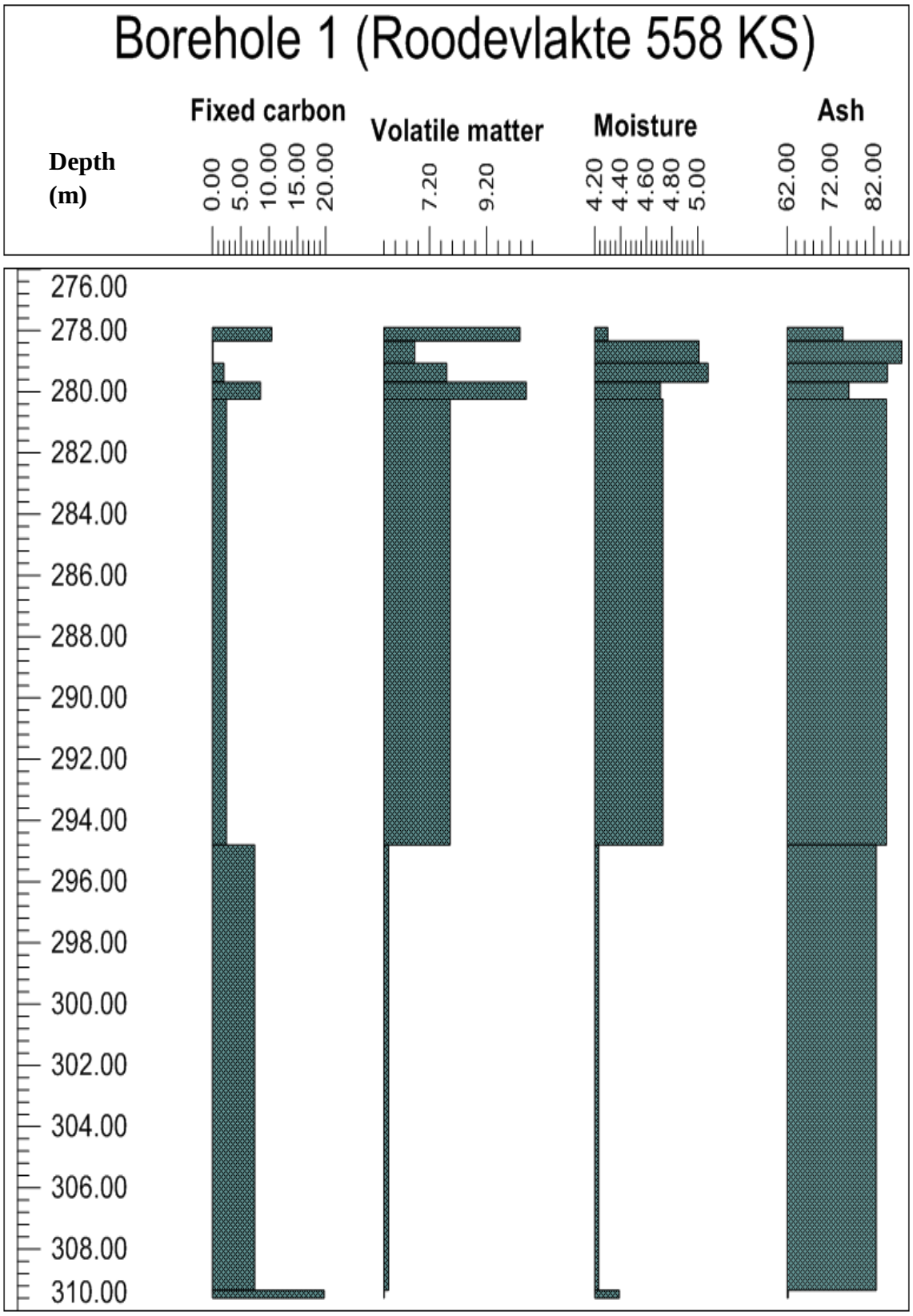


Figure 4. 1:Proximate analysis of coal samples from BH1 with increasing depth

4.1.2 BH2 (KROOMDRAAI 626 KR)

Figure 4.2 represents the proximate analysis for the 6.6 m thick coal zone in BH2, intersected from 251.3 m to 257.9 m. The fixed carbon average was 33.6% throughout the entire coal zone, and peaked at around 254.2 m registering 47.2% fixed carbon content. The Fixed carbon was slightly higher yet comparable to the 31.7% for samples from the Kroomdraai area in the CGS database.

The volatile matter ranges from 16.59% to 33.16%, averaging 24.3%; this is similar to the 23.6% volatile matter content of samples from the same area in the CGS database. The moisture content was fairly consistent throughout the coal zone; a difference of 1.01% was recorded between the minimum 2.35% and 3.36% maximum, averaging 2.76%, which was in line with the 2.1% moisture content from the samples in the CGS database.

The ash content averaged 40.79%, agreeing with the 40.3% recorded in the CGS database. The results were also in line with the 30%-55% ash content estimated by De Jager (1983). The 40.79% was however, higher than the 25%-30% inferred ash content by Petric Commission (1975).

The proximate analysis constituents for BH2 did not vary significantly throughout the coal zone, except for samples from 256.4 m to 258 m, which had relatively high ash content. The proximate results for the upper section of coal are similar to those used by collieries in South Africa for electricity generation (Pinhiero, 1999).

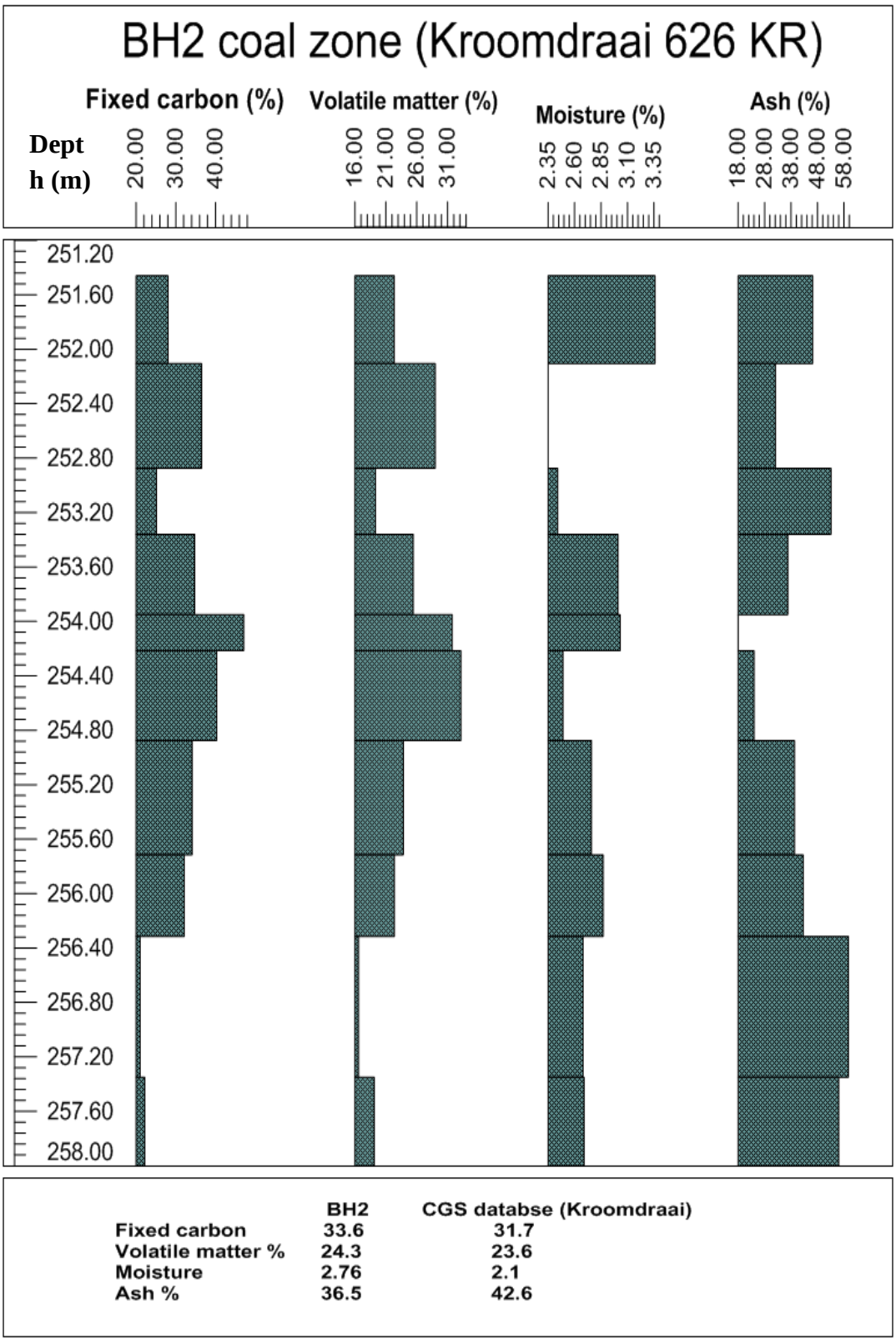


Figure 4. 2: Proximate analysis of coal samples from BH2 with increasing depth

4.1.3 BH3 (TUINPLAATS 678 KR)

Figure 4.3 represents the proximate analysis of BH3 from the 3.6 m thick coal zone (341.5 to 345.1 m). The fixed carbon content varied from 4.28% to 33.39%, averaging 19.5%. The fixed carbon values were low throughout the coal zone when compared to the 30.2% reported by Nel (2012), while also being lower than the 40.15% reported by Linning *et al*. (1983) for samples in the Tuinplaats region. The volatile matter content varied from 8.49% to 26.98%, with a mean value of 17.35%, lower than the 34.2% average reported by Linning *et al*. (1983) from the same region.

The moisture content of the coal samples from BH3 varied from 2.01% to 3.20%, and averaged 2.4%. The moisture content was comparable to the 2.1% reported by Nel (2012), and the 2.05% reported by Linning *et al*. (1983) for the Tuinplaats region. The ash content varied from 37.31% to 84.69%, and averaged 60.64%. The ash content was higher than the 30%-55% ash content estimated by De Jager (1983), and was higher than the 25%-30% inferred ash content by Petric Commission (1975). Nel (2012) recorded 27.8% ash content and Linning *et al.* (1983) reported 29.1% ash from the samples in the Tuinplaats region.

When one considers the entire coal zone in BH3, it can be noted that 64.4% of the 3.6 m coal zone contained samples with an ash content higher than 50%. For this reason, samples from 343.3 m to the end of the coal zone exhibited very poor coal quality, in terms of high ash content, low volatile matter, and low fixed carbon content compared to samples from 341.5 m to 343.3 m.

Figure 4.3 shows a 1.5 m region from 342 m to 343.5 m which had the best properties in the coal zone and the highest potential in terms of coal quality. The region contained a fixed carbon average of 28.21%, lower than the 40.15% reported by Linning *et al*. (1983), yet higher than the overall 19.5% fixed carbon. The 22.4% volatile matter average was lower than the 34.2% average reported by Linning *et al*. (1983) from the same region, and the 46.3% ash content is higher than the 29.1% reported by Linning *et al*. (1983), however both the volatile matter and ash content in this region exhibited better coal qualities compared to the rest of the coal zone.

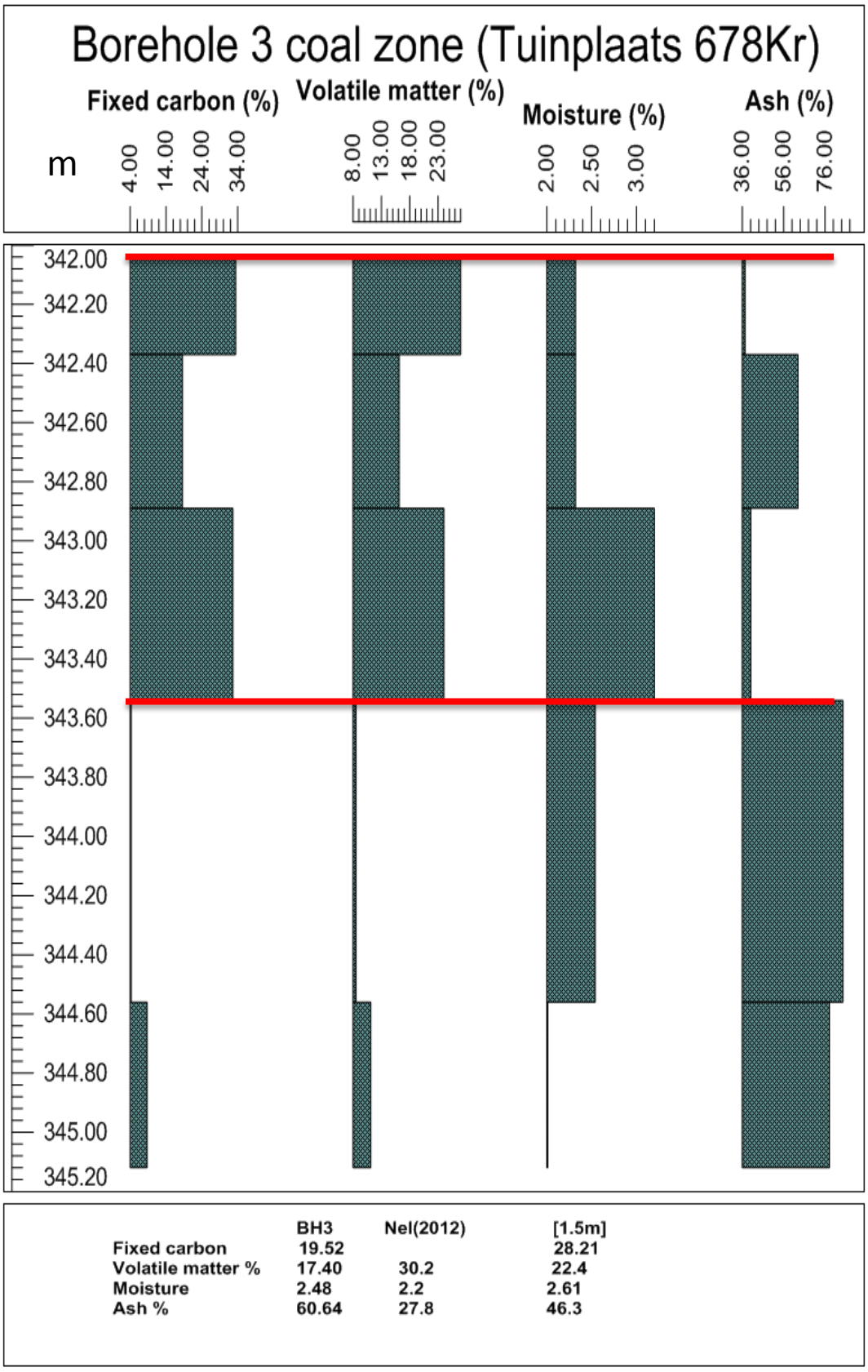
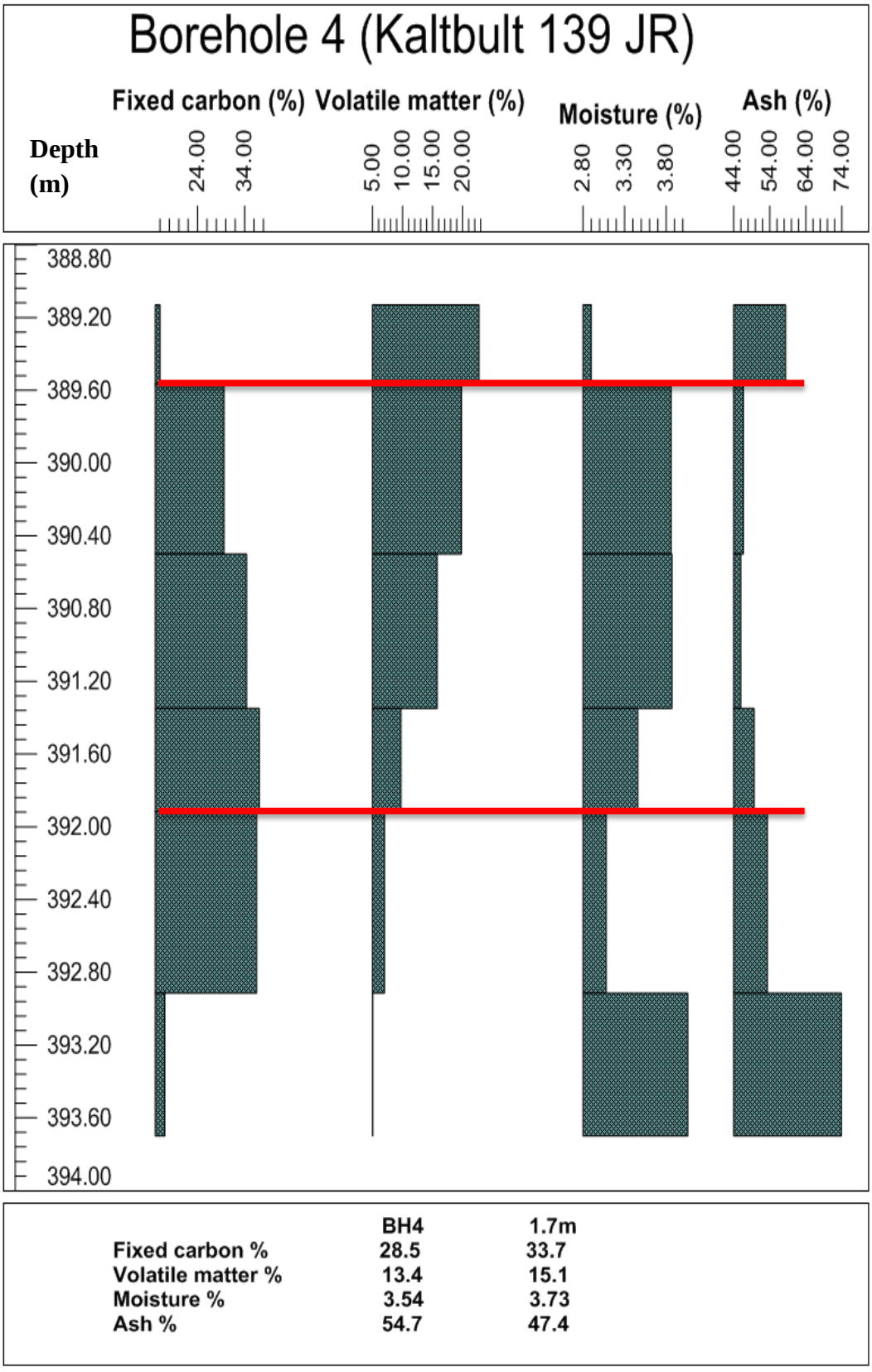


Figure 4. 3: Proximate analysis of coal samples from BH3 with increasing depth

4.1.4 BH4 (KALTBULT 139JR):

Figure 4.4 represents the proximate analysis for the 4.9 m thick coal zone intersected from 387.8 m to 393.7 m. The fixed carbon ranged from 15.98% to 37.13%. The BH4 coal zone averaged 28.5% fixed carbon, which was lower than the 35.9% reported by Linning *et al.* (1983) from the Kalkbult area. A volatile matter maximum of 22.7% was found at the top of the coal zone; the 13.3% volatile matter average was low, lower than 26.6% reported by Linning *et al.* (1983). A relatively high ash content average (54.65%) was observed, higher than the 25%-30% inferred ash content by Petric Commission (1975), whilst also being higher than the 30%-55% ash content estimated by De Jager (1983), and the 35% ash content reported by Linning *et al.* (1983) for samples from the Kalkbult region.

Similar to BH3, BH4 had a 1.7 m region that had the best potential of being mined in terms of coal quality (390 m -391.7 m), 33.7% fixed carbon was recorded, which was comparable to the 35.9% reported by Linning *et al.* (1983) and higher than the 28.5% average for the entire coal zone. The 15.1% volatile matter in this region was higher than the 13.3% reported earlier. Yet lower than the 26% reported by Linning *et al.* (1983), and the 47.4% ash content from this 1.7 m region was higher than the 35.9% ash content reported by Linning *et al.* (1983) for samples from the Kalkbult area.



	BH4	1.7m
Fixed carbon %	28.5	33.7
Volatile matter %	13.4	15.1
Moisture %	3.54	3.73
Ash %	54.7	47.4

Figure 4. 4: Proximate analysis of coal samples from BH4 with increasing depth

4.1.5 BH5 UCZ (WOLFHUISKRAAL 626JR)

Figures 4.5 and 4.6 represent the proximate analyses results for the coal zones in BH5, where two coal zones were sampled. The UCZ was intersected from 144.50 m -155.3 m, totaling 0.8 m of coal, followed by shale and sandstone. Coal was found again from 152.2 to 155.3 m, resulting in a 3.6 m total coal zone.The UCZ had an average 24.14% fixed carbon content, lower than the 34.9% reported in the CGS database for samples from the Wolfhuiskraal region. The volatile matter average was 6.8%, below the 21.0% volatile matter content recorded in the CGS database. The ash content was higher than 50% for every sample in the coal zone except in the last sample where the ash content was 43.3%; the average ash content for the borehole was 68.7%. The assh content in the UCZ was higher than the 25%-30% inferred ash reported by The Petric Commission (1975), whilst also being higher than the 30%-55% ash content estimated by De Jager (1983), and the 39.9% average recorded in the CGS database for samples from the same region. The proximate analysis results for the UCZ of BH5 are below the limits of typical South African coals. The proximate analysis for BH5 resembles shale qualities instead of coal (Martins *et al*., 2010)

4.1.6 BH5 LCZ (WOLFHUISKRAAL 626JR)

The LCZ was intersected from 344.67 m to 350.67 m, resulting in a 6 m thick coal zone. The LCZ has an average 24.4% fixed carbon content, lower than the 34.9% recorded in the CGS database. The 17.5% volatile matter average was lower than the 21% recorded in the CGS database. The ash content averaged 55.10%, which was higher than the 39.9% ash content in the CGS database, and higher than the 25%-30% ash content inferred coal estimated by The Petric Commission (1975), whilst also being higher than the 30%-55% ash content estimated by De Jager (1983). The region with the most promise in this coal zone is a 1.6 m area found from 346.3 m to 347.9 m, which had 31.6% fixed carbon, 20.5% volatile matter and 44.5% ash content. The 20.5% volatile matter content, compared well with other coals used in collieries in the country especially in the Mpumalanga region (Pinhiero, 1999). BH3 (342 m-343.5 m) and BH5 LCZ (346 m to 347.8 m) have similar depths of potential mineability; BH4's best region is lower (from 389.5 m)

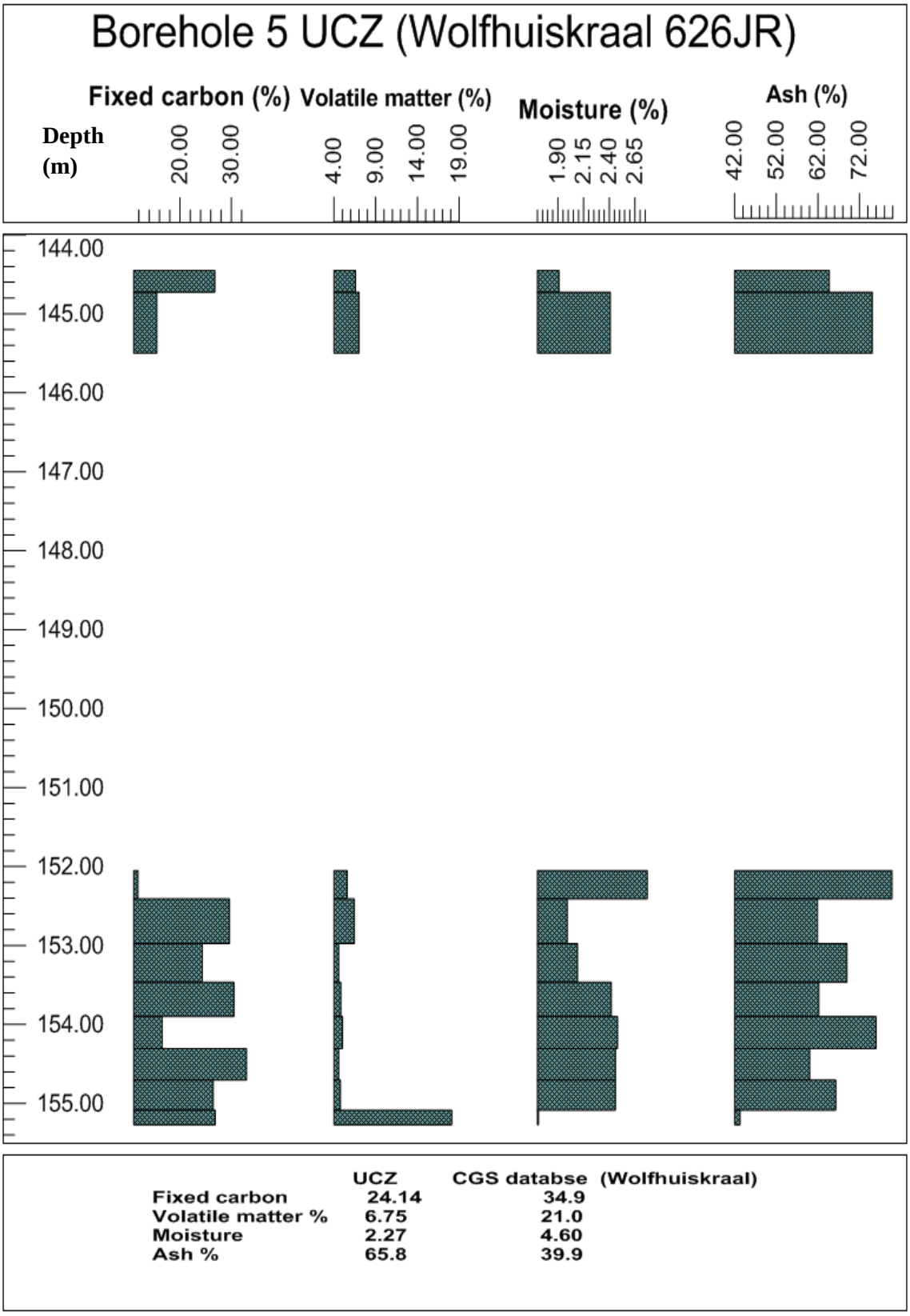
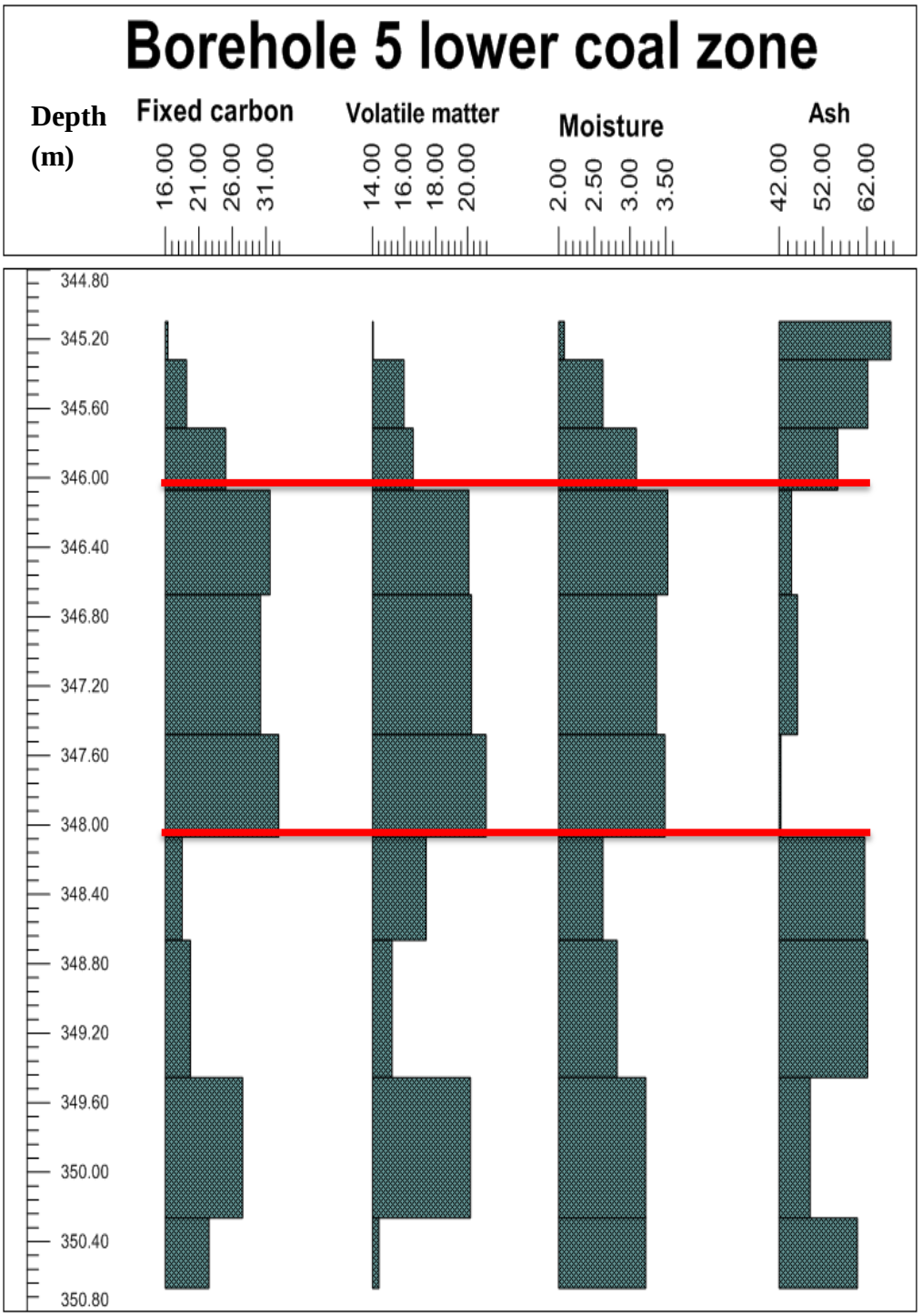


Figure 4. 5: Proximate analysis of coal samples from the UCZ in BH5



	LCZ	CGS databse (Wolfhuiskraal)	[1.6m]
Fixed carbon	24.4	34.9	31.6
Volatile matter %	17.3	21.0	20.5
Moisture	3.01	4.60	3.46
Ash %	55.7	39.9	44.5

Figure 4. 6: Proximate analysis of coal samples from BH4 with increasing depth

4.2 ULTIMATE ANALYSIS AND CV

Ultimate analyses were run on all 49 samples to determine the nitrogen, carbon, hydrogen and sulfur content present in the samples, with a key focus being the sulfur content, as this is important in determining possible harmful SO_2 emissions; the carbon content gives a measure of the coals combustibility. For this reason, these two elements will be discussed in more detail compared to the hydrogen and nitrogen content. The CV of the samples was studied to provide information pertaining to the energy released during combustion. Figure 4.7 gives the average CV per borehole. The full set of results can be found in Appendix A.

Figure 4.7 displays that BH1 had the lowest CV on average (1.8 MJ/kg). BH2 has the highest average CV (18.2 MJ/kg), displaying a coal zone that can be beneficial to the economy of the country. BH4 followed with the second highest CV average (11.8 MJ/kg), and the LCZ of BH5 had a slightly higher CV (10.9 MJ/kg), compared to BH3 (10.6 MJ/kg).

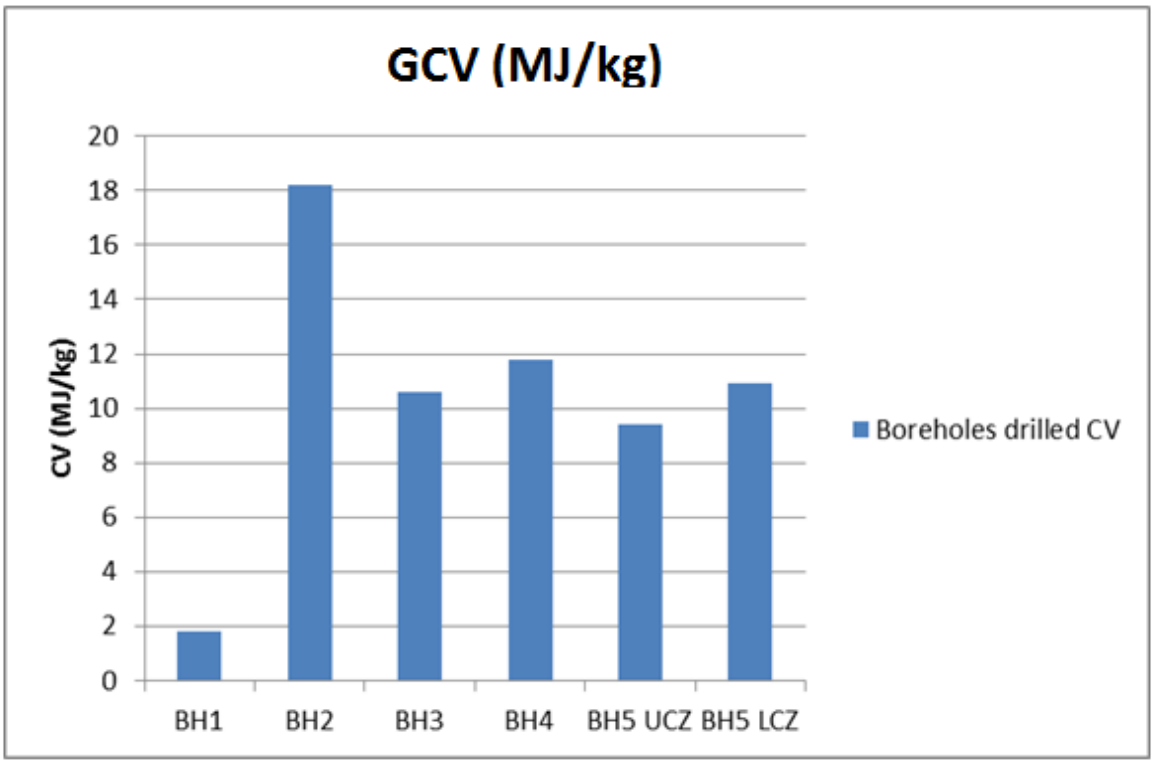


Figure 4. 7: CV values of the coal zones from BH1 to BH5

4.2.1 BH1 (ROODEVLAKTE 558 KS)

The carbon content in BH1 did not show a significant difference from a minimum of 4.10% to a maximum of 13.71%. Figure 4.8 shows the ultimate analysis results for the coal zone in BH1. The carbon content was highest at the top of the coal zone. The 7.3% average carbon content was extremely low. The carbon content describes a poor quality coal zone that can't be used for power generation by neither the local industry nor the export industry (Pinhiero, 1999).

The sulfur content was relatively low, peaking at a modest 0.24% and averaged 0.16%. Compared to South Africans coals, these results correspond well to the 1% by weight reported by Gonenc *et al.* (1990), while also being less than 0.4-1.29% reported by Wagner and Hlatshwayo (2005) and 1.47% by Roberts (2008). BH1 had the lowest average CV (1.8 Mj/kg) with one sample registering a CV value of 0. The maximum CV obtained from BH1 was 4.15 Mj/kg.

The CV of BH1 further confirms results obtained from proximate analysis, that this coal zone does not contain good quality coal, with properties alluding to the coal zone being made up of carbonaceous shale (Qing *et al*., 2013; Martins *et al*., 2010).

4.2.2 BH2 (KROOMDRAAI 626 KR)

BH2 had a carbon content ranging from 27.88% to 65.28%. Figure 4.9 shows the ultimate analysis results for the coal zone in BH2. The average carbon content throughout the coal zone was 44.56%. The carbon content for the 2.75 m region (253 m to 255.75 m) was 50.63%. This region is a particularly mineable region, with properties similar to coals used in the South African electricity generation industry (Pinhiero, 1999). The maximum sulfur content was 8.86%, averaging 3.16%. The sulfur content was slightly higher than the 2.83% recorded in the CGS database for samples from the same region. It must be noted that relative to South African coals, the 3.16% average, is higher than with the 1% by weight reported by Gonenc *et al.* (1990), while also being higher than 0.4-1.29% reported by Wagner and Hlatshwayo (2005), and 1.47% by

Roberts (2008). The sulfur content in this coal zone is extremely high and will require desulfurization methods should it mined.

The CV ranged from 11.65 MJ/kg to a maximum of 27.04 MJ/kg. The maximum CV correlated to the maximum carbon value obtained from ultimate analysis results. An average CV of 18.2 MJ/kg ROM coal was lower than the 22 MJ/kg estimated by De Jager (1983), for the SFC and was comparable to the 18.5 MJ/kg for samples found in the CGS database in Kroomdraai area.

BH2's coal quality resembles a typical South African bituminous coal (Falcon and Ham, 1988; Pinhiero, 1999) and, it could be of economic benefit to the country, depending on the available tonnages in the area. This coal zone should be encouraging to potential investors, especially considering that if this coal zone were to be beneficiated, the CV should increase and the ash content decrease making this coal zone even more suitable for local electricity generation, apart from the sulfur in certain horizons.

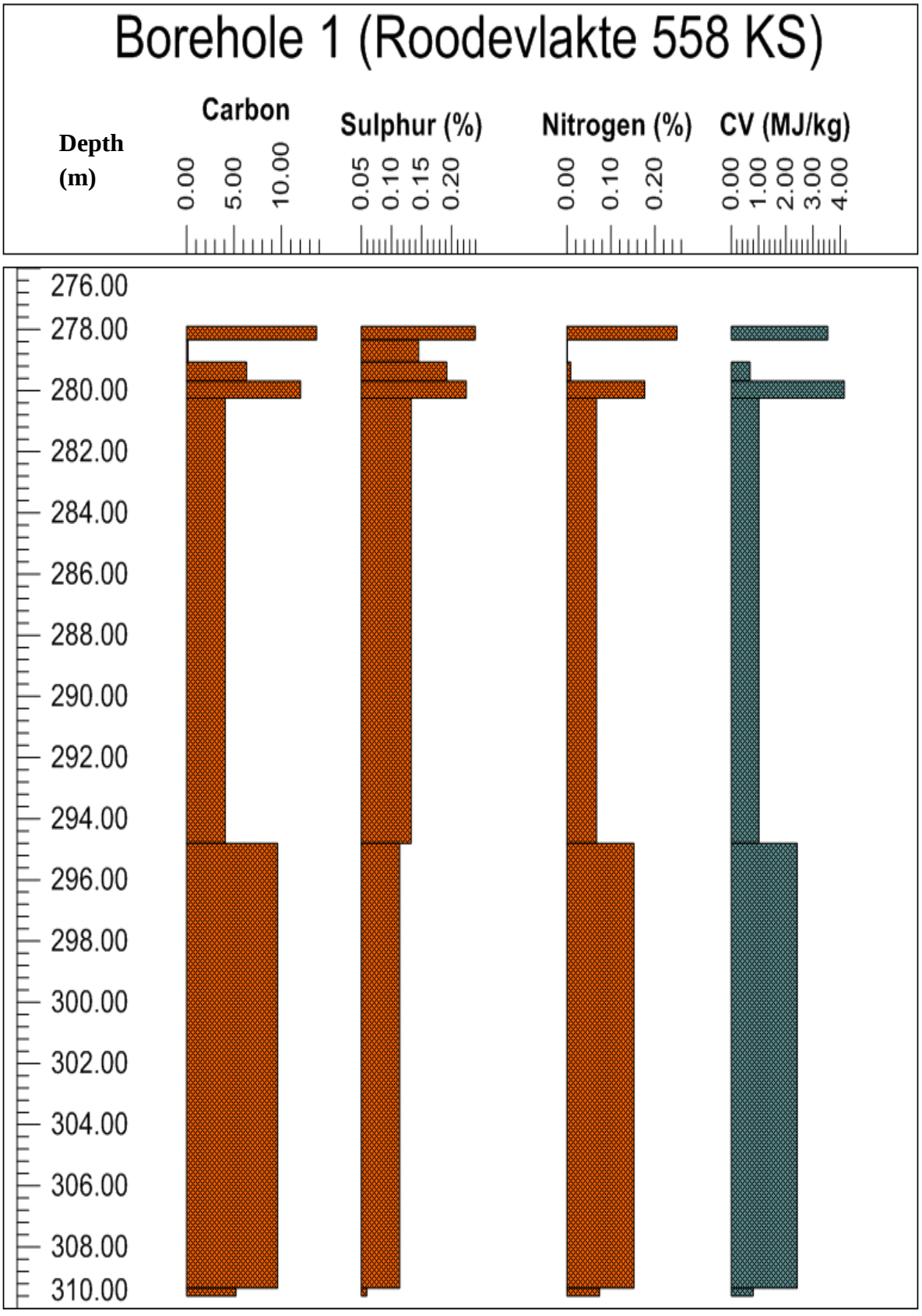


Figure 4. 8: Ultimate analysis and CV of BH

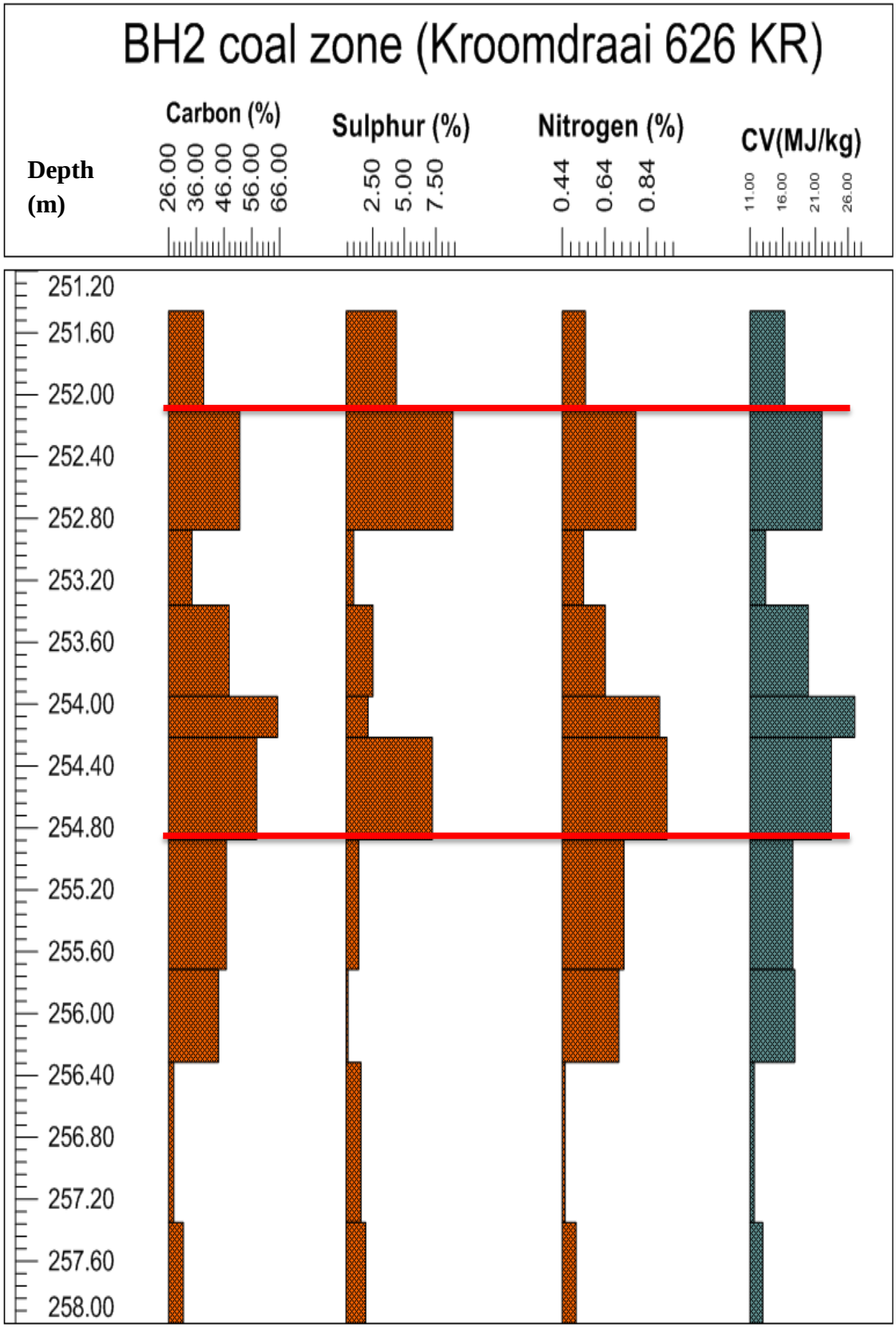


Figure 4. 9: Ultimate analysis and CV of BH2

4.2.3 BH3 (TUINPLAATS 678 KR)

The BH3 samples exhibited a wide range in carbon value; from a minimum 5.5% to the maximum 47.6%. The average carbon content (29.9%) was lower than the average 51% reported by Nel (2012) from samples in the Tuinplaats region.

The BH3 samples had moderate sulfur content relative to the other borehole core coal zones sampled. The maximum content was 3.59% with an average of 2.52%. The average was lower than the 2.69% reported by Nel (2012), for the Tuinplaats region; Relative to South African coals, the sulfur content was higher than the 1% by weight reported by Gonenc *et al.* (1990), while being higher than 0.4-1.29% reported by Wagner and Hlatshwayo (2005) and 1.47% by Roberts (2008).

The samples from the BH3 borehole displayed a difference of 18.8 MJ/kg, from the minimum value (1.72 MJ/kg) to the maximum value (19.8 MJ/kg). The average CV (10.6 MJ/kg) was lower than the 22 MJ/kg estimated by De Jager (1983), and lower than the 23.5 MJ/kg reported by Nel (2012), whilst also being lower than the 23.2 MJ/kg reported average by Linning *et al*. (1983), for samples from the Tuinplaats area.

The carbon content for the 1.5 m region (342 m to 343.5 m) was 38% which was better than the 29% for the entire coal zone; however it was still less than the 51% recorded by Nel (2012) for this region. Similar to the results found by proximate analysis, samples were seen to be of very low quality coal especially samples at a depth of 343.6 m to 345.1 m, which averaged 2.92 MJ/kg, compared to samples from 341.5 to 343.1 m that averaged 15.6 MJ/kg. Similar to the results found by proximate analysis, the carbon content seen in Figure 4.10 suggests that samples were of low quality coal at a depth from 343.6 to 345.1 m, compared to samples from 341.5 to 343.1 m

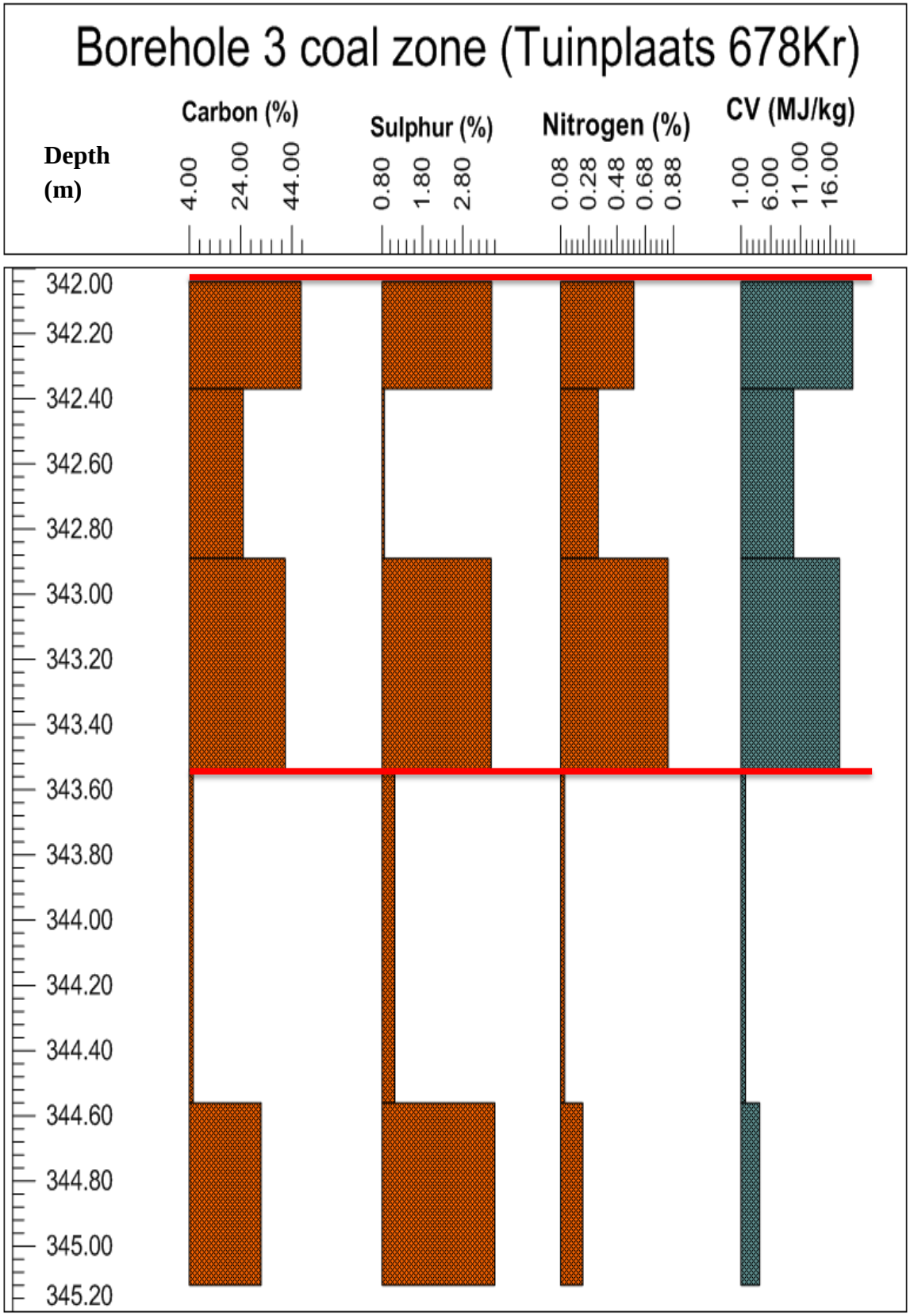


Figure 4. 10: Ultimate analysis and CV of BH3

4.2.4 BH4 (KALKBULT 139JR)

The BH4 coal zone had the second highest carbon content of the borehole core coal zones studied here, second only to BH2. Figure 4.11 shows the ultimate analysis results for the coal zone in BH4. The carbon content ranged from 18.98% to 41.232%, averaging 32.3%. Sulfur content averaged 1.78%, which was lower than the 2.43% recorded by Linning *et al*. (1983), for samples in the Kalkbult area. Relative to the coals in South Africa, the sulfur content was higher than the 1% by weight reported by Gonenc *et al.* (1990), while being higher than 0.4-1.29% reported by Wagner and Hlatshwayo (2005), and 1.47% by Roberts (2008). The higher sulfur contents are at the top of the coal zone where the coal zone is mostly shale, and decrease with increasing depth. This indicates a possible rise in sea water in the environment, during the coal formation stage, towards the top of the coal zone

BH4 displayed a fairly consistent CV ranging from 10.27 MJ/kg to 16.45 MJ/kg, a difference of 6.1 MJ/. The 11.8 MJ/kg average was the second highest CV of the boreholes drilled, however still lower than the 22 MJ/kg estimated by De Jager (1983) for the SFC, and slightly lower than the 20.8 MJ/kg reported by Linning *et al*. (1983) for the Kalkbult area .

BH4 could also be considered as a borehole of economic interest with alternatives such as Underground coal gasification (UCG) possibly pursued for this coal zone as it meets the criteria of being deeper than 200 m and ash content less than 60% while also having a decent carbon content of 32.3% (Dubinski, 2009)

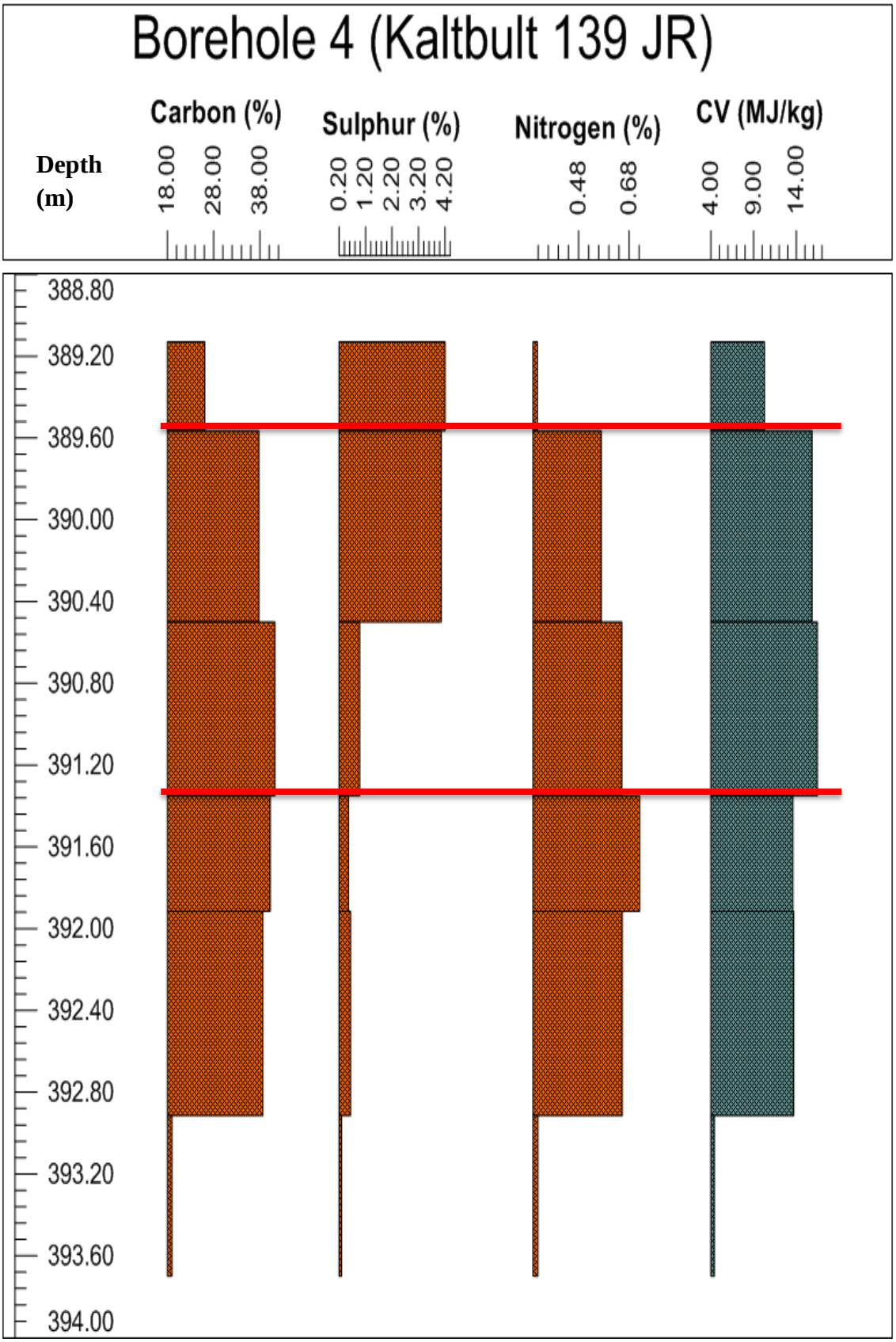


Figure 4. 11: Ultimate analysis and CV of BH4

4.2.5 BH5 UCZ (WOLFHUISKRAAL 626JR)

The average carbon content for the UCZ in BH5 was very low (26.6%). The carbon values resembled those of shale rather than coal as given in Martins *et al.* (2010). Figure 4.12 shows the ultimate analysis results for the coal zone in the UCZ in BH5. The UCZ of BH 5 had relatively low sulfur content; it had an average of 2.3% sulfur which was comparable to the 2.2% in the CGS database for samples from the Wolfhuiskraal region; however compared to South African coals, this was higher than the 1% by weight reported by Gonenc *et al.* (1990), while being higher than 0.4-1.29% reported by Wagner and Hlatshwayo (2005), and 1.47% by Roberts (2008)

The UCZ in BH5 had a very low CV, varying from 4.15 MJ/kg to 17.82 MJ/kg, averaging 9.39 MJ/kg which was lower than the 22 MJ/kg estimated by De Jager (1983) and lower than the 17.3 MJ/kg reported in CGS database for samples from the same area.

4.2.6 BH5 LCZ (WOLFHUISKRAAL 626JR)

The LCZ in BH5 had a higher carbon content than the UCZ, specifically in the horizon between 346 m and 348 m. Figure 4.13 shows the ultimate analysis results for the coal zone in the LCZ in BH5. The LCZ averaged a carbon content of around 31.8%, compared to the 26.6% registered by the UCZ. Thus, in terms of the combustibility, the LCZ had better coal quality than the UCZ. The region from 345.89 m to 347.9 m describes a zone where the average carbon content is 40%.

The LCZ had an average of 0.47% sulfur which was the second lowest of all the boreholes; relative to South African coals, the sulfur content was comparable to the 1% by weight reported by Gonenc *et al.* (1990), while being less than 0.4-1.29% reported by Wagner and Hlatshwayo (2005) and 1.47% by Roberts (2008). The maximum sulfur content in the coal zone is 1.47%, which is relatively low. The LCZ averaged a CV of 15.8 MJ/kg lower than the 22 MJ/kg estimated by De Jager (1983) and yet comparable to the 17.3 MJ/kg from samples found in the CGS database in the same area.

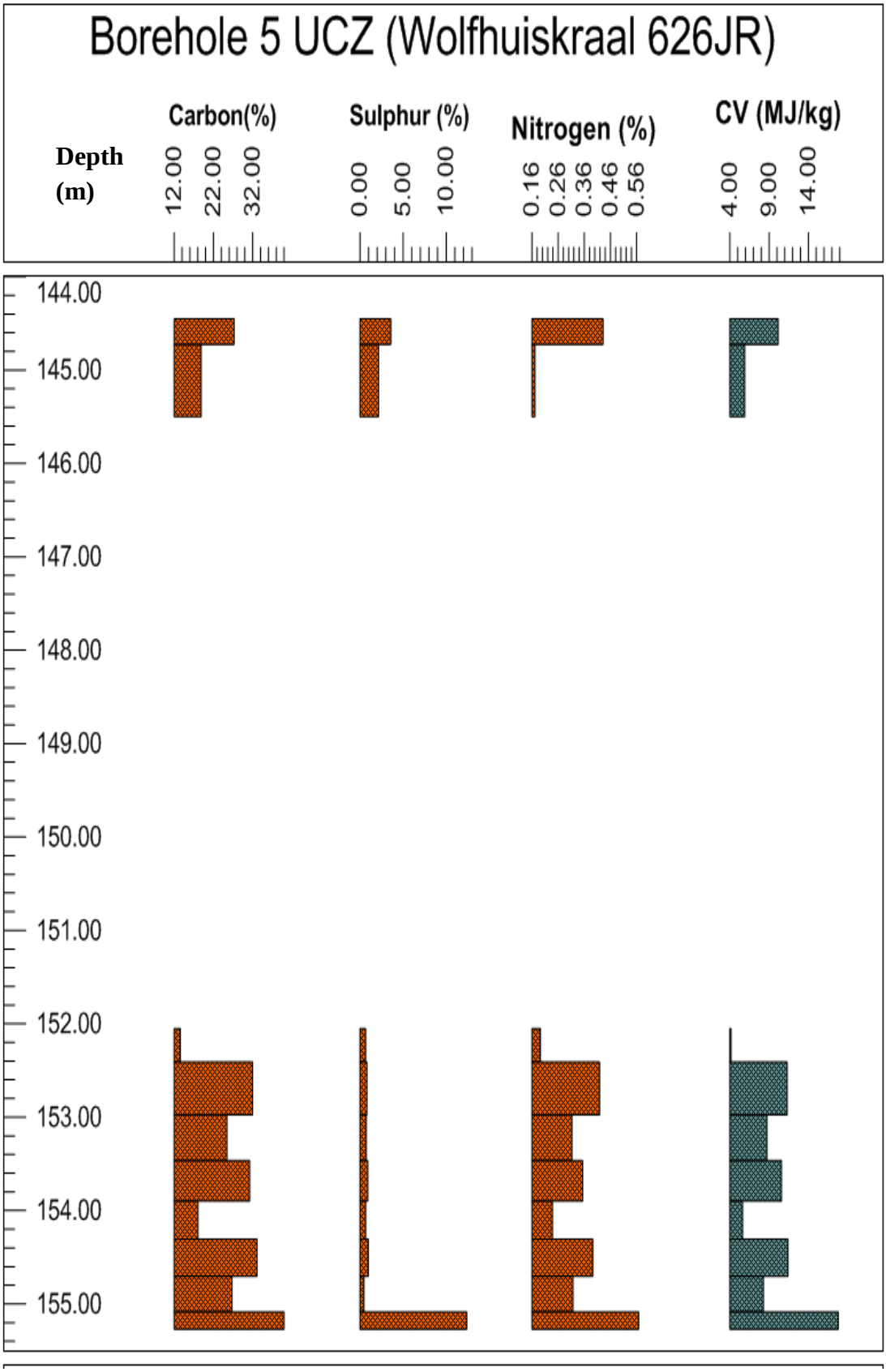


Figure 4. 12: Ultimate analysis and CV of the UCZ in BH5

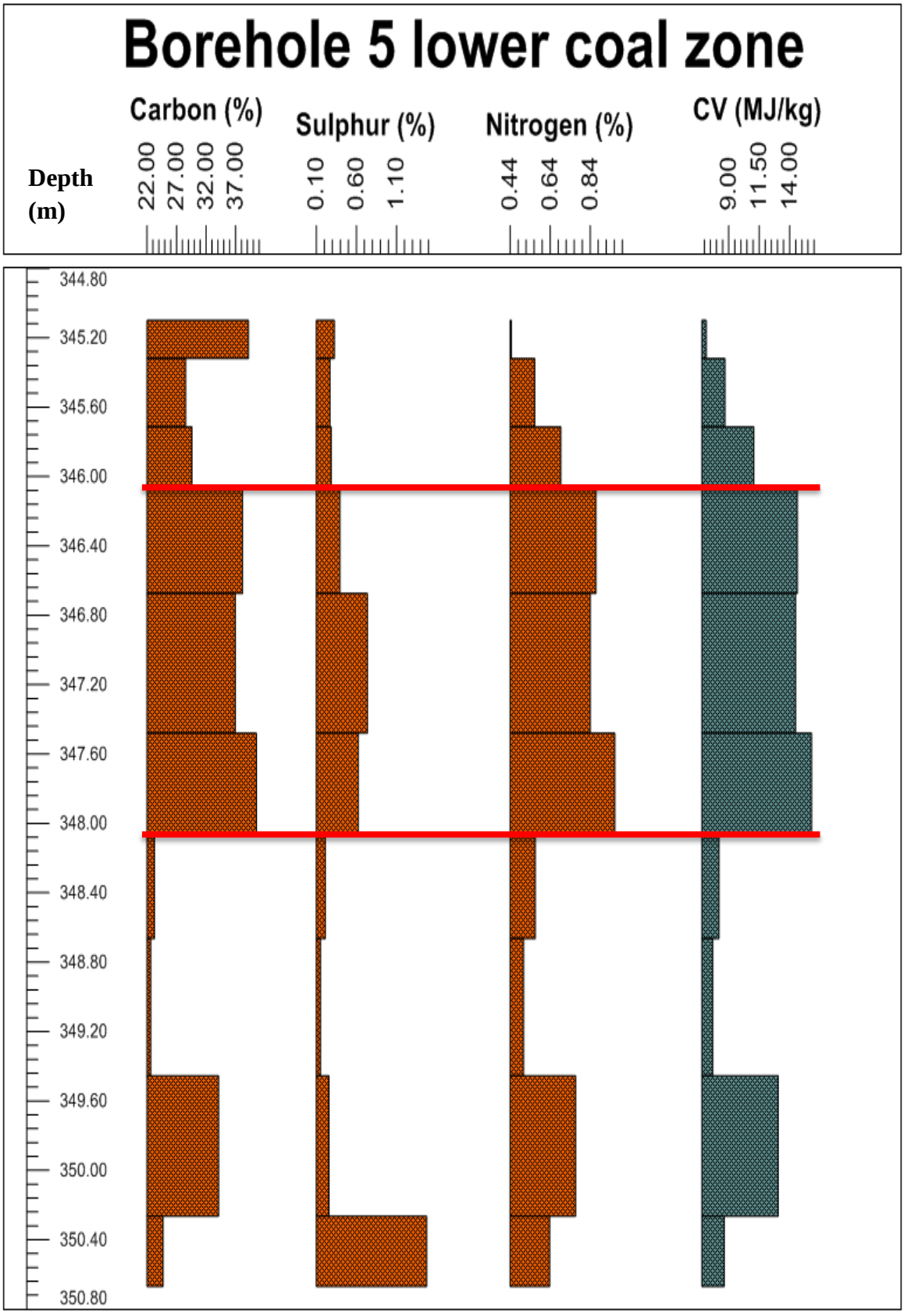


Figure 4. 13: Ultimate analysis and CV for the LCZ in BH5

4.3 XRF RESULTS

XRF was used to determine the major inorganic compounds present in the coal samples. Table 4.1 shows the average major constituents present in each borehole; due to the limited literature available on the SFC, it was hard to compare how these values rank relative to other coals from the areas. However Nel (2012) did conduct studies in the Tuinplaats farm studied in this research (BH3), and the values reported were compared in Table 4.1. The full set of results is found in Appendix C. The coal samples had high SIO_2 content, as expected, followed by Al_2O_3 and Fe_2O_3. BH1 had the highest average of SiO_2, followed by BH2 and BH3. The LCZ in BH5 had the highest Al_2O_3 content and the UCZ of BH5 had the lowest Al_2O_3 content. Fe_2O_3 content was highest in BH2 and BH4, the LCZ in BH5 had the lowest Fe_2O_3 content. Overall, BH3 had similar content in terms of SIO_2 Al_2O_3, and TiO_2 compared to those reported by Nel (2012); however BH3 registered higher Fe_2O_3 than the results from Nel (2012) and Nel (2012) reported higher CaO content.

Table 4. 1: Major constituents in coal ash samples by XRF (%)

	SIO2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	MnO_2	P_2O_5	SO_3
BH1	67.8	22.22	2.87	0.89	1.27	0.89	2.31	0.02	0.04	0.10
BH2	62.4	21.51	7.81	1.00	2.13	0.61	1.91	0.07	0.04	0.98
BH3	62.1	23.81	6.56	0.97	1.78	0.60	1.83	0.04	0.04	0.64
BH4	61.5	20.77	7.82	0.88	1.75	0.99	2.90	0.28	0.03	0.21
BH5 UCZ	61.51	19.41	7.16	0.77	2.45	1.16	2.54	0.15	0.04	0.71
BH5 LCZ	55.60	33.74	1.49	1.68	2.07	0.55	1.13	0.02	0.68	0.62
Nel (2012)	63.20	22.00	3.00	1.12	4.70	0.56	1.22	0.07	0.16	2.83

4.4 CONCLUSIONS ON COAL QUALITY

- BH1 and the UCZ in BH5 had ash content higher than 50% for all the samples collected throughout the coal zone. These coal zones are made up almost entirely of carbonaceous shale.

- BH2 had reported coal quality that resembles a typical of South African bituminous coal and could potentially be of economic benefit to the country depending on the available tonnages in the area.
- BH3 and BH4 had horizons that are potentially mineable, and could be of use in coal conversion industries.

4.5 URANIUM DETECTION ANALYSIS

ICP-MS analysis was conducted on the 49 samples from BH1 to BH5. A ^{238}U standard sample was used, and it was assumed that the U isotope detected in the SFC coal samples was ^{238}U. ^{238}U is the most abundant of the U isotopes found in nature (Edwards and Oliver, 2000). Confirmation will be achieved by INAA (Section 4.8). Figure 4.14 shows the average U content from BH1 to the LCZ in BH5. The full set of raw results are found in appendix B

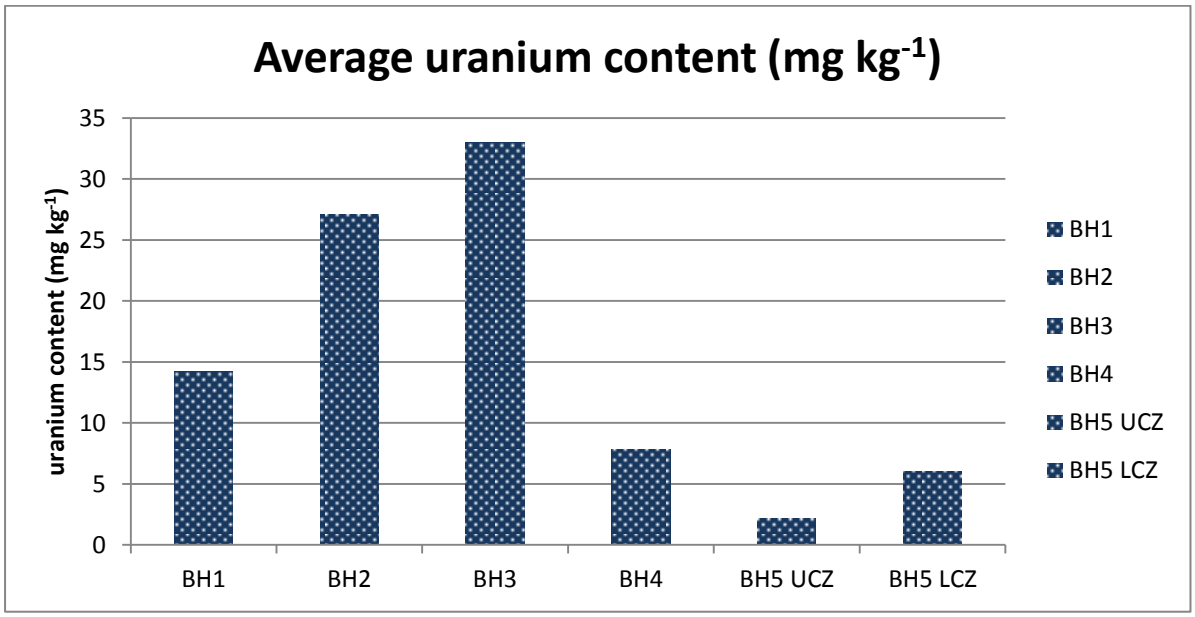


Figure 4. 14: Average U content in borehole coal zones (mg kg^{-1}) ICP-MS

In summary, BH3 had the highest U content average of all the borehole coal zones (33 mg kg^{-1}) followed by BH2 (26 mg kg^{-1}) and BH1 (14 mg kg^{-1}). BH4, the UCZ in BH5, and the LCZ in BH5 all had U content averages less than 10 mg kg^{-1}. All borehole coal zones studied had U content averages higher than the 2 mg kg^{-1} world average reported by Swaine (1990). Figure 4.15 shows the distribution of U in the borehole coal zones.

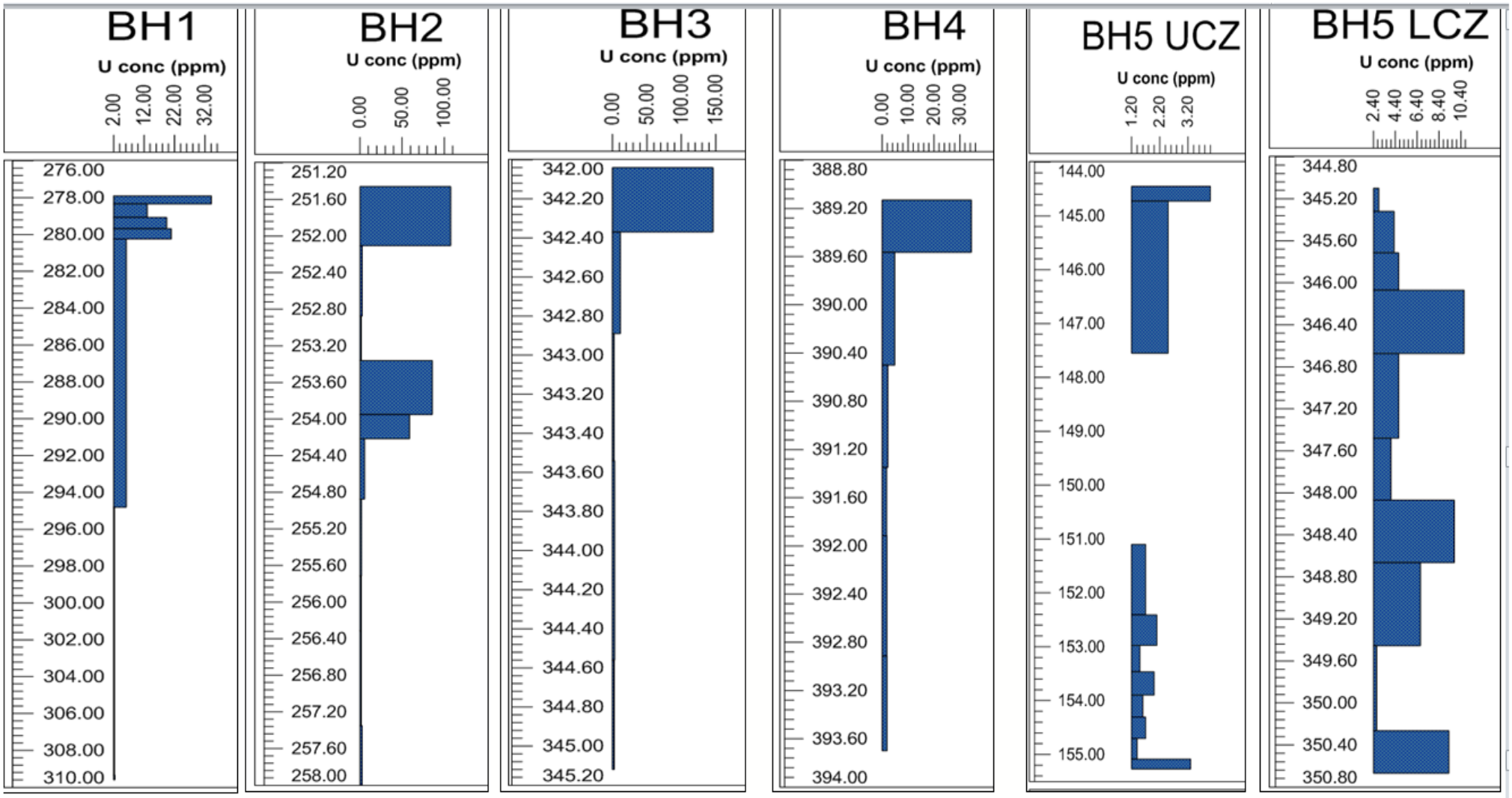


Figure 4. 15: U content relative to depth (m) of coal zone

4.5.1 BH1 (ROODEVLAKTE 558 KS)

The U content in samples from BH1 ranged from 2.3 mg kg^{-1} to 34.1 mg kg^{-1}, averaging 14 mg kg^{-1}. When one considers the coal quality results of the coal zone, BH1 was made up completely of carbonaceous shale and thus U in this coal zone occurred in the carbonaceous shale. The findings agree with those of Swanson (1956), where the U occurred primarily in organic-rich black shales studied from Pennsylvanian age coals, in Kansas and Oklahoma. The 14 mg kg^{-1} average was lower than the 76 mg kg^{-1} reported by Nel (2012) for coaly shale. The maximum U content (34.1 mg kg^{-1}) was found in the first 2 m of the coal zone, agreeing with studies by Nel (2012) and Christie (1989), which stated that U mineralization in the SFC occurred in the uppermost coal layer. Figure 4.16 shows the U content in BH1 to the UCZ in BH5, relative to the major proximate analysis and ultimate analysis constituents.

4.5.2 BH2 (KROOMDRAAI 626 KR)

Samples from BH2 had a U content that ranged from 1.6 mg kg^{-1} to 107.7 mg kg^{-1}, averaging 27 mg kg^{-1}. Relative to the coal quality, the region with the highest U content in this coal zone was predominately coal (% ash < 50%), with a significant peak occurring towards the middle of the coal zone (85.9 mg kg^{-1}), also a coal-rich zone. The 37.8 mg kg^{-1} average for the predominantly coal regions was lower than the 130 mg kg^{-1} reported by Nel (2012) for shaly coal in the SFC. The findings agree with results from Nel (2012), where the samples also had higher U content in the shaly coal compared to the coaly shale. U was found in the areas that are predominately carbonaceous shale (% ash > 50%) as well; the 2.03 mg kg^{-1} average for the carbonaceous shale regions, was significantly lower than the 76 mg kg^{-1} reported by Nel (2012) for coaly shale. Hancox and Gotz (2014) also reported that the U in the SFC is known to be found both in the coal and in the carbonaceous mudrock, and supported by Cole (2009) who concluded that U is disseminated throughout the coal and carbonaceous shale in the SFC. U content was highest at the top of the coal zone, agreeing with studies by Nel (2012) and Christie (1989), who concluded that U mineralization in the SFC occurred in the uppermost coal layer.

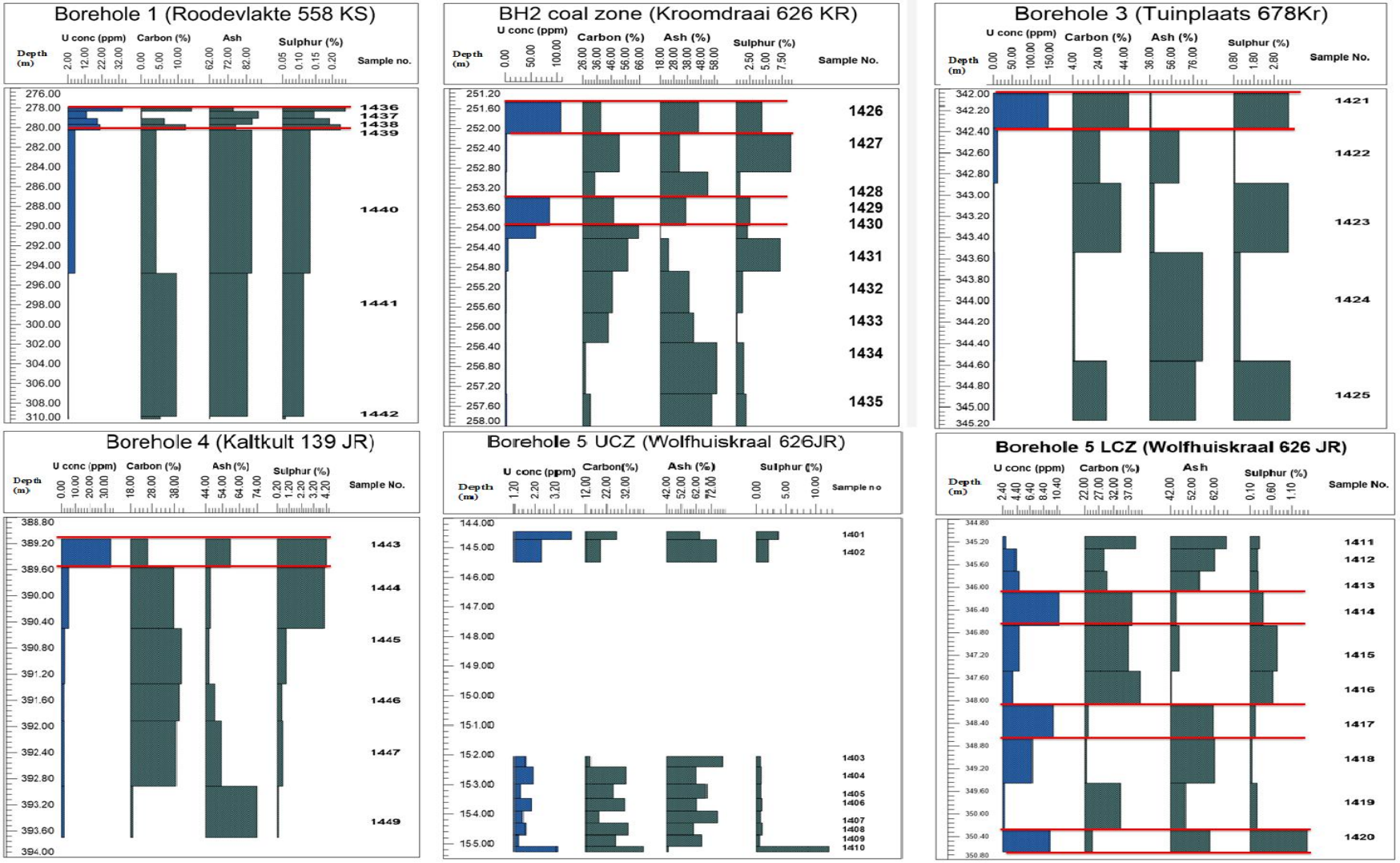


Figure 4. 16: U content in all coal zones relative to coal quality results

4.5.3 BH3 (TUINPLAATS 678 KR)

Samples from BH3 had the highest U content on average (33 mg kg^{-1}), ranging from 2.2 mg kg^{-1} to 145.9 mg kg^{-1}. The 5.67 mg kg^{-1} average for the carbonaceous shale region was significantly lower than the 76 mg kg^{-1} reported by Nel (2012) for coaly shale; the region with the highest U content in this coal zone was predominately coal, averaging 74.1 mg kg^{-1}, which was lower than the 130 mg kg^{-1} reported by Nel (2012) for shaly coal in the SFC. Thus both carbonaceous shale regions and coal regions contained U; however the predominately coal regions had a higher U content. The findings agree with those by Nel (2012) whose samples also had higher U content in the shaly coal compared to the coaly shale. Hancox and Gotz (2014), also reported that the U in the SFC is known to be found both in the coal and in the carbonaceous mudrock, and supported by Cole (2009) who concluded that U is disseminated throughout the coal and carbonaceous shale in the SFC. The maximum U content was found at the top of the coal zone, within the first 1 m of the coal zone, agreeing with studies by Nel (2012) and Christie (1989) who found that U mineralization in the SFC occurs in the uppermost coal layer.

4.5.4 BH4 (KALKBULT 139JR)

The BH4 U content varied from 1.7 mg kg^{-1} to 34.4 mg kg^{-1}, and averaged 7.8 mg kg^{-1}. The maximum U content occurred where the coal zone was carbonaceous shale, similar to the findings by Swanson (1956), where U occurred primarily in organic-rich black shales studied from Pennsylvanian age coals, in Kansas and Oklahoma. The carbonaceous shale regions averaged a U content of 12.7 mg kg^{-1}, lower than the 76 mg kg^{-1} reported by Nel (2012) for coaly shale; the 2.93 mg kg^{-1} average for the coal regions, again lower than the 130 mg kg^{-1} reported by Nel (2012) for shaly coal in the SFC. Although U was distributed in both coal and carbonaceous shale, as supported by Hancox and Gotz (2014), and Cole (2009), the carbonaceous shale regions contained more U which is different to what Nel (2012) reported, where he found that shaly coal had a higher U content compared to coaly shale. BH4 also had maximum U content at the top of the coal zone, within the first 1 m of the coal zone, agreeing with studies by Nel (2012) and Christie (1989) that U mineralization in the SFC occurs in the uppermost coal layer.

4.5.5 BH5 UCZ (WOLFHUISKRAAL 626JR)

The UCZ in BH5 had a U content that ranged from 1.5 mg kg^{-1} to 4 mg kg^{-1} and averaged 2.2 mg kg^{-1}. The entire coal zone had very little U present and the average 2.2 mg kg^{-1} was only slightly higher than the 2 mg kg^{-1} world average reported by Swaine (1990). The 2.2 mg kg^{-1} average was lower than the 76 mg kg^{-1} reported by Nel (2012) for coaly shale. Similar to BH1, the entire coal zone was made up of carbonaceous shale, and thus U in this coal zone occurred in the carbonaceous shale. The findings agree with findings by Swanson (1956), where U occurred primarily in organic-rich black shales studied from Pennsylvanian age coals, in Kansas and Oklahoma. Although the U maximum was found at the top of the other coal zone, the U in this coal zone was not extensively concentrated at the top of the coal zone, it was rather distributed almost evenly throughout the coal zone; with a difference of 2.5 mg kg^{-1} between the maximum and the minimum. This could be due to the lack of significant U mineralization in the borehole.

4.5.6 BH5 LCZ (WOLFHUISKRAAL 626JR)

The LCZ in BH5 had a U content that ranged from 6.4 mg kg^{-1} to 14 mg kg^{-1} and averaged 9.8 mg kg^{-1}. Similar to BH2, other peaks of interest were found further down the coal zone. The U in this coal zone was distributed in some areas that are coal, and in areas that were carbonaceous shale. The 10 mg kg^{-1} U content for the shale regions was lower than the 76 mg kg^{-1} reported by Nel (2012) for coaly shale, and the 9.55 mg kg^{-1} average for the coal regions was lower than the 130 mg kg^{-1} reported by Nel (2012) for shaly coal. The results agree with results obtained by Hancox and Gotz (2014), who reported that the U in the SFC is known to be found both in the coal and in the carbonaceous mudrock, and supported by results from Cole (2009) who concluded that the U is disseminated throughout the coal and carbonaceous shale in the SFC. A maximum U content was found in the first 1 m of the coal zone, agreeing with studies by Nel (2012) and Christie (1989), where U mineralization in the SFC occurred in the uppermost coal layer.

4.5.7 CARBON AND URANIUM CONTENT IN COAL

Figure 4.17 shows the relationship between the content of the carbon content and of the U in the coal samples studied. The samples with a U content >50 mg kg^{-1} (samples within circle), all had a carbon content higher than 40%. These samples occurred in horizons where coal quality was coal. Kyser and Cuney (2008) explained the correlation between carbon and U by stipulating that U in sedimentary environments is fixed through the several processes, including adsorption onto carbon rich organic matter, oxides and fine clays.

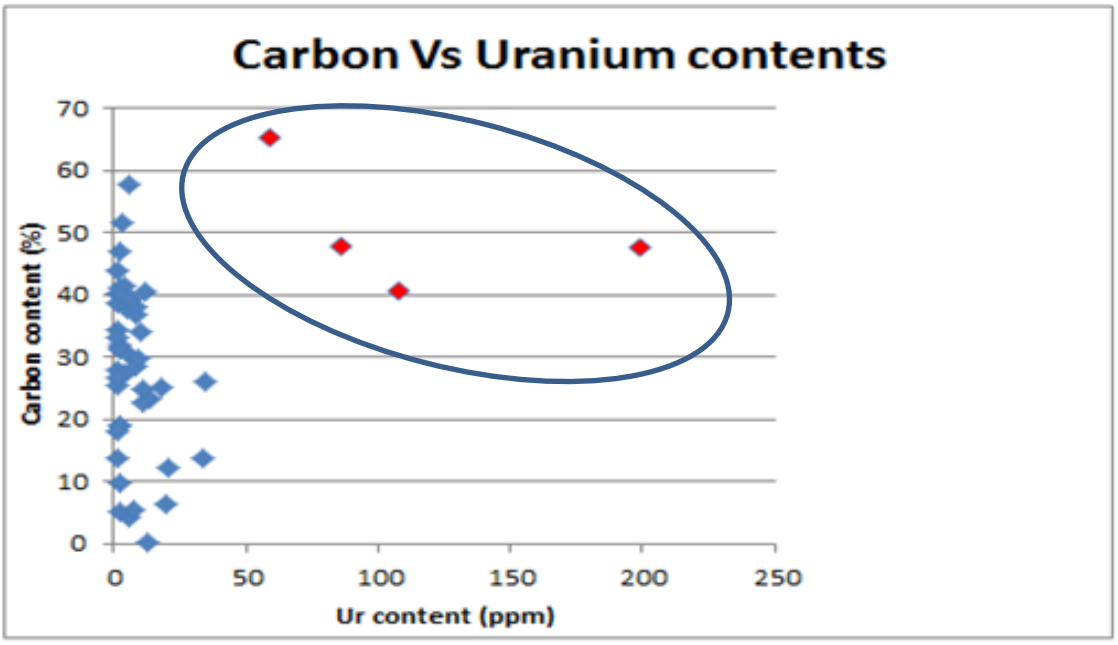


Figure 4. 17 Relationship between carbon content and U content for the samples in BH1- BH5

4.6 CONCLUSIONS ON URANIUM CONTENT IN BOREHOLE COAL ZONES

- All borehole coal zones studied had a U content averages higher than the 2 mg kg^{-1} world average reported by Swaine (1990).
- U in the SFC samples was disseminated throughout the coal and carbonaceous shale, findings in agreement with (2009) and Hancox and Gotz (2014).

- For all boreholes except BH5, U in the SFC samples was concentrated within the first 1 m of the coal zone, agreeing with studies by Nel (2012) and Christie (1989).

- The U in the coal zones was generally restricted to a single layer, usually the highest in the local sequence, except in BH2 and the LCZ in BH5 where U mineralization was seen in multiple locations in the coal zone. This finding is in agreement with Cole (2009) and Nel (2012).

- BH3 has the highest average U content (33 mg kg^{-1}). The highest U content was determined in a sample from this coal zone (145.9 mg kg^{-1}), and BH4, the UCZ in BH5 and the LCZ in BH5 all had an average U content less than 10 mg kg^{-1}.

- Samples with a U content >50 mg kg^{-1} all had carbon content higher than 40%.

4.7 XRD RESULTS

Some of the samples were taken for XRD analysis, with the purpose of quantifying the major minerals present in the samples with a high U content, and to determine the minerals that U has an affinity for; although low in U, sample 1410 was selected due to the high sulfur content with the purpose of correlating the sulfur content to the pyrite content. Table 4.2 shows that sample 1410 registered extremely high sulfur content (12.4%), and this value translated to high pyrite content (8%). Sample 1436 registered 0.2% sulfur, the lowest sulfur content of the selected samples; the pyrite content of the sample was less than the detection limit of the instrument. The correlation between the sulfur content and the pyrite content agreed with studies by Dai *et al*. (2003) and Descostes *et al*. (2010), which concluded that pyrite is the main carrier of sulfur in coal, and that sulfur is hosted primarily in pyrite. Figure 4.18 shows some of the pyrite granules seen under a microscope for the samples with high U content. Figure 4.19 shows sample 1410 in the UCZ in BH5; sulfides are clearly seen as the dominant minerals to the naked eye.

Table 4. 2: XRD constituents of selected samples (%)

Sample	Calcite	Siderite	Anatase	K-feldspar / Rutile	Plagioclase	Quartz	Mica	Kaolinite	**Pyrite**	**Total Sulfur**	**U content (mg kg-1)**
1410	22	-	-	1	-	38	3	25	**8**	**12.4**	**5.2**
1421	7	-	-	-	-	33	4	47	**7**	**3.5**	**145.9**
1426	3	-	1	-	-	43	5	37	**4**	**4.4**	**107.7**
1429	5	-	trace	-	-	50	5	34	**3**	**2.5**	**85.9**
1436	-	-	trace	1	-	51	5	31	**-**	**0.2**	**34.1**
1443	3	36	2	-	2	24	2	29	**4**	**4.2**	**34.4**

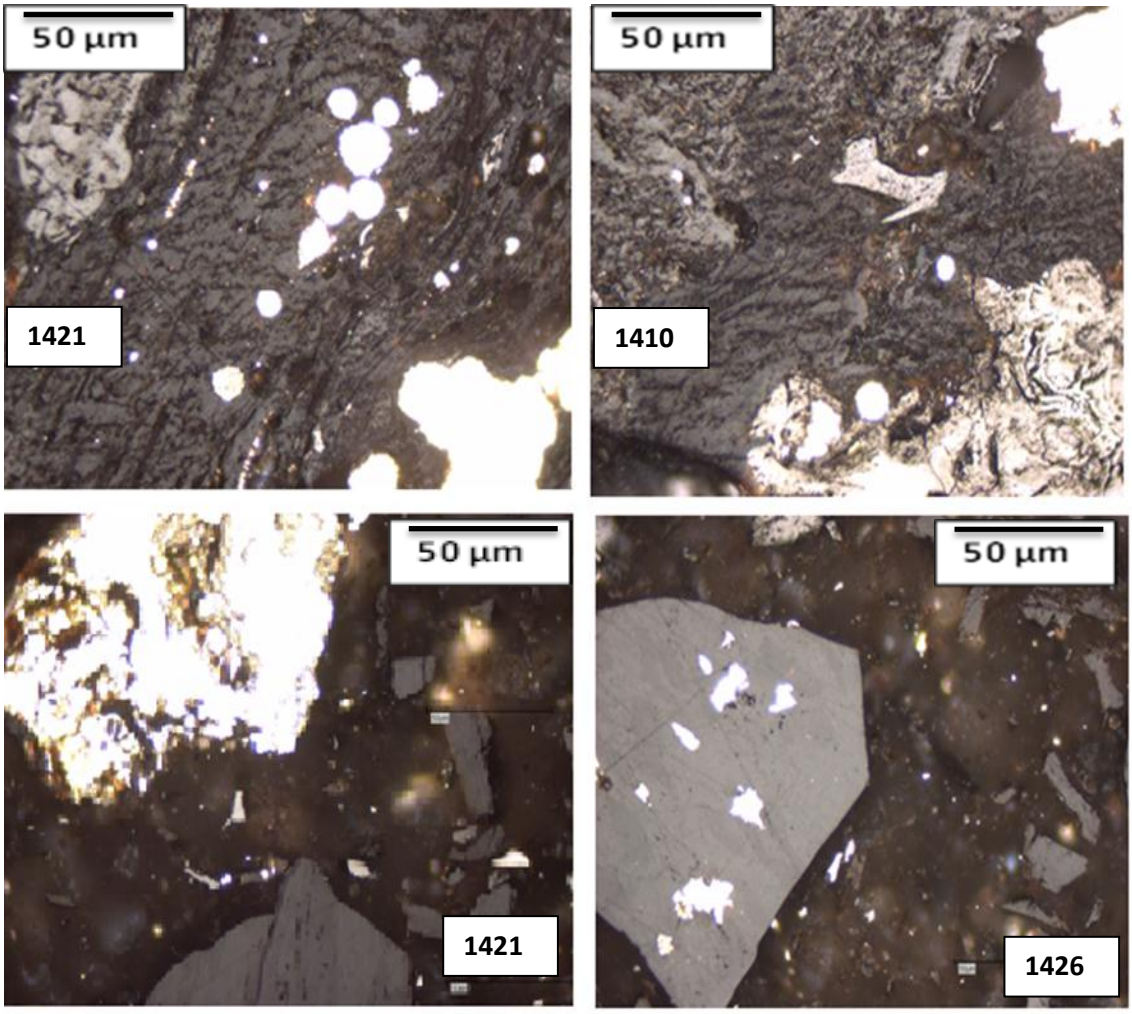


Figure 4. 18: Pyrite granules in selected samples (bright yellow component under reflected light, oil immersion lens)



Figure 4. 19: Pyrite in the UCZ of BH5 (Courtesy of Ms Valerie Nxumalo)

Table 4.2 shows the mineral content of the samples selected for XRD analyses. As expected, quartz and kaolinite made up the bulk of the mineral matter of the raw coal samples supported by Pinetown and Boer (2006) who studied Highveld coal samples and noticed the general trend. The kaolinite content was lowest in the sample with the lowest U content (1410); and maximum kaolinite content was in the sample with the highest U content (1421). The results agreed with those from Querol *et al.* (1994), and Pickhardt (1989), who concluded that the U is affiliated with clay minerals in coals, and kaolinite in particular. Wang *et al.* (2008) also confirmed that U has an aluminosilicate affinity (clay minerals) in coal. Figure 4.20 shows the results with a best fitted linear curve when U content is correlated to kaolinite.

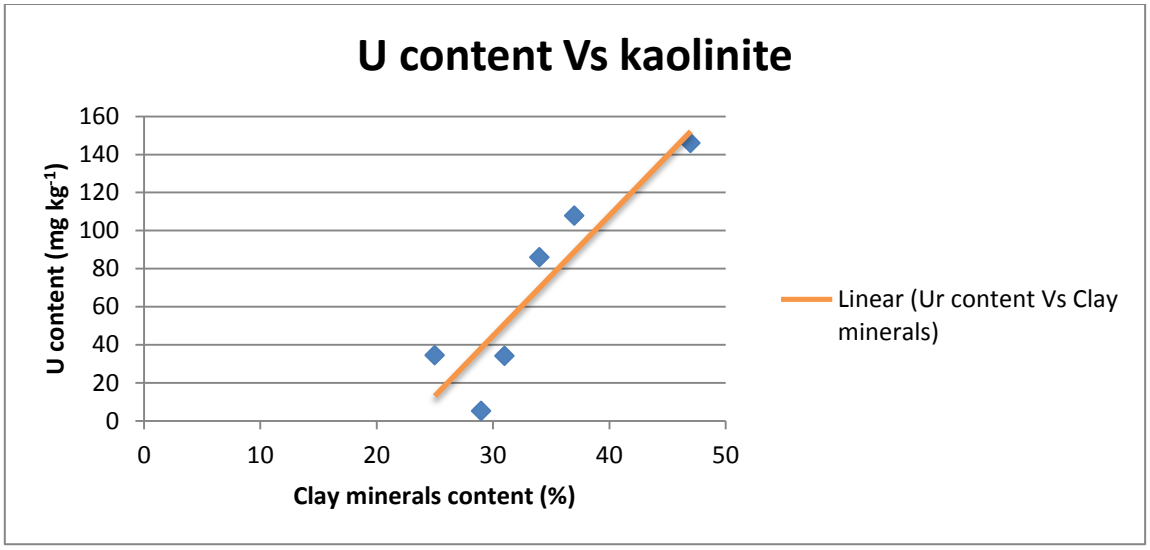


Figure 4. 20 : The correlation of U content and the clay mineral amount

4.8 URANIUM CONTENT FOR SELECTED SAMPLES

XRF was also used to quantify the U quantity in the coal samples. Table 4.3 gives the U content of the selected samples. The full set of XRF results for U content in all samples is found in Appendix B. Based on XRF results determined in Table 4.3, 11 samples with U content higher than 10 mg kg^{-1} were selected and taken for ICP-MS and INAA analysis to confirm the XRF results. Due to the limited available sample quantity, each sample was analyzed once.

Table 4. 3: U content in selected samples determined by XRF, INAA and ICP-MS (mg kg^{-1})

Sample name	Borehole	U [XRF]	U [INAA]	U [ICP-MS]
1416	BH5 LCZ	12	8.93	8.6
1417	BH5 LCZ	14	11.8	9.8
1421	BH3	199	161	145.9
1422	BH3	18	15.6	11.3
1429	BH2	96	86.9	85.9
1436	BH1	73	64.6	34.1
1437	BH1	52	43.2	13
1438	BH1	51	39.4	19.4
1439	BH1	36	29.3	20.9
1440	BH1	14	11.5	6.2
1443	BH4	52	33.5	34.4

Generally, INAA provided higher U values than ICP-MS, and was closer to the XRF values; ICP-MS provided the lowest U values of all the techniques used. XRF gave the highest U content results. XRF and INAA results for these samples were comparable. The variation caused by the ICP-MS in some sample results lead to the conclusion that an error could have occurred during analysis, either mechanical or human error. The extremely complicated chemical digestion and separation procedures prior to insertion into the ICP-MS instrument have been well documented (Yoshida *et al*., 1992), and could have been the cause of the error experienced. The biggest concern when dealing with ICP-MS analyses occurs mostly in solid samples, where incomplete sample decomposition and digestion is possible (Orihashi and Hirata, 2003).

INAA was also used to determine the U isotope present in the selected coal samples shown in Table 4.3. The energy peaks were correlated to the known energy peaks characteristic of U, and the products of the U decay series. INAA results confirmed ICP-MS results, that the ^{238}U isotope was the dominant isotope, with every peak encountered representing the ^{238}U isotope or a decay series product of the isotope. Again, this was not surprising, since ^{238}U is the most abundant of the U isotopes found in nature (Edwards and Oliver, 2000)

4.9 LEACHING RESULTS

To extract U from the selected coal samples, the 11 selected samples underwent leaching using sulfuric acid under different conditions as outlined in Section 3.12. Once the results from the initial leaching were obtained, the conditions that gave the highest extraction were combined to create optimum U leaching conditions.

4.9.1 LEACHATE INAA RESULTS

INAA was initially used to obtain U values for the leachates. Figure 4.21 shows that only 1 visible spectrum was observed. Figure 4.22 shows the same spectrum, zoomed in at different energies; the background peak is seen in black, and sample peaks characteristic of U, and the U decay series products are in color. The difference between the background peak and the sample peak would give the amount of U present in the sample. The vital peaks zoomed into are found at 511 keV, 1461 keV and 2618 keV.

Figure 4.22 shows that the spectra from the sample was almost identical to the spectra produced by the background without the sample; this meant that the U content in the samples was lower than the detection limit of the instrument. This was true of the bulk of the leachate samples analyzed using the instrument; thus this meant that the bulk of the leachate samples had U content less than the 1 mg L^{-1} detection limit of the instrument.

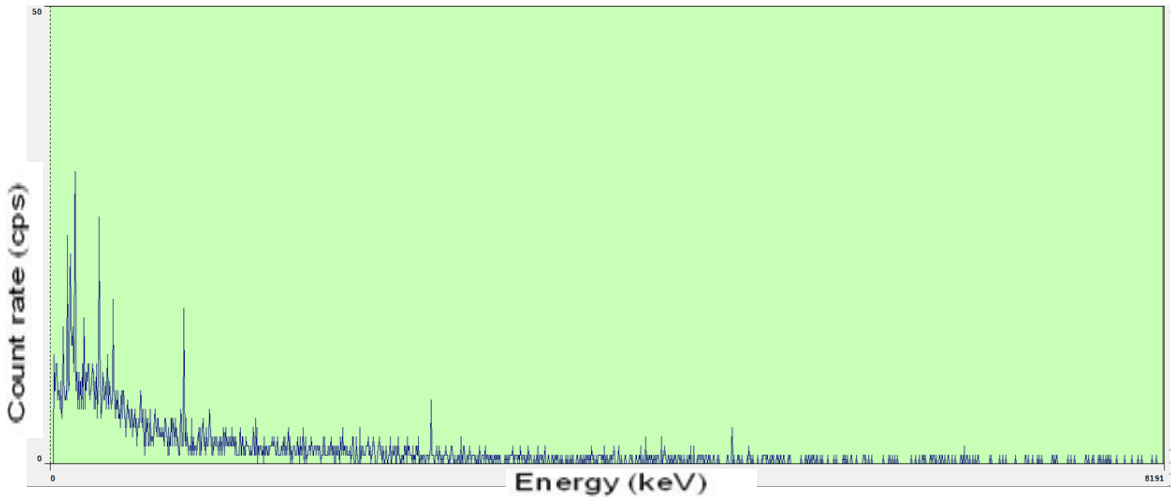


Figure 4. 21: Sample 1421 leachate spectra (INAA)

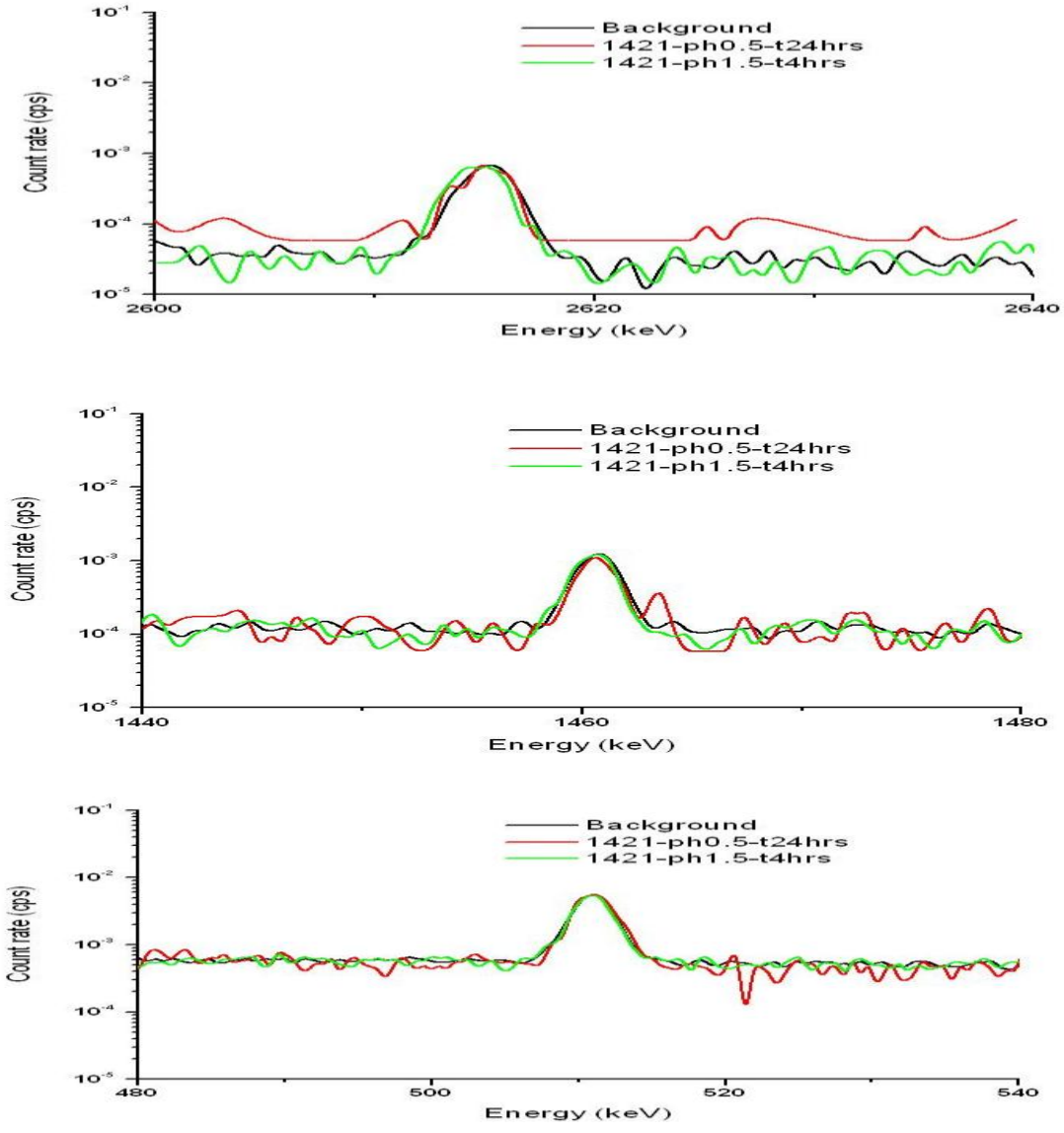


Figure 4. 22: U content in leachate less than detection limit

It was clear that the samples required a more sensitive quantitative method to analyze the leachates, thus ICP-MS was chosen as the method of analysis for the samples, as it costs less and is known to give high precision results for solutions which do not require chemical digestion. The samples were then submitted for ICP-MS, at the CGS chemistry lab for analysis. The results are given in section 4.9.2.

4.9.2 LEACHATE ICP-MS RESULTS

To determine the U content leached into solution, the leachates were submitted for ICP-MS, and the results are discussed. The effects of time, temperature and pH on U extraction into solution are given. Due to cost of analysis, all 11 samples were only analyzed once.

4.9.2.1 EFFECT OF TIME

The effect of time was studied by leaching the coal samples for 4 hours, 8 hours and 24 hours, at pH=0.5 and T=25^{o}C. Figure 4.23 is a pie chart of the percentage of samples that registered maximum U extraction at different time intervals; Table 4.4 displays the U content in the leachate samples in $\mu g\ L^{-1}$;

Increasing the leaching time from 4 hours to 8 hours yielded a higher U extraction for 72.7% of the samples as seen in Table 4.4. A further increase in leaching time gave varying results where, 54.5% samples recorded higher U extraction after leaching for 24 hours. The other 45.5% registered maximum extraction after leaching for 8 hours. No samples recorded maximum U extraction after leaching for 4 hours; as such the pie chart excluded 4 hours, as it contributed 0% to maximum extraction. These results agree with studies conducted by Gajda *et al.* (2015), who found that increasing leaching time increased U extraction when leaching Triassic sedimentary rocks.

The U content extracted into solution varied from 64 $\mu g\ L^{-1}$ to 1789 $\mu g\ L^{-1}$. Sample 1421 had the highest extraction of U into solution at every time interval as well as the highest U content in all raw coal samples (145.9 mg kg^{-1}). The sample registered a maximum 1789 $\mu g\ L^{-1}$ of U after leaching for 24 hours. Sample 1436 had the second

highest U content extracted into solution for all time intervals, peaking after 24 hours at 1107 µg L^{-1} (Figure 4.24). Wang *et al.* (2008) reported a maximum 119 µg L^{-1} after 60 hours, lower than the 1789 µg L^{-1} maximum reported here after 24 hours.

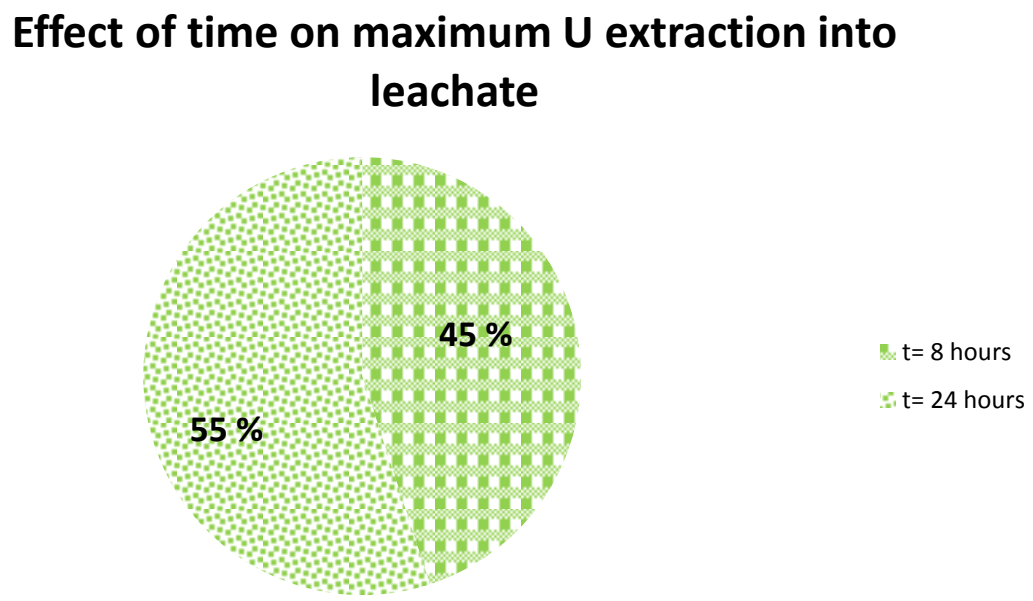


Figure 4. 23: Effect of leaching time on maximum U extraction shown as a percentage of samples, using ICP-MS

Each sample behaved differently when leaching time was increased; Table 4.4 displays the trends each sample displayed with increasing leaching time. 45.5% of the samples had a U content was low initially, and then increased to a maximum after 8 hours; U content decreased again after 24 hours leaching time. 18.2% of the samples had a U content that was high after leaching for 4 hours, then decreased to a minimum after 8 hours leaching and increased after 24 hours leaching. 27.3% of the samples had a U content that increased steadily from 4 hours to 8 hours, and reached its maximum after 24 hours. Sample 1422 had constant U content from 4 hours to 8 hours, and increased to its maximum after 24 hours leaching.

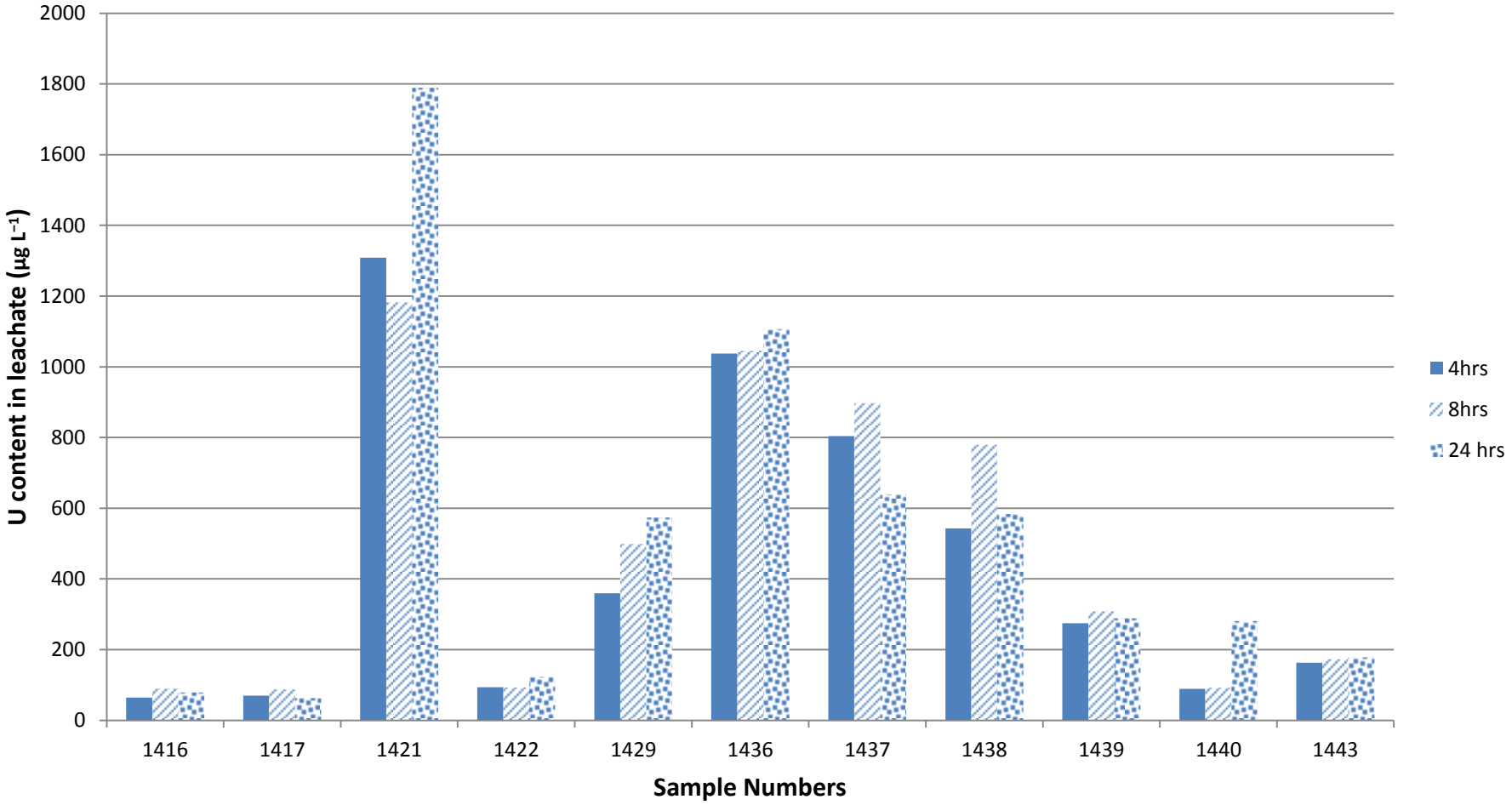


Figure 4. 24: U content in leachate samples using ICP-MS, varying time (µg L^{-1}))

Table 4. 4: U content in leachate determined by ICP-MS for varying time (µg L^{-1})

Sample name	4 hours	% Diff	8 hours	% Diff	24 hours	Trend
1416	64	40.63	90	-12.22	79	∧
1417	70	24.29	87	-27.59	63	∧
1421	1308	-9.63	1182	51.35	1789	V
1422	94	-1.06	93	32.26	123	_/
1429	359	39.00	499	15.03	574	/
1436	1037	-4.53	990	11.82	1107	V
1437	804	11.57	897	-28.65	640	∧
1438	543	43.65	780	-25.13	584	∧
1439	274	12.77	309	-6.47	289	∧
1440	89	57.30	140	100.71	281	/
1443	163	6.13	173	2.89	178	/

4.9.2.2 EFFECT OF PH

The effect of pH on the maximum U extraction was studied by varying the pH from pH=0.5, 1.0, to pH=1.5, at T=25^{o}C for 4 hours. It was noted, that based on Section 4.9.2.1 results, that increasing the leaching time resulted in higher U extraction, however, all samples underwent leaching tests concurrently and hence when the effect of pH was studied, the result was unknown. This necessitated that conditions which led to maximum U extraction should be combined to create an optimum U leaching. Figure 4.25, shows that 72.7% of samples registered maximum U content when pH=0.5; the remaining 27.3% samples registered maximum extraction when the pH=1. No samples recorded maximum extraction when the pH was 1.5; as such the pie chart excluded pH. =1.5, as it contributed 0% in maximum extraction.

Table 4.5 gives the U content in the leachates, and Figure 4.26 is a bar chart of the same leachate results. For the most part, solutions with a higher acidity, gave a higher U content in solution. Wang *et al.* (2008) did not study the pH ranges as was studied in this research, but one can see in Table 4.5 that, 64% of the samples leached at pH=0.5 at time=4 hours, in this study, recorded U content values higher than the 105.5 µg L^{-1} for samples leached at pH=2, reported by Wang *et al.* (2008) for the same time period

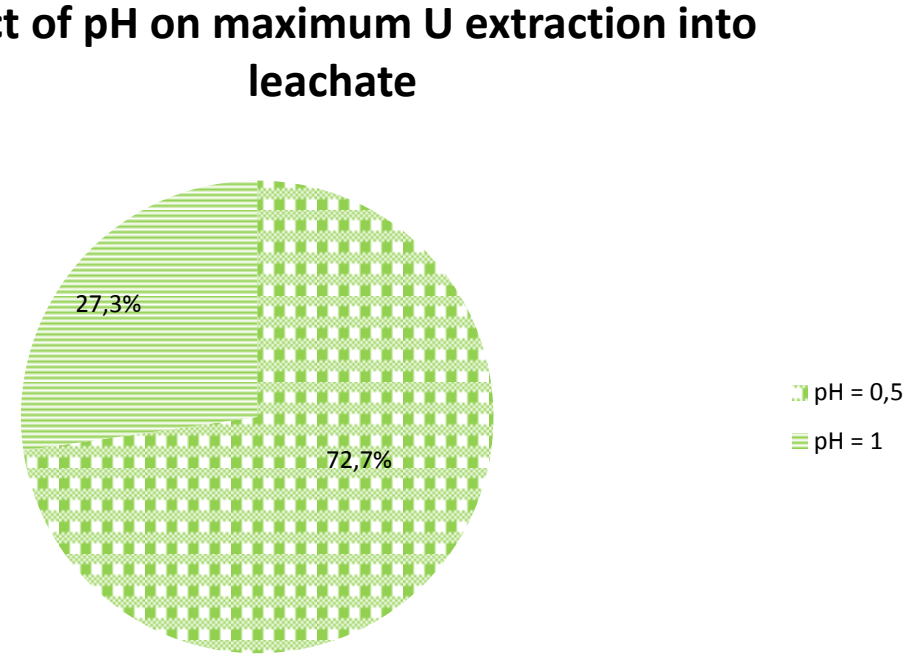


Figure 4. 25: Effect of leaching pH on maximum U extraction shown as a percentage of samples, using ICP-MS

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Overall the U content in leachates in this study was higher than those recorded by Wang *et al.* (2008) who leached at higher pH values. It was concluded that an increase in acidity gives an overall increase in U content recovered into solution. These findings agree with Wang *et al.* (2008), and Maslov *et al.* (2010), who found that increasing acidity resulted in an increase in U recovery.

Studying the samples' individual behavior relative to the increase in acidity, Table 4.5 shows that each sample behaved differently to an increase in acidy. The percentage difference in U content experienced by each sample due to a change in pH is also given in Table 4.5. 73% of the samples had U content that increased gradually with increasing acidity; the same trend was seen in samples studied by Wang *et al*. (2008). Sample 1438 displayed the "$\overline{I}$" trend, where U content was at its minimum when pH= 1.5, and increased to its maximum when pH=1, thereafter, U content remained relatively constant until pH=0.5

Table 4. 5: 5 U content in leachate determined by ICP-MS for varying pH (µg L^{-1})

Sample name	pH1,5	% Diff	pH=1	% Diff	pH=0,5	Trend
1416	5	89.58	48	25	64	/
1417	4	90.91	44	37.14	70	/
1421	75	92.05	943	27.91	1308	/
1422	81	23.58	106	-12.77	94	ʌ
1429	151	62.25	400	-11.42	359	ʌ
1436	515	56.58	1186	-14.37	1037	ʌ
1437	196	-71.93	114	85.82	804	V
1438	144	73.38	541	0.37	543	/¯
1439	52	79.84	258	5.84	274	/
1440	41	40.58	69	22.47	89	/
1443	16	78.95	76	53.37	163	/

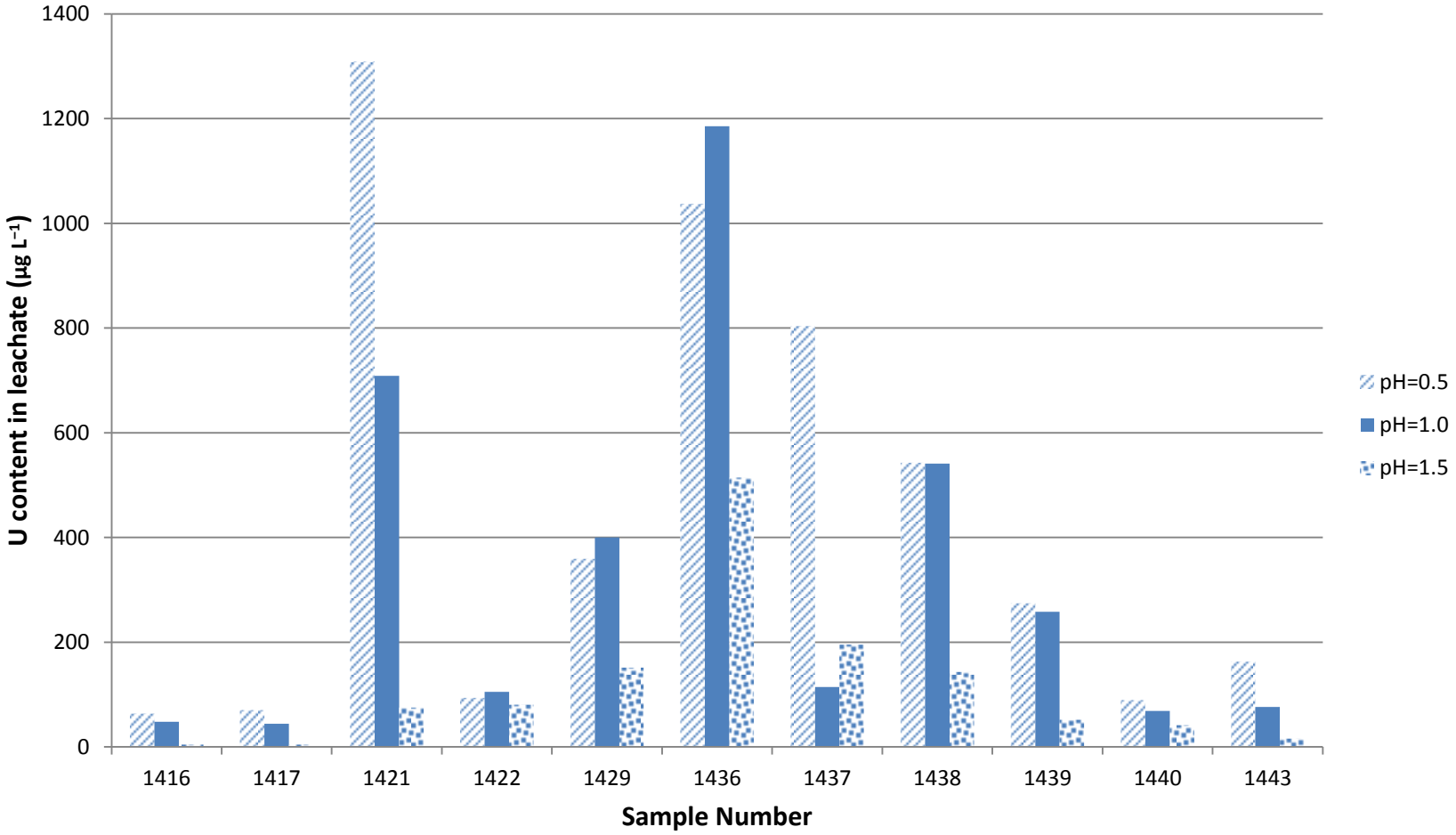


Figure 4. 26: Leachate results from ICP-MS, varying pH (µg L^{-1})

4.9.2.3 EFFECT OF TEMPERATURE

The effect of temperature on the maximum U extraction was studied by varying leaching temperature, from T=25^{0}C, to T=45^{0}C, and to T=65^{0}C, at pH=1 for 4 hours. Figure 4.27 is a pie chart of the percentage of samples that registered maximum U extraction at different temperature intervals. 45% of the samples produced maximum U extraction at T= 25^{0}C, and 45% of the samples registered maximum extraction when T=45^{0}C, one sample registered maximum extraction at T=65^{0}C.

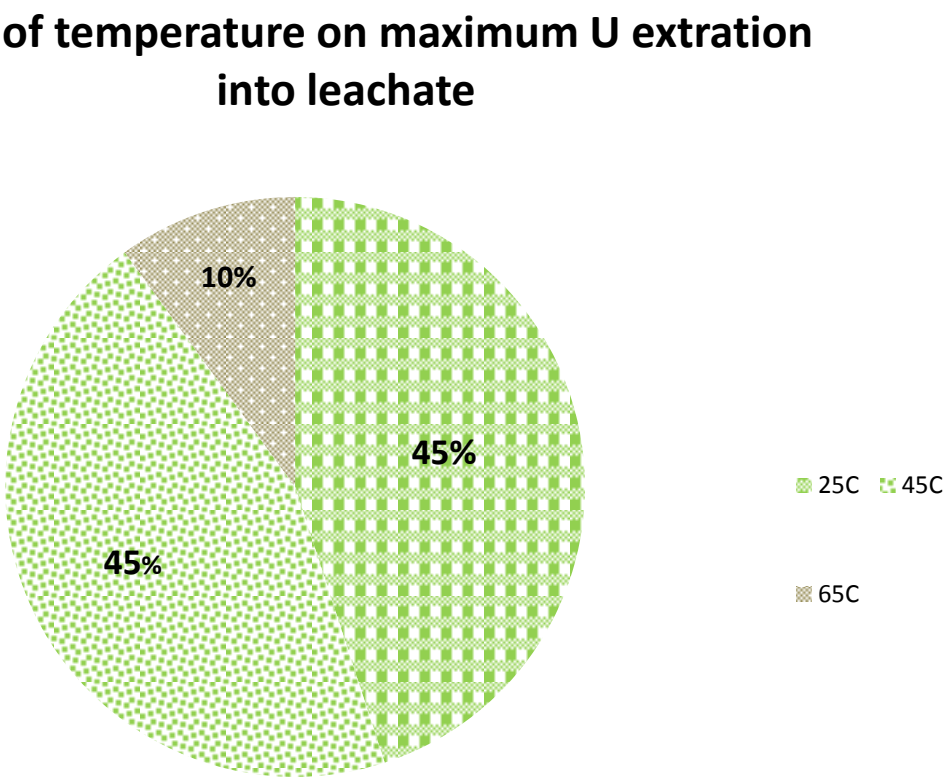


Figure 4. 27: Effect of leaching temperature on maximum U extraction shown as a percentage of samples, using ICP-MS

Table 4.7 gives the U content in the leachates, and Figure 4.28 is a bar chart of the same leachate results; sample 1436 had the highest extraction of U into solution at T=25^{0}C (1185 $\mu g\, L^{-1}$). When the temperature was raised to 45^{0}C and 65^{0}C, sample 1421 had highest U extraction compared to the other samples (979 $\mu g\, L^{-1}$ and 771$\mu g\, L^{-1}$ respectively).

Figure 4.27 displays that 55% of the samples recorded maximum U extraction at elevated temperatures; the obvious correlation between temperature and rate of reaction is described by the Arrhenius equation in equation 11. Higher temperatures increase the rate constant, and thus speed up the reaction. These results agreed with studies by Ram (2013), Roshani and Mirjalili (2009), and Demopoulos (1985), who reported an increase in U content for U bearing ores when leaching at higher temperatures.

$k = Ae^{-E_a/RT}$ ..... eq 11

Where k= rate constant, T= temperature, A= pre-exponential factor, E_a = Activation energy and RT= average kinetic energy.

Table 4.7 displays the trends each sample displayed with increasing leaching temperature. 45.5% of the samples displayed the "**Λ**" trend, 36.4% of the samples displayed the "**V**" trend, 9% of the samples displayed the "***/***" trend, and sample 1438 displayed the **"_"** trend, where U content was at its maximum when T=25 ^{O}C, decreased when T=45^{O}C, and remained relatively constant thereafter when T=65^{O}C.

Table 4. 6: U content in leachate determined by ICP-MS (µg L^{-1}), varying temp

Sample Name	25^{o}C	% Diff	45^{o}C	% Diff	65^{o}C	Trend
1416	48	-20.83	38	7.89	41	V
1417	44	-34.09	29	48.28	43	V
1421	943	3.82	979	-21.25	771	Λ
1422	105	14.29	120	32.5	159	/
1429	400	17.25	469	-2.99	455	Λ
1436	1186	-42.24	685	10.80	759	V
1437	114	529.82	718	-28.69	512	Λ
1438	541	-17.74	445	-0.23	444	_
1439	258	-25.97	191	5.76	202	V
1440	69	27.54	88	-17.05	73	Λ
1443	76	92.11	146	-56.85	63	Λ

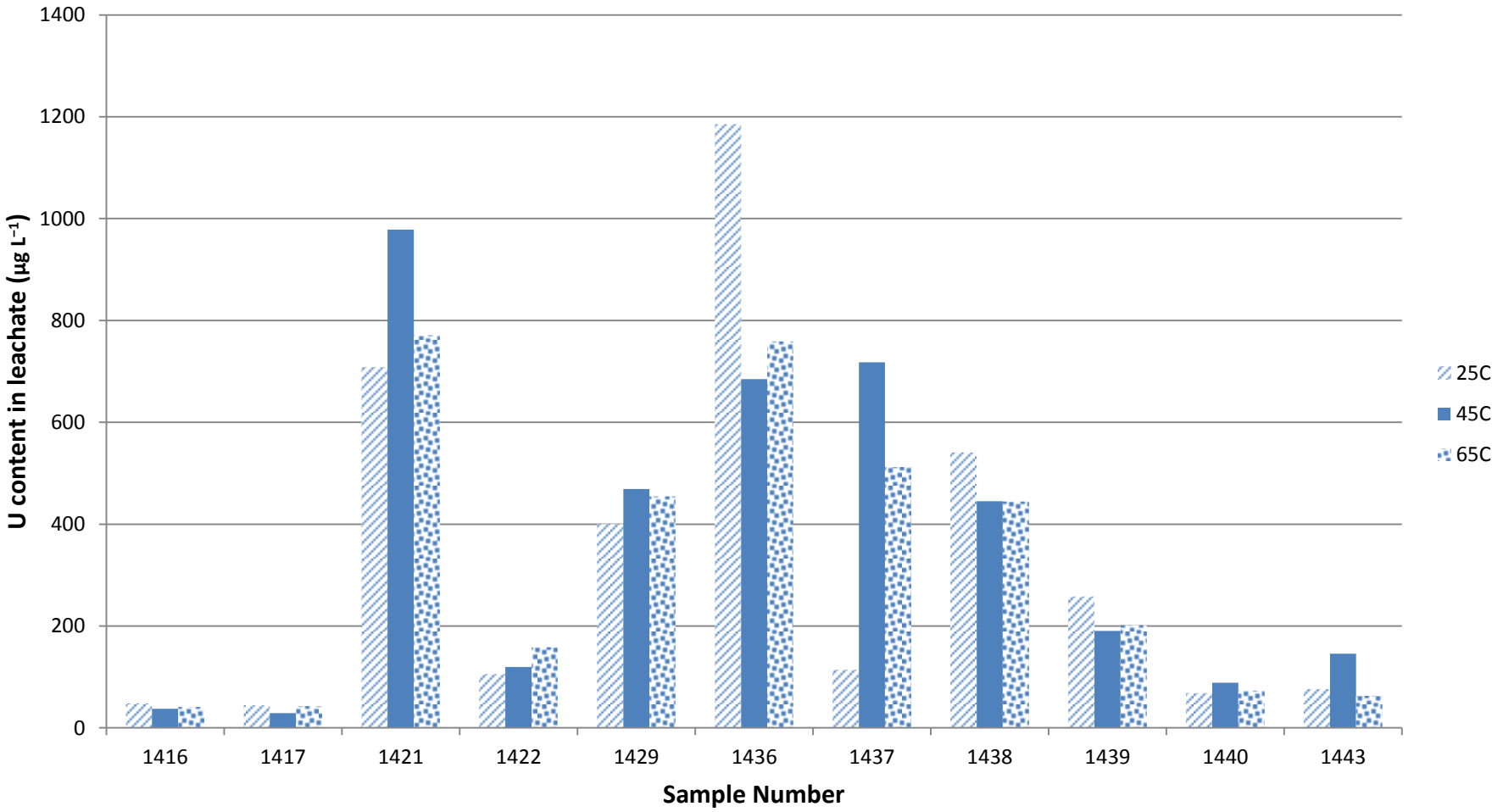


Figure 4. 28: Leachate results with increasing temperature using ICP-MS

4.10 OPTIMIZATION RESULTS

Based on the leachate results, it was observed that samples 1421, 1436 and 1437 reported relatively high U extraction rates. The conditions at which maximum U was attained were selected for optimization experiments to discern whether U extraction could be improved in this manner. To determine the U percentage leached from the original coal samples, the filter cakes were submitted for XRF trace element analysis, and the leachates were submitted for ICP-MS; the results are discussed here.

Sample 1421, recorded the highest U content when T=45^{o}C, after 24 Hours at pH=0.5, thus sample 1421 was leached at T=45^{o}C, for 24 hours and the acid concentration was varied at 5 M, 10 M and 15 M. Sample 1436, recorded maximum U content when T=25^{o}C, after 24 hours at pH=1, thus this sample was leached at T=25^{o}C, for 24 hours and acid concentration was varied at 5 M, 10 M and 15 M. Sample 1437, recorded the highest U content when T=45^{o}C, after 8 Hours at pH=0.5, thus sample 1437 was leached at T=45^{o}C, for 8 hours and acid concentration was varied at 5 M, 10 M and 15 M. Table 4.8 gives the results after the samples had been subjected to their optimal leaching conditions. The samples recorded higher U content for almost every optimization condition. Figure 4.29 shows the optimization results compared to the initial leaching results for the selected samples. The results were compared to the initial maximum values displayed in Table 4.8. Sample 1421 recorded 38% increase in U content from a previous maximum of 1789 $\mu g\, L^{-1}$ to 2462 $\mu g\, L^{-1}$leached at 15 M. Sample 1436 displayed the highest increase in U content leachable (106%) from 1186 $\mu g\, L^{-1}$ to 2438 $\mu g\, L^{-1}$ leached into solution leached at 15 M. Sample 1437 recorded a 25% increase from a previous high of 897 $\mu g\, L^{-1}$ to 1124 $\mu g\, L^{-1}$ leached at 10 M.

Table 4. 7: Optimized U content in leachate ($\mu g\, L^{-1}$)

Samples	Previous max	M=5 M	M=10 M	M=15 M	Trend
1421	1789	1788	1513	2462	V
1436	1186	1959	1550	2438	V
1437	897	1124	886	1010	V

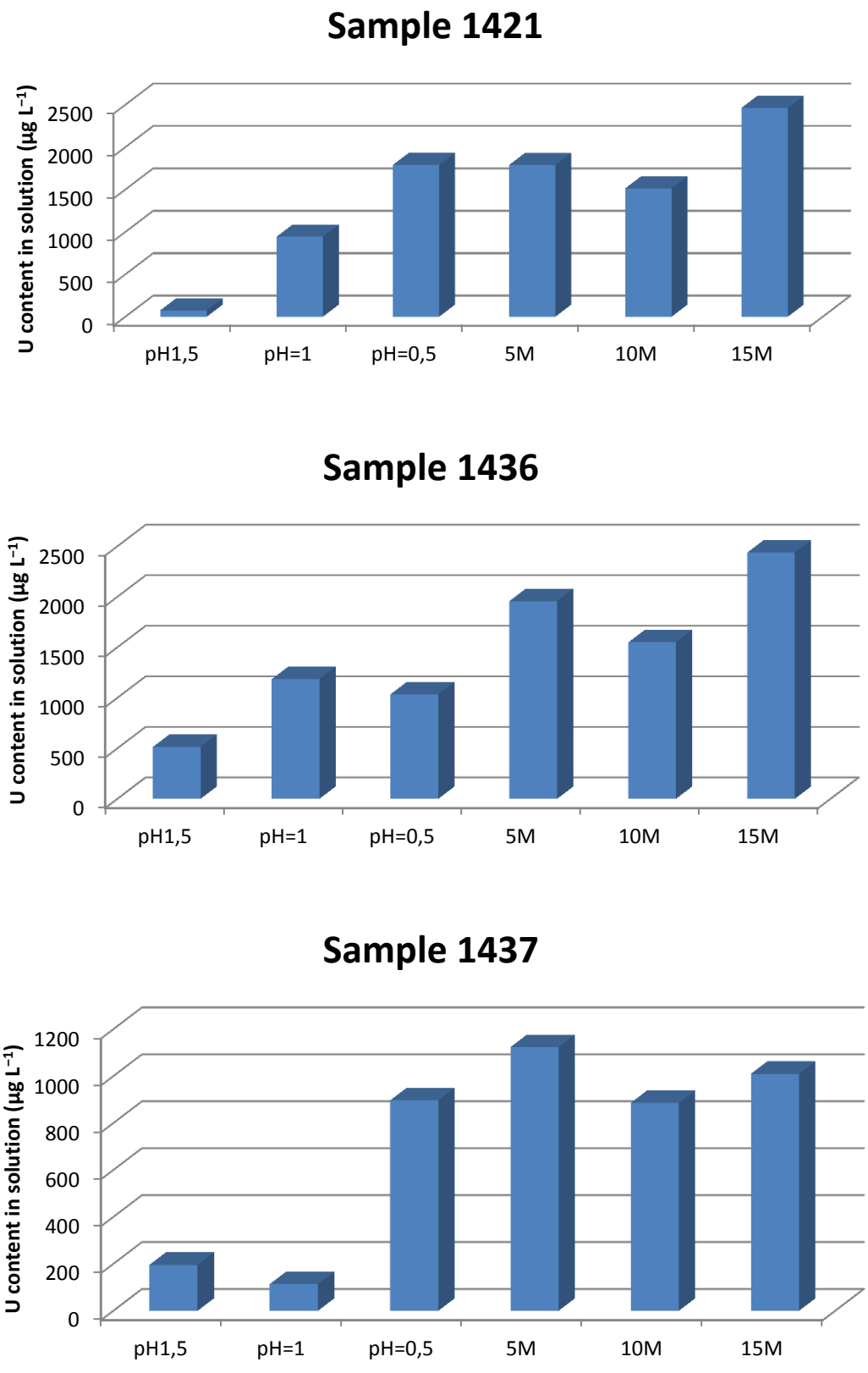


Figure 4. 29: Optimization leachate results (ICP-MS) for samples 1421, 1436, 1437

Figure 4.29 shows the critical role molarity plays in the reactions to liberate U from the coal samples. As mentioned previously in section 2.3, U needs to be oxidized into its hexavalent state (U(VI)) before it can be dissolved by the sulfuric acid (Edwards and Oliver, 2000). The dissolution of hexavalent U in a sulfuric acid leaching system follows equations 4 to 6.

When the pH was lowered by increasing the molarity of the solution used, the SO_4^{2-} ion ($2H^+$) was increased, and the rate of producing UO_2SO_4 increased. Similarly for reactions 5 and 6, $[UO_2(SO_4)_2]^{2-}$ and $[UO_2(SO_4)_3]^{4-}$ were produced at a faster rate due to the increased SO_4^{2-} ion. Zavodska *et al.* (2009) stated that at low pH values, U is predominantly in the mobile oxidized state (U(VI)). Thus, increasing molarity increased the mobility of U into solution and thus U was readily leached. The increase in U content due to the increase in molarity was expected and the findings agreed with Wang *et al.* (2008), and Maslov *et al.* (2010), who found that decreasing pH resulted in an increase in U recovery.

4.11 OPTIMIZATION FILTER CAKE RESULTS

Filter cake samples leached using the 5 M and 10 M solutions were taken for XRF trace element analysis. Filter cake samples leached at 15 M could not be attained; this was due to the highly acidic nature of the solution. The acid dissolved the filter membrane and no substantial amount of cake retention was possible.

Table 4.9 displays the U percentage extracted from the SFC coal samples. The U percentage extracted from samples leached at 5 M ranged from 37.7% to 50.7%. The % U extracted range was higher than the 10-20% U extracted reported by Slivink *et al*. (1985) on coal samples from Zirovski, Yugoslavia, leached between pH =0.5- 1.2.

Samples 1436 and 1437 recorded higher extraction rates than the 45.4% U extracted from Mongolian coal ash samples reported by Maslov *et al.* (2010).

The U percentage extracted from samples leached at 10 M ranged from 58.9% to 67.3%. The U extracted range was higher than the 10-20% U extracted by Slivink *et al*. (1985) on coal samples from Zirovski, Yugoslavia, leached at pH =0.5- 1.2. All samples leached at 10 M recorded higher extraction rates than the 45.4% U extracted from Mongolian coal ash samples reported by Maslov *et al.* (2010).

Table 4.9: U content in filter cakes determined by XRF (mg kg^{-1})

	1421 5M	**1421 10M**	**1436 5M**	**1436 10M**	**1437 5M**	**1437 10M**
U content in original coals (XRF)	199	199	73	73	52	52
U content in filter cakes (XRF)	124	79	36	30	26	17
% U extracted	**37.7**	**60.3**	**50.7**	**58.9**	**50**	**67.3**

Increasing the molarity of the leaching solution from 5 M to 10 M increased the % U extracted for all coal samples. Sample 1421 experienced the highest increase in % U extracted due to the change in molarity of leaching solution (22.6% increase), followed by 1437 (17.3% increase), and 1436 recorded 8.2 % increase. Increasing molarity translates to an increase in acidity, and as such, these findings agree with Wang *et al.* (2008), and Maslov *et al.* (2010), who found that increasing acidity resulted in an increase in U recovery. It was interesting to note that ICP-MS leachate results for the same samples showed that U content in solution was higher.

Comparing the optimized cake results to the leachate results; Leachate results recorded a **'v'** trend, in that samples leached at 5 M recorded higher U content in solution than samples leached at 10 M. Cake results reported an expected steady increase in U content extracted with increasing molarity of solution. ICP-MS precision does degrade considerably when detecting low levels of trace and ultra-trace elements (Munro *et al*., 1986). Fischer *et al.* (1998) explains that accurate measurement of ultra-trace content of rare metals and platinum group elements using ICP-MS is complicated by interferences in complex matrices and preferential elemental partitioning. The highly acidic 5 M, 10 M, and 15 M H_2SO_4 solutions used in this project may have caused

molecular ion interferences with the instrument (Munro *et al.*, 1986); dilute HNO3 is the most suitable acid matrix in giving accurate results

Based on the cake results determined from XRF, overall optimization conditions displayed that using sulfuric acid to leach U from SFC was possible and can be successful.

4.12 LEACHING CONCLUSIONS

- U was successfully leached from coal samples into solution.

- Maximum extraction was experienced by 45.5 % of the samples after leaching for 8 hours. The other 54.5% samples leached recorded a higher U extraction after leaching for 24 hours No samples recorded maximum U extraction after leaching for 4 hours, in agreement with studies by Gajda *et al.* (2015), that leaching time has an effect on U extraction.

- Maximum extraction was registered for 72.7% of samples when pH=0.5, the remaining 27.3% samples registered maximum extraction when pH=1. No samples recorded maximum extraction when pH was 1.5, agreeing with studies by Wang *et al.* (2008), and Maslov *et al.* (2010) that pH has an effect in U extraction.

- Increasing temperature gave an increase in samples experiencing maximum extraction with 45% of the samples attaining maximum U extraction at T= 25^0C, and 55% of the samples registered maximum extraction at elevated temperatures T=45^0C and T=65^oC. These results were in agreement with Roshani and Mirjalili (2009), and Demopoulos (1985), who reported an increase in U content, for U bearing ores when leaching at higher temperatures.

- Sample 1421, 1436 and 1437 recorded high U extraction rates and were selected for optimization reactions.

- All 3 samples recorded higher U content for every optimization condition. Sample 1421 recorded 38% increase in U content from a previous maximum of 1789 μg L^{-1} to 2462 μg L^{-1}. Sample 1436 displayed the highest increase in U content leachable (106%) from 1186 μg L^{-1} to 2438 μg L^{-1} leached into solution. Sample 1437 recorded a 25% increase from a previous high of 897 μg L^{-1} to 1124 μg L^{-1}.

- The U percentage extracted from coal samples leached at 5 M ranged from 37.7% to 50.7%. The % U extracted range was higher than the 10-20% U extracted reported by Slivink *et al*. (1985) on coal samples from Zirovski, Yugoslavia, leached between pH =0.5- 1.2. Samples 1436 and 1437 recorded higher extraction rates than the 45.4% U extracted from Mongolian coal ash samples reported by Maslov *et al.* (2010).

- The U percentage extracted from coal samples leached at 10 M ranged from 58.9% to 67.3%. The U extracted range was higher than the 10-20% U extracted by Slivink *et al*. (1985) on coal samples from Zirovski, Yugoslavia. All samples leached at 10 M recorded higher extraction rates than the 45.4% U extracted from Mongolian coal ash samples reported by Maslov *et al.* (2010).

- Increasing molarity of leaching solution from 5 M to 10 M increased % U extracted for all coal samples, Sample 1421 experienced the highest increase in % U extracted due to the change in molarity of leaching solution, recording a 22.6% increase.

- Using sulfuric acid in the SFC samples was a viable and successful method of extracting U from the coal samples.

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The aim in the project was to assess the feasibility of extracting U from selected SFC coal samples using acid leaching. To achieve this, 5 freshly drilled SFC borehole cores were obtained and 49 coal samples were characterized for coal quality using proximate and ultimate analysis. The type of U isotope was identified using INAA, and U present in coal samples was quantified using ICP-MS, XRF, and INAA to identify the coal samples with high U content. 11 samples with U content higher than 10 mg kg^{-1} were selected, and leached with H_2SO_4 under different conditions. The U content post leaching in leachates was quantified to determine the effects leaching time, temperature, and pH on U extracted into solution. Three samples with the highest U extraction rates were selected and underwent leaching at optimum conditions. Based on the results obtained from optimum leaching, the viability of using sulfuric acid to leach U in the coal samples was then assessed and determined.

Proximate and ultimate analysis described the chemical nature of coal samples obtained from 5 freshly drilled SFC borehole cores. The analysis displayed that BH2 and certain horizons in BH3 and BH4 included coals that could be considered to be typical of South African coals, used in power generating plants in the country. Generally, BH1 and BH5 had high ash content; these coal zones were almost completely made up of carbonaceous shale, and the samples were omitted from further investigation. A petrographic microscope was used to view pyrite cleats present in the coal samples with high sulfur content. XRD showed that quartz and kaolinite made up the bulk of the mineral matter of the raw coal samples supported by Pinetown and Boer (2006) and that U was affiliated with clay minerals in coals, and kaolinite in particular.

The U content was quantified in the borehole core coal samples using ICP-MS, XRF and INAA. Generally, XRF gave the highest U results of all the techniques used, and INAA provided U values higher than ICP-MS (Table 4.3). The low U content reported by ICP-MS was attributed to possible incomplete decomposition and digestion of the solid coal

samples. XRF results were used as the basis since the filter cakes samples were analyzed using XRF. The percentage U extracted was calculated using XRF.

All borehole coal zones studied had an average U content higher than published data on global U content (Swaine, 1990). U in the SFC samples was distributed throughout the coal zones and carbonaceous shale regions in the zones sampled. U in the coal zones was generally restricted to a single layer, usually within the first 1 m in the local sequence, with the exception of BH2 and LCZ in BH5; here U mineralization occurred in multiple horizons. BH3 had the highest average U content (33 mg kg^{-1}), followed by BH2 (26 mg kg^{-1}) and BH1 (14 mg kg^{-1}). BH4 (7.8 mg kg^{-1}), the UCZ in BH5 (4.3 mg kg^{-1}), and the LCZ in BH5 (5.9 mg kg^{-1}) all had U content averages less than 10 mg kg^{-1}.

INAA was used to determine the U isotope present in coal samples, INAA results determined that the ^{238}U isotope was the dominant isotope present in the coal samples, with every peak encountered representing the ^{238}U isotope or a decay series product of the isotope. This was expected since ^{238}U is the most abundant of the U isotopes found in nature.

Based on XRF results, 11 samples with a U content higher than 10 mg kg^{-1} were selected to be leached using sulfuric acid (Table 4.3). The U was successfully leached from the coal samples into solution using sulfuric acid. A number of variables were tested to determine the impact on leaching potential, namely time, temperature and pH. Time played a role in U extraction, with 4 hours producing low U content. 45% of the samples leached recorded maximum extraction after leaching for 8 hours; 55% of the samples recorded their maximum U extraction after leaching for 24 hours. Thus, increasing leaching time resulted in more samples recording high U content leached into solution. Reducing the pH resulted in improved U extraction into solution; no samples recorded maximum extraction when pH was 1.5; 27.3% samples registered maximum extraction when pH=1, and 72.7% of samples registered maximum U content when pH=0.5. Increasing leaching temperature resulted in more samples recording high U content in solution; 45% of the samples produced maximum U extraction at T= 25^0C, and 55% of the samples registered maximum extraction at elevated temperatures (T=45^0C and T=65^oC).

3 samples (1421, 1436 and 1437) with relatively high U content extracted into solution were selected for optimization experiments; conditions providing maximum U extraction for each sample were sought. All samples recorded higher U content for every optimization condition. Sample 1421 recorded 38% increase in U content from a previous maximum of 1789 $\mu g\, L^{-1}$ to 2462 $\mu g\, L^{-1}$ leached at 15 M. Sample 1436 displayed the highest increase in U content leachable (106%) from 1186 $\mu g\, L^{-1}$ to 2438 $\mu g\, L^{-1}$ leached into solution leached at 15 M. Sample 1437 recorded a 25% increase from a previous high of 897 $\mu g\, L^{-1}$ to 1124 $\mu g\, L^{-1}$ leached at 10 M.

Based on filtered cake results, the U percentage extracted from coal samples leached at 5 M ranged from 37.7% to 50.7%, and from 58.9% to 67.3% for coal samples leached at 10 M. All samples recorded % U extraction higher than the 10-20% U extracted by Slivink *et al*. (1985) on coal samples from Zirovski, Yugoslavia. Increasing molarity of leaching solution from 5 M to 10 M resulted in an increased in U extracted for all coal samples. Sample 1421 experienced the highest increase in U extracted due to the change in molarity of leaching solution, recording a 22.6% increase.

The research was successful in addressing the aims and objectives set out for the project, in that samples from the SFC were successfully characterized in terms of coal quality, and U occurrence within the horizons of the borehole coal zones. U was successfully extracted from SFC coal samples, and relatively high U extraction was reported. Additionally, this research will contribute to the public domain information available on the separation of coal and U and will be a pioneer for SFC raw coal samples. Overall, sulfuric acid leaching of SFC coal samples was found to be a viable and successful method of extracting U.

5.2 RECOMMENDATIONS

- Due to the quality and depth of the coal zone in the SFC, conventional underground mining is currently not an option. Had the majority of the resources been in the opencastable range (0-75 m), perhaps the coal quality would have been more suitable to opencast mining by micro to medium enterprises. New extraction methods and technologies exploiting the energy

content of the coal *in situ* and markets for low-grade, high ash coal are necessary before South Africa can utilize this vast coal resource, in agreement with Jeffrey (2005).

- Due to the alarmingly high sulfur content, should BH2, BH3 and BH4 minable areas be pursued, then probably, flue gas desulfurization (FGD) would be a requirement for these coal zones to diminish the expected high SO_2 emissions into the atmosphere and environment.
- It should be noted that if the areas surrounding BH2 was to be mined, the beneficiated product may be employed in the steel industry as a blended coking coal (Jeffery 2005). The coals can be upgraded by using dense medium beneficiation techniques.
- Other factors that could influence the U extraction rate should be researched such as impact of particle size, slurry density, degree of agitation, and oxidation potential. Probably the first to be researched could be agitation, as this is a relatively inexpensive addition to the research. Studies have shown that the U content increases in the leachate when agitation rate and time are increased (Bailes *et al,* 1956). Adding an oxidant such as hydrogen peroxide or adding iron containing compounds through the leach slurry has also been seen to significantly influence the U solubility and hence enhance extraction into solution (Lottering *et al*. 2008).
- The effect of the solids to liquids ratio should be studied by leaching smaller portions of sample using the same amount of acid.
- Other means of leaching such as column leaching could also be studied to see the impact they would have on the overall leaching of U with literature showing relative success in using column leaching to extract U from coal and its combustion by products (Wang *et al.*, 2008).
- Further studies using different lixiviants eg nitric acid or sodium carbonate should be done as a comparative study. Sodium carbonate leaching has been done in North America for in-situ leaching of U.

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Appendix - Tables

Appendix A- Coal quality results

Table A1- BH1: Coal Quality

sample name	Depth (m)	Moisture	Volatile matter	Fixed carbon	Ash	Carbon	Nitrogen	Sulfur	CV
1436	277.0 - 277.9	4.3	10.37	10.47	74.86	13.711	0.25012	0.2392	3.54
1437	278.0 - 278.78	5.01	6.68	0.1	88.41	0.14607	0.00082	0.1452	0
1438	278.78 - 279.37	5.08	7.8	2.03	85.09	6.321	0.00869	0.19194	0.69
1439	279.37 - 280.0	4.71	10.59	8.49	76.21	12.038	0.17711	0.2244	4.15
1440	280.0 - 280.5	4.73	7.92	2.46	84.89	4.0806	0.06731	0.13312	1.01
1441	308.73- 309.1	4.23	5.76	7.47	82.53	9.5987	0.1521	0.11364	2.42
1442	309.1- 309.6	4.39	5.61	19.75	62.18	5.2272	0.07442	0.05899	0.8

Table A2- BH2: Coal quality

Sample name	Depth (m)	Moisture (%)	Volatile matter (%)	Fixed carbon (%)	Ash (%)	Carbon (%)	Nitrogen (%)	Sulphur (%)	CV
1426	251.34-251.46	3.36	22.37	28.04	46.23	38.618	0.54828	4.387	16.3
1427	252.30 - 252.75	2.35	29.01	36.53	32.1	51.67	0.78457	8.8593	21.98
1428	252.75-253.0	2.44	19.33	25.14	53.09	34.443	0.53926	0.98551	13.39
1429	253.12 - 253.72	3.01	25.44	34.77	36.78	47.797	0.64114	2.5288	19.93
1430	253.72 - 254.18	3.03	31.76	47.15	18.06	65.2795	0.8953	2.1349	27.04
1431	254.14-254.25	2.49	33.16	40.32	24.04	57.735	0.9303	7.2293	23.45
1432	254.6 - 255.5	2.76	23.84	34.11	39.29	46.84	0.72846	1.3889	17.52
1433	255.5-255.93	2.87	22.39	32.15	42.59	43.989	0.70498	0.54374	17.86
1434	256.33-256.70	2.68	16.59	21.04	59.7	27.882	0.45322	1.5738	11.65
1435	257.78 - 258.00	2.69	19.12	22.16	56.03	31.356	0.5047	1.9438	12.94

Table A3- BH3: Coal quality

Sample name	Depth (m)	Moisture (%)	Volatile matter (%)	Fixed carbon (%)	Ash (%)	Carbon (%)	Nitrogen (%)	Sulphur (%)	CV
1421	341.52- 342.04	2.32	26.98	33.39	37.31	47.613	0.60029	3.519	19.8
1422	342.1.0- 342.7	2.32	16.15	18.57	62.96	24.963	0.34589	0.85327	9.87
1423	342.7 – 343.08	3.2	24.03	32.66	40.1	41.378	0.84266	3.5045	17.6
1424	343.56 – 344.0	2.54	8.49	4.28	84.69	5.4628	0.10885	1.115	1.72
1425	344.0-344.3	2.01	11.11	8.71	78.16	32	0.23654	3.5949	4.12

Table A4- BH4: Coal quality

Sample name	Depth (m)	Moisture (%)	Volatile matter (%)	Fixed carbon (%)	Ash (%)	Carbon (%)	Nitrogen (%)	Sulphur (%)	CV MJ/kg
1443	387.81 -389.13	2.9	22.71	15.98	58.4	26.1	0.31714	4.2063	10.27
1444	389.1 -390.0	3.86	19.81	29.63	46.7	37.77	0.56986	4.0571	15.83
1445	390.0 - 391.0	3.87	15.77	34.42	45.94	41.22	0.65118	0.9779	16.45
1446	391.0 -391.7	3.46	9.73	37.13	49.68	40.24	0.72214	0.5574	13.58
1447	391.7 -392.13	3.08	6.98	36.57	53.36	38.63	0.65326	0.6346	13.69
1449	393.0 -393.7	4.06	5.03	17.04	73.87	18.98	0.31913	0.2926	4.4

Table A5- BH5 UCZ: Coal quality

Sample name	Depth	Moisture (%)	Volatile matter (%)	Fixed carbon (%)	Ash (%)	Carbon (%)	Nitrogen (%)	Sulphur (%)	CV
1401	143.90-144.45	1.91	6.58	26.78	64.74	27.271	0.43135	3.5754	10.16
1402	144.5- 145.0	2.41	7.02	15.5	75.06	18.878	0.17168	2.1705	5.91
1403	151.6-152.10	2.77	5.59	11.82	79.81	13.575	0.19256	0.64696	4.15
1404	152.10-152.72	1.99	6.45	29.65	61.92	31.957	0.41845	0.79386	11.3
1405	152.72- 153.23	2.09	4.56	24.36	69	25.417	0.31263	0.74248	8.72
1406	153.23-153.70	2.42	4.83	30.51	62.24	31.222	0.35369	0.90661	10.58
1407	153.7-154.1	2.48	5.03	16.52	75.98	18.03	0.23815	0.65181	5.62
1408	154.1-154.51	2.46	4.56	32.95	60.04	33.1	0.39206	0.97267	11.41
1409	154.51-154.9	2.46	4.78	26.47	66.29	26.72	0.31668	0.47063	8.27
1410	154.9-155.27	1.71	18.11	26.88	43.3	39.99	0.56804	12.376	17.82

Table A6- BH5 LCZ: Coal quality

Sample name	Depth	Moisture	Volatile matter	Fixed carbon	Ash	Carbon (%)	Nitrogen (%)	Sulphur	CV
1411	344.67 – 345.10	2.08	14.05	16.4	67.48	39.18	0.44572	0.32478	7.16
1412	345.10 345.54	2.62	15.99	19.17	62.21	28.54	0.5626	0.27092	8.7
1413	345.54-345.89	3.09	16.58	24.99	55.34	29.607	0.69367	0.28526	11.06
1414	345.89-346.25	3.53	20.08	31.61	44.78	38.177	0.86907	0.39362	14.63
1415	346.25-347.10	3.37	20.26	30.17	46.21	36.925	0.84012	0.73826	14.48
1416	347.10-347.86	3.49	21.18	32.91	42.42	40.515	0.96256	0.62493	15.8
1417	347.86-348.28	2.62	17.39	18.5	61.49	23.262	0.56608	0.21249	8.2
1418	348.28-349.05	2.82	15.24	19.75	62.18	22.62	0.5073	0.15155	7.7
1419	349.05-349.86	3.22	20.19	27.52	49.07	34.113	0.76654	0.25761	13.06
1420	349.86-350.67	3.22	14.42	22.52	59.84	24.732	0.6375	1.4767	8.64

Appendix B- Ur detection results

Table B1- BH1: Ur content

sample name	Depth (m)	XRF (mg kg^{-1})	ICP (mg kg^{-1})
1436	277.0 -277.9	73	34.1
1437	278.0 -278.78	52	13
1438	278.78 -279.37	51	19.4
1439	279.37 - 280.0	36	20.9
1440	280.0 -280.5	14	6.2
1441	308.73-309.1	5.6	2.3
1442	309.1-309.6	5.3	2.4

Table B2- BH2: Ur content

Sample name	Depth (m)	XRF (mg kg^{-1})	ICP (mg kg^{-1})
1426	251.34-251.46	130	107.7
1427	252.30 - 252.75	2.9	2.8
1428	252.75-253.0	2.9	1.7
1429	253.12 - 253.72	96	85.9
1430	253.72 - 254.18	74	58.9
1431	254.14- 254.25	9.9	5.6
1432	254.6 - 255.5	2.9	1.9
1433	255.5-255.93	3.6	1.6
1434	256.33- 256.70	4.3	1.7
1435	257.78 - 258.00	4.8	2.7

Table B3- BH3: Ur content

Sample name	Depth (m)	XRF (mg kg^{-1})	ICP (mg kg^{-1})
1421	341.52- 342.04	199	145.9
1422	342.1.0- 342.7	18	11.3
1423	342.7 – 343.08	4.2	2.2
1424	343.56 – 344.0	7.9	3.2
1425	344.0-344.3	6	2.5

Table B4- BH4: Ur content

Sample name	Depth (m)	XRF (mg kg^{-1})	ICP (mg kg^{-1})
1443	387.81 -389.13	52	34.4
1444	389.1 -390.0	8.3	4.9
1445	390.0 - 391.0	3.6	2.2
1446	391.0 -391.7	3.9	1.7
1447	391.7 -392.13	3.2	1.8
1449	393.0 -393.7	4.5	1.9

Table B5- BH5 UCZ and LCZ: Ur content

Sample name	Depth	XRF (mg kg^{-1})	ICP (mg kg^{-1})	Sample name	Depth	XRF (mg kg^{-1})	ICP (mg kg^{-1})
1401	143.90-144.45	7.9	4	1411	344.67 – 345.10	6.4	2.9
1402	144.5-145.0	4.4	2.5	1412	345.10 345.54	8.8	4.3
1403	151.6-152.10	4.2	1.7	1413	345.54-345.89	8.9	4.7
1404	152.10-152.72	3.2	2.1	1414	345.89-346.25	8	10.7
1405	152.72-153.23	4	1.5	1415	346.25-347.10	8.2	4.7
1406	153.23-153.70	3.3	2	1416	347.10-347.86	12	4
1407	153.7-154.1	4.1	1.6	1417	347.86-348.28	14	9.8
1408	154.1-154.51	3.3	1.7	1418	348.28-349.05	11	6.7
1409	154.51-154.9	2.9	1.4	1419	349.05-349.86	10	2.7
1410	154.9-155.27	5.2	3.3	1420	349.86-350.67	11	9.3

Table B6- Selected samples: Ur content

Sample name	Borehole	U [INAA] (mg kg^{-1})
1416	BH5 LCZ	8.93
1417	BH5 LCZ	11.8
1421	BH3	161
1422	BH3	15.6
1429	BH2	86.9
1436	BH1	64.6
1437	BH1	43.2
1438	BH1	39.4
1439	BH1	29.3
1440	BH1	11.5

Table B6- Selected samples: Ur content in leachates

Samples	1421 5m	1421 10m	1436 5m	1436 10m	1437 5m	1437 10m	1421 15M	1436 15M	1437 15M
Li (7)	51	50	292	293	441	404	103	444	565
Be (9)	49	71	275	392	114	111	218	443	101
B (10)	< 40	< 40	< 40	< 40	45	< 40	< 40	< 40	< 40
Na (23)	9366	8409	41954	44006	63737	58520	10422	40418	57845
Mg (24)	5866	6064	16468	19095	30673	30504	6946	16542	22110
Al (27)	23810	31562	154035	262561	241756	345120	35188	281699	308476
K (39)	5808	2587	30601	17076	50615	30165	3549	14903	25859
Ca (43)	91513	29190	73570	42093	86788	43342	451311	304262	301849
V (51)	148	123	298	341	188	177	422	580	187
Cr (52)	427	665	3858	4057	207	185	2137	6412	245
Fe (54)	87613	67898	236474	195777	275649	206568	98693	233487	211235
Mn (55)	8207	7808	3305	2647	4627	3176	14015	3955	3913
Co (59)	1746	1258	420	360	212	153	1733	471	159
Ni (60)	1153	967	1197	1348	243	200	1546	1861	207
Cu (63)	177	79	179	114	191	180	111	382	198
Zn (66)	1599	3978	6610	4869	2526	2625	8843	8344	4239
Ga (69)	12	23	38	72	52	111	80	133	119
As (75)	5458	4366	1121	518	598	482	1008	212	279
Se (82)	< 0.4	332	160	236	< 0.4	271	176	59	38
Rb (85)	143	34	558	217	615	352	34	142	228
Sr (88)	715	716	2521	1804	2684	2663	2207	3789	4140
Mo (95)	362	333	258	237	18	17	393	278	16
Ag (107)	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Cd (111)	27	40	125	90	3	2	51	139	4
Te (128)	1	2	5	2	4	3	1	2	3
Ba (137)	35	671	54	1868	59	4205	2276	4287	3581
Tl (205)	62	57	5	3	6	4	53	3	3
Pb (208)	212	317	93	227	70	156	531	986	473
Bi (209)	4	< 0.2	7	1	7	< 0.2	3	22	4
U (238)	1788	1513	1959	1550	1124	886	2462	2438	1010

Table B7- Selected samples: Ur content in cakes

	1421 10 M	1437 10 M	1436 10 M	1421 5 M	1437 5 M	1436 5 M
As	75	7.5	8.2	109	12	6.5
Ba	80	124	107	125	198	193
Bi	<3	<3	<3	<3	<3	<3
Br	<2	<2	<2	<2	<2	<2
Ce	65	18	119	92	28	176
Co	21	5.2	13	30	11	16
Cr	90	38	107	75	42	84
Cs	<5	11	<5	<5	6.8	8.1
Cu	5.9	6.5	8.3	6.1	9.1	11
Ga	5.8	12	11	7.5	18	17
Ge	1.5	<1	<1	2.6	1.8	1.2
Hf	<3	3.3	<3	<3	5.3	3.7
La	37	<10	64	50	13	90
Mo	17	<2	6.4	23	<2	5.7
Nb	8.8	14	15	10	18	18
Nd	32	<10	56	46	12	84
Ni	36	18	31	48	24	38
Pb	19	16	16	26	21	22
Rb	9.7	46	42	13	62	54
Sc	3.1	4.1	3.1	5.1	4.9	6.2
Se	<1	<1	6.4	2.6	<1	7.5
Sm	<10	<10	<10	<10	<10	14
Sr	33	32	33	46	44	35
Ta	<2	<2	<2	<2	<2	<2
Th	<3	3.3	6.3	4.9	7.2	8.5
Tl	<3	<3	<3	<3	<3	<3
U	79	17	30	124	26	36
V	30	35	41	44	45	60
W	3.4	<3	<3	6.2	<3	<3
Y	53	10	56	76	13	68
Yb	3.5	<3	4.9	4.4	<3	6
Zn	59	19	67	98	33	83
Zr	85	89	118	132	127	163

Appendix C- Major Components results (XRF)

Table C1- BH1: Majors (%)

Sample	**1436**	**1437**	**1438**	**1439**	**1441**
SiO2	50.65	64.29	59.97	60.17	54.62
TiO2	0.74	0.87	0.81	0.87	0.82
Al2O3	16.10	19.75	20.25	20.25	18.67
Fe2O3	2.26	2.87	2.50	2.10	2.81
MnO	0.050	0.030	0.028	0.024	0.032
MgO	0.59	0.62	0.66	0.60	1.04
CaO	2.18	1.17	1.20	0.98	1.22
Na2O	0.53	0.29	0.41	0.57	1.05
K2O	1.87	1.97	1.95	2.15	2.60
P2O5	0.033	0.020	0.028	0.027	0.033
Cr2O3	0.004	0.003	0.003	0.003	0.005
LOI	24.34	7.56	11.67	11.65	16.56

Table C2- BH2: Majors (%)

Sample	**1426**	**1427**	**1428**	**1429**	**1430**	**1431**	**1432**	**1433**	**1434**	**1435**
SiO2	27.37	16.00	32.21	21.81	9.99	10.92	23.94	28.30	39.44	31.79
TiO2	0.46	0.22	0.49	0.34	0.14	0.22	0.38	0.47	0.60	0.52
Al2O3	10.59	4.67	9.58	6.23	3.13	3.39	8.23	9.36	12.63	11.82
Fe2O3	4.19	2.76	1.10	2.22	1.83	6.94	1.08	0.62	2.27	2.00
MnO	0.112	0.115	0.012	0.094	0.055	0.124	0.011	0.010	0.028	0.071
MgO	0.26	0.10	0.22	0.18	0.12	0.12	0.21	0.26	0.35	0.31
CaO	4.92	3.75	0.18	4.56	1.72	3.40	0.18	0.17	0.44	1.40
Na2O	0.10	0.06	0.16	0.06	0.04	0.08	0.16	0.30	0.35	0.28
K2O	0.67	0.36	0.94	0.50	0.33	0.37	0.84	1.21	1.68	1.35
P2O5	0.037	0.006	0.015	0.009	0.009	0.008	0.011	0.015	0.019	0.020
Cr2O3	0.003	0.001	0.003	0.001	0.002	0.005	0.002	0.002	0.002	0.003
LOI	50.35	70.84	54.58	62.87	81.74	73.39	64.38	58.78	41.49	49.79

Table C3- BH3: Majors (%)

Sample	**1421**	**1422**	**1423**	**1424**	**1425**
SiO2	21.69	44.39	23.64	57.83	50.40
TiO2	0.35	0.63	0.49	0.90	0.77
Al2O3	7.90	15.65	10.66	20.52	18.33
Fe2O3	3.85	1.37	4.24	2.92	6.20
MnO	0.057	0.016	0.024	0.024	0.040
MgO	0.15	0.35	0.22	0.56	0.42
CaO	2.61	0.46	0.26	0.36	0.43
Na2O	0.07	0.13	0.09	0.28	0.26
K2O	0.39	0.98	0.73	2.65	2.06
P2O5	0.022	0.028	0.023	0.040	0.031
Cr2O3	0.017	0.025	0.017	0.029	0.037
LOI	62.04	35.56	58.88	13.34	20.32

Table C4- BH4: Majors (%)

Sample	**1443**	**1444**	**1445**	**1446**	**1447**	**1448**	**1449**
SiO2	21.37	27.97	24.45	30.33	37.18	44.15	45.49
TiO2	0.33	0.44	0.42	0.44	0.52	0.67	0.72
Al2O3	6.48	9.39	8.71	11.00	12.58	14.34	17.07
Fe2O3	15.80	3.39	2.31	1.14	1.53	2.51	2.23
MnO	0.988	0.047	0.068	0.065	0.054	0.052	0.037
MgO	0.41	0.38	0.45	0.57	0.71	0.86	1.06
CaO	2.65	0.91	1.73	1.68	1.29	1.66	0.86
Na2O	0.20	0.45	0.61	1.09	1.49	1.12	1.29
K2O	0.55	1.21	1.31	1.46	1.81	2.30	2.77
P2O5	0.016	0.017	0.013	0.015	0.017	0.024	0.028
Cr2O3	0.001	0.002	0.002	0.002	0.001	0.005	0.002
LOI	50.69	55.21	59.21	51.51	42.17	31.68	27.86

Table C5- BH5 UCZ: Majors (%)

Sample	**1401**	**1402**	**1403**	**1404**	**1405**	**1406**	**1407**	**1408**	**1409**	**1410**
SiO2	39.85	49.35	53.44	38.77	46.50	41.67	51.49	40.37	44.49	17.32
TiO2	0.47	0.52	0.75	0.57	0.62	0.51	0.65	0.54	0.59	0.22
Al2O3	11.69	11.99	16.69	12.54	13.58	13.05	15.76	12.43	13.96	6.60
Fe2O3	7.40	5.61	2.66	4.25	2.74	1.89	2.47	1.92	2.23	13.06
MnO	0.087	0.089	0.033	0.048	0.036	0.030	0.040	0.031	0.036	0.139
MgO	1.09	1.34	1.02	0.96	0.80	0.69	0.92	0.63	0.73	0.19
CaO	0.69	3.52	0.97	0.88	0.62	0.72	0.61	0.48	0.51	5.39
Na2O	2.28	2.00	2.46	2.76	2.90	2.51	2.33	2.29	2.33	0.07
K2O	1.52	1.88	2.74	1.61	2.21	2.12	2.64	2.07	2.38	0.49
P2O5	0.034	0.026	0.036	0.022	0.024	0.026	0.029	0.022	0.023	0.016
Cr2O3	0.025	0.027	0.015	0.013	0.017	0.013	0.019	0.016	0.017	0.046
LOI	34.22	22.92	18.27	36.94	29.44	36.16	22.46	38.67	31.91	55.22

Table C6- BH5 LCZ: Majors (%)

Sample	1411	1412	1413	1414	1415	1416	1417	1418	1419	1420
SiO2	45.77	37.00	32.75	24.92	25.44	23.63	35.12	36.08	27.69	33.54
TiO2	0.94	0.73	1.02	0.80	0.83	0.92	1.17	1.08	0.86	1.44
Al2O3	19.22	20.18	18.62	17.63	17.38	15.28	22.68	24.22	17.90	21.31
Fe2O3	0.68	0.43	0.46	0.43	1.02	0.86	0.53	0.44	0.55	3.12
MnO	0.010	0.007	0.013	0.009	0.015	0.014	0.014	0.006	0.014	0.023
MgO	0.28	0.22	0.23	0.20	0.25	0.23	0.29	0.23	0.27	0.40
CaO	0.19	2.01	1.64	0.76	1.24	1.56	1.76	0.28	2.08	0.23
Na2O	0.15	0.14	0.15	0.12	0.14	0.11	0.16	0.13	0.13	0.39
K2O	1.05	0.74	0.76	0.60	0.68	0.62	0.73	0.67	0.59	0.67
P2O5	0.045	1.570	0.867	0.435	0.185	0.277	0.225	0.105	0.172	0.039
Cr2O3	0.024	0.008	0.015	0.007	0.008	0.009	0.014	0.010	0.012	0.028
LOI	31.05	36.31	42.90	53.50	52.15	55.86	36.59	36.11	49.01	38.35