DETERMINATION OF ASH CONTENT OF SOME NIGERIAN COALS USING GAMMA TRANSMISSION MEASUREMENTS

BY

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Dedication

Above all, I dedicated this research work to God Almighty. To Him alone be the glory for ever and ever, Amen.

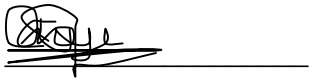
Secondly, it is dedicated to all who are very close to my heart – my wife, daughter, father and all my siblings.

Finally, this research is dedicated to my late mother – Mrs. Agnes Omeje, of the blessed memory who departed even before I could complete first degree programme.

Declaration

I declare that the work in the thesis entitled 'Determination of the Ash Content of some Nigeria Coals Using Gamma Transmission Measurements' has been performed by me in the Department of Physics under the supervision of Dr. I. O. Okunade and Prof. S. A. Jonah.

The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at any university.



Omeje, Cornelius Uchenna

Date: 08 – 02 – 2008

Certification

This thesis entitled "DETERMINATION OF THE ASH CONTENT OF SOME NIGERIA COALS USING GAMMA TRANSMISSION MEASUREMENTS" by Omeje, Cornelius Uchenna meets the regulations governing the award of Master of Science degree in Physics (Nuclear option) of Ahmadu Bello University, Zaria, and is approved for its contribution to knowledge and literary presentation.

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Abstract

An experimental facility which utilizes gamma transmission technique has been developed for routine determination of ash content of coal. It consists of ^{241}Am and ^{137}Cs radioisotope sources and NaI(Tl) detector coupled with single channel analyzer, characterized with relatively high sensitivity and with windows set at appropriate energy for determination of transmitted γ-counts from the sample. The facility is based on principles of Absorption and attenuation of low energy γ-rays which depend on the mean atomic number of elements and thus can be used to determine the ash content of coal since the mean atomic number of ash is greater than that of coal matter. The system was calibrated using simulated standard prepared by doping graphite powder with different concentrations of incombustible elements in their compound form. The calibration coefficients determined from measurements of simulated standards containing different amounts of ash in single and dual energy mode were used for the determination of ash content of various coal samples obtained from different areas in Nigeria namely; Okaba, Ogboyoga, Okpara, Ogwashi/Azagba, Owukpa, Lafia-obi and Inyi. The results compare reasonably well with results from chemical assay of the coal samples. The predicted ash for single energy also largely agrees with prediction based on dual energy transmission measurements. The accuracy of ash determinations however depends to some extent on variation in chemical composition of the ash and the coal matter. With proper control of sources of experimental error the facility shows great promise in accurate determination of raw and washed coal samples and favourably lends itself to adaptation to industrial on-line quality control of coal.

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CHAPTER ONE

1.0 Introduction

Accurate determination of the ash content of coal is an important aspect of coal production and processing. Existing methods based on chemical assay usually involve a lot of time and effort and does not lend itself to representation of bulk composition of coal. This is because the heterogeneous nature of coal requires byline analysis of several samples from which the mean ash content is obtained in order to come close to a value that is representative of the bulk composition of the coal. Thus grading of coal using these methods require a lot of time and effort, making it difficult to be adapted for integration into standard industry protocols for quality control. Coal is essentially made up of coal matter, mineral matter and moisture. The coal matter consists of carbon, hydrogen, oxygen and nitrogen; while the mineral matter include aluminum and other silicates, iron sulphide and oxides of several metals of varying composition. Thus when coal is subjected to combustion for the purpose of extracting heat energy, the byproduct is the oxidized incombustible residue in form of ash having concentration that is closely correlated with the mineral matter content.

X-ray, low energy γ-ray (Fookes et al, 1977; Boyce et al, 1977), annihilation γ-rays (Sowerby and Ngo, 1981) and neutron techniques (Sowerby, 1979; Borsaru and Mathew, 1980) had been employed for non-destructive and accurate determination of ash content of coal. Absorption and attenuation of low energy and annihilation γ-rays depend on the mean atomic number of elements and thus can be used to determine the ash content of coal since the mean atomic number of ash is greater than that of coal matter. In the case of neutron techniques, the ash content is usually determined via

analysis of the bulk coal sample in terms of concentration of individual elements that constitute the ash content or indirectly by analysis of carbon and hydrogen content.

The accuracy of ash determinations by each of the above techniques depends to some extent on variation in chemical composition of the ash and the coal matter. For example, consideration of iron variation in the ash is very important when using the X-ray absorption techniques since it is particularly sensitive to variations in iron content of the ash (Sowerby, 1979). In addition, the technique requires sampling of the coal from the conveyor and considerable sample preparation before analysis. The annihilation technique which requires gamma ray energy above 1.02 MeV is much less sensitive to iron variations. Neutron based analytical techniques including nuclear activation analysis, inelastic scatter and capture γ-ray, capable of determining concentrations of Al and Si in coal are based on the assumption that a strong correlation exist between ash content and concentrations of these two elements. Even if the techniques are used to analyze several elements in coal, the series of steps and relatively longer analysis time makes them unattractive. The only justification in such cases would be requirement of ash content as well as elemental concentrations of the coal samples.

Some the above mentioned techniques had been applied in determination of ash content for coal that were sampled from the conveyor belt, which may not necessarily be representative of the entire batch. In a situation whereby the sample presentation can be automated, the sampling and sampling presentation systems are rather complicated and expensive. Direct on-line measurement of coal on conveyors using γ-ray transmission technique has the potential to overcome these problems since it has the capability of averaging the ash content determination over larger weights of coal. Errors may

however be introduced as a result of segregation on the main-stream conveyors, and also by variable measurement geometry due to changes in profile of coal on the belt and changes in belt thickness.

The present work utilizes γ-ray transmission technique for determination of ash content of coal on laboratory scale using both the single energy and dual energy options. This is done by calibrating the system with simulated standard prepared by doping graphite with different concentrations of elements of interest. The set-up consists of radioisotope sources of appropriate energy, NaI(TL) detector and predetermined sample volume all enclosed in a lead shield. A single channel analyzer with relatively higher sensitivity and with windows set at appropriate energy was utilized in determining transmitted γ-counts from the sample.

1.1 Objectives of the Study

The main objective of this work is to determine the ash content of coal using gamma transmission technique. Specific objectives are as follows;

- To set up an experimental facility for determination of ash content of coal using γ-transmission technique.
- To develop an analytical procedures for the determination of ash content of coal using γ-transmission technique.
- To use the facility to determine ash content of some Nigerian coals.
- To explore the possibility of adapting this technique for industrial on-line quality control facility for coal seams.

1.2 Previous Works

One of the earliest works recorded was carried out at the request of the Mineral Survey of Southern Nigeria by the Imperial Institute, London, between 1903 and 1911 on the characterization of Southern Nigerian Lignites. Being limited then, by the availability of modern facilities in gamma spectroscopy, and mainly focusing on the potentiality of coals as a fuel source, the Imperial Institute submitted reports on the Proximate and Ultimate Analysis of Nigerian coal (Dunstan, 1911; Wilson, 1925 and Ewa, 1992). These reports were based on the calorific properties of Nigerian coal and therefore have little relationship with measurement of the ash content. The final analysis provided results on the principal fuel related elements of carbon, hydrogen, nitrogen, sulphur and oxygen.

Sowerby, (1979) reported the method for specific energy dependence on a combination of a measurement of 4.43 MeV ^{12}C γ - rays from neutron inelastic scattering and ^{60}Co γ - ray scattering measurement on essentially the same sample volume. The γ - ray scattering measurement corrects the neutron gauge for variable such as sample bulk density, bulk density gradients and sample thickness. He applied this method on approximately 50 kg coal samples from coalfields in Sutherland, New South Wales, Australia and found that carbon specific energy and ash were 0.44 MJ/kg and 1.4 wt. % respectively.

Another coal related work was reported by Sowerby, et al. (1981) where they carried out Annihilation Radiation measurement on 57 bulk coal samples, each weighing 100-200 kg, from three different areas of Australia and using ^{60}Co source and 7.6 cm x 7.6 cm NaI(Tl) detector in backscatter geometry. They gave that the root mean square

deviations between chemical laboratory ash and ash measured on the backscatter gauge were in the range of 0.46 to 1.37 wt. %.

Further attempt at the characterization of Nigerian coal was reported by Ndiokwere, et al. (1983). Their report, though not exclusive was limited to Okpara, Onyeama and Ekulu mines. Also constrained by the economy of reactor time, the long-lived irradiation was limited to only three hours, meaning that data for all long-lived radionuclides that require longer irradiations were not determined. Seventeen elements (Al, Br, Ce, Co, Eu, Fe, Ga, K, La, Mn, Na, Sb, S, Si, Sm, Ti and V) were therefore determined by them using Instrumental Neutron Activation Analysis (INAA).

Fookes, et al. (1983) using Low Energy γ-ray Transmission Measurement on suites of 100kg samples from each of four different areas of Australia gave that errors in ash determination were 0.99, 1.20, 1.59 and 2.24 wt. % (1σ), respectively, for mean ash contents of 20.0, 27.1, 24.5 and 17.1 wt. % ash.

Also Fookes, et al. (1983) reported a gauge based on Measurement of the Transmission through Coal of Low and High Energy γ - rays developed for on-line determination of the ash content. As they determined, the root mean square difference between ash determined on-line and ash determined by chemical assay of coal sampled from the conveyor was 0.45 wt. %. The gauge measures coal directly on the conveyor.

Another coal related study was reported by Ewa, et al. (1996). They used Instrumental Neutron Activation Analysis (INAA) to determine the concentration of thirty three trace elements in both feed-coal and ash obtained from coal-fired power station in Nigeria. They measured the Ash Enrichment Factors (EFs) for each of the elements; used it to asses the environmental contamination and found that most of the elements

had EFs less than 1 while As, Fe, Hf, Na and Ti had EFs within the range of 1-10 and that obtained for Mn and U appeared significant.

Again, Ewa, et al. (1996) used Instrumental Neutron Activation Analysis to determine the concentration of some alkali elements (Na, Ca and Mg) associated with Ash Fouling for eight Nigerian coals mined at Onyeama, Ogbete, Enugu, Gombe, Okaba Afikpo, Lafia and Asaba. They found that sodium levels were generally low (0.001-0.036%) and also determined the oxygen concentrations which they considered as an indicative measure of the wettability for each of the coal samples and discussed the ash fouling based on the possible effects of the concentration of these elements.

Also, Ewa, et al. (1996) reported the pattern of ten Rare Earth Elements (La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Yb and Lu) for the same eight Nigerian coal samples using Instrumental Neutron Activation Analysis. Their results showed that the existence of fractionations with the highest index of 13.19 for Lafia coal, depletion in Heavy Rare Earth Elements, negative Eu anomaly for most of the coals, Rare Earth Elements patterns that are consistent with chondritic trends; prominent (Eu/Eu*)cn for Okaba and Gombe coals. These variations in the geochemical data, they observed could suggest strong departures from band metamorphism during the coalification events of the Benue trough geosynclines, where the coal deposits are all located.

Another coal related work was reported by Raja, et al. (1999). This work assessed and detailed the dependence of useful heat value (UHV) on parameters such as fixed carbon, volatiles, ash and moisture for samples of coal using Gamma ray Transmission Technique. They obtained a correlation between the attenuation coefficient and UHV for the coal samples.

Adaikpoh et al. (2005) reported that heavy metals (Mn, Cr, Cd, As, Ni and Pb) which they analyzed for were present in both the coal samples and sediments from River Ekulu in Enugu, Coal City of Nigeria throughout the period of monitoring. They pointed out that heavy metals have a higher residence period in the coal than the sediments around the river, a possible reason for the higher concentration of heavy metals in the coal.

1.3 Present work

In this work, gamma transmission measurement was used to determine the ash content of eight coal samples from different locations in Nigerian. The samples were irradiated using a low energy and high energy sources, ^{241}Am and ^{137}Cs respectively. The intensities (counts per second) with and without the samples were measured in both single and dual energy modes.

Simulated coal samples were prepared using graphite and known amounts of compounds to obtain a simulated standard of known concentration of ash. The elemental concentrations of these simulated standards were calculated using spread sheet.

Three different samples (water, simulated standard and sand) were used to measure optimal thickness, to be used for calibration of the set-up. Sample depths ranging from 0.0 cm to 35.0 cm were used and from the plot of the normalized counts rate versus depth, the normalized counts rate rises from 0.0 cm and saturates between 25.0 cm and 30.0 cm.

The intensities of the γ-rays with and without samples were measured and used to determine the calibration constants. Then using equations (3.6) and (3.10) in chapter

three, the ash content of the coal samples was determined in both the single energy and the dual energy gamma transmission methods respectively.

CHAPTER TWO

2.0 Review of Related Literature

2.1 Radioactivity and Types of Radioactive Decay

The types of radioactive decay products which are likely to occur and which may be used to identify and measure radioactivity are alpha and beta particles, gamma and x-rays and neutron emission.

Alpha particles are emitted during the course of the decay chain of naturally occurring radioactive species and are not usually emitted as the result of decay of any neutron activation process, except where the activation process results in the production of a nuclide in the natural decay chain, for example ^{235}U decaying to ^{231}Th with emission of an alpha particle or, in the case of neutron – induced reactions of lithium and boron, $^{6}Li(n,\alpha)^{3}H$ and $^{10}B(n, \alpha)^{7}Li$, when prompt alpha particles are emitted. Alpha particles are mono-energetic and have energies in the range 2 – 10 MeV. The range of an alpha particle is small, for example a 5 MeV alpha particle will travel only 0.03 mm in silicon. Consequently, before counting, an alpha emitter would normally be chemically isolated from the original sample matrix and plated onto a support so it could be measured. For these reasons alpha particles are rarely used in activation analysis for the determination of elemental concentration. Notable exceptions are the determination of uranium by measuring the alpha particles produced by fission during neutron activation, and the determination of boron in steel. The alpha particles are recorded using a film made of cellulose nitrate, cellulose acetate or a polycarbonate placed in close contact with the surface of the material under examination. When an alpha particle is emitted, it creates tracks in the film. The number of tracks recorded will indicate the concentration of the alpha emitter in the sample.

Beta particles are charged particles with either a negative (β^-) or a positive (β^+) charge. They are not mono-energetic but have a band of energy from zero up to a maximum energy in the range 0.1- 20 MeV, although the majority is below 10 MeV. Most neutron-activated nuclei decay by emission of beta activity giving rise to a daughter with either an atomic number one above (in the case of β^- emission), or one below (in the case of β^+ emission). For example, the decay of ^{60}Co with emission of a β^- produces ^{60}Ni and the decay of ^{65}Zn with emission of a β^+ gives ^{65}Cu. The major disadvantage is the wide band of energies exhibited by beta particles. A mixed source containing several beta emitters would give a range of energies which could only be identified by their different half-lives and by chemical separation of the components. This is applied to some analysis but since it is a specialized technique usually confined to single elements. It is not suitable for multi-elemental analysis.

X-rays are produced as a result of internal conversion or electron capture during the decay of radionuclides produced by neutron activation. In the case of electron capture, the nucleus captures an electron from the K or L shell, with the production of a daughter with an atomic number one less and emission of the characteristic X-ray of the daughter. For example, ^{58}Co decays by electron capture and positron emission to give ^{58}Fe and the characteristic X-ray of the iron. Internal conversion occurs when a gamma ray emitted from the nucleus interacts with an orbital electron producing a conversion electron. Rearrangement of the orbital electrons results in production of an X-ray characteristic of the parent. The percentage of internal conversion is often high for isomeric transitions, such as the decay of ^{60m}Co to ^{60}Co, when virtually all the gamma rays (59 keV) are converted in the K shell and the characteristics X-ray of cobalt is seen (Parry, 1991). The X – rays produced during these decay processes may be used in

activation analysis to measure elements. Being mono-energetic they are suitable for multi-elemental analysis. The main problems of X-ray counting are associated with interferences from other processes, secondary X-rays due to fluorescence, high backgrounds due to beta particles and absorption in the matrix. The latter is a major drawback for analyzing thick samples since the attenuation effects of X-rays, with energies between a few and 100 keV is large. It can be overcome using very thin samples.

Gamma rays are produced as a result of a transition between excited levels of a nucleus. These may be prompt gamma rays produced when a neutron is absorbed during activation of the (n,γ) type, or a delayed gamma ray which occurs when the radioactive product is decaying. In the first case, the gamma rays are emitted during irradiation, as the highly excited level decays to the zero level of the activation product. This transition can be seen while the sample is being irradiated. The gamma ray spectra tend to be quite complex and have a number of very high energy gamma rays (up to 6 MeV). Delayed gamma rays are emitted during the decay of the parent and normally follow the beta decay. Therefore, they have the characteristics half-life of the parent. The transitions are between energy levels of daughter and therefore, there may be a number of different gamma ray lines. Each photon has a characteristic well-defined energy and there may be several energy transitions for each disintegration. Typical energies are in the range 0.05 – 4 MeV.

When a fissionable material (uranium, thorium, neptunium or plutonium) is activated with neutrons to induce fission, shot-lived fission products with half-lives of up to 54 s are produced. They are very unstable and decay sometimes with emission of a neutron from the nucleus. These delay neutrons have an average energy of 0.5 eV. They

provide a specific technique for measuring fissionable material. The method is applied in particular to the determination of uranium in mineral exploration samples (Amiel, 1981). It is very specific technique and its applications are limited to fissionable material.

2.1.1 Radioisotopes

Many of the chemical elements have a number of isotopes. The isotopes of an element have the same number of protons in their atoms (atomic number) but different masses due to different numbers of neutrons. In an atom in neutral state, the number of external electrons also equals the atomic number. These elements determine the chemistry of the atom. There are 82 stable elements and about 275 stable isotopes of these elements, (Lowenthal and Airey, 2001).

When a combination of neutrons and protons, which does not already exist in nature, is produced artificially, the atom will be unstable and is called a radioactive isotopes or radioisotope. There are also a number of unstable natural isotopes arising from the decay of primordial uranium and thorium. Overall there are some 1800 radioisotopes. At present there are up to 200 radioisotopes used on regular basis, and most must be produced artificially, (Lowenthal and Airey, 2001).

Radioisotopes can be manufactured in several ways. The most common is by neutron activation in a nuclear reactor. This involves the capture of a neutron by the nucleus of an atom resulting in an excess of neutron (neutron rich). Some are manufactured in a cyclotron (proton rich). The nucleus of a radioisotope usually be comes stable by emitting an alpha and/or beta particle. These particles may be accompanied by the

emission of electromagnetic radiation known as gamma rays. This process is known as radioactive decay.

They have very useful properties: radioactive emissions are easily detected and can be tracked until they disappear leaving no trace. Alpha, beta and gamma radiations, like X-rays, can penetrate seemingly solid objects, but are gradually absorbed by them. The extent of penetration depends upon several factors including the energy of the radiation, the mass of the particle and the density of the solid. These properties lead to many applications for radioisotopes in the scientific, medical, forensic and industrial fields. Some industrial radioisotopes which are artificially produced include;

1. ^{241}Am: Used in backscatter gauges, smoke detectors, fill height detectors and in measuring ash content of coal.
2. ^{14}C: Used to measure the age of water (up to 50,000 years).
3. ^{137}Cs: Use for radiotracer technique for identification of sources of soil erosion and deposition, in density and fill height level switches.
4. ^{60}Co: Used for gamma sterilization, industrial radiography, density and fill height switches (Lowenthal and Airey, 2001).

2.1.2 Activity of a Radioisotope Source

The activity of a radioisotope source is defined as its rate of decay, and is given by the fundamental law of radioactivity;

$$\frac{d\,N}{d\,t} = -\lambda\,N \qquad (2.1)$$

where N is the number of radioactive nuclei and λ is defined as the decay constant. The historical unit of activity has been the curie (Ci), defined as exactly 3.7 x 10^{10}

disintegrations per second, which owes its definitions to its origin as the best available estimate of the activity of one gram (1g) of pure ^{226}Ra. Its submultiples, millicurie (mCi) or mirocurie (μCi), generally are more suitable units for laboratory-scale radioisotope sources. Although still widely used in the literature, the curie is destined to be gradually replaced by its SI equivalent, the Becquerel (Bq). 1Bq which is defined as one disintegration per second is given by; 1 Bq = 2.703 x 10^{-11} Ci.

In the laboratory, radioactive sources of convenient size are more reasonably measured in kilobequerels (kBq) or megabequerels (MBq) (Knoll, 1979).

2.1.3 Statistical Nature of Radioactive Decay

For an ensemble of radioactive nuclei, the population of the parent nuclei goes on decreasing in time, t following an exponential law. If at a time t = 0, there are N_o radioactive parent atoms present, then at t = t (seconds) their number will be N(t) given by;

$$N(t) = N_o e^{-\lambda t} \qquad (2.2)$$

where λ is the decay constant and it denotes the probability that an undecayed nucleus will decay in the next second.

Radioactive decays are usually described in terms of half-life, $T_{½}$ rather than the decay constant, λ. The half-life is equal to the time taken for the number of parent atoms to decrease by a factor 2. Therefore, putting $N(t)=\frac{N_0}{2}$ at t = $T_{½}$ in equation (2.2), it gives

$$\frac{N_0}{2} = N_0 \exp^{-\lambda T_{½}} \qquad (2.3)$$

From where $\text{half-life}\left(T_{½}\right) = \frac{0.963}{\lambda}$ (2.4)

It should be emphasized that activity measures the source disintegration rate, which is not synonymous with the emission rate of radiation produced in its decay. Frequently, a given radiation will be emitted in only a fraction of all the decays, so the knowledge of the decay scheme of the particular isotope is necessary in order to infer a radiation emission rate from its activity. Also, the decay of a given radioisotope may lead to a daughter product whose activity also contributes to the radiation yield from the source. A given nuclear state can be stable or unstable. In the latter case, it will decay by alpha, beta and gamma ray emission and this decay will be characterized by a decay constant, λ or a mean lifetime, τ (τ is equal to the reciprocal of the decay constant, λ). For a general case, when the nuclear state can decay in more than one fashion (say by beta decay as well as gamma decay), the total constant, λ is given by;

$$\lambda = \lambda_1 + \lambda_2 + \lambda_3 + \lambda_4 + \ldots \qquad (2.5)$$

where λ_1, λ_2, λ_3, λ_4, etc are partial decay constants of each mode and also the total mean lifetime, τ is given in the expression;

$$1/\tau = 1/\tau_1 + 1/\tau_2 + 1/\tau_3 + 1/\tau_4 + \ldots \qquad (2.6)$$

where τ_1, τ_2, τ_3, τ_4, etc are partial mean lifetimes.

2.1.4 Interaction of radiation with matter

There are three main processes which occur when gamma rays interact with matter: photoelectric absorption, Compton scattering and pair production.

Photoelectric Effect

The photoelectric effect occurs when a gamma ray interacts with an atom of the absorber and a photoelectron is emitted. The energy of the photoelectron is equal to that of the gamma ray less the binding energy of the photoelectron in its original shell

(usually the K shell). The binding energies are typically a few keV for low Z materials to tens of keV for higher Z material. The vacancy in the absorber atom is filled through capture of a free electron in the absorber material, accompanied by a characteristic X-ray or Auger electron. Normally, they are reabsorbed in the material. Photoelectric absorption is the effect which is used to detect and measure the energy of the gamma ray in a semiconductor detector (Parry, 1991).

Compton Effect:

The second effect of the interaction of gamma rays with matter is Compton scattering. In this case, the gamma ray interacts with an electron in the absorber and some of the energy of the gamma ray is transferred by inelastic scattering to the recoil electron. The result is a gamma ray of some undefined lower energy plus an electron with the residual energy, dependent on the scattering angle, which can range from zero up to a maximum which occurs in the case of a head-on collision. The maximum energy can be calculated from the rest mass energy of the electron (0.511 MeV) and the incident photon energy. The difference in the energy between the gamma ray energy and the maximum Compton recoil electron energy tends towards 0.256 MeV when the incident gamma ray energy is large. Therefore, this Compton effect results in a broad range of gamma ray energies below the energy of the original gamma ray, which will continue to interact by the photoelectric effect or others. The result of this effect is the production of a continuous background which can interfere with the detection of gamma rays which undergo the photoelectric effect.

Pair production

The third interaction is the pair production, where the gamma ray loses energy by the production of an electron-positron pair. This can only occur if the energy of the gamma

ray exceeds 1.02 MeV, which is twice the rest mass energy of an electron (0.511 MeV). All the energy of the gamma ray is lost to the electron-positron pair, so any energy above the 1.02 MeV appears in the form of kinetic energy. The positron will normally annihilate an electron in the absorber, with the production of two annihilation gamma ray photons each with energy of 0.511 MeV. These gamma rays may be absorbed in the material or escape. If the detector is small, then both may escape and only kinetic energy will remain. The result is a photo peak with energy equal to the gamma ray energy minus the 0.511 or 1.02 MeV.

The interaction of gamma rays with matter as described above may be used as a means to detect them. For a material to be a suitable gamma ray detector, it must respond to the gamma ray interactions to produce electrons and also have a means of detecting them (Parry, 1991).

2.1.5 Absorption of Photons

A beam of photons passing through a material is usually attenuated. As the photon transverse through the material, the resulting attenuation may either be caused by absorption or scattering and can be characterized by a fixed probability of occurrence per unit length in the material (absorber). The sum of these probabilities is simply the probability per unit path length that the gamma ray photon is removed from the beam; and is called the linear attenuation coefficient, μ. The number of transmitted photons, I is then given in terms of the number without an absorber, I_o as;

$$I = I_o \exp^{-\mu t} \qquad (2.7)$$

where t is the time taken by the photon to pass through.

2.2 Gamma Radiation Detection and Measurement

The field of gamma ray spectroscopy is one of the most highly developed techniques in experimental nuclear physics because gamma ray detection and gamma spectrum determination forms the essential measurement at every step in nuclear spectroscopic experiments. Until recently, sodium iodide scintillation spectrometer (which was used in this thesis) was the most successful and popular method of gamma ray spectroscopy. The scintillation spectrometers with their high detection efficiency and moderately good energy resolution have made a tremendous contribution to our knowledge of nuclear properties. The recent development of this semiconductor radiation detector (particularly lithium-drifted germanium detectors) has further revolutionized the experimental techniques and has helped push the frontiers of the knowledge to newer horizons (Singru, 1972).

2.2.1 Scintillation Counters

There are several substances, certain organic and inorganic materials, which emit light flashes or scintillations when charged particles, x-rays or gamma rays pass through them. These substances are called scintillators. In a scintillation counter or detector, these light flashes are allowed to fall on the photocathode of a photomultiplier tube and a pulse is extracted out to signal the passage of nuclear radiation. The height of this output pulse can be made proportional to the energy dissipated by the ionizing radiation in the scintillator and can be used not only for counting but also for energy analysis (Singru, 1972). The most widely applied scintillators include the inorganic alkali halide crystals, of which sodium iodide is the favorite and organic-based liquids and plastics. The inorganic tend to have the best light output and linearity, but are relatively slow in

their response time. Organic scintillators are much faster, but yield less light. The intended application also has a major influence on scintillator choice. The high Z-value of the constituents and high density of inorganic crystals favors their choice for gamma ray spectroscopy, whereas organics are often preferred for beta spectroscopy and fast neutron detection (Knoll, 1979).

2.2.2 Semiconductor Detector

The basic element of a semiconductor detector is a single crystal of semiconductor material with a P- I- N diode structure. {N- and P- refers to the nature of the impurities in the crystal. N-impurities are pentavalent atoms, thus acting as electron donors, while P-impurities are trivalent atoms, acting as electron acceptors. I represent the intrinsic layer} (IAEA TECDOC-564, 1990). Semiconductor detector can be considered as ionization chamber where the gaseous medium is replaced by a semiconducting solid. In a semiconductor detector, ionizing radiation produces ion pairs which are collected by the electric field applied externally, and the detector gives an electrical pulse which is proportional to the energy of ionizing radiation. The semiconductor detector has many definite advantages over the gas-filled or scintillation detectors which are: smaller, compact and convenient size; fast (few n sec.) rise time of output pulses; linear response over wide energy range; excellent energy resolution and; choice of sensitive depth, area and geometry.

2.2.3 Photomultiplier Tube

The wide spread use of scintillation counting in radiation detection and spectroscopy would be impossible without the availability of devices to convert the extremely weak

light output of a scintillation pulse into corresponding electrical signal. The photomultiplier tube accomplishes this task remarkably well, converting light signals that typically consist of no more then a few hundred photons into a usable current pulse without adding a large amount a random noise to the signal. A great variety of commercially available photomultiplier tubes are sensitive to radiant energy in the ultra-violet, visible and near infrared regions of electromagnetic spectrum. They find many applications in optical spectroscopy, laser measurements, and astronomy.

The photomultiplier tube consists of photosensitive layer called the photocathode, coupled to an electron multiplier structure. The photocathode serves to convert as many of the incident light photons as possible into low-energy electrons. If the light consists of pulse from a scintillation crystal, the photoelectrons produced will also be a pulse of similar time duration. Because only a few hundred photoelectrons may be involved in a typical pulse, their charge is too small at this point to serve as a detectable electrical signal. The electron multiplier section in a photomultiplier tube provides efficient collection geometry for the photoelectrons as well as serving as a near-ideal amplifier to greatly increase their number. After amplification through the multiplier structure, a typical scintillation pulse will give rise to 10^7 - 10^{10} electrons, sufficient to easily serve as the charge signal for the original scintillation event. This charge is conventionally collected at the anode or output stage of the multiplier structure (Knoll, 1979).

2.2.4 Preamplifier

The pulse coming out of a nuclear radiation detector is first fed to a preamplifier which is located close to the detector. The length of the input cable connecting the detector to the preamplifier is kept as short as possible so that its capacitance is low. The main

purpose of a preamplifier is to perform impedance matching between the preamplifier input of low capacitance and its output of high capacitance. The preamplifier is not designed to give high gain and usually its gain is of the order of $1\text{-}10^2$ (Singru, 1972).

2.2.5 Amplifier

The output pulse from a preamplifier is taken to an amplifier whose function is to provide a voltage gain of the order of $10\text{-}10^4$ or so. The amplifier also shapes the pulse for suitable analysis in following stage. In the gamma ray spectroscopy, the main amplifier functions are: linear amplification of the pulses from the preamplifier to levels suitable for pulse height analysis (0-10 V); improvement of signal-to-noise ratio by shaping of the signal pulses and direct current (DC) power supply to the preamplifier. Amplifier performance is defined by energy resolution at low count rate and by gain and resolution stability as function of count rate (Singru, 1972).

2.2.6 Counter and Timer

As the final step in the counting system, the logic pulses must be accumulated and their number recorded over a fixed period of time. The device used for this purpose may be a simple digital register which is incremented by one count each time a logic pulse is presented to its input. In nuclear pulse counting applications, such devices are often called scalars as a historic anomaly that dates from the time when digital registers of reasonable size were not widely available. Counters are commonly operated in one of the two modes: preset time and preset count. In the preset time mode, the counting period is controlled by an external timer. This timer may be built as part of a common chassis with the counter or separate timers can be obtained as individual modules. In

the preset count mode, the counter will accumulate pulses until a specified total has been achieved, at which point the counting period is terminated. The preset count mode has the advantage that a given statistical precision can be specified before the start of the measurement, and the duration of counting will be prolonged until enough counts have been accumulated to guarantee the desired statistical precision.

The function of a timer is simply to start and stop the accumulation period for an electronic counter or other recording device. Obviously, its most important property is the precision to which the time interval is controlled. Two general methods of control are commonly encountered. The simplest and least expensive method is to base the timing interval on the frequency of the alternating current of the power line to which the unit is connected. The precision of the timing is therefore determined solely by the accuracy and stability of the power line frequency. On the other hand, the frequency may wander substantially over short periods of time, and timers based on power line synchronization thus may give rise to substantial timing interval errors if the interval is less than a few hours. In order to guarantee better accuracy, timers which are based on interval crystal-controlled circuits are preferred for exacting measurements. The most important specification in this case then becomes the stability of the timing frequency to changes in temperature (Knoll, 1979).

2.2.7 Single Channel Analyzer

A single channel analyzer (SCA) is another linear-to-logic converter which involves two independent discriminator levels: the lower level discriminator (LLD) and upper level discriminator (ULD). A single channel analyzer or differential discriminator produces a logic output pulse only if the input linear pulse amplitude lies between the

two levels. The action of the unit is therefore to select a band of amplitudes or "window" in which the input amplitude must fall in order to produce an output pulse. In some units, the LLD and UPD are independently adjustable from front-panel controls. In others, the lower level is labeled the E level, and the window width or difference between levels is labeled ΔE and can be separately varied without affecting the E level. In counting system, the single channel analyzer can serve to select only a limited range of amplitudes from all of those generated by the detector. A common example is one which the window is set to correspond only to those events in the detector which deposit the full energy of an incident radiation. In this way, one type or energy of radiation often can be selectively measured in the presence of other radiations. In normal single channel analyzers, the time of appearance of the logic pulse is not closely coupled to the actual event timing and use of these logic pulses in timing measurements will often give imprecise results. However, incorporating into the single channel analyzer design a time pickoff takes care of this; modules with this feature are often called timing single channel analyzers and are used in coincidence applications or other timing measurements (Knoll, 1979).

2.2.8 Multi-channel Analyzer

When a large number of channels are required, the reliability of any scheme based on the independent operation of a large number of single channel elements would likely be less than ideal. A device designed to carry out this function is known as multi-channel analyzer (MCA) (Knoll, 1979).

Recording data with SCA involves many operations and it takes long time to go from one end of the spectrum to the other. A multi-channel analyzer overcomes these

difficulties by recording the entire spectrum in a single operation. The vital part of a multi-channel analyzer is an analog-to-digital converter (ADC) which converts each pulse amplitude (or energy) into an equivalent time interval. A built-in periodic oscillator sends out clock pulses and the number of such pulses occurring in this time interval is recorded in a Scaler (address register). This digital information (address) is identified with certain channel in which the pulse is stored in the magnetic core memory of the analyzer. Each channel can store up to 10^6 counts and there can be as many as 400, 512, 1024 or higher number of total channels available. The stored data in the memory can be viewed on an oscilloscope or may be read out in the external printer. In this way, the entire histogram plot of counts versus pulse height can be recorded almost simultaneously (Singru, 1972).

2.3 Nuclear Techniques in Coal Assay

Nuclear techniques are increasingly used in industrial and environmental management. The continuous analysis and rapid response of nuclear techniques, many involving radioisotopes, meaning that reliable flow and analytic data can be constantly available. This results in reduced cost with increased product quality (Lowenthal et al, 2001). Techniques are however confined to those using penetrating radiation such gamma-rays, high energy X-rays (/ 50 keV) and neutrons, if sampling is to be avoided (Sowerby, 1979). These nuclear techniques include Gamma Transmission Technique, X-ray Techniques, Neutron Technique, Pair Production and Annihilation Technique, etc.

2.3.1 Gamma – Transmission Technique

Gamma - ray transmission is the technique employed in this work. Gamma - ray transmission or scattering can be used to determine the ash content of coal on line on a conveyor belt. The gamma ray interactions are atomic number dependent, and the ash is higher in atomic number than the coal combustible matter. Also the spectrum of gamma rays which have been inelastically scattered from the coal can be measured (Compton Profile Analysis) to indicate the ash content.

2.3.2 X-ray Technique

X–rays from a radioactive element can induce fluorescent X–rays from other non–radioactive materials. The energies of the fluorescent X–rays emitted can identify the elements present in the material, and their intensity can indicate the quality of each element present.

This technique is used to determine element concentrations in process stream of mineral concentrators. Probes containing radioisotopes and a detector are immersed directly into slurry streams. Signal from the probe are processed to give the concentration of the elements being monitored, and give a measure of the slurry density. Elements detected this way include iron, nickel, copper, zinc, tin and lead.

2.3.3 Neutron Technique

Neutrons can interact with atoms in a sample causing the emission of gamma rays which, when analyzed for characteristic energies and intensity, will identify the types and quantities of elements present. The two main techniques are Thermal Neutron Capture (TNC) and Neutron Inelastic Scattering (NIS). TNC occurs immediately after a

low-energy neutron is absorbed by a nucleus, NIS takes place instantly when a fast neutron collides with a nucleus. Most commercial analyzers use californium-252 neutron sources together with sodium iodide detector and are mainly sensitive to TNC reactions. Others use Am-Be-241 source and bismuth germinate detectors, which registers both TNC and NIS.

NIS reactions are particularly useful for elements such as carbon, oxygen, aluminum and silicon which have low neutron capture cross section. Such equipment is used for a variety of on-line and on-belt analysis in the cement, mineral and coal industries. A particular application of NIS is where a probe containing a neutron source can be lowered into a borehole where the radiation is scattered by collisions with surrounding soil. Since hydrogen (the major component of water) is by far the best scattering atom, the number of neutrons returning to a detector in the probe is a fraction of the density of the water in the soil.

To measure soil density and water content, a portable device with an americium-241–beryllium combination generates gamma rays and neutrons which pass through a sample of soil to a detector. (The neutrons arise from alpha particles interacting with ^{9}Be.) A more sophisticated application of this is in borehole logging.

2.3.4 Pair Production and Annihilation Technique

When a sample is irradiated with gamma-rays of energy >1.022 MeV, it is possible to produce electron-positron pairs having a total energy equal to the energy of the incident gamma-ray. This pair production process only takes place in the field of charged particles, mainly in the nuclear field. The positron will rapidly lose most of its energy by collisions with electrons and ions, and will subsequently annihilate by colliding with

an electron. Both the positron and electron will disappear with the appearance of two oppositely directed gamma-rays each of energy 0.511 MeV; this is annihilation radiation.

The cross section for pair production is proportional to Z^2. Its probability per unit weight is, therefore, proportional to the ratio Z^2/A of the target material (where, Z is the atomic number while A is the mass number). This Z^2/A dependence forms the basis of the present method. The cross section for pair production increases rapidly with increasing gamma-ray energy, particularly for energies just above the threshold of 1.022 MeV.

2.4 Chemical assay of ash content of coal

The ash content of coal is the incombustible residue left after the combustion of coal. As stated earlier, this is the mineral mater component of coal and usually consists of mainly trace and heavy elements such as silicon, iron, manganese, lead, sodium, magnesium, etc. The higher the concentrations of these elements in coal, the more the ash content of the coal and the lesser the quality of the coal sample; and vice versa.

2.5 Characteristics of Coal

2.5.1 Origin and Occurrence of Coal

Coal is essentially the end – product of the compaction in its original place, the accumulated organic matter, resulting from altered remains of terrestrial materials such as bark, root, leaves, spores and seeds (Petrascheck, 1956). As the geological time scale progressed, these materials form sedimentary strata usually identified in coal

petrography as coal beds. The beds have a distinctive non migratory characteristic that differentiates them from other fossil fuels such as oil or gas.

The origin of the Nigerian coal could be traced back to the geochemical events that took place during the Paleozoic era and dates much younger as having occurred during the second era of humolith formation, probably during the Late Cretaceous (Van Krevelen, 1981 and Ewa 1992). Petrascheck (1956), in his discussion on coalification noted that 43% of the world's coal resources are accounted for by events that must have occurred between the Upper Carboniferous and the Permain while about 51% is accounted for by events during the Upper Cretaceous and Tertiary. This implies that 94% of the world's coal was formed in about 60% of the time that passed since the Upper Carboniferous. On a conservative geological time scale, Nigerian coal deposits must have been formed between the Late Carboniferous to the Permain during which an uninterrupted swamp covered the extensive areas of the Northern Hemisphere. This was followed by a process of subsidence of the swamps in stratigraphic sequence. The resulting geosynclines formed by strong lateral compressive forces acting on the earth's crust, did not sink at a constant rate rather alternated between periods of rapid and slow subsidence. The slow subsidence allowed for the formation of shallow lagoons leading to luxuriant growth of primitive aquatic plants that eventually died, decayed and were acted upon by micro-organisms. This debris eventually transformed into peat deposits that accumulated with time, before being overtaken by increased rate of subsidence. The final step must have been the submerging of peat under sedimentary minerals of clay, silt and sand, thus forming coal beds.

It can therefore be inferred that the extent of the lagoons must have accounted for the stretch of coal seams while the dipping and depth of the overburden must have been as

a result of the subsidence. However, coal researchers have proposed several widely different coal formation theories (Petrasheck, 1956; Nicholls. 1968; Ensminger, 1977 and Ewa, 1992) as well as tend to accept two basic stages of coal formation namely:

- The biochemical period of accumulation and preservation of plant material as peat and
- The geochemical period of conversion, this is summarized below in figure 2.1.

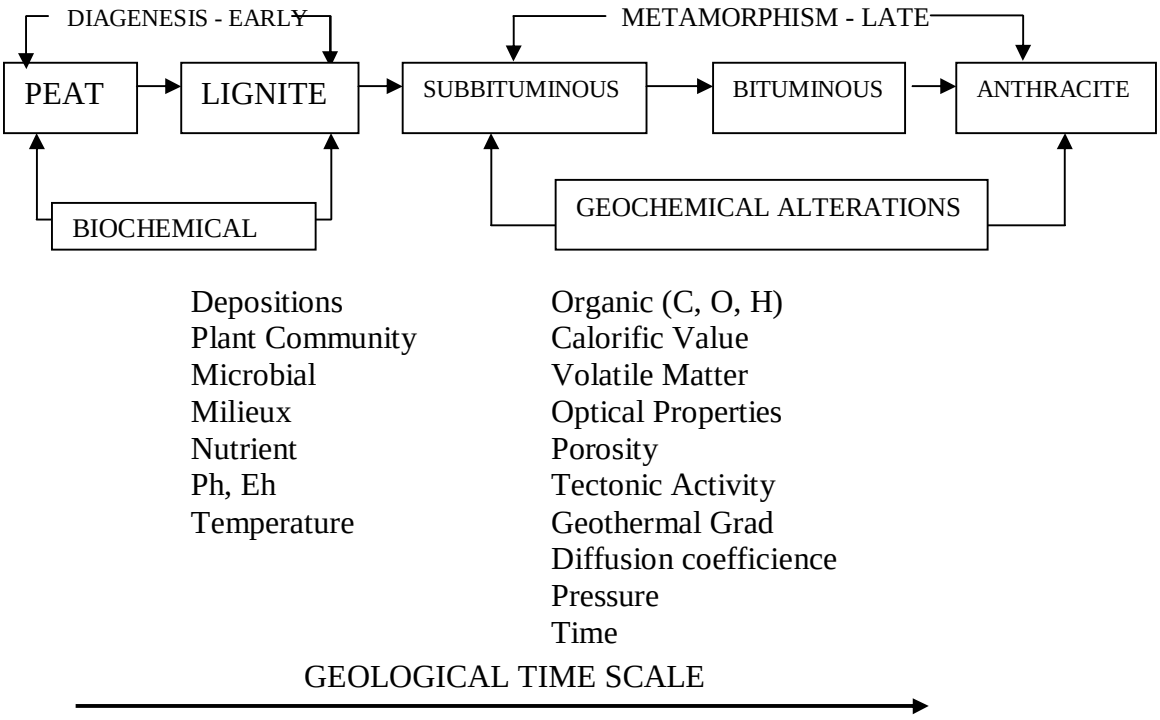


Figure 2.1: Geological stages during coalification.

Therefore, coalification starts with the biochemical process of peatification of the dead plant debris which is followed by a complex process of metamorphism as the peat is covered by sediments. Tectonic movements account for the subsidence of the coal environment either during the diagenesis or through the late metamorphic stages.

However, in both cases, the degree of subsidence is severe limitation on the coalification process and at the early diagenesis or the floral stage, a rapid subsidence leads to a dieing-off, of the plant community resulting in severe pollution of the peat by inorganic sediments, while a too slow subsidence accounts for continuous oxidation and rotting of the ‘wood’ produced. Therefore, coal deposits are associated with favorable climatic conditions as well as appropriate tectonic movements.

By the mode of formation, coal beds will contain water-borne dissolved elements as well as those associated with eroded rocks from which the sediments are derived. This is anticipated for, after the burial of the formed peat, the inventory of the elements in the coal beds must have been altered either by magmatic vein infiltration of ground water or through possible ion-exchange in clays and organic matter relevant to the geological setting of the Benue Trough (Ewa, 1992).

2.5.2 Classification of Coal

The classification of coal is based on coal rank and coal type.

2.5.3 Coal Ranking

The degree of 'metamorphism' or coalification undergone by a coal, as it matures from peat to anthracite, has an important bearing on its physical and chemical properties, and is referred to as the 'rank' of the coal. Lignite and sub-bituminous coals (the low rank coals), are typically softer, friable materials (easily reduced to tiny particles) with a dull, earthy appearance; they are characterized by high moisture levels and a low carbon content, and hence a low energy content. Higher rank coals are typically harder and stronger and often have a black vitreous luster. Increasing rank is accompanied by a rise in the carbon and energy contents and a decrease in the moisture content of the

coal. Anthracite is at the top of the rank scale and has a correspondingly higher carbon and energy content and a lower level of moisture as shown in figure 2.2.

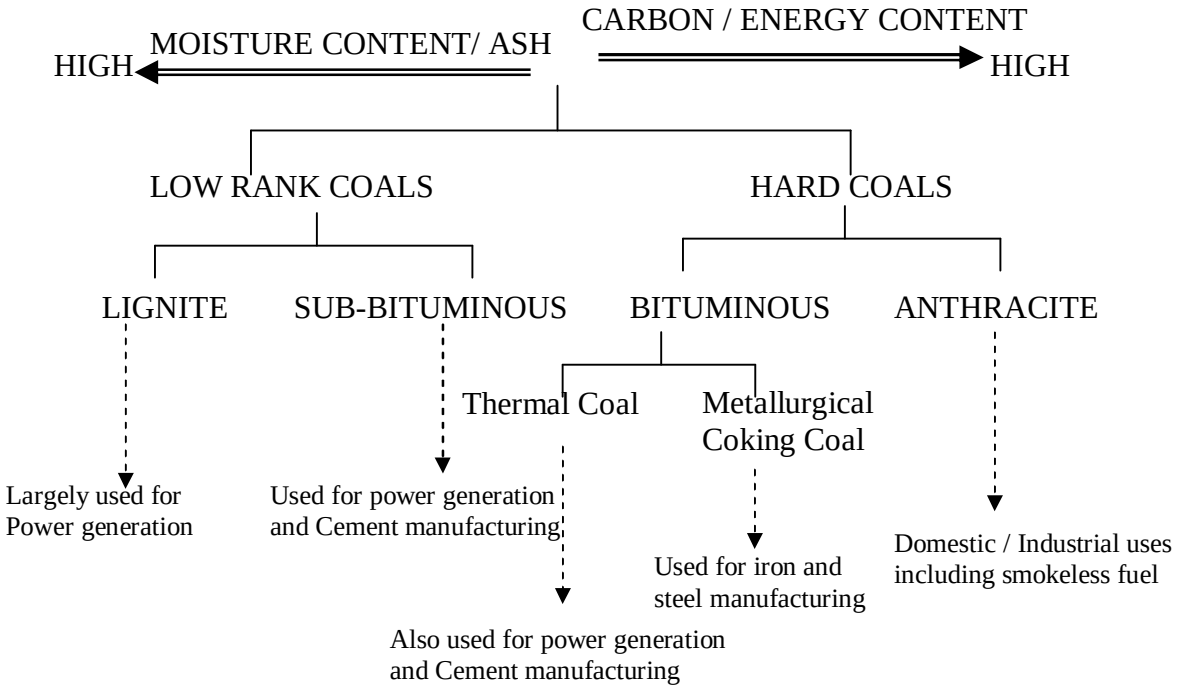


Figure 2.2: A summary of the coal classification and uses.

Between anthracites and peat there are three broad coal rankings. Bituminous coals are dense black solids, frequently containing bands with a brilliant lustre. The carbon content of these coals ranges from 78 to 91% and the water content from 1.5 to 7%.

The bituminous coals are suited to the production of metallurgical coke. Non-coking bituminous coals are used for power generation, cement making and to provide heat and steam in industry.

Sub-bituminous coals usually appear dull black and waxy. They have carbon content between 71 and 77% and a moisture content of up to 10% and are used for electricity generation or can be converted to liquid and gaseous fuels.

The lower ranked coals are browner and softer. Brown coals or lignite have a high oxygen content (up to 30%), a relatively low carbon content (60 -75% on a dry basis), and a high moisture content (30 -70%). Brown coals are used for power generation but generally are uneconomic to transport because of their high moisture content. These coals are also susceptible to spontaneous combustion.

Fig. 2.2 shows that the carbon/energy content increases from lower to higher ranking coals (i.e. from lignite to anthracite). This means that the ash content decreases in that order because the higher the carbon content, the lower the ash content and vice versa.

2.5.4 Coal Types

Coal types are classified by Geologists according to the organic debris, called macerals, from which the coal is formed. Macerals are identified microscopically by reflected light-the reflective or translucent properties of the coal indicating the individual component macerals and the way they have combined to form the coal. The purpose of classifying coal in this way is to determine its best uses. There is a finite supply of the resource and, therefore, type and chemical composition must be matched to the most suitable end use.

The mineral or inorganic content of coal is another significant factor affecting end use. Mineral content is assessed by burning coal and measuring the amount of incombustible material remaining, referred to as the ash content of coal.

2.5.5 Coal Combustion

Combustion is the main process by which coal is utilized whether it be for the utility, industrial, commercial or domestic sectors. It is achieved using pulverized-fuel burners

in power generation and by stoker firing at the industrial and commercial scale with static grate combustion used in household appliances. All these combustion systems are mature technologies albeit with significant potential for improvement. In more recent years, much research and development has been directed towards developing fluidized bed technologies for application in the utility and industrial sectors.

Competition is fierce from the alternative fuels, particularly natural gas. Thus there is the need to strive towards reducing capital and operating costs, improving the efficiency and reliability of coal-fired plant and reducing their emissions of pollutants. Improved amenity is particularly important for small and medium sized appliances where there has been much scope for improved coal handling, storage and operation of equipment. The development of advanced, clean coal power generation technologies through the use of combined cycles is another major area of development as it offers the prospects for low cost electricity with improved efficiencies and lower emissions of pollutants.

The great driver over the last decade has been the environmental concerns associated with coal use, in particular the need to control SO_2, NOx (x may be 1 or 2) and particulate emissions to meet emission standards. These pollutants are very dangerous to health which may lead to death of any living organism within that vicinity. When they are released to the atmosphere, it causes acid rain which increases the soil ph level. This is very harmful to living organisms in that environment. Because of this non-environmental friendly nature of the combustion of coal, there should be a system for measuring and controlling emissions from coal-fired equipment to meet current and future emissions requirements, otherwise, those using coal should cease to stop further

endangering of human race. This is why coal ash determination is necessary, so that only coals of low ash content would be used.

2.5.6 Coal Conversion

The trigger for substantial research and development into coal conversion were the major oil price increases of the 1970s. In particular, it was considered important for strategic reasons to develop technology to enable coal to be converted into liquid fuels, substitute natural gas (SNG) and chemical feed stocks. As a result, major research programmes were undertaken by British Coal on coal liquefaction and British Gas for the manufacture of SNG.

The early research and development on coal liquefaction was carried out in the laboratory and on small pilot plant at CRE. In 1991, direct coal liquefaction moved away from the laboratory when a large pilot plant-scale facility started operations at Point of Ayr in North Wales. This pilot plant programme, recently concluded, showed that the British Coal Liquid Solvent Extraction (LSE) process is technically ready to be taken forward to the demonstration stage. The process can convert almost any coal into low boiling liquids, which, after a simple upgrading step, yield petrol and diesel fuel that can be substituted directly for their conventional counterparts. This ability to produce directly substitutable transport fuels will allow coal liquefaction to be phased in gradually at the appropriate time, without the need for infrastructural changes.

Coal liquefaction is not economically viable at current oil prices. However, economic modeling studies indicate that the LSE process is a lower cost route than competing technologies. Although a wide range of assumptions is necessary, it has the potential to be commercially viable at a crude oil price as low as $25 per barrel in favourable

circumstances. The abilities to process low-grade coals and to integrate with existing oil refinery operations give it a very large potential market, both in Europe and worldwide. By way of indication, a commercial scale plant processing 5 million tones per year of coal would meet only about 0.5% of current European transport fuel demand.

Similarly, substantial effort has been deployed in the research, development and demonstration of the British Gas/Lurgi slagging gasifier. The technology, which is based on the development of the conventional fixed-bed gasifier so that the coal ash is rejected as molten slag, is now commercially available. Whilst initially developed for the manufacture of SNG, it is considered particularly suitable also for use in Integrated Gasification Combined Cycle (IGCC) plant for power generation.

Underpinning these coal conversion developments and other processes for producing energy from coal, are the many projects carried out in Universities and industrial laboratories, aimed at adding to our basic knowledge of the fundamental processes involved. For example, major advances have been made in the area of coal characterization and analysis using modern analytical techniques, including nuclear magnetic resonance (NMR) and proton magnetic resonance - thermal analysis (PMRTA). This fundamental research has yielded invaluable basic knowledge, which can be applied in many areas. It contributes to the better selection of coals and the ability to predict with greater confidence the performance of coals in all utilization processes.

However, in Nigeria, little or no attention has been directed towards this area of research even though our country is very much endowed with huge deposits of coal and even the other natural resources.

2.5.7 Uses of Coal

All ranks of coal have some economic value. For centuries, peat has been used as a fuel for open fires, and more recently peat and lignite have been made into briquettes for burning in furnaces. Electric utilities and general industry use bituminous coal. Steel producers use coke, or metallurgical coal, a fuel that is almost pure carbon, produced by distilling coal (heating it strongly in the absence of air, so that it does not burn).

This process of producing coke yields a number of chemical by-products, including coal tar, which is used in the manufacture of many other products. Coal was also used, from the early 19th century to the World War II era, for the production of fuel gas, and coal liquefaction techniques were used to produce liquid oil products. Manufacture of fuel gas and other products from coal diminished as natural gas became widely available. In the 1980s, however, industrialized nations again became interested in gasification and new clean coal technology. Indeed, coal liquefaction supplies all of the Republic of South Africa's oil needs.

Coal is used in alumina refineries to generate process heat to separate alumina from the impurities in the ore. Under high temperatures and pressure the alumina is dissolved while the impurities remain solid.

Paper manufacturers and breweries use coal for steam raising and for heating and processing, and bricks, tiles and earthenware pipes are fired at high temperatures, often in coal fired kilns.

Several chemical products can be produced from the by-products of coal. Refined coal tar is used in the manufacture of a range of chemicals - pitch, creosote oil, naphthalene, phenol, pyridine, benzene and toluene. Ammonia gas recovered from coke ovens is used to manufacture ammonia salts, nitric acid and agricultural fertilizers-sulphates of

ammonia and ammonium nitrate. Thousands of different products have coal or coal by-products as components. Soap, aspirin, solvents, dyes, plastics and fibres like rayon and nylon are some of them. Given the large deposits of brown coal in the tertiary sediments east and west of River Niger; Nigeria can cash in on foreign investors' technology to produce coal pellets for industrial use, coal briquettes for domestic use; that is, to replace firewood.

The main uses of coal include cooking, heating, road construction, power generation, metallurgical processes, electricity generation and production of some chemical products.

2.5.8 Coal Research, Development and its Benefits

The purpose of undertaking coal research and development is primarily to help improve the economics of coal use and environmental protection. Thus, research and development is needed to help coal to compete with alternative energy sources, such as natural gas, in its various markets viz. utility, industrial, commercial and domestic sectors.

The immediate aim of coal research and development is to provide technical benefits, either through direct industrial application or as the basis for further development and demonstration of technologies. Technology transfer is a key element in order to help ensure that project results are taken up by industry, so that commercial benefits can be realized. In addition, most areas of coal use need research and development to provide environmental benefits because of the ever-increasing pressures to reduce their environmental impact. These benefits clearly contribute to the general public good, towards cleaner and more competitive energy from coal. Nor should the benefits be

ignored which arise from the development of skilled scientists and engineers in the energy and environmental fields, and the opportunities for technology transfer to other industries, e.g. the process industries which have benefited from work done on solids handling/transport and solids separation.

Technology transfer is key to the Coal research and development programme because of the importance of industry taking up the results of the research as soon as possible. To help in the dissemination of information, it is good to have a medium that produces and publishes comprehensive series of Project Profiles, Project Summaries and Project Reports. It also contributes to relevant national and international conferences as well as organizing a variety of meetings to encourage and promote technology transfer.

This will led to a much better awareness of the successes and benefits, which have resulted from coal research in this country.

The various bodies (e.g. Government and Industries) from time to time should analyze to varying degrees the cost and benefits of funding research. It could lead to a detailed evaluation of coal technology and utilization research in terms of realized technological, commercial, environmental and regional benefits. The success of each research project could be assessed under certain categories in terms of some potential objectives and achievements.

In United Kingdom (UK), the Coal Research Forum has been formed. This Forum has been an important focus for the coal community in the UK for promoting coal research by providing opportunities for dissemination of information on Coal research and development progress and achievements. It has seven Research Divisions; viz. Coal Preparation, Coal Characterization, Combustion, Advanced Power Generation, Liquefaction, Carbonization and other Metallurgical Uses, and Environment. They hold

regular meetings and symposia to discuss the research and development being undertaken in the various areas and to identify future research and development needs. These meetings provide valuable opportunities for industrial and university groups to consider how best to co-ordinate their various activities. As a result, the coal research and development undertaken by non-industrial organizations has been targeted better for addressing the needs of industry, thus greatly increasing the relevance and resulting benefits of such research. Although historically, in UK – based markets for clean coal, an increasing emphasis is being placed now on the development and exploitation of UK know-how worldwide by British companies, and the resulting benefits to the UK economy. The overseas opportunities are vast: the potential worldwide market for Clean Coal Technology is at least £500 billion over the next 15 years or so. Also, successful research and development made a major contribution in helping to defend the market for coal in the UK. Now the successes are helping the UK economy by enabling British companies to develop and sell clean coal technology equipment, services and expertise overseas.

In Nigeria however, the few research works are being conducted at the universities with little or no government attention. These researchers on coal should be encouraged and assisted by the government and coal companies in Nigeria to help them form a formidable organization to carryout coal research and development in Nigeria.

CHAPTER THREE

3.0 Materials and Methods

3.1 Description of gamma transmission technique

When radiation emitted by a gamma ray source passes through matter (transmission), it is attenuated, the amount of attenuation being dependent on thickness, density and composition of the absorber. A scintillation detector, which is very sensitive to gamma radiation, is used to measure the attenuated radiation. This supplies a digital signal which is proportional to the intensity of the attenuated radiation. Also, the absorption of low – energy gamma radiation from ^{241}Am increases as a function of the atomic number of the material through which the radiation passes. The ash components in the coal have a higher atomic number than the coal matter and thus give a higher absorption level which is a direct measure of the ash content (Trost, 1966).

Absorption of Gamma-rays is widely used in non-destructive characterization of opaque materials. However, other methods could be used but the former has the following advantages;

(a) Its simplicity for handling, instrumentation and processing;

(b) It can provide representative analysis without the need of sample preparation procedures;

(c) It can give an early indication of the mineral quality by allowing direct determination of concentration of sensitive elements and the derivation of important economic parameters, such as ash content values in samples in conveyor belts and in ores; and

(d) It is non-destructive, accurate, economic and low cost analytical tool (El-Kateb, A.H., et al, 2000).

3.2 Theoretical considerations (The Principle of Gamma Transmission Technique)

The gamma ray interactions are atomic number dependent, and the ash is higher in atomic number than the coal combustible matter. Gamma-ray transmission methods are frequently used in industrial measurement systems: A radiation source is placed on one side of the process vessel and a detector on the other side, as shown below in figure 3.1.

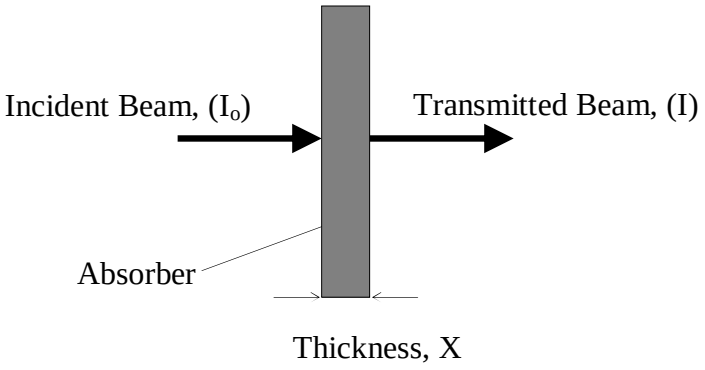


Fig. 3.1: Attenuation of a parallel beam of gamma - ray in an absorber.

The absorption mechanisms of X-rays and gamma - rays are totally different from those of particles. A gamma-ray photon may travel a long distance in a material without being affected at all, but its history is terminated once it interacts. Energetic photons are said to interact catastrophically.

The attenuation of a narrow and parallel beam of mono-energetic photons penetrating a thin slab of homogeneous material, as shown in the figure 3.1, follows Lambert-Beer's exponential decay law, equation (3.1):

$$I_{(x)} = I_0 e^{-\mu x} \qquad (3.1)$$

where I_o is the incident or initial intensity

x is the thickness of the absorber

$I_{(x)}$ is the remaining beam intensity and

μ is the linear attenuation coefficient, usually with unit cm^{-1}.

This expresses the photon interaction probability per unit path length in the absorber. The value of the linear absorption coefficient μ (cm^{-1}) is dependent upon the energy of the radiation and the atomic number of the absorbing medium (Trost, 1966). This equation may thus be solved with respect to either of these variables.

Equation (3.1) can be written as:

$$I_{(x)} = I_0 e^{-(\mu/\rho)\rho x} \qquad (3.2)$$

Where $\frac{\mu}{\rho}$ is the mass absorption coefficient.

$\frac{\mu}{\rho}$ is dependent on the atomic composition and the density *(ρ)* depending on radiation energy. Gamma ray transmission may consequently be used to measure thickness, average density, effective atomic number and component fractions or interface.

With electromagnetic radiation of low energy less than 100keV the absorption is brought about chiefly by the photoelectric process and the photoelectric absorption is strongly dependent upon the atomic number. As the average atomic number of chemical components of the ash content is higher than that of the pure carbon and the combustible part respectively, with low energy gamma rays, an ash content determination may be carried out by measuring the beam absorption (Trost, 1966).

3.2.1 Single Energy Gamma Transmission

The attenuation of gamma-rays through materials follows Lambert-Beer's exponential decay law, (equation 3.1). The intensities I and I_0 of transmitted gamma-rays are respectively the intensities with and without the samples. Equation 3.1 could also be expressed as;

$$\left(\frac{I}{I_0}\right) = \exp(-\mu_c \rho x) \quad = \exp\left(-\sum_i (\mu_i C_i)\rho x\right) \qquad (3.3)$$

Where μ and C are respectively the mass absorption coefficient and concentration, the subscripts c and i respectively are coal and the ith element in the wet coal and $\sum_i C_i = 1$.

Using the mixture rule $\mu_C = \sum_i \mu_i C_i$, equation (3.3) can be written for coal sample as:

$$\mu_c = \mu_{cm} C_{cm} + \mu_{ash} C_{ash} + \mu_w C_w \quad = \left(-\frac{1}{\rho x}\right) In\left(\frac{I}{I_0}\right) \qquad (3.4)$$

Where the subscripts cm, w and ash respectively are coal matter, water and ash, C is the concentration in the wet coal and $C_{cm} + C_{ash} + C_w = 1$. For low energy gamma ray, $\mu_{cm} = \mu_w$. Hence, equation (3.4) for the single energy method becomes:

$$C_{ash} = \left(-\frac{1}{\rho x}\right) In\left(\frac{I}{I_0}\right) + \mu_{cm}(C_{cm} + C_w)$$

$$= \left(-\frac{1}{\rho x}\right) In\left(\frac{I}{I_0}\right) + \mu_{cm} - \mu_{cm} C_{ash} \qquad (3.5)$$

And therefore,

$$C_{ash} = \frac{\left(-\frac{1}{\rho x}\right) In\left(\frac{I}{I_0}\right) + \mu_{cm}}{(1 + \mu_{cm})} = a_1 \, In\left(\frac{I}{I_0}\right) + a_2 \qquad (3.6)$$

The calibration constants a_1 and a_2 [in equation (3.6)] can then be obtained from measurements on coal of known ash contents. Simulated standards were prepared from which these values were obtained. The plot of the ash content in wt. % against the logarithm of intensity ratio per mass thickness, where these calibration constants were obtained is shown in figure 3.2.

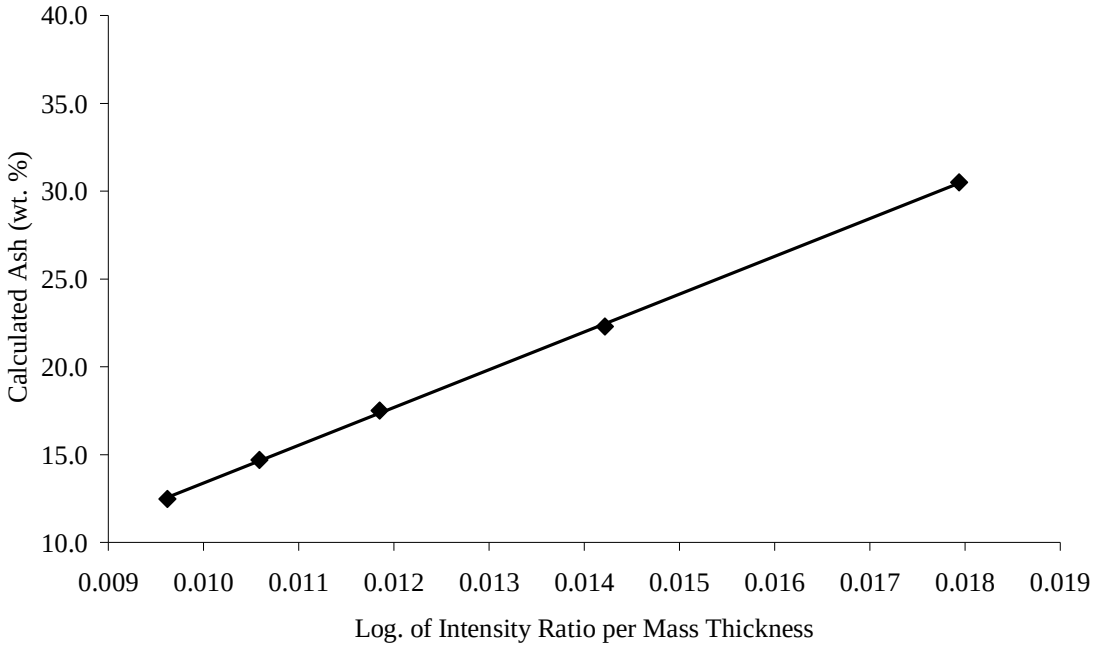


Figure 3.2. Variation of the Ash with log. of intensity ratio per mass thickness

3.2.2 Dual Energy Gamma Transmission

However, for the dual energy method, the ash content of coal could often be determined by combining separate measurements of transmission of high (H) and low (L) energy gamma-rays. Two equations similar to equation 3.4 combine to give:

$$C_{ash} = \frac{\left(R\mu_{cmH} - \mu_{cmL}\right) + \left\{R\left(\mu_w - \mu_{cm}\right)_H - \left(\mu_w - \mu_{cm}\right)_L\right\} C_w}{\left[\left(\mu_{Ash} - \mu_{cm}\right)_L - R\left(\mu_{ash} - \mu_{cm}\right)_H\right]\left[1 - C_w\right]} \quad \text{(Fookes et al, 1983)} \qquad (3.7)$$

$$\text{where } R = \frac{\mu_L}{\mu_H} = \frac{\log\left(\frac{I}{I_0}\right)_L}{\log\left(\frac{I}{I_0}\right)_H} \qquad (3.8)$$

and C_{ash} is the ash content dry weight. For the high energy gamma-rays, $\mu_{ash} \approx \mu_{cm} \approx \mu_w$ and for the low energy gamma-rays, $\mu_{cm} \approx \mu_w$ and equation 3.7 can be approximated by:

$$C_{ash} \approx \frac{\left(R\mu_{cmH} - \mu_{cmL}\right)}{\left(\mu_{ash} - \mu_{cm}\right)\left(1 - C_w\right)} \text{ (Fookes et al, 1983)} \qquad (3.9)$$

From equation 3.9, C_{ash} can be determined by measuring R when μ_{cm}, μ_{ash} *and* C_w are constant. Equation 3.9 then reduces to:

$$C_{ash} = a_1 R + a_2 \qquad (3.10)$$

where a_1 and a_2 are constants depending on the mean water content and composition of the matter and ash, which were determined by the measurements on the coal standards since they are of known ash contents, using ^{137}Cs (high) and ^{241}Am (low) energy sources. Figure 3.3 shows the curve used to obtain these constants for the dual energy method.

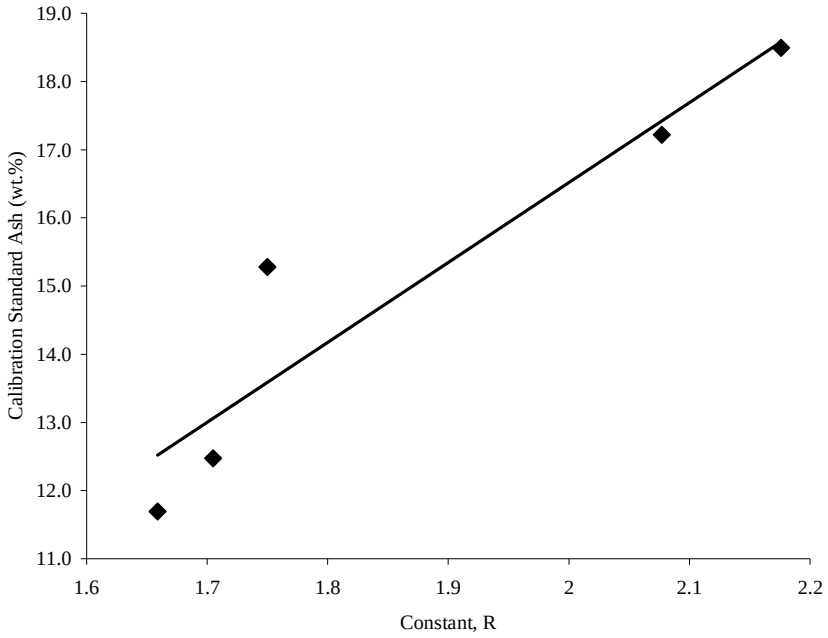


Figure 3.3: Variation of Coal Standard Ash with Constant, R.

3.3 Experimental Arrangement

3.3.1 Sample- Source-Detector Arrangement

The schematic diagram of the nuclear electronic system used is shown in fig. 3.4 below. The ^{137}Cs and ^{241}Am sources were used to provided the gamma (γ)-ray spectrometry which was detected with a thallium activated sodium iodide {NaI(Tl)} - Canberra 200P detector, which operates at a bias voltage supply of 950 volts. The counting was done with a single channel analyzer (SCA) -TENNELEC, TC 512 dual counter and timer, and amplified by TENNELEC, TC 246 amplifier. The sample container was placed inside the lead shield. The sample container was placed inside the lead shield and directly on top of the detector and the position made reproducible with the aid of a mark a small graph paper placed on top of the detector. Similarly, the source position was also kept constant on top of the sample container.

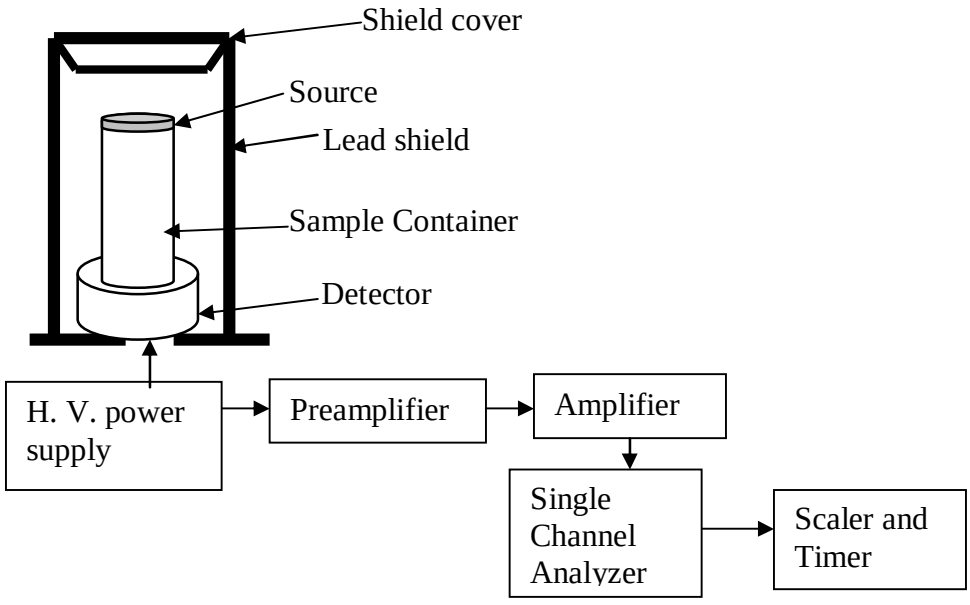


Fig. 3.4: Schematic diagram of sample – source – detector Arrangement

3.3.2 Instrumentation

The gamma-transmission technique for both single and dual energies requires a gamma source, which were provided by a lower energy source ^{241}Am for the single energy method and two gamma sources ^{241}Am and ^{137}Cs, which respectively provided lower and higher energy intensities, for the dual energy method. ^{241}Am source has a half-life of 432.20 years, gamma intensity of 35.90 % and energy of about 60keV while ^{137}Cs source has a half-life of 30.14 years, gamma intensity of 85.10 % and energy of about 661 keV.

In both cases, transmitted intensities through the simulated standards as well as the coal samples placed between the source and the detector were counted in the single channel analyzer (SCA)-TENNELEC, TC 512 dual counter and timer connected to a NaI (Tl) detector. The detail information on the radioisotope sources used is given below in Table 3.1.

Table 3.1: Radioisotope sources used

Radioisotope	Half-life (Years)	Date of production	Activity at the date of production (kBq)	Gamma intensity (%)	Approximate Energy (keV)
^{241}Am	432.2	July 1st , 2004	36.5	35.90	60.0
^{137}Cs	30.14	July 15th , 2004	36.9	85.10	661.0

3.3.3 Single Channel Analyzer and Energy Window Setting

The single channel analyzer (SCA) offers four modes of operation which includes: Integral (INTG), Normal (NORM), Asymmetry (ASYM) and Symmetry (SYM) modes.

In the INTG mode, all amplifier output pulses with amplitudes exceeding the threshold setting of the lower level control will produce a digital output signal which can operate a counter or ratemeter. In one of the three SCA modes, all amplifier output pulses which fall between two adjustable threshold levels will produce a digital SCA output pulse, while amplifier output pulses falling outside these levels will be excluded.

In the asymmetrical window (WINDOW ASYM) mode, as the UPPER/WINDOW control is advanced, the window opens above the lower setting to include a desired region of spectrum. In the symmetry window (WINDOW SYM) mode, as the UPPER/WINDOW control is advanced, the window opens symmetrically above and below the LOWER level setting to include a desired spectral line centred around the lower level setting. It operates well in the temperature ranges of 0 – 50 ^{0}C. After connecting the experimental set-up as shown in figure 3.4 above, the SCA dual counter could then be reset to count for more than one (1) second which is the default settings. The following should be done to achieve this;

(i) Press the MODE button and immediately followed by the PROG. PRESET button.

(ii) Then, press the CHANNEL SEL or ENTER button. This would bring out the default counter (1.00 second).

(iii) The OPER, PROG. INPUTS, PROG. PRESET and COUNTING MODULE buttons would then be used to change the preset value.

(iv) Then, press the ENTER button and followed by the CHANNEL SEL (SCROLL) button to exit.

(v) Press the ENTER button to select the channel which is connected.

(vi) To count, use the STOP/START button.

When the counter is put “ON”, it may register little or no count at all. Therefore, to the energy window, the coarse and fine gain is chosen. The lower level is adjusted by opening the knob so that the registered count increases to an appreciable value. This is followed by adjusting the upper level until the counts is approximately repeating itself for the same time. When the energy window is set appropriately, the counts registered for a particular time is reproducible each time the SCA is to be used. The settings used in this work for the low and high energy sources are respectively given in Table 3.2.

Table 3.2: Single Channel Analyzer Settings

Settings	Low energy	High energy
Coarse gain	100	50
Fine gain	14.38	0.70
Lower level	1.76	2.92
Upper level	0.27	0.13
Mode	ASYM	ASYM
Input polarity	Positive	Positive

3.3.4 NaI(Tl) Scintillation Detector

One of the most efficient methods of counting gamma rays and measuring their energies is their detection by a scintillation gamma ray spectrometer. This spectrometer employs a scintillation detector which is usually a thallium activated sodium iodide [denoted by NaI (TI)] crystal as a scintillator.

3.4 Analytical procedures

3.4.1 The Single Energy

A cylindrical sample container which fits well into the detector geometry was used. It has a height of 11.0 cm and 2.2 cm in diameter. The source position was kept constant throughout the measurement at the top of the container and the position of the sample container made reproducible on the detector by placing a graphical sheet on which the bottom outline of the container were traced on top of the detector window. The background intensity and the intensities with and without samples I and I_0 respectively were measured with the counter of the SCA in each case for the coal standards and the coal samples. The counting time was 20 seconds and each measurement was repeated ten times with standard deviation of 1.2 and 1.1 for I and I_o respectively. The depth of the sample in the container was 9.5 cm which was maintained throughout the measurement.

3.4.2 The Dual Energy

The cylindrical sample container used here has the same diameter with that used in the single energy method but with a height of 34.6 cm. Also the source position was kept constant throughout the measurement at the top of the container and the position of the sample container made reproducible. The background intensity and the intensities with and without sample I and I_0 respectively were measured in each case for the coal standards and the coal samples. However, the counting time in this case was 300 seconds and each measurement repeated five times with standard deviation of 0.0 and 0.1 for I and I_o respectively.

3.4.3 Determination of sample size/volume

The sample size/volume used was determined by measuring the gamma-rays transmission through three different samples which include sand, water and the simulated standard. Figures 3.5 and 3.6 below show the plot of the normalised count rate per second against the thickness in centimetres. The three samples in both figures 3.5 and 3.6 showed similar variation of the normalized count rate against sample depth. In figure 3.5 obtained with the high energy (^{137}Cs) source, normalised count rate rises from 0.0 cm and saturates between the sample thickness of 15.0 cm to 35.0 cm for the three samples while in figure 3.6 obtained with the low energy (^{241}Am) source, a kind of direct proportionality exists from the thickness of 0.0 cm to 20.0 cm for the three samples and saturates between the sample thickness of 23.0 cm to 35 cm for the three samples. However, the two graphs (fig. 3.5 and fig. 3.6) show that the optimal thickness lies between 25.0 cm and 35.0 cm and the variation is in agreement with the theory. In both keys in figures 3.5 and 3.6, Istd, Isand and Iwt respectively represent the normalized count rates for the coal standard, sand and water while Cs and Am represent caesium and americium. From both graphs, it could be seen that there is a good plateau at a thickness of 28.0 cm. This was used as the optimal thickness for the samples during the experimental work.

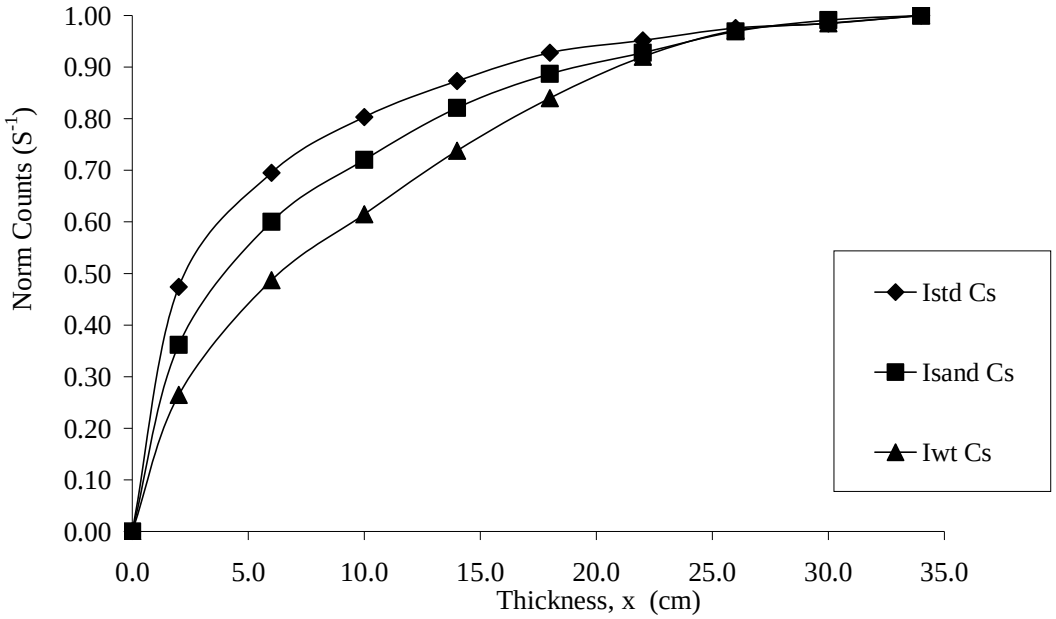


Fig. 3.5: Variation of Norm. Count rate with Thickness Using high Energy Source (Cs-137)

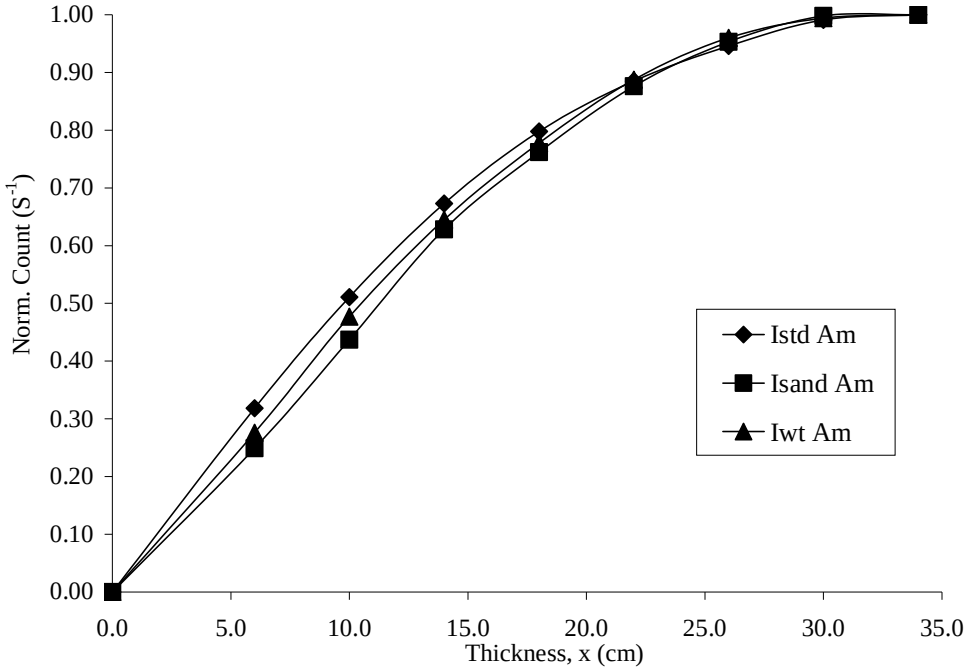


Fig. 3.6: Variation of Norm. Count rate with Thickness Using low Energy Source (Am -241)

From equation (3.2), the intensity of the gamma ray absorbed varies with the thickness and other parameters such as mass absorption coefficient and the ash content. This effect of variation in sample depth and density, which has considerable effect on the amount of transmitted gamma rays measured were investigated and eliminated by taking the counts of transmitted gamma rays with increasing sample depth. The point where the curves show less variation was chosen for the optimal thickness. The other dependants were eliminated by dividing the logarithm of the intensity ratio with the mass thickness (ρx) leaving the variation of the intensity ratio to depend only on the ash content.

3.4.4 Preparation of calibration standards

In order to obtain the calibration constants, a_1 and a_2, eight different simulated standards were prepared with different compositions of compounds and carbon (graphite). These compounds includes: As_2O_3, Ga_2O_3, Mn_2CO_3, Co_2O, $NiCO_3$, MoO_3, Fe_2O_3, $CaCO_3$, K_2CO_3, MgO, BaO and Aluminum powder. The amount of each compound in each of these simulated standards varies from one sample to the other, because the amount of each of these compounds added to the carbon (graphite) varies in each case as shown in Table 3.3.

Also, the compositions and the amount of each compound added in simulated standard were calculated. This was done using spread sheet and as well, the concentration of each element in these simulated standards were also calculated in the same spread sheet. The concentration of each of the elements in standard one (STD1) (as shown in Table 3.4) and others were based on the amount of the compounds added. Table 3.5 below shows the concentration of each of the elements in the simulated standards.

Different tables in spread sheet were used for each of the eight simulated standards. In each case, the sum of the elemental concentration in the simulated standard is 100% (Table 3.5). This serves as a form of validation for the simulated standards. These concentrations were then used in the calculation of the ash content of each of the eight simulated standards.

Table 3.3: Compound additives of simulated standard

Standards	Graphite Dilution (g)	Compound additives (g)											
		As_2O_3	Ga_2O_3	Mn_2CO_3	Co_2O	$NiCO_3$	MoO_3	Fe_2O_3	$CaCO_3$	K_2CO_3	MgO	BaO	Al
STD 1	89.0	0.5	0.2	0.2	2.0	2.0	2.1	2.0	2.0	2.0	2.0	2.0	2.0
STD 2	97.0	0.5	0.2	0.2	2.0	2.0	2.1	2.0	2.0	2.0	2.0	2.0	2.0
STD 3	97.0	0.1	0.09	-	0.11	0.1	0.2	0.1	0.1	-	0.1	0.1	0.1
STD 4	97.0	-	-	-	0.2	0.2	0.4	0.2	0.2	-	0.2	0.2	0.1
STD 5	97.0	-	-	-	0.1	0.1	0.2	0.1	0.1	-	0.1	0.1	0.1
STD 6	97.0	-	-	-	0.1	0.2	0.1	0.1	0.1	-	0.1	0.1	-
STD 7	97.0	-	-	-	0.1	0.1	0.1	0.1	0.1	-	0.1	0.1	0.1
STD 8	97.0	-	-	-	0.1	0.1	0.1	0.1	0.1	-	0.1	0.2	0.2

Table 3.4: Simulated Standard One Calculation.

COMPOUNDS	ELEMENTAL COMPOSITION			AMOUNT ADDED (g)
As_2O_3	As(2)	C	O(3)	
AT WT	74.92168	0	15.9994	
VALENCY	2	0	3	
	0.378695	0	0.121305	0.5
Ga_2O_3	Ga(2)		O(3)	
AT WT	69.72		15.9994	
VALENCY	2	0	3	
	0.148785	0	0.051215	0.2
$MnCO_3$	Mn	C	O(3)	
AT WT	54.938	12.01115	15.9994	
VALENCY	1	1	3	
	0.095588	0.020899	0.083513	0.2
CoO	Co		O	
AT WT	58.9332		15.9994	
VALENCY	1	0	1	
	1.572966	0	0.427034	2
$NiCO_3$	Ni	C	O(3)	
AT WT	58.71	12.01115	15.9994	
VALENCY	1	1	1	
	1.354004	0.277008	0.368988	2
Mo_2O_3	Mo(2)		O(3)	
AT WT	95.94		15.9994	
VALENCY	2	0	3	
	1.679802	0	0.420198	2.1
Fe_2O_3	Fe(2)		O(3)	
AT WT	55.847	0	15.9994	
VALENCY	2	0	3	
	1.398866	0	0.601134	2
$CaCO_3$	Ca	C	O(3)	
AT WT	40.08	12.01115	15.9994	
VALENCY	1	1	3	
	0.800884	0.240009	0.959107	2
K_2CO_3	K	C	O(3)	
AT WT	39.1	12.01115	15.9994	
VALENCY	2	1	3	
	1.131617	0.173811	0.694572	2
MgO	Mg	C	O	
AT WT	24.305	0	15.9994	
VALENCY	1	1	1	
	1.206072	0	0.793928	2
BaO	Ba		O	
AT WT	137.34	0	15.9994	
VALENCY	2		3	
	1.702501	0	0.297499	2
Al	Al		O	
AT WT	26.9815	0	0	
VALENCY	1		5	
	2	0	0	2

Table 3.5: Elemental Concentration of Simulated standards (calculated)

	CONCENTRATIONS (wt. %)							
ELEMENTS	STD1	STD2	STD3	STD4	STD5	STD6	STD7	STD8
Fe	1.04	1.18	1.30	1.46	1.59	1.71	1.84	1.95
Ca	0.59	0.68	0.74	0.83	0.91	0.98	1.05	1.10
K	0.84	0.82	1.05	0.79	0.77	0.76	0.75	0.73
Mg	0.90	1.02	1.12	1.26	1.37	1.48	1.58	1.68
Ba	1.26	1.42	1.58	1.77	1.93	2.09	2.24	2.55
Al	1.49	1.69	1.85	1.85	2.04	2.00	2.19	2.57
As	0.28	0.46	0.35	0.44	0.43	0.42	0.41	0.41
Ga	0.11	0.27	0.14	0.26	0.25	0.27	0.24	0.24
Mn	0.07	0.07	0.09	0.07	0.07	0.06	0.06	0.06
Co	1.17	1.35	1.46	1.66	1.80	1.92	2.08	2.21
Ni	1.01	1.14	1.25	1.41	1.53	1.81	1.93	2.03
Mo	1.25	1.60	1.56	2.28	2.59	2.73	2.85	2.96
O	3.58	4.11	4.46	4.92	5.32	5.69	6.01	6.33
C	86.41	84.19	83.05	81.00	79.40	78.08	76.77	75.18
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

The calculated and predicted ash content of each of the eight standards is showed below in Table 3.6.

Table 3.6: The simulated standards and its predicted ash content

Simulated Standards	Calculated Ash (wt. %)	Predicted Ash (wt. %)	r.m.s errors
CAL-STD1	10.0	18.8	3.11
CAL-STD2	11.7	11.5	0.07
CAL-STD3	12.5	13.3	0.32
CAL-STD4	14.1	11.8	0.81
CAL-STD5	15.3	13.5	0.64
CAL-STD6	16.2	14.7	0.53
CAL-STD7	17.2	18.0	0.28
CAL-STD8	18.5	17.0	0.53

From Table 3.6, it could be seen that the values of the ash content obtained for the simulated standards are in the range of 10.0 wt. % and 18.5 wt. % while the predicted ash for each of the simulated standards ranges from 11.5 wt. % to 18.8 wt. % with their root mean square (r.m.s.) errors in the range 0.07 - 3.11 wt. % indicating that the values are close to each other. The masses of the various compounds used lie between 0.09 g to 2.10 g (see Table 3.3). It was found out from the calculation that when smaller masses were used, lower ash values were obtained and vice versa.

3.5 Analysis of Coal Samples

3.5.1 Sample Collection

Coal is one of the major natural resources among others such as oil found in southern and north central parts of Nigeria. Most of these other resources are deposited across the different parts of the country. The coal samples used in this work which are listed below were collected from the Nigerian Coal Corporation Enugu. These includes Owukpa coal (Benue State), Okaba coal (Kogi State), Okpara coal (Enugu State), Ogwashi/Azagba (Delta State), Inyi coal (Enugu State), Ogboyoga coal (Kogi State), Fire-clay (Enugu State) and Lafia - Obi coal (Nasarawa State).

3.5.2 Preparation of Coal Samples

The bulk coal samples supplied by the Nigerian Coal Corporation Enugu were crushed to powdered form to make them homogeneous. The crushing were achieved using mortar and pestle. In doing this, care was taken in order not to contaminate or mix the samples together by washing the mortar and pestle and drying same before proceeding to the next sample. After reducing each sample to powdered form, they were packed and labeled using different containers.

3.5.3 Analysis of ash content of coal

The ash content of the coal samples obtained from eight different locations in Nigeria were analyzed, first by measuring the intensities of the gamma ray transmitted with and without the coal samples, I and I_o respectively. Secondly, using the calibration constants a_1 and a_2 and equations 3.6 and 3.10, the values of the ash content were obtained respectively for the single and dual energy methods.

CHAPTER FOUR

4.0 Results and Discussion

The ash compositions of Nigerian coals were determined using the coefficients obtained from the relationship between concentration of ash content and logarithm of R, the ratio of fractional transmitted gamma rays (with respect to initial gamma rays) for high and low radioactive sources. In calculating R, the effect of variation in sample depth and density, which has considerable effect on the amount of transmitted gamma rays measured were eliminated. The effect due to variation in sample depth was investigated by taking the counts of transmitted gamma rays with increasing sample depth for coal standard, water and sand as shown in figure 3.5 and 3.6 for low and high energy gamma rays. The point where the curve shows negligible variation of counts with sampling depth was chosen as the working depth for all the samples used in this work. The effect due to variation in density was taken care of by normalizing the R values calculated from initial and final counts for low and high energy gamma rays to the density of the samples. It was also ensured throughout that the samples were measured in their loose form to avoid changes in density due to compression.

Using the values of the coefficients a_1 and a_2 calculated for single and dual gamma transmission methods from the measurements of the standards, the determination of ash contents of the various Nigerian coal samples was achieved and these are presented in Table 4.1.

From Table 4.1, it could be seen that the values obtained for Okaba, Ogboyoga, Owukpa and Lafia-obi coal samples in the dual energy mode agrees considerably well with the supplied values and in the single energy mode, Okaba, Ogboyoga and Inyi coal samples also agree with the supplied values.

Table 4.1: Ash Content of the Coal Samples

Coal Samples	Ash Supplied (wt%)	Cal. Ash for the Single Energy (wt%)	r.m.s. value for the single energy	Cal. Ash for the Dual Energy (wt%)	r.m.s. value for the dual energy
OKABA	7.30	7.12	0.06	8.71	0.50
OGBOYOGA	8.00	8.63	0.22	9.13	0.40
INYI	6.50	6.42	1.61	-	-
OWUKPA	9.60	5.40	0.01	10.54	0.33
LAFIA-OBI	14.70	3.49	1.49	15.11	0.14
OKPARA	-	3.86	3.96	10.45	0.72
OGWASHI/AZAGBA	-	4.22	0.03	-	-
FIRECLAY	-	5.77	2.04	13.83	4.89

This shows that more of the values obtained in the dual energy mode agree better with the supplied values, which is an indication that the dual energy mode is better than the single energy mode. Also, Table 4.1 shows that Nigerian coals generally have low ash contents and are high ranking coals because low ash content is an indication of high carbon/energy content (section 2.5.3, chapter two).

The root mean square (r.m.s.) error quoted for the combination of ^{241}Am and ^{137}Cs sources were obtained by least squares regression analysis in which the predicted and known values of the ash were compared using the equation:

$$C_{ash} = a_1 \log \frac{(I/I_o)_{Am}}{(I/I_o)_{Cs}} + a_2 \qquad (4.1)$$

Where, a_1 and a_2 are constants and Am and Cs refer respectively to measurements with these radioisotopes. The r.m.s. error in simulated standards determined by γ -

transmission measurements on the standards vary in the range 0.06 – 3.12 wt. % ash, while it varies in the range 0.14 - 4.89 wt. % for the coal samples. It has been suggested that variations in ash composition are the greatest sources of error in the determination of coal samples and in particular iron oxide causes the greatest part of the total error (Fookes et al, 1983). Since the concentration of iron was not particularly determined in these samples, the effect of iron variation is not quite clear. However the results compare reasonably well with results from chemical assay of the coal samples. The predicted ash for single energy also agrees with prediction based on dual energy transmission measurements except for one of the coal samples.

The most promising areas of application for low energy gamma transmission technique for ash determination should be considered based on the above results. Most of the errors in the above determinations are caused by variation in composition of the ash, particularly iron. It should be noted that the measurements were made on raw (i.e. unwashed coal). Since errors due to chemical composition of the ash are proportional to the ash content, it is expected that smaller errors would be obtained on washed products from a coal washery plant since the washing often selectively reduces Fe_2O_3 relative to Al_2O_3 and SiO_2 so that the ash in washed coal has lower Fe_2O_3 than feed coal. However, the apparatus can easily be calibrated to allow for the effect of iron variation due to mining in different areas over a given period. The accuracy of the apparatus can be enhanced by inclusion of a collimator in order to obtain narrow transmission. Hence the most promising areas of application for low energy gamma ray transmission technique are the determination of ash content of washed and unwashed coal in which iron variations are low and more accurate determination is possible.

The method can also be adapted to industrial online quality control of coal on conveyor belts. This can be achieved using a conveyor belt powered by an electric motor to move the coal samples to the source/detector assembly, which is mounted below the conveyor belt so that it is parallel to the direction of the belt movement. A time delay can also be incorporated to ensure that the output from the source/detector assembly refers to the particular batch of the coal when ash content is calculated. In the case of dual energy transmission arrangement two sources of low and high energies (i. e. ^{241}Am and ^{137}Cs) can be mounted in one holder and placed below the conveyor belt, while a NaI (Tl) Scintillation detector based spectrometer with energy analysis used to resolve the transmitted intensities of the two different gamma rays. With these arrangements, gamma rays from ^{241}Am and ^{137}Cs bombard the coal stream and the attenuation of gamma rays through the coal stream which is related to the ash content of the coal is determined.

It should however be noted that coal on the conveyor belt can segregate both vertically and transversely. This segregation can be minimized by meticulously feeding the coal samples onto the conveyor belt, but it cannot be completely avoided. When narrow beam transmission, which provide accurate results is used, the results of the ash content determination is also affected by variation in height of the coal samples. In such situation, instantaneous measurement of both high and low γ-ray intensities should be made and converted to logarithms of the intensities and to ash content using the above equation. The mean of these various ash content values would give the ash content of the coal samples. The two constraints for adaptation of low energy γ-ray transmission technique for on-line quality control for coal streams identified above, namely segregation of coal on the conveyor belt and variation in the height of the coal can be

circumvented however, by using a cylindrical container for the coal samples. This ensures a fixed height and volume of coal when it is being moved to the measuring apparatus by the conveyor belt and so segregation of coal on conveyor and variation in height of coal can be avoided.

CHAPTER FIVE

5.0 Summary, Conclusion and Recommendations

5.1 Summary and Conclusion

In this work, an experimental facility which is based on the principles of absorption and attenuation of γ - rays has been developed for routine determination of ash content of coal samples. The facility consists of ^{241}Am and ^{137}Cs radioactive sources and NaI(Tl) detector coupled with SCA.

The system was calibrated with simulated standards which were prepared from calculated concentrations of graphite and incombustible elements in their compound form. The calibration coefficients was determined from the measurements of the ratio of the fractional transmitted γ - rays to the initial γ - rays for ^{241}Am and ^{137}Cs radioactive sources and using the coefficients determined for single and dual energy γ - transmission methods, the ash content of eight Nigerian coal samples obtained from different locations in Nigeria were determined.

The results of these analyses compare very well with previous works, however, there were a few areas of difference. Moreover, the values determined show very low ash content for these coal samples and therefore, they contain low pollutants which could be released to the environment during combustion. In addition with their low ash content, they have very high calorific and market values which could attract a lot of foreign exchange earnings to Nigeria.

This technique could be applied to the on-line measurement of ash content of coal, since the detector-source arrangement could be incorporated into the conveyor belt carrying the coal because of its less time consuming, non destructive nature, fastness and because it takes care of some other analytical problems and will serve as industrial

on-line quality control for coal than the other existing techniques that have been used in the by-line analysis of coal ash with a lot of disadvantages.

5.2 Recommendations.

Based on the observations, findings and experience in the course of this work, the following are recommended:

- Further research work on industrial scale should be carried out using this same technique but however, with stronger sources.
- The apparatus should be enhanced including a collimator in order to obtain narrow transmission of the gamma rays.
- Coal companies and other firms that use coal should use this technique and incorporate a source-detector arrangement into the conveyor belt to control the quality of coal they use.

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