Environmental and Health Related Assessment Of NORMs And Trace Elements From The Pozzolana Industry In Ghana

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Declaration

This is to certify that this thesis is the result of research undertaken by Natharius Nimbashabira towards the award of the degree of Master of Philosophy in Nuclear Science and Technology in the Department of Medical Physics, School of Nuclear and Allied Sciences, College of Basic and Applied Sciences, University of Ghana, Legon.

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Dedication

This work is dedicated to my Parents Mr. Joseph Kakwara and Ms. Purikeria Barindirize.

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I wish to acknowledge the contributions and technical guidance given throughout this study by my supervisors Prof. E.O Darko and Rev Dr. S.A. Bamford.

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Table of Contents

List of Tables

List of Figures

List of Plates

Abstract

The cement industry processes and uses raw materials with varying concentrations of Naturally Occurring Radioactive Materials (NORMs), some being of more radiological significance than others. Additionally, these raw materials may contain hazardous trace elements from which the workers and the public might be exposed to as a result of the various processes involved in the manufacture of cement. Therefore, it is important to establish the levels of the radionuclides in cement types for radiation protection purposes and also investigate the effect of cement industry activities on the surrounding environment. This study therefore, focused on estimating possible radiological health hazards associated with the manufacture and use of Crystal cement, a product of mixing clay Pozzolana with Ordinary Portland Cement as well as the investigation of the factory surroundings for possible pollution from trace elements and radionuclides. A total of one hundred cement samples representing four major brands of Ordinary Portland Cement used in Ghana were collected from various cement dealers. Additionally, samples of Palm Kernel Shells (PKS), raw clay and clay Pozzolana were collected from Pozzolana Ghana Limited while 62 soil samples were collected within and around the factory premises. All the samples were analyzed for the activity concentrations of Ra-226, Th-232 and K-40 using the High Purity Germanium Detector. Soil samples and clay Pozzolana were further analyzed for elemental concentrations of Pb, Cr, Cd, As and Hg using the Atomic Absorption Spectroscopy (AAS). Results showed that after mixing clay Pozzolana with Ordinary Portland cement, there was enhancement in the individual activity concentrations of Ra-226, Th-232 and K-40 in some mixed cement types while there was reduction in the activity concentrations of the same radionuclides in other mixed cement types. The resultant effect of alterations in activity concentrations on the indoor absorbed gamma dose rate was insignificant in CEM (CEMENT) IA (0.47% increase from CEM I) and CEM IIC (1.38% decrease from CEM III). However, these alterations were significant in CEM IIB and CEM IVD as there was an increase of 5.45% in indoor absorbed gamma dose rate from CEM II to CEM IIB and a 48.48% reduction in the indoor absorbed gamma dose rate from CEM IV to CEM IVD. Regardless of the enhancement or reduction in individual activity concentrations of the radionuclides, results revealed that the annual indoor effective dose from gamma radiation in Crystal cement ranged between 0.28±0.01 and 0.40±0.02 mSv, the maximum value in this range being lower than 1 mSv per year considered as the limit for public exposure. Similarly, estimation of internal exposure from the alpha activity in all Crystal cement types indicated that the maximum indoor radon concentration of 73.02 Bq/m^3 was lower than 300Bq/m^3 which is considered as the action level in dwellings and other buildings for members of the public. The natural radioactivity in soil samples around the factory indicated that the average annual outdoor effective dose was 0.03±0.01 mSv still lower than 1 mSv per year considered as the limit for public exposure. The range of calculated Pollution Index, (P_{ij}), Ecological risk factor (E_r^i) and Geo-accumulation index (I_{geo}) indicated the following: P_{ij}: 0.06-0.49 <1; E_r^i: 0.14-14.70 <40; I_{geo}:-5.98- -2.91$\leq$ 0. The calculated value of improved comprehensive pollution index P_{ij} was 0.54 indicating clean soils around the factory. Hence, both the single and integrated indices indicated no possible environmental pollution with trace elements. Therefore, the use of Crystal cement as a building material is considered safe and no soil pollution with radionuclides and trace elements from the factory activities was established by this study.

CHAPTER ONE
INTRODUCTION

1.0 Background

Several types of human activities and non-nuclear industries contribute to the enhancement of concentrations of some of the natural radionuclides in the earth's crust and this affects both the humans and the environment (Samad et al., 2012). All building materials such as concrete, cement, brick, sand, aggregate, marble, granite, limestone, gypsum, etc., contain mainly natural radionuclides whose contents in cement materials vary in regard to geological source as well as geochemical characteristics (Turhan et al., 2008). These radionuclides include uranium (U-238) and thorium (Th-232) and their decay products and the radioactive isotope of potassium (K-40) (Eštoková & Palaščáková, 2013; Turhan et al., 2008). When building materials are processed, the concentration levels of radionuclides within them may be enhanced. Enhancement is said to have occurred when a naturally occurring radioactive material has its composition, concentration, availability or proximity to people altered by human activity (European Commission, 1999).

The cement industry has been identified as one of the industries which processes materials that contain naturally occurring radioactive material (NORM) and are considered to be of potential significance with regard to public exposure (European Commission, 2003). There are many types of cements according to the chemical composition and hydraulic properties for each one (El-Taher et al.,2010), some construction materials have more natural radioactivity than others.

It is important to note that even though there can be low-level natural radioactivity in construction materials, there is still internal and external exposure arising from these materials (Righi & Bruzzi, 2006). The external radiation exposure comes from the gamma radiation emitted from members of the uranium and thorium decay chains as well as from K-40.The internal radiation exposure that mainly affects the respiratory tract, comes from the short-lived daughter products of radon that escapes from construction materials and released into room air (Khan & Khan, 2001). It has also been demonstrated in various studies (Arafa, 2004; Stoulos et al., 2003) that, if building materials with high natural radioactivity concentration are used, dose rates indoors will be elevated accordingly. Exposure to excess level of background ionization radiation may cause somatic and genetic effects that tend to damage critical and/or radiosensitive organs of the body, which ultimately can lead to death (Avwiri, 2006).

The cement industry is one of the manufacturing industries whose workers may be exposed to the emitted dust that contains natural radionuclides and trace elements among other compositions at various manufacturing and production processes. The aerodynamic diameter of cement dust particles dispersed is respirable and therefore, exposure to the dust can cause a number of health hazards that include acute or chronic respiratory diseases as well as respiratory function deficits (Meo, Al-Drees, Masri, Rouq, & Azeem, 2013).

Apart from occupational exposure, since dust travels large distances depending on the metrological conditions at the facility, members of the public may also be severely exposed (both ingestion and inhalation) depending on the quality of dust. The cement dust comes from the raw materials used during the production process and therefore, the quality of the dust depends on the raw materials. The major raw material used by Pozzolana Ghana Limited is clay. Most clay types have some mineral compositions such as: kaolinite (the major component of most clays); silica (free crystalline silica-SiO_2); talc (a complex mineral which may be contaminated with asbestos-related minerals or free silica) and vermiculite (a mica-like mineral, which may also be contaminated with asbestos)[1]. Minerals are essentially inert chemicals, and are not usually hazardous when ingested or when they come in contact with the skin. However, they can be hazardous when their dusts are inhaled. Most mineral dusts seem to irritate the lungs to some degree, but because they do not readily dissolve or break down, once they begin to accumulate, they overload the lung clearing mechanisms[1]. The biological effects of clay minerals are influenced by their mineral composition and particle size. However, of all of the mineral compositions listed above, the most and severe lung effects are silicosis and asbestosis caused by inhalation of silica and asbestos respectively. Crystalline silica causes various lung diseases, including silicosis and lung cancer (WHO, 2005)

Apart from direct occupational and public exposure to cement dust, cement dust may adversely affect the soil ecological communities especially downwind areas where elevated pH levels have been exhibited (Ahiamadjie et al., 2011). Air pollutants especially heavy metals are the major causes of vegetation injury as well as crop yield losses when in excesses. For example, in one study by (Ade-Ademilua & Umebese, 2007), they found out that levels of chromium, silica, iron and calcium were high and

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[1] http://www.cheminfonet.org/art/ceramics1.pdf; accessed on 4/04/2015

their contamination levels decreased with distance from the factories. As a result, the growths of plants in the area were being affected by those compositions.

Knowledge of the occurrence and concentration of natural radioactivity in construction materials is essential for estimating the radiological hazards to human health (El-Taher et al., 2010) since the majority of individuals spend 80% of time indoors (El-Taher et al., 2010; Righi & Bruzzi, 2006). Similarly, knowledge of the ecological effect of cement dust on the soil around Pozzolana Ghana Limited (PGL) is important in estimating the extent of environmental pollution. Hence, this study will address the radiological significance of radionuclides in cement products as well as the effect of cement dust generated during the production process on the physicochemical characteristics of the soil in the vicinity of the cement factory.

1.2 Statement of Problem

The cement industry is considered as one of the basic industries that plays an important role in the national economy of developing countries (El-Taher et al., 2010). Unfortunately, most of the raw materials used in the manufacture of cement contain varying radionuclide concentrations of natural origin that are known to be of radiological significance if in excess concentrations. In Ghana, the environmental impact of ordinary Portland cement production processes and the radiological health risks in the products have been documented (Kpeglo et al., 2012; Addo et al., 2012; Adukpo et al., 2011; Ahiamadjie et al., 2011; Kpeglo et al., 2011). These studies however, have been restricted to imported cement or locally produced using imported clinker and gypsum without taking into consideration the amount of radionuclides and trace element in the raw materials. Furthermore, the assessment of natural radioactivity in building materials used along the Coast of Central Region of Ghana has been reported by Otoo et al., (2011). However, the building materials were considered individually without taking into account of possible composite mixtures. Though the above studies addressed the environmental and radiological health risk associated with the cement production processes and other building materials, no similar studies have been done at the cement factory operated by Pozzolana Ghana Ltd. Hence, there is insufficient data on the possible radiological health risks from use of crystal cement (Portland-Pozzzolana) as well as the environment impact on the surrounding from the activities of the cement factory operated by Pozzolana Ghana Limited. Therefore, this current study addressed the radiological health risk from use of crystal cement as a building material and possible soil pollution with trace elements and radionuclides from the activities of the cement factory operated by Pozzolana Ghana Limited located at Gomoa Mprumem, Apam in the central region.

1.3 Objectives

The primary objective is to study the environmental and health impact of NORMS and trace elements from cement produced by replacing part of Portland cement with locally manufactured clay Pozzolana.

This study was guided by the following specific objectives:

- To investigate possible enhancement or reduction in NORM concentration from Crystal Cement (Portland-Pozzolana).

- To assess radiological health risks from the use of crystal cement as a building material.
- To assess environmental impact of trace elements and natural radionuclides from production of crystal cement.

1.4 Relevance of the Study

Cement is the most widely used construction material throughout the world. This leads to an enormous production of cement to meet the increasing demand for housing and infrastructure. Cement production is, however, harmful to the environment and the population since the materials out of which cement is made, are of soil origin that contains radionuclides that contribute approximately 80% of the total radiation dose a person receives in a year. Additionally, the dust from the production processes may consist of toxic heavy metals and natural radionuclides with varying concentrations that may further concentrate the natural existence of these elements and radionuclides in soil around the factory. Therefore, analyses of radionuclide concentration and accumulation of heavy metals in the soils around the factory, raw materials and cement products from the cement factory would provide information to evaluate the extent, degree and routes of the radiological risk and environmental impact. This information would then contribute to formulation of necessary guidelines that ensure best cement production processes by relevant bodies responsible for environmental protection (Environmental Protection Agency-EPA), consumer protection (Ghana Standards Authority-GSA) and radiation protection (Radiation Protection Institute -RPI). Therefore, the findings of this study can be used as a tool for controlling anthropogenic activities capable of contributing to pollution within the environment of the study area as well as adding on the frontiers of the existing knowledge on environmental and health impacts of various cement products in Ghana.

1.5 Scope and Limitation of Work

The scope of this work was limited to assessment of radiological significance of terrestrial radionuclides (U-238 or Ra-226, Th-232 and K-40) in crystal cement and its raw materials as well as estimation of possible environmental pollution with natural radionuclides of U-238 or Ra-226, Th-232 and K-40 and trace elements in soils within and around Pozzolana Ghana Limited cement factory. This was achieved by collecting samples of raw clay, clay Pozzolana and Palm Kernel Shells (PKS) from the factory premises, soils from within and around the factory, Ordinary Portland cement from various cement dealers in Ghana and analyzing them for natural radioactivity by the gamma spectrometry using High Purity Germanium detector at Radiation Protection Institute (RPI). Clay Pozzolana and soil samples were further analyzed for presence and concentration levels of some selected trace elements (Pb, Cr, Cd, As and Hg) using Atomic Absorption Spectroscopy at the National Nuclear Research Institute (NNRI), Ghana Atomic Energy Commission.

1.6 Structure of the Thesis

This work is presented in five chapters. A brief description of the contents in each chapter is provided below.

Chapter One is the introduction of the study and comprises of the background, statement of the problem, objectives of the study, justification/relevance of the work and the scope of the work.

Chapter Two contains a literature review on Pozzolana cement, categories of NORMs and their existence in building materials. Additionally, the chapter further discusses some trace elements associated with the cement industry. The chapter also provides the theory on Gamma Spectrometry and Atomic Absorption Spectroscopy (AAS). Chapter Three describes the study area, sample collection and preparation protocols, detailed analytical procedures and, mathematical expressions employed to achieve the stated objectives. Chapter Four presents results and discusses on the major observations and their significance with regard to the stated objectives. Chapter Five contains the conclusions regarding the significance of the work and the various recommendations.

CHAPTER TWO

Literature Review

2.0 Pozzolana

Pozzolana is defined as a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties (Barger et al., 2001). Massazza (1998) defines pozzolana as those inorganic materials, either natural or artificial, which harden in water when mixed with calcium hydroxide (lime) or with materials that can release calcium hydroxide. Hence, pozzolana covers a large number of materials in terms of origin, composition and structure. Within the building industry, the term pozzolana covers all the materials which react with lime and water giving calcium silicate and aluminate hydrates possessing cementing properties (Bensted and Barnes, 2002). As a consequence, all pozzolana have to be rich in reactive silica or alumina plus silica. The major sources of natural and manmade pozzolanas include volcanic mineral deposits, fired and crushed clay, and flyash that is created during the burning of coal for power generation (Al-Chaar et al., 2013). Pozzolana-lime mixes have been used until earlier in the last century, but nowadays they are generally replaced by pozzolanic cements which have higher early and ultimate strength, while they keep the typical property of high chemical resistance of ancient mortar and concrete, unaltered. However, pozzolana-lime mixes can be successfully used also today for casting durable mortars and concrete where high strength is not necessary, or supply of cement is difficult (Bensted and Barnes, 2002).

2.1 History of Pozzolana Industry in Ghana

Initial studies on possible pozzolanic materials in Ghana were undertaken by Hammond, (1978; 1976) using bauxite waste from the Awaso mines. Other materials that possessed pozzolanic properties were identified as the vast clay deposits in the Greater-Accra region of Ghana and agricultural wastes such as rice husks, coconut fibres, groundnut husks, sugar-cane bagasse, etc., (Hammond, 1987). The research on bauxite wastes indicated that with a 20 to 30% replacement of Ordinary Portland Cement (OPC) with calcined (700-900 ºC) bauxite-wastes, mortars and concretes produced with these blended cements, exhibited strength comparable to those using OPC only.

In 2001, the Council for Scientific and Industrial Research (CSIR) built a small, prototype plant to produce clay pozzolana from clay deposits at Mfensi (north-west of Kumasi). The plant consisted of a ball mill for grinding of raw clay and palm kernel shells and also for pulverizing calcined clay. In addition, the plant also included a small nodulizer that nodulized a ground clay/palm kernel shell mix. The role of palm kernel shells (waste products of the oil-palm production industry) is to boost the calcination temperature to the required 700-900^{0}C range. Ash, which is the end-product of the kernel burning, has some low level lime content, which is a plus to the pozzolanic process. Its main role, however, is that of providing fuel.

Since early 2007, the prototype plant has been upgraded with the installation of a hammer mill for grinding raw clay; addition of 1500 mm diameter noddlezer; horizontal mixer for ground clay and palm kernel shells, prior to nodulization ; installation of 9 tonnes/batch brick vertical up-draft kiln, for calcinations; a pulverizing plant with the capacity of pulverizing 5 tonnes of pozzolana per hour.

In 2011 BRRI expanded their production by constructing a production plant operated by Pozzolana Ghana Limited (PGL) at Gomoa Mprumen, Apam. Figure 2.1 shows the manufacturing process used by Pozzolana Ghana limited to manufacture Crystal cement (Portland- Pozzolana). Clay and palm kernel shells are used as raw materials.

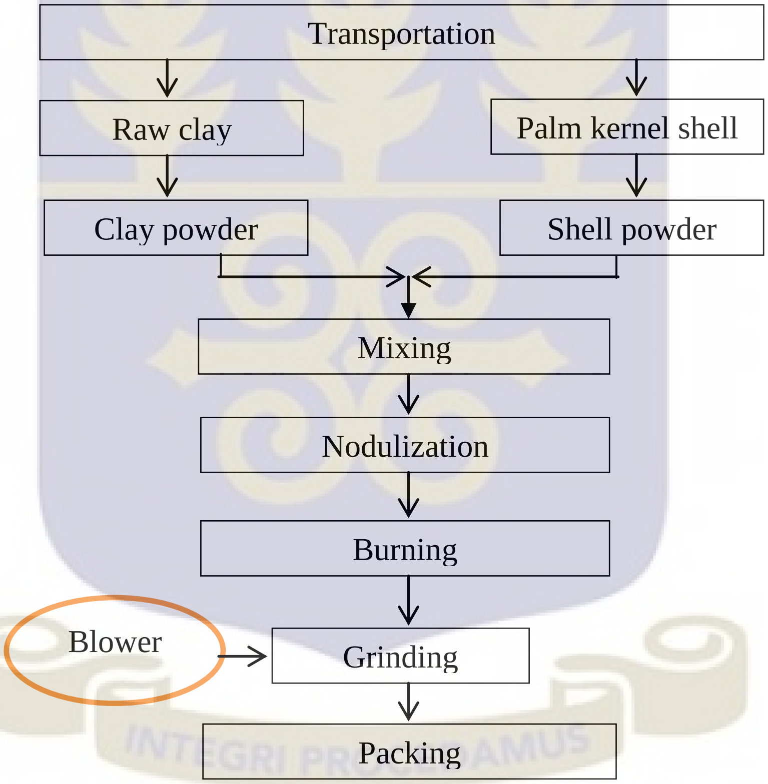

Figure 2.1: Manufacture process of clay Pozzolana[2]

The production process begins with transportation of raw materials (clay and palm kernel shells). They are then homogenized differently using the palm shell machine crusher and

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[2] http://www.bk.tudelft.nl/fileadmin/Faculteit/BK/Actueel/Symposia_en_congressen/African_Perpectives/Programme/Building_in_Africa/doc/APD_wp_5_ayeh_paper1.pdf

hammer mill for palm husks and clay respectively. The two powdered materials are then mixed using a horizontal mixer and carried to the noddlezer by the conveyer belt. From noddlezer, the mixture is carried by the conveyer belt to the bucket advectors that feed the mixture into the kiln for firing. After the firing process, the fired material is carried by the conveyer belt to the jaw crusher and then to the silo by the bucket advectors and to the ball mill (Pulverizer). The ball mill has three sections to ensure that a fine powder is produced. Finally the fine powder is taken to the second silo by the bucket advectors before being lowered to the bagging machine. The process described above completes the production of clay Pozzolana at PGL. However, separate machines are available for mixing this clay pozzolana with Portland cement in the ratio of 1:3

2.2 Classification of Pozzolana

The most commonly accepted classification concerns the origin of pozzolanas in terms of natural and artificial materials. In this case, natural materials require no further treatment except grinding while artificial pozzolanas require chemical and/or structural modifications of materials that originally had no or only weak pozzolanic properties (Massazza, 1998). Artificial Pozzolana can be residues of certain production methods or products manufactured from selected raw materials. The classification between natural and artificial pozzolanas is further shown in Figure 2.2 detailing the different raw materials for each.

2.2.1 Natural Pozzolanas

Natural pozzolanas can be classified according to their origin and their essential active constituent. On the basis of these criteria, according to Bensted and Barnes (2002), natural pozzolanas are usually classified as, volcanic, incoherent, rich in unaltered or partially-altered glass; tuffs, where volcanic glass has been transformed, entirely or partially, into zeolitic compounds; sedimentary, rich in opaline diatoms; and diagenetic, rich in amorphous silica, resulting from the weathering process of siliceous rocks. However, according to Barger et al., (2001), natural pozzolana can as well be defined as either a raw or calcined natural material that has pozzolanic properties (for example, volcanic ash or pumicite, opaline chert and shales, tuffs, among others).

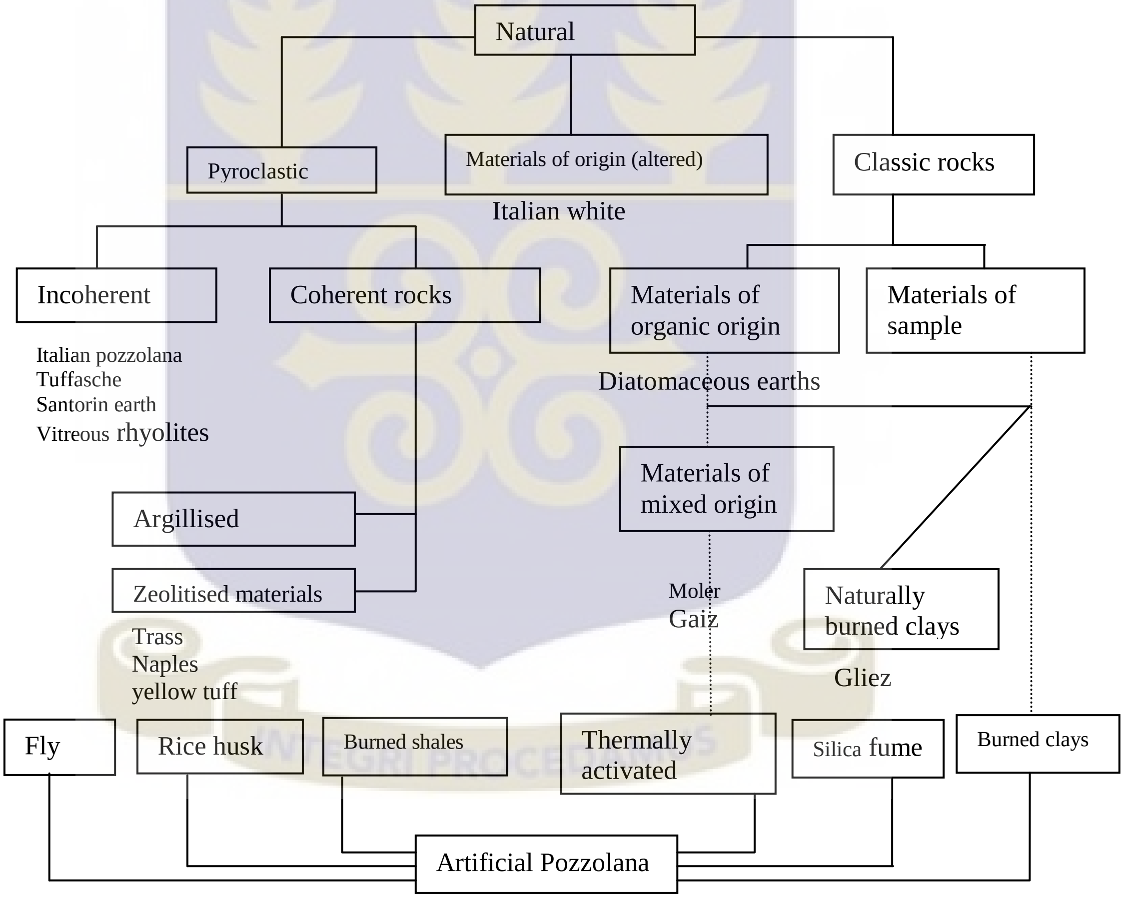

Figure 2.2: Classification of pozzolanas. Source: (Massazza, 1998)

All pozzolanas contain variable amounts of non- reactive or low reactive constituents (quartz, andesite, horneblende, leucite and feldspars). The active phases are conventionally assimilated to the components of pozzolana which are dissolved by an acid attack followed by a basic one (Bensted and Barnes, 2002). Pozzolanas are often polluted by clay minerals coming from the weathering of the siliceous constituents of the original deposit or, as in the case with diatomaceous earth, from the concomitant precipitation with diatoms in waters (Bensted and Barnes, 2002).

The properties of natural pozzolanas vary considerably depending on their origin. This is because of the variable proportions of the constituents and the variable mineralogical and physical characteristics of the active materials (Barger et al., 2001). Most natural Pozzolanas contain substantial amounts of constituents other than silica, such as alumina and iron oxide, which will react with calcium hydroxide and alkalies (sodium and potassium) to form complex compounds.

2.2.2 Artificial Pozzolana

Artificial pozzolans mostly used are from by-product materials such as fly-ash produced by burning pulverized coal in power stations; burned clay and shale that are mostly composed of silica and alumina; microsilica obtained from the manufacturing processes of silicon metal and ferrosilicon alloys in an electric arc furnace. The main features of microsilica are a high silica content, amorphous structure as well as high specific surface area. These characteristics account for the substantial pozzolanic activity of microsilica in terms of both its capacity of binding lime and rate of reaction. Another example of artificial pozzolana is the use of burned rice husks within certain temperature ranges (Massazza, 1998).

2.3 Pozzolanic Cements and Pozzolana Cements

When mixed with Portland cement and water, pozzolana reacts with the calcium hydroxide formed during hydration of the calcium silicates in the clinker (Bensted and Barnes, 2002). As a result of this reaction, the resulting portlandite content in the hydration products is at all times lower than that found in the control Portland cement. This applies to all pozzolanas, both natural and artificial, as well as to suspensions, pastes, mortars and concretes. The simultaneous presence of Portland cement and pozzolana modifies the respective reactions of hydration. Depending on the replacement level, portlandite can be partially or entirely combined giving calcium silicate and aluminate hydrates (Massazza, 1998).

Pozzolanic materials can be used either as an addition to the cement in the manufacturing process or as a replacement for a portion of the cement in the mortar and concrete production (Appiah Boakye, 2012). Hence pozzolanic cements are by definition mixes of Portland cement and pozzolana which, if dispersed in excess water and kept under certain conditions, eventually give rise to unsaturated calcium hydroxide solutions (Massazza, 1998). Conversely, pozzolana cements do not comply with this requirement. This is because they contain insufficient Pozzolana content in terms of both quality and quantity to combine all the portlandite which forms during the hydration process. As a consequence, whilst hardened pozzolanic cements lack at least theoretically free lime, pozzolana cements do not.

In principle, Pozzolana can be added to Portland cement either at the building site or at the cement plant. When mixing is done at the cement plant, Pozzolana undergoes either simultaneous grinding with clinker and gypsum or separate grinding followed by mixing and homogenization with suitable equipment. However, when mixed at the building site, Pozzolana is introduced with Portland cement into the concrete mixer. This procedure improves the quality of concrete both in terms of strength and durability when Pozzolana is added with the purpose of improving grading of the fine aggregates. However, this causes a certain decline in the properties of concrete when Pozzolana is used as a partial replacement for Portland cement. Hence, this procedure is not recommended (Massazza, 1998) since:

a) generally, the degree of homogenization that can be reached by mixing Pozzolana with Portland cement at the building site is lower than that reached by using the facilities of a cement plant;

b) replacing a relatively large portion of Portland cement with pozzolana reduces early strength;

c) building yards rarely have all the personnel, equipment and time required for checking the properties of pozzolana and the mixes.

2.4 Naturally Occurring Radioactive Materials (NORMs)

All minerals and raw materials have natural radionuclides of natural origin and the most important for the purposes of radiation protection are the radionuclides in the U-238 and Th-232 decay series and K-40 (International Atomic Energy Agency, 2007). The levels of human exposure arising from the minerals and raw materials containing these radionuclides are not significantly greater than normal background levels. However, some activities may give rise to significantly enhanced exposures and hence the need for regulatory control. Materials giving rise to these enhanced exposures are known as naturally occurring radioactive materials (NORMs) (International Atomic Energy Agency, 2007).

The radionuclides of U-238, Th-232 and K-40 are very long lived and some of their progenies are also long-lived such as R-226. The distribution of radionuclides in the geosphere depends on the distribution of the geological media from which they are derived and the processes which concentrate them at a specific location in specific media (International Atomic Energy Agency, 2003). The list of isotopes which contributes to natural radiation is divided into those materials that come from the ground (terrestrial sources) and those that are produced as a result of the interaction of atmospheric gases with cosmic rays (cosmogenic).

2.4.1 Cosmogenic NORM

Cosmogenic NORM is formed from the interactions between certain gases in the Earth's atmosphere and cosmic rays. Cosmic rays are extraterrestrial radiations and consist of galactic particles that originate outside the solar system and solar particles emitted by the sun (James, 2006). As they strike the atmosphere they produce cascades of nuclear interactions that yield many secondary particles which are very important in production of cosmogenic radionuclides. Some of the cosmogenic radionuclides of interest are shown in Table 2.1 while the distribution of cosmic ray components and energy spectra is shown in Figure 2.3.

Table 2.1: Radiological Characteristics of Cosmogenic NORM

Nuclide	Decay mode	Half-life (y)	Global inventory (PBq)	Inventory in Biosphere	
				Distribution (%)	Activity (PBq)
C-14	β-	5730	8500	4	340
H-3	β-	12.3	1300	27	350
Na-22	β+ and electron capture	2.6	0.4	21	0.08
Be-7	Electron capture	0.146	37	8	3

Source: ([3], Radiation Protection Division, 2004)

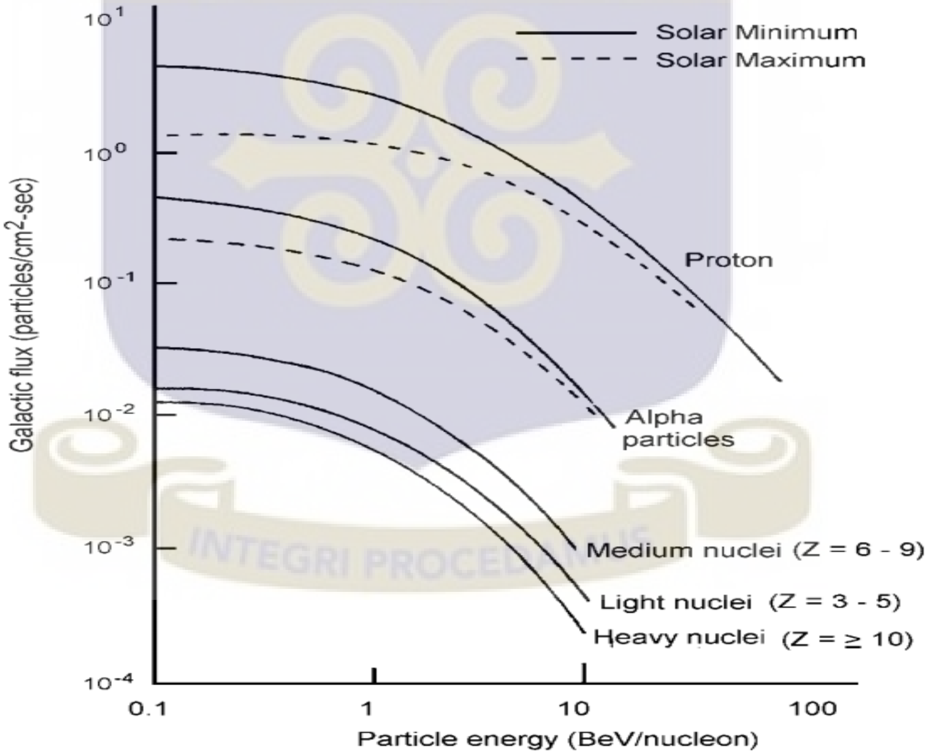

Figure 2.3: Components and energies of galactic cosmic radiation. Adapted from (James, 2006)

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[3] http://www.world-nuclear.org/info/ Safety-and-Security/Radiation-and-Health/Naturally-Occurring-Radioactive-Materials-NORM/[3]

Most cosmic radiation is deflected by the Earth's magnetic field or absorbed by the atmosphere and therefore, very little reaches the Earth's surface. As a result of this effect, cosmogenic radionuclides contribute more to dose at low altitudes than cosmic rays. Radiation dose rates at the earth's surface due to cosmic radiation are largely caused by muons and electrons, and both vary with elevation and with latitude. The atmospheric shield is a column of air that weighs 1033 g/cm^2 at sea level; the effectiveness of this shield is related to the atmospheric thickness or depth in units of g/cm^2 of overlying air (James, 2006). Consequently, the total dose rate from cosmic rays will increase with altitude as the thickness of the atmosphere decreases (Radiation Protection Division, 2004). This is further demonstrated in Figure 2.4 which contains data averaged over geomagnetic latitudes between 43° and 55° and over two periods of solar activity (James, 2006).

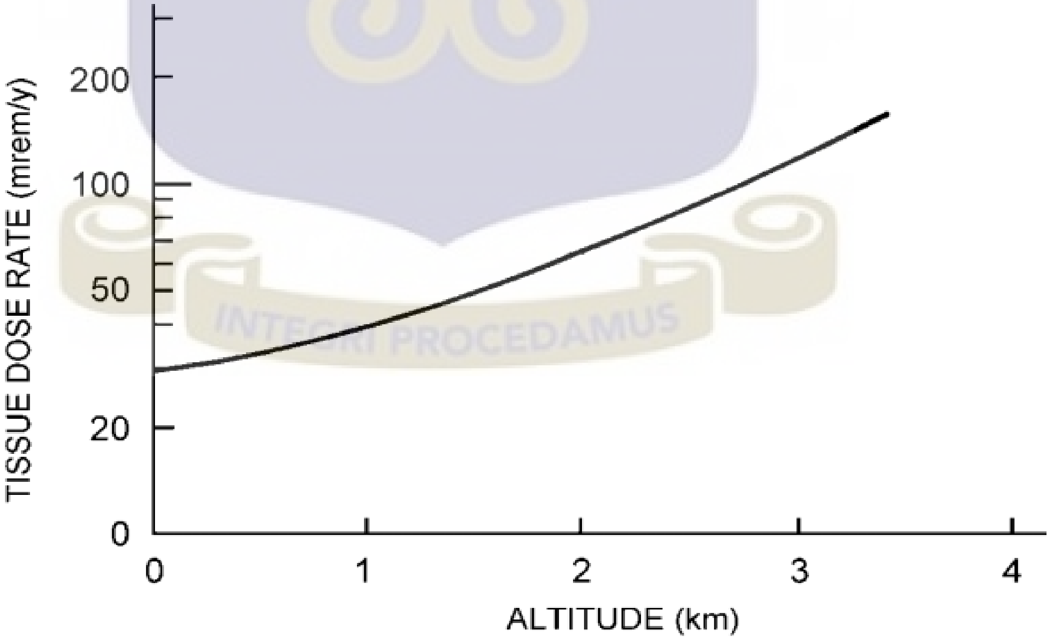


Figure 2.4: Long-term average outdoor total dose equivalent rate (charged particles plus neutrons) due to cosmic radiation at 5 cm depth in a 30 cm thick slab of tissue. *Adapted from (James, 2006)*

Cosmogenic NORM barely contributes to population dose perhaps a few tens of microsieverts per year. However, terrestrial NORM especially radon contributes to the majority of natural dose usually over 1mSv per year (James, 2006). It should be noted that cosmogenic radionuclides because of their relative paucity and insignificant contribution to the dose from naturally occurring radioactivity, they are of little or no importance in the context of health physics (Cember & Thomas, 2009).

2.4.2 Terrestrial NORM

Terrestrial NORM consists of radioactive material that comes out of the Earth's crust and mantle. The materials may be original (such as uranium and thorium) or decay products thereof, forming part of characteristic decay chain series. The two most important chains that provide nuclides of radiological significance in NORM are the thorium series (Th-232) and the uranium (U-238) series (International Atomic Energy Agency, 2013). Appendix 1 shows the decay chains as well the other radionuclides from these series that contribute to both external and internal exposure.

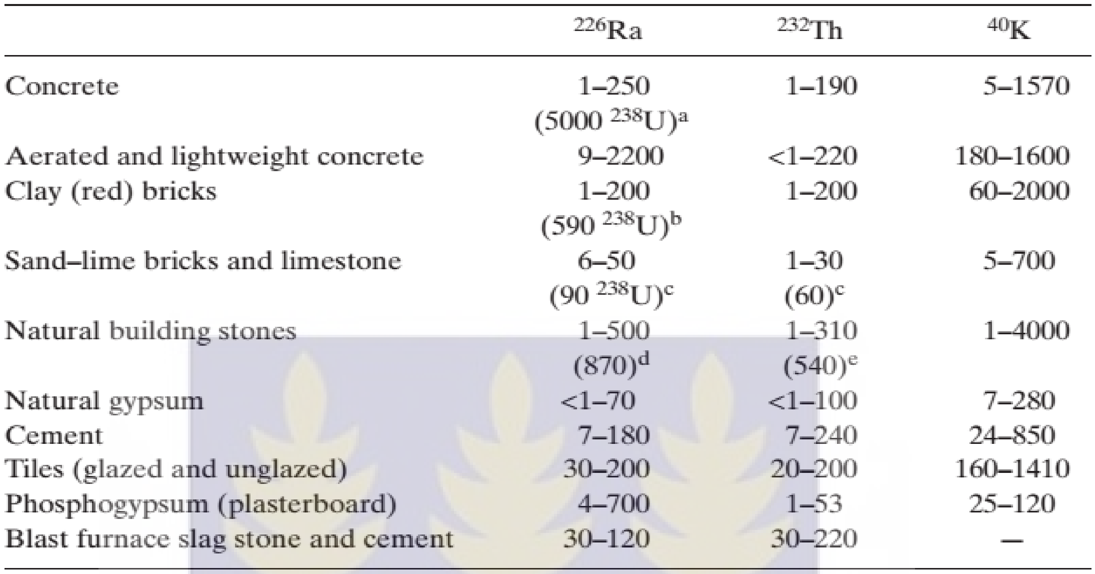
Another major source of terrestrial NORM is potassium 40 (K-40) of half-life of 1.25 billion years (International Atomic Energy Agency, 2013). The long half-life means that it still exists in measurable quantities today. K-40 decays by beta emission, mostly to calcium-40, and forms 0.012% of natural potassium which is otherwise made up of stable K-39 and K-41. Some of human activities have contributed to the redistribution or enhancement of these NORMs. These activities include industrial activities such as: mining and milling of metalliferous and non-metallic ores; production of non-nuclear fuels, including coal, oil and gas; extraction and purification of water, for example for the generation of geothermal energy, as drinking and industrial process water, and in paper and pulp manufacture; production of industrial minerals including phosphate, clay and building materials; use of radionuclides, such as thorium, for properties other than their radioactivity among others (International Atomic Energy Agency, 2003).

2.6 NORM in Building Materials and their Radiological Significance

Building materials can contain NORMs that are of natural origin i.e., contained in the raw material (e.g., natural stone), or it can be due to the addition of industrial products (e.g., zircon sand), intermediates or by-products (e.g., coal ash, phosphogypsum and furnace slags) (International Atomic Energy Agency, 2003). In particular, if clays are used as one of the raw materials, they usually have concentrations of the radionuclides from the decay chains of U-238 and Th-232 of the order of 35 Bq kg^{-1} (European Commission, 2003). The NORM content in natural resources may also vary considerably over short distances, for example in granite quarries (International Atomic Energy Agency, 2003).

The abstraction of sediments, such as sands and gravel, which typically have low radioactivity content, per se does not lead to elevated concentrations in the product or waste stream. However, it could be envisaged that slimes and fines from aggregate plants may be relatively enriched, as typically the NORM resides in these fractions (International Atomic Energy Agency, 2003). The concentration of radionuclides in building materials is summarized in Table 2.2.

Table 2.2: Activity Concentrations (Bq/kg) of Natural Radionuclides in Building Materials



	^{226}Ra	^{232}Th	^{40}K
Concrete	1–250 (5000 ^{238}U)[a]	1–190	5–1570
Aerated and lightweight concrete	9–2200	<1–220	180–1600
Clay (red) bricks	1–200 (590 ^{238}U)[b]	1–200	60–2000
Sand–lime bricks and limestone	6–50 (90 ^{238}U)[c]	1–30 (60)[c]	5–700
Natural building stones	1–500 (870)[d]	1–310 (540)[e]	1–4000
Natural gypsum	<1–70	<1–100	7–280
Cement	7–180	7–240	24–850
Tiles (glazed and unglazed)	30–200	20–200	160–1410
Phosphogypsum (plasterboard)	4–700	1–53	25–120
Blast furnace slag stone and cement	30–120	30–220	—

Source: (International Atomic Energy Agency, 2003)

The radiological significance of naturally occurring radioactive materials and radiation sources is closely linked to the physical behavior of the materials in the source and how they change with time (James, 2006). NORM in its unaltered natural state can pose potential radiological concerns. However, such unaltered NORM is mostly not amenable to regulatory control. On the other hand, exposures to NORM that has been altered in the course of exploitation of natural resources to meet human needs can, in principle, be controlled. There are two effects of human exploitation that are relevant in the case of potential effects of NORM on human health and the environment (International Atomic Energy Agency, 2003):

a) The concentrations of NORM can be enhanced above its natural levels in a product, by-product or residue.

b) The availability for release into the biosphere of the NORM in products, by-products or residues can be enhanced through physicochemical changes or simply due to the method by which the residues are managed.

Basing on the above therefore, the requirements for planned exposure situations apply in building materials if the activity concentration of any radionuclide in the uranium or thorium decay chains is greater than 1 Bq/g or the activity concentration of K-40 is greater than 10 Bq/g (International Atomic Energy Agency, 2013).

2.5 Background Radiation

Background radiation is the sum of the external radiation doses that accrue from the naturally occurring radiation sources (U-238, Th-232, Ra-226, K-40, C-14, etc.,), cosmic radiation, and anthropogenic sources, such as debris from weapons tests, fallout from accidental releases, and releases from the routine operations of reactors and the nuclear fuel cycle. The exact background dose rate varies from place to place, depending mainly on the mineral content in the ground and the cosmic ray intensity (which in turn depends on the altitude and the latitude) (Cember & Thomas, 2009; Radiation Protection Division, 2004).

In most places, the external background dose rate varies from about 70 to 150 millirads (700–1500μGy) per year (Cember & Thomas, 2009). However, there are many places throughout the world where the background is very much higher than the average. Table 2.3 shows some of reported places with their respective specific background dose/ range values.

Table 2.3: Places with high background radiation doses per year

Country	Location	Specific dose/range (µGy per year)
Brazil	Beach	430,000
India (Kerala region)	Soil	5000–6000
China	Densely populated areas	3000–4000
USA	Denver	2000

Source: (Cember & Thomas, 2009, Radiation Protection Division, 2004)

It is important to note that no harmful radiation effects have been observed among the populations living in the high-radiation areas (Cember & Thomas, 2009). Therefore, background is significant to the health physicist because the background radiation must be accounted for when measuring radiation from a source and also it substantiates the validity of the radiation safety standards for incremental doses that are within the range of variability of background dose rate levels (Cember & Thomas, 2009).

2.7 Health and Environmental Effects of a Cement Plant

The major pollution problem in the cement industry is dust, which is emitted from various parts of the production process such as the raw material crusher, rotary kiln, cranes, mills, storage silos and packing sections (Mwaiselage et al., 2006). For the case of clay pozzolana production, this dust consists of the fine dust called Respirable Crystalline Silica (RCS) that is known to cause silicosis, Chronic Obstructive Pulmonary Disease (COPD) and lung cancer among other lung diseases (Health and Safety Executive, 2013). Deposition of cement dust in the respiratory tract causes a strong basic reaction leading to increased pH values (12.5–13.0) that irritate the exposed mucous membranes (Dietz et al., 2004).

In a cement plant, the main potential source of aerial discharge is from volatilisation of Po-210 and Pb-210 due to very high temperature of the raw materials in the kilns (European Commission, 2003). Table 2.4 shows estimates of typical discharge of the cement plant. The discharge figure for Po-210 is based on the assumption that 50% of the polonium escapes from the thermal process in analogy with the assumption used for the production of bricks and roofing tiles (European Commission, 2003).

Table 2.4: Annual aerial discharges for a typical cement plant with a 2000 kt per year ore throughput of different types of cement

Nuclides	GBq per year
U-238	0.2
Th-228	0.05
Ra-226	0.2
Rn-222	157
Pb-210	0.2
Po-210	78
K-40	0.4

Source: (UNSCEAR, 2000)

Apart from Po-210, Rn-222 is one of the main radionuclides released to air by cement industries (UNSCEAR, 2000). Doses by inhalation result from the presence in air of dust particles containing radionuclides of the U-238 and Th-232 decay chains. The dominant component of inhalation exposure is the short-lived decay products of radon.

Radon is a radioactive transformation product of U-238, U-235, and Th-232 and it exists in various concentrations in all soils and minerals. Of all the radon isotopes, Rn-222 is of major radiological significance since its half-life of 3.82 days is long enough for it to accumulate in the homes unless they are constructed in ways that preclude entry of radon gas, or provisions are made to remove the radon (James, 2006).

Once radon accumulates in a home it will undergo radioactive transformation and the resulting transformation products are no longer gases but are solid particles, which, due to an electrostatic charge, become attached to dust particles that are inhaled by occupants, or the particles can be inhaled directly. Because they are electrically charged, the particles readily deposit in the lung, and since they have half-lives of the order of minutes or seconds their transformation energy is almost certain to be deposited in lung tissue. Radon transformation products (commonly called daughters) emit alpha particles with energies ranging from 6 to 7.69 MeV (James, 2006) and because alpha particles (as helium nuclei) are massive and highly charged, this energy is delivered in a huge jolt to the cellular structure of the surface of the bronchi and the lung, which damages and kills these cells. The body can tolerate and replace killed cells, but damaged lung tissue cells can replicate, and cellular defects may eventually lead to lung cancer (James, 2006). Therefore, the release of gaseous Rn-222 from building materials for example cement, may result in elevated levels of exposure to this radionuclide by those involved in the use of these materials potentially causing elevated health risks for example cancer (Brigden et al., 2002).

Many studies have been carried out on the radiological significance of NORMs in building materials. The outcomes of these findings are briefly stated below.

In a study aimed at determining the effect of long-term exposure to cement dust on lung function in non-smoking cement mill workers, (Meo et al., 2013) found out that long term exposure to cement dust outstandingly resulted in decreased pulmonary function. The findings also found out that cement mill workers whose exposure time was greater than 10 years showed a significant reduction in Forced Vital Capacity (FVC), Forced Expiratory Volume in one second (FEV_1), Peak Expiratory Flow (PEF) and Maximal Voluntary Ventilation (MVV) relative to their matched controls.

Ndontchueng et al., (2013) investigated Naturally Occurring Radionuclides in some six representative cement types commonly used in Cameroon as building material and found out that four out of the six types had specific activities of radium-226 exceeding the recommended value of 32 Bq/kg^{-1} and subsequently the absorbed dose rates in air were higher than the world average population-weighted value of 59 $nGyh^{-1}$ (UNSCEAR, 2000).

Kpeglo et al., (2011) assessed the natural radioactivity and its associated radiological hazards in five brands of cement (pozzolana exclusive) manufactured and used in building construction in Ghana. Results indicated a range Radium equivalent in the five studied cement types to be 61.72-139.60 Bq/kg. This maximum value (139.60 Bq/kg) of Radium equivalent was lower than the recommended of 370 Bq/kg (UNSCEAR, 2000). Additionally, the calculated hazard indices were all less than 1 which is considered the safe limit for use of such materials.

Adukpo et al., (2011) assessed NORM at Diamond cement factory and its effects in the environment. Results of the study revealed that the annual effective doses from soils and water were 0.094±0.041 mSv and water 0.180±0.080 mSv respectively. These values were found to be lower than the recommended ones and hence the factory activities did not pose health problems to the host communities. However, these values were expected to increase with longer period of operation.

Turhan, (2008) assessed natural radioactivity and radiological hazards in Turkish cement and its raw materials. He found out that the mean specific radioactivity of Ra-226 in some composite cement samples was higher than the world mean value, and the indoor absorbed dose rate in the cement types was 87.3 nGy/h slightly higher than the population-weighted average of 84 nGy/h. This was attributed to higher radioactivity values in some raw materials.

Mwaiselage et al., (2006) investigated acute respiratory health effects among cement factory workers in Tanzania and found out that out of 84 workers who completed the questionnaire and the ventilatory test, 51 were highly exposed while 33 were least exposed. The group that was highly exposed had significantly more acute respiratory symptoms such as acute cough, stuffy nose and shortness of breath than the low exposed group. This scenario was attributed to the high concentration of dust in the work environment as well as to specific components in the cement dust. This was because about 37.5% (9/12) of the respirable dust samples exceeded the occupational exposure limit (OEL) of 5 mg/m^3, whereas 54.5% (6/11) of the total dust samples exceeded the OEL of 10 mg/m^3.

2.8 Gamma Spectrometry

The activity of gamma-emitting radionuclides present in the environmental samples can be determined using gamma spectrometric system based on the analysis of the energies and the peak areas of the gamma lines. This technique allows the identification and the quantification of the radionuclides since gamma photons are emitted at sharp energies which characterize each radionuclide allowing easy identification of radionuclides quantitatively and qualitatively (Radiation Protection Division, 2004).

The samples of different environmental media soil, water, vegetation, etc., are measured to determine background levels of radiation, or to assess the levels of contamination as a consequence of manmade radioactivity (Gordon, 2008). The radionuclides usually measured by gamma spectrometry are terrestrial radionuclides K-40, U-238, Th-232 and cosmogenic radioisotopes. Uranium-238 and Th-232 are accompanied by their daughter radionuclides. Gamma spectrometry of environmental media poses a number of challenges. This is due to the fact that the activity levels are quite low and if statistically better results are required, it needs long counting times while minimizing the background radioactivity levels around spectrometer. In addition, annihilation peaks and fluorescence X-rays contribute in the background. Any activity in the environmental sample itself must be detected above the background activity. There lie also a large number of mutual spectral interferences between many radionuclides in the decay series of uranium and thorium (Gordon, 2008).

Several applications with high purity germanium (HPGe) detector spectra entail identifying particular gamma rays with specific nuclides. The sharp peaks in the HPGe spectra together with a precise energy calibration, enable a unique determination of the nuclides in a sample[3]. The CANBERRA HPGe/ computer-based gamma spectroscopy systems identify nuclides through peak searches of spectra and scans of standard as well as user-generated nuclide libraries using different software such as the Genie 2000 that is capable of resolving overlapping peaks into individual components[4].A schematic diagram of the HPGe detector is shown in Figure 2.5 while the block diagram, is shown in Figure 2.6.

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[4] http://www.canberra.com/literature/fundamental-principles/pdf/Spectrum-Analysis.pdf

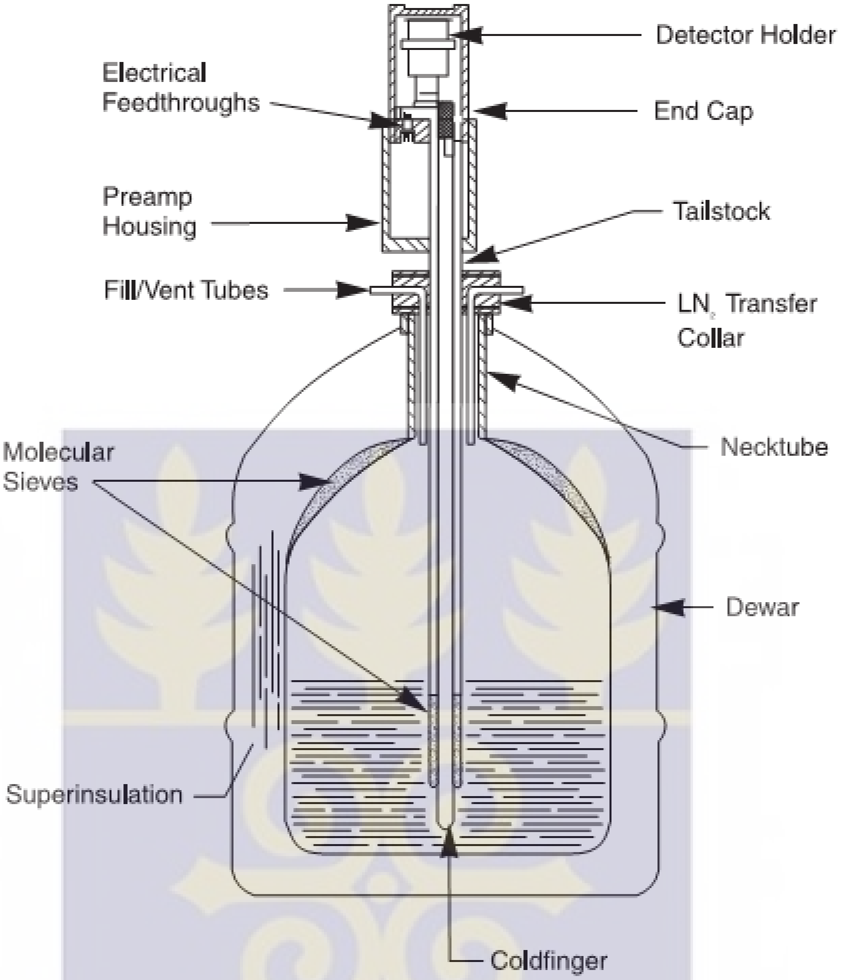

Figure 2.5: Model 7500SL Vertical Dipstick Cryostat[5]

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[5] http://www.canberra.com/literature/fundamental-principles/pdf/Gamma-Xray-Detection.pdf

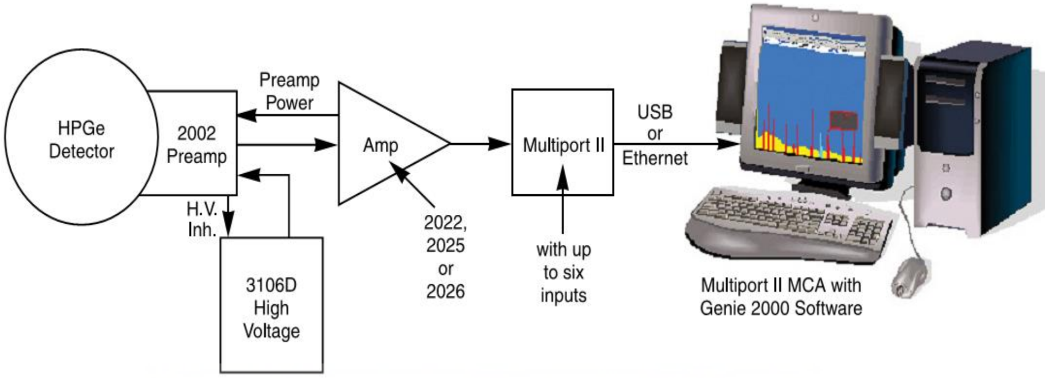

Figure 2.6: Detector and analog MCA Configuration[6]

When a gamma photon enters a detector, it interacts with the detector material by ionization process and deposits its energy in the detector volume in the form of an electric charge which in turn generates an electric signal. The electric signal is converted to a pulse by a preamplifier connected to the detector and is then amplified in the amplifier. Further amplification is done to the pulse to give it shape and reduce the electronic noise before being sent to the Multi-Channel Analyzer (MCA). The MCA sorts out the pulses into full energy peaks that correspond to gamma energy lines that are characteristic of specific radionuclides (Khandaker, 2011).

2.9 Secular Equilibrium

Secular equilibrium occurs in a radioactive decay chain if the half-life of the parent radionuclide is much greater than that of the daughter product (Cember & Thomas, 2009; James, 2006). In such a situation, the decay rate of the patent, and hence the production rate of the daughter is approximately constant since the half-life of the parent is very long

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[6] http://www.canberra.com/literature/fundamental-principles/pdf/Basic-Counting-System.pdf

compared to the timescales being considered. The quantity of the daughter radionuclide builds up until the number of daughter atoms decaying per unit time becomes equal to the number being produced per unit time and the quantity of the daughter radionuclide then reaches a constant or the equilibrium value (Cember and Thomas 2009). For example, the build-up of Rn-222 from the transformation of Ra-226 in the U-238 decay series is a good example of secular equilibrium. In this case the activity of the product (Rn-222) will increase until it is the same (99%) as that of the parent and this happens after about 6.7 half-lives of the product nuclide (James, 2006). The transformation and attainment of secular equilibrium between Rn-222 and Ra-226 is further illustrated in Figure 2.7

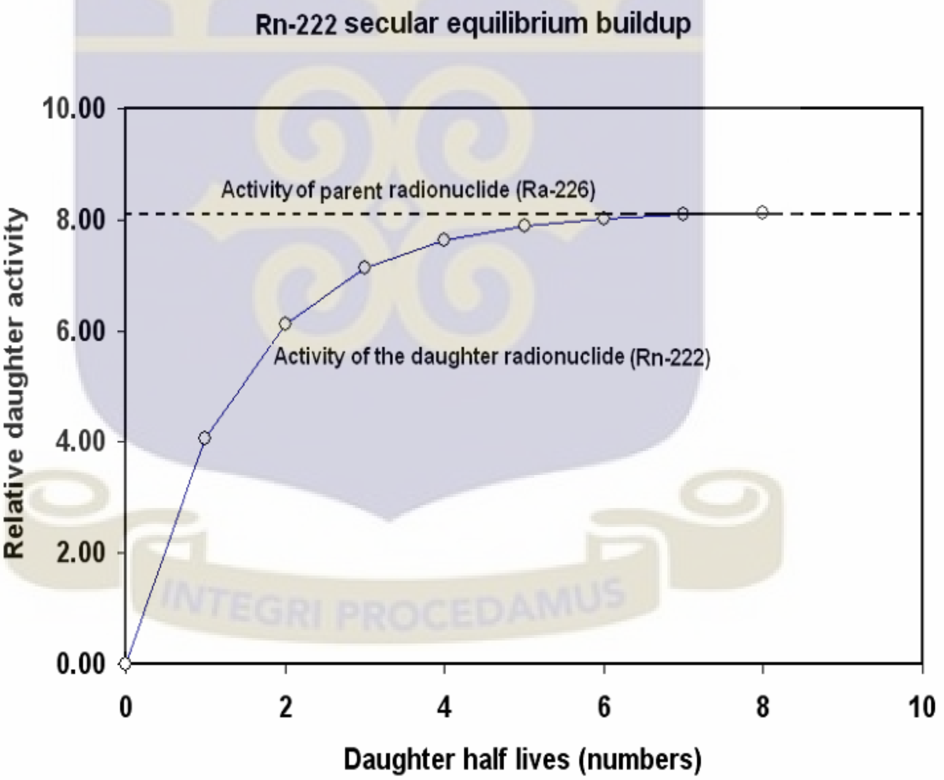


Figure 2.7: Secular equilibrium showing buildup of a very short-lived daughter radionuclide from a very long-lived parent radionuclide. The activity of the parent radionuclide remains constant

Secular equilibrium phenomenon is, thus, used to measure the activities of terrestrial radionuclides U-238 and Th-232 accompanied by their daughter radionuclides respectively as well as cosmogenic radionuclides. The daughter radionuclides of U-238 and Th-232 that emit gamma rays are shown in Appendix I.

2.10 Atomic Absorption Spectroscopy (AAS)

Atomic absorption is defined as the absorption of light by atoms (Evans et al., 1998). Figure 2.8 shows a simplified energy-level diagram where E_0 represents the ground state in which the electrons of a given atom are in their lowest energy level and E_1, E_2, E_3 etc. represent higher excited energy levels

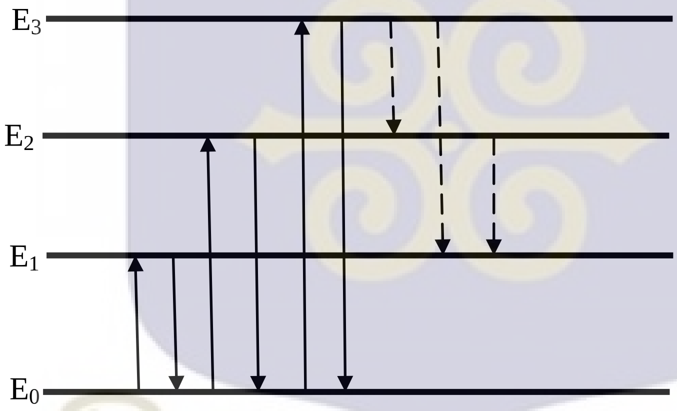


Figure 2.8: Energy-level diagram

A transition between two quantized energy levels for example from E_0 to E_1 corresponds to the absorption of radiant energy given by Equation (2.1) while the transition from higher energy levels to lower energy levels (indicated by full lines) say E_1 to E_0, corresponds to the emission of radiation of frequency ν.

$$\Delta E = E_1 - E_0 = h\nu = \frac{hc}{\lambda} \tag{2.1}$$

Where c is the velocity of light, h is the Planck's constant, ν is the frequency and λ is the wavelength of the radiation absorbed.

Atomic absorption corresponds to transitions from lower to higher energy states and thus, the degree of absorption depends on the population of the lower level. When thermodynamic equilibrium has prevailed, the population of a given level is determined by Boltzmann's law (Evans et al., 1998). The population of the excited levels is generally very small compared to that of the ground state (that is, the lowest energy state peculiar to the atom) and therefore, absorption is greatest in lines resulting from transitions from the ground state i.e. resonance lines (Evans et al., 1998).

Atomic Absorption Spectroscopy works on the principle that if light of the resonance wavelength is passed through a flame containing the atoms in the ground state, then part of the light will be absorbed and the extent of absorption will be proportional to the number of ground state atoms present in the flame (Jeffery et al., 1989). For atomic absorption to occur, light of the correct wavelength (energy) is absorbed by ground -state electrons, promoting them to a higher, excited state. The intensity of the light leaving the analytes is therefore diminished. The amount by which it is diminished is proportional to the number of atoms that were absorbing it (Evans et al., 1998). In atomic absorption spectroscopy, the absorbance A is given by the logarithmic ratio of the intensity of incident light signal I_0 to that of the transmitted light I_t as shown in Equation (2.2) (Jeffery et al., 1989).

$$A = \log\left(\frac{I_0}{I_t}\right) = K\,L\,N_0 \qquad (2.2)$$

Where,

N_0 is the concentration of atoms in the flame (number of atoms per mL)

L is the path length through the flame (cm)

K is a constant related to the absorption coefficient

It can be shown that K and hence A, are proportional to atom (analyte) concentration, and the plot of absorbance against atom concentration is a straight line for small values of A (Evans et al., 1998; Jeffery et al., 1989).

Figure 2.9 shows a schematic disposition diagram for Atomic Absorption Spectroscopy (AAS). Only major components have been included.

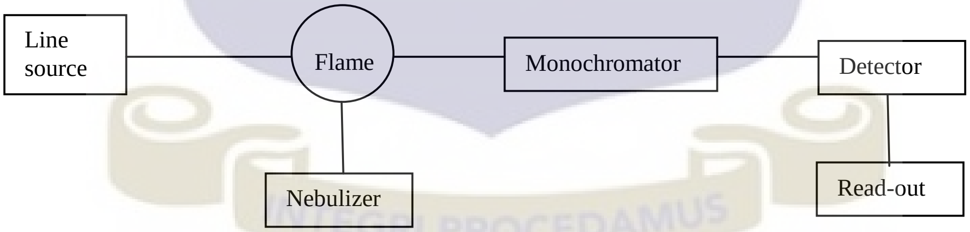


Figure 2.9: Instrumentation of AAS

For AAS the resonance line source is placed in line with the detector. The functions of each component are briefly discussed below (Jeffery et al., 1989).

Nebulizer: This is used to convert the test solution into gaseous atoms.

Monochromator: In AAS, the function of the monochromator is to isolate the resonance line from all non-absorbed lines emitted by the radiation source.

Detector: In atomic absorption spectrometers, the detectors consist of photomultipliers to improve spectral sensitivity. The output from the detector is fed to suitable read-out system that may include; meters, chart recorders and digital displays.

Resonance Line Sources: The source for atomic absorption is a hollow cathode lamp that consists of a cathode and anode enclosed within a glass tube and filled with a low pressure of Ne or Ar (Figure 2.10).

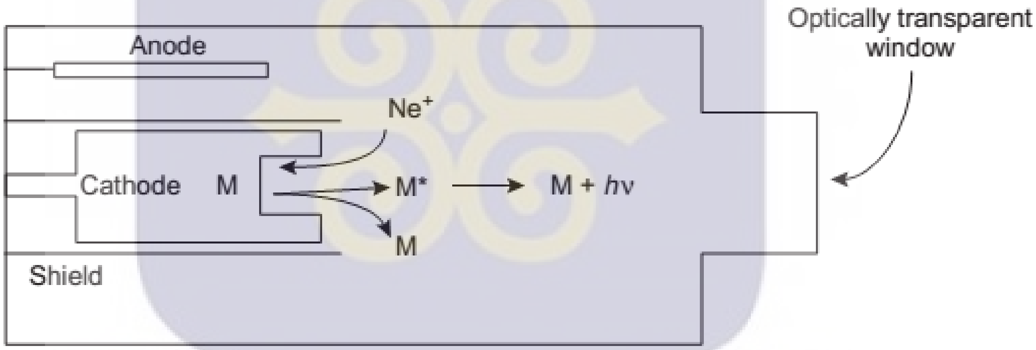


Figure 2.10: Schematic diagram of a hollow cathode lamp. *Source:* (David, 2000).

When a potential is applied across the electrodes, the filler gas is ionized and the positively charged ions collide with the negatively charged cathode, dislodging, or sputtering, atoms from the cathode's surface. The sputtered atoms in the excited state then emit radiation characteristic of the metal from which the cathode was manufactured (David, 2000). Multi-element lamps are available in which the cathodes are made from alloys (Jeffery et al., 1989).

2.11 Trace Elements

From the geochemical point of view, trace elements are metals whose concentrations are less than 1000 ppm or whose percentages in rock composition do not exceed 0.1% (Zovko & Romic, 2011). Trace metals occur naturally in rocks and soils, but increasingly higher quantities of metals are being released into the environment by anthropogenic activities (Zovko & Romic, 2011; Raikwar et al., 2008). One of the major routes from these anthropogenic activities is the rapid industrialization including dust emissions from the cement production and its heavy metal contamination of the environment (Ogunkunle & Fatoba, 2013).

Various terms like heavy metals, metalloids and microelements are the most commonly encountered in ecological studies when referring to trace elements. In particular heavy metal refers to a group of 53 metals with density higher than 5 g/cm^3 (Zovko & Romic, 2011) According to (Raikwar et al., 2008), heavy metals can be classified into four major groups on their health importance. These groups are ;

i. **Essential:** Cu, Zn, CO, Cr, Mn and Fe . These metals also called micronutrients (Reeves & Baker, 2000) and are toxic when taken in excess of requirements (Monni et al., 2000; Blaylock & Huang, 2000).

ii. **Non essential:** Ba, Al, Li and Zr

iii. **Less toxic** : Sn and Al and

iv. **Highly toxic** : Hg, Cd and Cr.

Other heavy metals such as Ni, As, and Pb pose a number of hazards to humans since they are also potent carcinogenic and mutagenic (Ravichandran, 2011; Raikwar et al., 2008).

Heavy metals are non-biodegradable and persistent environmental contaminants, which may be deposited on the soil surfaces and then adsorbed into tissues of vegetables (Hong-gui, et al., 2012). Soils are regarded as the ultimate sink for heavy metals discharged into the environment (Ogunkunle & Fatoba, 2013) and plants take up heavy metals from the tissue parts exposed to the air in polluted environment as well as from contaminated soil (Hong-gui et al., 2012). Soil pollution is one of the most serious problems in the world, with long term consequences on human life (Ene et al., 2011). In recent years, with the rapid development of industry, various dangerous pollutants such as heavy metals (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Se, V, and Zn) have been released due to production, smelting and tailings, and got deposited in soils around industrial areas causing serious pollution and soil quality degradation (Ata et al., 2013).

Studies have shown that heavy metals are potentially toxic to crops, animals and humans when contaminated soils are used for crop production. This is because heavy metals are easily accumulated in vital organs to threaten crop growing and human health (Liang et al., 2011). Humans and animals that consume such crops are also prone to potential toxicity (Ogunkunle & Fatoba, 2013).

Heavy metals may enter the human body through food, water, air, or absorption through the skin when they come in contact with humans in agriculture and in manufacturing, pharmaceutical, industrial, or residential settings (Ravichandran, 2011). However, the food chain contamination is one of the important pathways for the entry of these toxic pollutants into the human body (Kodom et al., 2012). This is because of consumption of plants and vegetables grown in polluted areas (Ata et al., 2013).

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues (Ata etal., 2013). Heavy metals rank high amongst the chief contaminants of leafy vegetables and medicinal plants because they are non-biodegradable and thus can cause serious health hazards in humans and animals (Ajasa et al., 2004). Heavy metal contamination in vegetables may pose a direct threat to human health, and it is one of a range of important types of contaminants that can be found on the surface and in the tissues of fresh vegetables (Chiroma et al., 2012).

Some of the health effects of the heavy metals considered in this study are briefly discussed in the next subsections.

2.11.1 Cadmium (Cd)

Cadmium is a soft, silvery gray metal that is malleable and ductile, similar to zinc. In nature, essentially all cadmium exists as seven stable isotopes and one radioactive isotope. The seven stable isotopes and their approximate abundances are cadmium-106 (1.3%), cadmium-108 (0.9%), cadmium-110 (12%), cadmium-111 (13%), cadmium-112 (24%), cadmium-114 (29%), and cadmium-116 (7.5%) while the primary radioactive isotope, is cadmium-113, that comprises about 12% of natural cadmium and has an extremely long half-life (Peterson et al., 2007). Nine major radioactive isotopes of cadmium exist, of which only three – cadmium-109, cadmium-113, and cadmium-113m – have half-lives long enough to warrant potential concern because the half-lives of the other six are less than 45 days. The radioactive properties of key cadmium isotopes are shown in Table 2.5.

Of the heavy metals present in cement dust, the presence of elevated concentrations of the cadmium is of greatest concern because of its toxicity and ability to accumulate in soils as well as bioaccumulate in plants and animals (Brigden et al., 2002). There is a clear association between the cadmium concentration in soil and in the plants grown on that soil (Brigden et al., 2002). The accumulation of cadmium in the food chain has important implications for human exposure (Brigden et al., 2002).

Table 2.5: Radioactive properties of key Cadmium isotopes (Peterson et al., 2007)

Isotope	Half-life *(yr)*	Natural Abundance *(%)*	Specific Activity *(Ci/g)*	Decay mode	Radiation Energy *(MeV)*		
					α	β	γ
Cd-109	1.3	<<1	2,600	EC	-	0.083	0.026
Cd-113	9.3×10^{15}	12	0.34 trillionth	β	-	0.093	-
Cd-113m	14	<<1	240	β	-	0.019	-

EC= electron capture, *MeV*= million electron volts

Human exposure to Cadmium occurs mainly from consumption of contaminated food, active and passive inhalation of tobacco smoke and inhalation by workers in the non-ferrous metal industry (WHO, 2007a). Gastrointestinal absorption from food or water is the principal source of internally deposited cadmium in the general population (Peterson et al., 2007), with the liver and kidney tissues being the two main sites of cadmium storage(WHO, 2007a). While it concentrates in the liver and kidneys, cadmium can also deposit in other organs and tissues depending on its chemical form.

Chronic exposure to Cadmium may result in emphysema and chronic bronchitis while repeated low exposures may also cause permanent kidney damage, leading to kidney stones and other health problems (Peterson et al., 2007). More effects of human exposure to cadmium have been reported. For example painful bone disorders, including osteomalacia, osteoporosis and spontaneous bone fracture, have been observed in humans chronically exposed to cadmium in food (WHO, 2007a), high-level occupational exposure is associated with lung changes, primarily characterized by chronic obstructive airway disease (Straif et al., 2009). Additionally, the International Agency for Research on Cancer (IARC) has classified cadmium and cadmium compounds as carcinogenic to humans(Group 1), meaning that there is sufficient evidence for their carcinogenicity in humans (IARC, 1993).

2.11.2 Lead (Pb)

Lead is a metal belonging to group IV and period 6 of the periodic table with atomic number 82, atomic mass 207.2, density 11.4 g cm^{-3}, melting point 327.4ºC, and boiling point 1725ºC (Wuana & Okieimen, 2011). It is a naturally occurring, bluish gray metal usually found as a mineral combined with other elements, such as sulphur (i.e., PbS, $PbSO_4$), or oxygen ($PbCO_3$), and ranges from 10 to 30 mg kg^{-1} in the earth's crust

(Wuana & Okieimen, 2011). Typical mean Pb concentration for surface soils worldwide averages 32 mg kg^{-1} and ranges from 10 to 67 mg kg^{-1} (Kabata & Pendias, 2001).

Inhalation and ingestion of Lead are the two routes of exposure to humans and the effects from both are the same. Lead accumulates in the body organs (i.e., brain), which may lead to poisoning or even death. The gastrointestinal tract, kidneys, and central nervous system are also affected by the presence of lead. Children exposed to lead are at risk for impaired development, lower IQ, shortened attention span, hyperactivity, and mental deterioration, with children under the age of six being at a more substantial risk (Wuana & Okieimen, 2011). Adults usually experience decreased reaction time, loss of memory, nausea, insomnia, anorexia, and weakness of the joints when exposed to Lead (Wuana & Okieimen, 2011).

Lead is not an essential element. It is well known to be toxic and its effects have been more extensively reviewed than the effects of other trace metals. Lead can cause serious injury to the brain, nervous system, red blood cells, and kidneys (Baldwin & Marshall, 1999). Exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Various effects occur over a broad range of doses, with the developing young and infants being more sensitive than adults. Lead poisoning, which is so severe as to cause evident illness, is now very rare. Lead performs no known essential function in the human body, it can merely do harm after uptake from food, air, or water. Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, but also in entire food chains. Generally, plants do not absorb or accumulate lead in the fruiting parts of vegetable and fruit crops. However, it is possible for some lead to be taken up that might lead to higher concentrations in leafy vegetables e.g. lettuce and on the surface of root crops e.g. carrots. As mentioned earlier, plants do not take up large quantities of soil lead and hence, the lead levels in soil that are considered safe for plants, will be much higher than soil lead levels where eating of soil is a concern.

Chronic exposure to Lead results in birth defects, mental retardation and potential toxic effects on fetus (Ata et al., 2013). According to Zhuang et al., (2009), Lead is considered potential carcinogen and is associated with etiology of a number of diseases, especially cardiovascular, kidney, blood, nervous, and bone diseases.

2.11.3 Arsenic (As)

Arsenic is a widely distributed metalloid, occurring in rock, soil, water and air (Järup, 2003). Arsenic occurs everywhere in the environment (in soils, plants, animals, and humans) both inorganic and organic forms; inorganic forms being most abundant (Peterson et al., 2007). Inorganic arsenic is not only associated with other metals contained in both igneous and sedimentary rocks but also occurs in combination with many other elements, especially oxygen, chlorine, and sulfur. Weathering of rock is the major natural source of inorganic arsenic, and it is also released by human activities (Peterson et al., 2007). Inorganic arsenic is present in groundwater used for drinking in several countries all over the world whereas organic arsenic compounds (such as arsenobetaine) are primarily found in fish, which thus may give rise to human exposure (WHO, 2001). Smelting of non-ferrous metals and the production of energy from fossil fuel are the two major industrial processes that lead to arsenic contamination of air, water and soil, smelting activities being the largest single anthropogenic source of atmospheric pollution (Järup, 2003). Other sources of contamination are the manufacture and use of arsenical pesticides and wood preservatives (Straif et al., 2009).

The primary organs affected when Arsenic is inhaled or ingested are the skin, lung and cardiovascular system (Peterson et al., 2007). The general population is exposed to arsenic mainly via intake of food and drinking water. However, contaminated soils such as mine-tailings are also a potential source of arsenic exposure (WHO, 2001).

Ingested, dissolved arsenic compounds are readily absorbed (80-90%) through the gastrointestinal tract and distributed in the blood to the liver, kidney, lung, spleen, aorta, and skin (Peterson et al., 2007). Depending on the amount ingested, arsenic can be beneficial or adverse. The acute lethal dose to humans can be about 2 to 20 mg/kg body weight per day (mg/kg-day) (Peterson et al., 2007).

Inorganic arsenic is acutely toxic and intake of large quantities leads to gastrointestinal symptoms, severe disturbances of the cardiovascular and central nervous systems, and eventually death (Järup, 2003). In survivors, bone marrow depression, haemolysis, hepatomegaly, melanosis, polyneuropathy and encephalopathy may be observed. Ingestion of inorganic arsenic may induce peripheral vascular disease, which in its extreme form leads to gangrenous changes.

Populations exposed to arsenic via drinking water show excess risk of mortality from lung, bladder and kidney cancer, the risk increasing with increasing exposure (Järup, 2003). Ingesting high doses of arsenic irritates the stomach and intestines, with symptoms including nausea, vomiting, diarrhea and liver swelling (Peterson et al., 2007) while ingesting small amounts for long period of time produces chronic effects such as increased risk of skin cancer and other skin lesions (Järup, 2003), damage to peripheral nerves, cardiovascular system effects, hair and appetite loss, and mental disorders (Peterson et al., 2007).

Studies on various populations exposed to arsenic by inhalation, such as smelter workers, pesticide manufacturers and miners in many different countries consistently demonstrate an excess lung cancer. Although all these groups are exposed to other chemicals in addition to arsenic, there is no other common factor that could explain the findings. The lung cancer risk increases with increasing arsenic exposure in all relevant studies, and confounding by smoking does not explain the findings (Järup, 2003).

The evaluation by (WHO, 2001) concludes that arsenic exposure via drinking water is causally related to cancer in the lungs, kidney, bladder and skin, the last of which is preceded by directly observable precancerous lesions.

2.11.4 Chromium (Cr)

Chromium is a first-row d-block transition metal of group VIB in the periodic table with the following properties: atomic number 24, atomic mass 52, density 7.19 g cm^{-3}, melting point 1875ºC, and boiling point 2665ºC (Wuana & Okieimen, 2011). Chromium is less likely to occur naturally in elemental form but in compounds. The major sources of Cr contamination include industrial disposal of Cr containing wastes (tanning factories, steel works, wood preservation, etc.), releases from electroplating processes, and artificial fertilizers (Tuzen & Soylak, 2007).

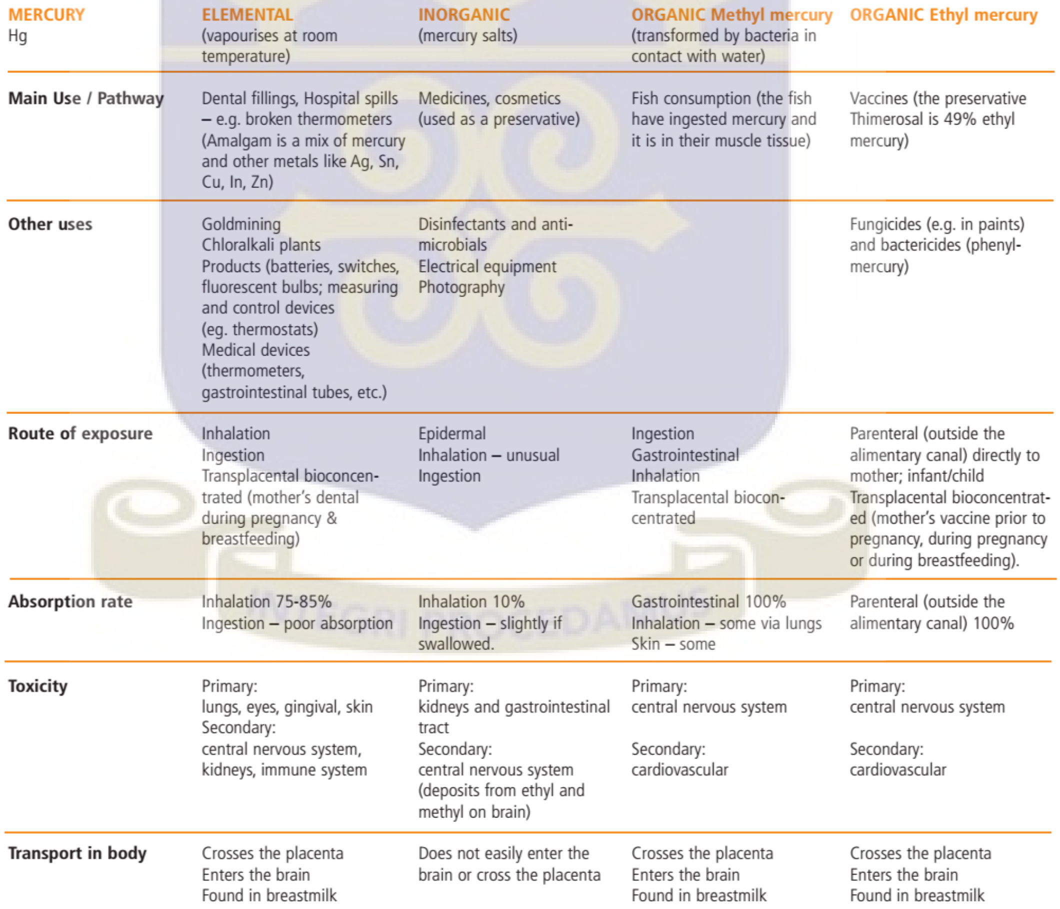
Chromium can be transported by surface run off to surface waters in its soluble or precipitated form. Soluble and un-adsorbed chromium complexes can leach from soil into groundwater and the leachability of Cr (VI) increases as soil pH increases (Wuana & Okieimen, 2011). Most of Cr released into natural waters is particle associated, and is ultimately deposited into the sediment (Smith & Brauning, 1995). Chromium is associated with allergic dermatitis in humans and elevated levels are responsible for lung, renal and cardiovascular diseases (Ata et al., 2013).

2.11.5 Mercury (Hg)

Mercury metal occurs naturally and its primary store is within the planet. According to (WHO, 2007b), Mercury releases are from volcanic activity, weathering of rocks, water movements, biological processes, combustion of fossil fuels (specially coal), electricity-generating power stations, gold and mercury mining, manufacture of cement, pesticides, chlorine, caustic soda, mirrors and medical equipment, industrial leaks, dentistry, waste and corpse incineration, and remobilization of historic sources: mercury in soil, sediment, water, landfill, waste.

Mercury exists in different forms (refer to Table 2.6) most of which are toxic to humans, wild-life and ecosystems. Although, exposure to high doses of mercury can be fatal to humans, relatively low doses of mercury containing compounds can also have serious adverse neurodevelopmental impacts. These impacts have been linked with possible harmful effects on the cardiovascular, immune and reproductive systems (European Commission., 2005). Additionally, mercury and its compounds affect the central nervous system, kidneys, and liver and can disturb autoimmune processes; cause tremors, impaired vision and hearing, paralysis, insomnia, and emotional instability[7].

Table 2.6: Use, exposure routes and toxicity of mercury and its compounds



MERCURY Hg	**ELEMENTAL** (vapourises at room temperature)	**INORGANIC** (mercury salts)	**ORGANIC Methyl mercury** (transformed by bacteria in contact with water)	**ORGANIC Ethyl mercury**
Main Use / Pathway	Dental fillings, Hospital spills – e.g. broken thermometers (Amalgam is a mix of mercury and other metals like Ag, Sn, Cu, In, Zn)	Medicines, cosmetics (used as a preservative)	Fish consumption (the fish have ingested mercury and it is in their muscle tissue)	Vaccines (the preservative Thimerosal is 49% ethyl mercury)
Other uses	Goldmining Chloralkali plants Products (batteries, switches, fluorescent bulbs; measuring and control devices (eg. thermostats) Medical devices (thermometers, gastrointestinal tubes, etc.)	Disinfectants and anti-microbials Electrical equipment Photography		Fungicides (e.g. in paints) and bactericides (phenyl-mercury)
Route of exposure	Inhalation Ingestion Transplacental bioconcentrated (mother's dental during pregnancy & breastfeeding)	Epidermal Inhalation – unusual Ingestion	Ingestion Gastrointestinal Inhalation Transplacental bioconcentrated	Parenteral (outside the alimentary canal) directly to mother; infant/child Transplacental bioconcentrated (mother's vaccine prior to pregnancy, during pregnancy or during breastfeeding).
Absorption rate	Inhalation 75-85% Ingestion – poor absorption	Inhalation 10% Ingestion – slightly if swallowed.	Gastrointestinal 100% Inhalation – some via lungs Skin – some	Parenteral (outside the alimentary canal) 100%
Toxicity	Primary: lungs, eyes, gingival, skin Secondary: central nervous system, kidneys, immune system	Primary: kidneys and gastrointestinal tract Secondary: central nervous system (deposits from ethyl and methyl on brain)	Primary: central nervous system Secondary: cardiovascular	Primary: central nervous system Secondary: cardiovascular
Transport in body	Crosses the placenta Enters the brain Found in breastmilk	Does not easily enter the brain or cross the placenta	Crosses the placenta Enters the brain Found in breastmilk	Crosses the placenta Enters the brain Found in breastmilk

Source: http://www.env-health.org/IMG/pdf/How_toxic_is_Hg.pdf

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[7] http://www.env-health.org/IMG/pdf/How_toxic_is_Hg.pdf

2.12 Joint Toxicity

Joint toxicity refers to the outcome of two or more chemicals acting together. The three categories of joint toxicity are: greater than additive (synergism and potentiation); additive (no interaction); and less than additive (antagonism and inhibition). Additivity is the default assumption for evaluating health effects of multiple chemicals. Toxicological interactions can either increase or decrease the apparent toxicity of a mixture relative to that expected from simple addition (Peterson et al., 2007). A few studies have investigated the effects of three metals in combination, but most have studied pairs as indicated in Table 2.7). The lead-cadmium pair has been studied most, including in human epidemiological studies and oral animal studies.

Table 2.7: Joint Toxicity for Selected Organ/System Endpoints following Ingestion

End point	**Arsenic on**			**Cadmium on**			**Chromium on**			**Lead on**		
	Cd	Cr	Pb	As	Cr	Pb	As	Cd	Pb	As	Cd	Cr
Nervous system			↑			↑				↑	↔	
Kidney	↔	↓	↓	↔	↔	↓	↓	↔		↓	↔	
Hematological system	↓		↓	↓		↓				↓	↔	
Reproductive: male	↓			na		↑	na			na	↑	
Skin	na	na	na		na	na	↑	na	na		na	
Cancer	na	na	na		na	na	↑	na	na		na	na

↑ = interactive effects are more than additive or one metal enhances an effect induced only by the other metal; ↓ = interactive effects are less than additive or one metal protects against an effect induced only by the other metal; ↔ = results are inconclusive or do not suggest that effects are more or less than additive; blank = relevant information is not available; na = not applicable because oral exposure to this metal does not cause the indicated health endpoint.

Source: Peterson et al., (2007)

For neurological effects, the predicted direction of joint toxic action for the mixture is greater than additive for several pairs (Arsenic-Lead, Cadmium-Lead, Lead-Arsenic), which indicates the health hazard of those mixtures might be somewhat greater than that estimated by endpoint-specific hazard indices for this endpoint. The same higher-than-additive effect is indicated for the male reproductive system (testes) for cadmium and lead acting on each other. In contrast, for effects on the kidney and blood, the predicted direction of joint toxic action is less than additive for several metal pairs, indicating that the health hazard might be somewhat less than estimated by endpoint-specific hazard indices (Peterson et al., 2007). The primary organs/systems affected following ingestion of Arsenic, Cadmium, Chromium and Lead are shown in Figure 2.11

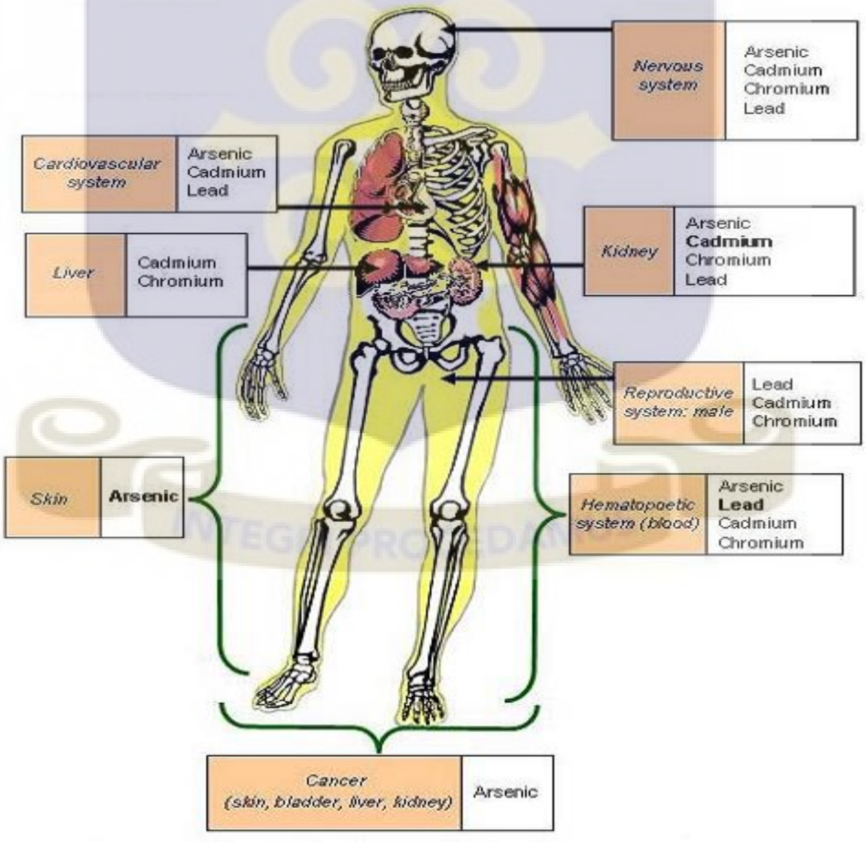

Figure 2.11: Primary target organs for different toxic metals
Source: (Peterson et al., 2007)

2.13 Possible Natural Ways to Eliminate Toxic Heavy Metals

Heavy metals can generally be removed from the body by use of chelating agents in form of drugs or foods that are specific to particular heavy metals. Chelating agents create a chemical bond with heavy metals in the body making them less active (Ravichandran, 2011)

Ravichandran (2011) suggests the following chelating agents in the form of drugs that are given orally, intramuscularly, or intravenously; Ethylene Diamine Tetraacetic Acid (EDTA) and dimercaprol (also known as BALor British AntiLewisite).

Other oral chelating agents used as alternatives to BAL are 2,3-demercaptosuccinic acid (DMSA), dimercaptopropanesulfonate (DMPS) and Dpenicillamine. Ravichandran further recommended the use of the following as natural chelation at home; Cilantro, Chlorella, Garlic, Malic acid (found in unripe fruit, salt and vinegar, potato chips as well as sour candies), Raw apple cider vinegar and pectinis (found in apples, bananas, grapes, okra, beets, carrots and the pith in all citrus fruits).

CHAPTER THREE

Materials and Methods

3.1 Study Area

The research was conducted at Pozzolana Ghana Limited (PGL) located in Gomoa Mprumem, Apam in the central region of Ghana. The geographical location of the facility is 5.361831ºN and 0.742215ºW. The location of Gomoa in Ghana is shown in Plate 3.1 together with distribution of sampling points.

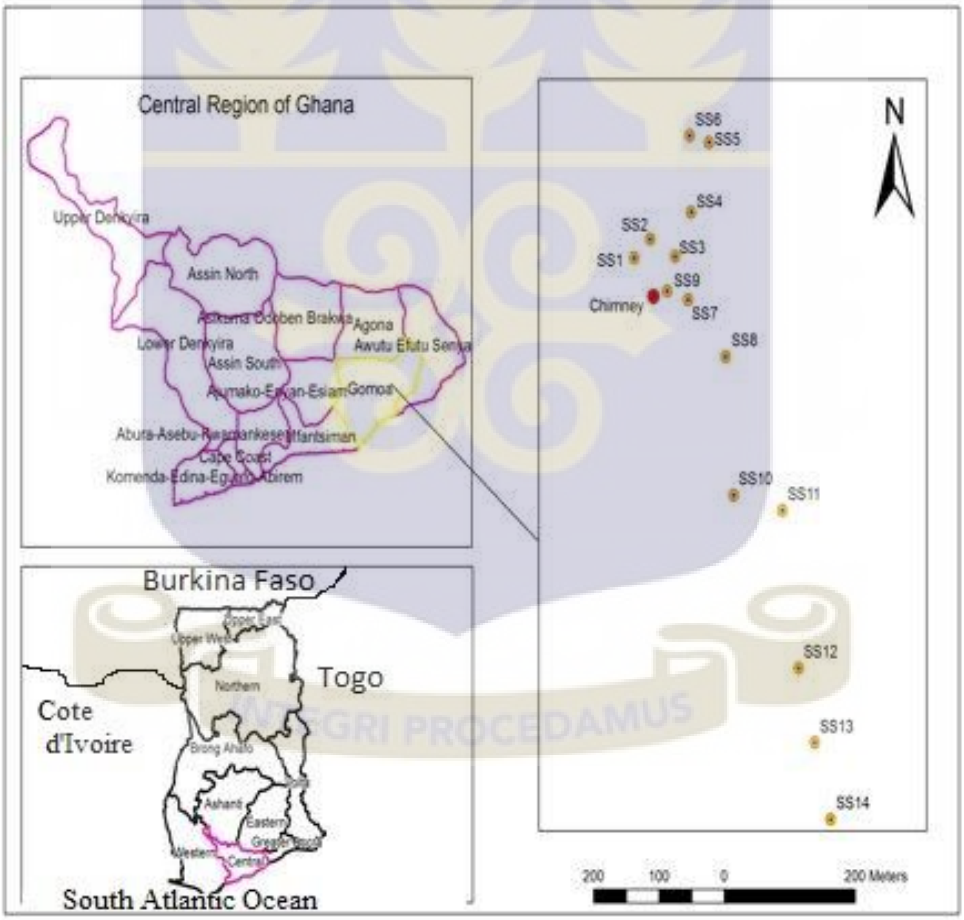

Plate 3.1: Location of Gomoa and sample collection points

3.2 Sample Collection and Characterization

3.2.1 Soil Samples

In order to assess the environmental impact (possible soil contamination with heavy metals and radionuclides) from the activities of the factory, a total of 62 soil samples representing 14 sampling points were carefully collected from the upper horizon (approximately 15 cm depth of top soil) of soils within and around the factory premises at varying distances. The soil sampling strategy adopted was random sampling suggested by the International Atomic Energy Agency, (2004). Sixty (60) soil samples were collected from open fields (gardens) since the factory is surrounded with thick cattle grass while two samples (2) were collected from the compound. To avoid any possible inclusion of possible radionuclides from fall out, the upper surface soil was first removed and the samples were taken using a shovel. In every garden, a total of five samples each of about 1 kg were collected from different locations and independently placed in water tight plastic bags, labelled and transported to the laboratory. Since one shovel was used for sampling in all the gardens, to avoid cross contamination, after each sampling in any garden, the following procedures were followed to decontaminate the shovel.

- Rinse with potable water;
- Scrub with a brush to remove soil and residual contamination material;
- Double rinse with potable water;
- Wash or rinse with acetone;
- dry with a lint-free paper towel.

3.2.2 Palm Kernel Shells (PKS) and Raw Clay Samples

Palm kernel shells and raw clay samples shown in Plates 3.2 (a) and (b) respectively were collected from the factory and placed in plastic bags before being transported to the analytical laboratory. These are part of the raw material input for production of Crystal cement.

Plate 3.2 (a): Palm Kernel Shells

Plate 3.2 (b): Raw Clay

3.2.3 Clay Pozzolana

The fine ground powder of clay Pozzolana (Plate 3.3) was collected from the factory, placed in water tight plastic bags and transported to the analytical laboratory.

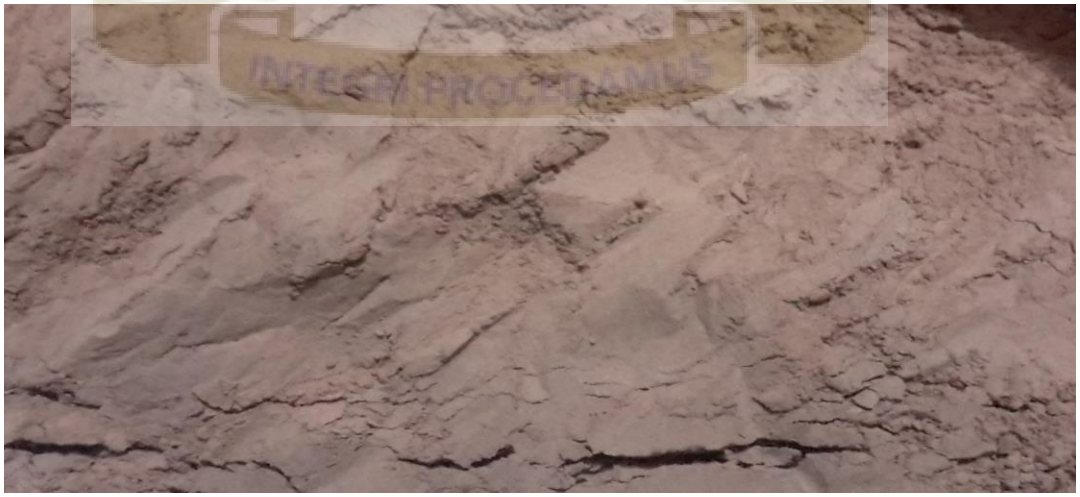

Plate 3.3: Clay Pozzolana powder

3.2.4 Cement Samples

A total of one hundred (100) cement samples representing Diamond cement (Portland limestone), Ghacem (Portland limestone), Dangote (Ordinary Portland) and WP (Ordinary Portland) were collected from different suppliers of cement in Ghana. For each cement type, twenty (20) samples each of about 5kg were collected and placed in water tight plastic bags before being transported to the analytical laboratory.

3.3 Sample Preparation

3.3.1 Soil and Clay Samples for Activity Concentration Measurements

The different soil samples collected from each garden were mixed together and homogenized to make one composite sample representing the whole garden. The composite samples were air dried for five days after removing the stones, pebbles, grass roots etc. The samples were crushed into small pieces using a manual hammer and dried again in a temperature controlled oven at 105 ^{o}C for 12 hours in order to remove the moisture content in the samples. To obtain the representative samples, the dried samples were thoroughly mixed, ground to fine powder using an electric grinder and passed through a sieve of mesh size of 500 µm. The samples were then packed into a plastic 1 litre Marinelli beaker, weighed and hermetically sealed with masking tape. The samples were stored for four weeks before counting so that secular equilibrium would be attained between the parent radionuclides (U-238 and Th-232) with their short lived progenies (Otoo et al., 2011).

3.3.2 Soil Samples for Heavy Metal Determination

For each prepared soil sample for radionuclide identification, a portion of each sample was placed in air tight plastic bag and reserved for elemental analysis.

Acid digestion method was used for preparation of samples for elemental determination. Ig of sieved soil was accurately weighed and transferred into a 100mL borosilicate beaker. About 25 mL of acqua regia prepared in the ratio of 1mL concentrated HCl to 3mL of concentrated HNO_3 was added to the beaker and covered with clingfilm and left for overnight. The contents were then placed on a hot plate and digested for 3 hours and then left to cool at room temperature. The cooled suspension was filtered into a 100mL measuring cylinder and topped up to the 50mL using distilled water. The filtrate was transferred to a plastic container ready to be analyzed. Two reference soil materials (Estuarine sediment-SRM 1646a and 114 ISE 4) were prepared and digested the same way as the actual samples.

3.3.3 Palm Kernel Shell Samples

The palm kernel shells were first manually sorted out to remove foreign particles such as dry leaves, grass and stones. The shells were then thoroughly washed and flushed using tap water with some added detergent to remove dirt and dust coated on the shells. The shells were air-dried for 4 days and later oven dried at 105^0C for 12 hours before being crushed into a fine powder using an electric grinder. The powder was then sieved through a 630μm mesh and a portion packed into a plastic 1 litre Marinelli beaker, weighed and hermetically sealed with masking tape. The sample was stored for four weeks before counting so that secular equilibrium would be attained. The remaining portion of the powder was kept in air-tight containers for elemental content analysis.

3.3.4 Clay Pozzolana and Cement Samples

All the four types of cement samples and clay Pozzolana were used without any processing since they were already in the powdered form. The samples were dried in a temperature-controlled furnace at 105ºC for 24 hours to remove moisture. After moisture removal, the samples were cooled in moisture-free atmosphere and passed through a 500 µm sieve. Clay Pozzolana was uniformly mixed with each type of Ordinary Portland Cement in the ratio of 1:3. The samples were packed into a plastic 1litre Marinelli beaker weighed and hermetically sealed. The sample containers were the same in size and geometry as the reference materials MBSS 2 used for calibrations. The sealed samples were also kept for four weeks before being analyzed. However, samples of mixed cement were analyzed immediately after sealing before being kept to attain secular equilibrium. This was to allow for determination of net count rate of Rn-222 at the time of sealing the sample container to be used for calculation of radon emanation coefficient from cement samples. A portion of clay pozzolana was kept in air-tight containers for elemental content analysis.

3.4 Instrumentation of the Gamma Spectrometry System for Activity Concentration Measurement

The detection and measurement of radionuclides in all the sample types was carried out by gamma spectrometry system using HPGe detector. The spectrometry system consisted of a Canberra high purity germanium (HPGe) connected to a Multi-Channel Analyzer (MCA). The detector specifications and performance data are provided below;

Detector Model: GX4020
Cryostat Model: 7500SL
Pre-amplifier Model: 2002CSL
Relative efficiency: 40%
Resolution: 2.0 keV (FWHM) at 1.33 MeV, 1.10 keV (FWHM) at 122 keV
Physical Characteristics
Geometry: Coaxial one open end, closed end facing window
Diameter: 60.5 mm
Length: 61.5 mm
Distance from window (outside): 6 mm

The equipment set up at the analytical laboratory is shown in Plate 3.4.

Plate 3.4: Set up of Gamma Spectrometry Equipment

3.4.1 Calibration of the Gamma Spectrometry System

a) Energy Calibration

Energy calibration of the detector was done to interpret the spectrum in terms of energy and this helped in radionuclide identification. The calibration was done because nuclear states have very well-defined energies and therefore, the energies of gamma rays emitted in state-to-state transitions are also very specific (Knoll, 2010). Energy calibration generally involves a means of determining the energy at a particular channel location of a spectrum. The energy calibration of the detector was done by use of a radioactive mixed standard MBSS 2. The standard was counted for 10 hours and the peaks were analysed using the Genie 2000 software. Following the spectrum analysis, the channel number/centroid of each radionuclide at its respective energy was determined and the results were used to generate a linear graph of energy versus channel number.

b) Efficiency Calibration of the Gamma Spectrometry System

The efficiency of a detector is a measure of how many pulses occur for a given number of gamma rays. The efficiency of detectors used in gamma analysis varies significantly with energy and depends on the following: energy of the incident gamma ray; the detector crystal (intrinsic); materials surrounding the crystal; source/sample - detector geometry; attenuation in the source matrix[8]. Therefore, each counting geometry requires an efficiency calibration, using a known standard in the same geometry which includes multiple energies. The detector efficiency was done using radionuclide mixed standard MBSS 2 with the following specifications: activity 41.02 kBq (tot.); Reference date:

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[8] http://www.canberra.com/literature/fundamental-principles/pdf/Spectrum-Analysis.pdf

20/3/2014. The radionuclides and their activities in the standard are shown in Appendix II. The standard was counted on the detector for 10 hours and the peaks at various energies of the radionuclide mixed standard analysed for the net counts. Following the determination of the present activity of the radionuclides in the mix from Equation (3.1), the efficiency of each gamma line was calculated from Equation (3.2).

$$A_{st(p)} = A_{o(st)} \times e^{-\lambda t} \tag{3.1}$$

$$\varepsilon = \frac{\text{Net count/area}}{A_{p(st)} \times p_{\gamma} \times T_c} \tag{3.2}$$

Where;

$A_{p(st)}$ is the present activity of the standard

$A_{o(st)}$ is the initial activity of the standard at the time of manufacture

t is the delay time

λ is the decay constant

p_{γ} is the emission probability of the gamma line

T_c is the counting time

ε is the efficiency of the gamma line

From the series of data pairs, a curve of efficiency versus energy was generated and fitted with the polynomial choice of fourth degree. The equation of the curve was then used to calculate efficiency at any energy in the calibrated energy range (60-2000 keV).

3.4.2 Sample Measurement by Gamma Spectrometry System

a) Background and sample Measurement

The background radioactivity levels at the laboratory were determined by counting five empty 1 litre Marinelli beakers filled with distilled water for 10 hours. The average counts obtained under each peak were then used to correct for the net area counts in each radionuclide. In order to determine the radionuclide contents in the samples, each prepared sample was placed on the High Purity Germanium detector and the gamma spectra was generated for the same time (10 hours) as for the background measurements to reduce the uncertainties in the net count.

b) Minimum Detectable Activity (MDA)

The MDA is defined as the smallest quantity of radioactivity that could be distinguished from the blank under specified conditions (Cember & Thomas, 2009). Determination of MDA for each nuclide in a sample is required in order that a measurement can be expected to correctly imply the presence, and correctly quantitatively assay the activity with a predetermined degree of confidence. Therefore, the calculation of Minimum Detectable Activity for a given nuclide, at the 95% confidence level, was determined based on Currie's derivation formula (Equation 3.3)[9].

$$\mathrm{MDA}(\mathrm{Bq/kg}) = \frac{2.71 + 4.66\,(\delta)}{T_c \times \varepsilon \times Y \times w_s} \tag{3.3}$$

Where;

δ is the standard deviation of the background during the time T_c (s) over the energy range of interest;

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[9] http://www.canberra.com/literature/fundamental-principles/pdf/Spectrum-Analysis.pdf

ε is the efficiency at the energy of interest

Y is the branching ratio

w_s is sample weight/mass

The above formulation takes into account both kinds of errors i.e. false positive (deciding there is sample activity when there is in fact none) and false negative (concluding there is no sample activity when there is some), and yields the smallest level of activity which can be detected with 95% confidence, while also having 95% confidence that "activity" is not detected falsely from a null sample. In this study the MDAs were calculated for K-40, U-238 and Th-232.

3.4.3 Analysis of Samples by Gamma Spectrometry System

The peaks of gamma emitting radionuclides from soil, cement, clay and PKS were analyzed using the Genie 2000 software from which the net count per second and corresponding error in counts were determined.

3.4.3.1 Determination of the Activity Concentration in Samples

Following the spectrum analysis, count rates for each detected photopeak and activity per unit mass (specific activity or radiological concentration) for each of the detected nuclides major of interest (Bi-214, Pb-214, Ac-228 and Bi-212) (Appendix I) was calculated using equation (3.4) (Beck et al., 1972).

$$A = \frac{N}{p_\gamma \times \varepsilon \times w_s \times T_c} \tag{3.4}$$

Where, A = Activity of the sample in Bq/kg

N = net counts per second,

= cps for the sample minus cps for background,

p_{γ} = emission probability

ε = The counting efficiency of the gamma energy

w_s = The net weight of the sample (in kg)

T_c = counting time

Each of these counting rates has its own standard deviation and therefore, the corresponding error e_A in all activity calculations was computed using equation (3.5).

$$e_A = A\sqrt{\left(\frac{\Delta N}{N}\right)^2 + \left(\frac{\Delta \varepsilon}{\varepsilon}\right)^2 + \left(\frac{\Delta p_{\gamma}}{p_{\gamma}}\right)^2 + \left(\frac{\Delta w_s}{w_s}\right)^2} \qquad (3.5)$$

Where;

ΔN, $\Delta \varepsilon$, Δp_{γ} and Δw_s are the respective errors in net count, efficiency of the gamma energy, emission probability and net weight of the sample.

The activity concentration of U-238 was taken as the average from activities of Pb-214 at 351.932 keV and Bi-214 at 609.312 keV while that of Th-232 was taken as the average of activities from Ac-228 at 911.204 keV and Bi-212 at 727.33 keV. In the U-238 series, the decay chain segment starting from radium (Ra-226) is radiologically the most important and, therefore, reference was made to Ra-226 instead of U-238 (Turhan, 2008). The Activity of K-40 was determined directly by measurement of its gamma-ray energy at 1460.83 keV.

3.4.3.2 Determination of Radiological Parameters

The activity concentration of Ra-226, Th-232 and K-40 calculated in equation (3.4) was used to compute different radiological parameters using suitable equations. These radiological parameters and suitable equations are briefly described below.

a) Radium Equivalent Activity (Ra_{eq})

The distribution of natural radionuclides in building material samples is not uniform (Eštoková & Palaščáková, 2013). Therefore, Radium Equivalent Activity (Ra_{eq}), was defined to compare the activity concentration of samples containing different amounts of U-238, Th-232 and K-40, and was computed using equation (3.6) (Beretka & Mathew, 1985).

$$Ra_{eq}\ (Bq/kg) = A_{Ra} + 1.43\ A_{Th} + 0.07A_{K} \tag{3.6}$$

where A_{Ra} , A_{Th} and A_K are the activity concentrations in Bq/kg of Ra-226, Th-232 and K-40, respectively. In the definition of Ra_{eq}, it was assumed that 10 Bq kg^{-1} of Ra-226, 7 Bq kg^{-1} of Th-232 and 130 Bq kg^{-1} of K-40 produce equal gamma-ray dose rate (Eštoková & Palaščáková, 2013). The maximum value of Ra_{eq} in raw building materials and products must be less than 370 Bq kg^{-1} for safe use, i.e., to keep the external dose below 1.5 mSv y^{-1} (UNSCEAR, 2000).

b) Hazard Indices

The hazard indices are defined in order to examine the applicability of using materials in construction. These indices were determined by the use of appropriate equations each briefly described on the next page.

i) External Hazard Index $\left(H_{ex}\right)$

The external hazard index $\left(H_{ex}\right)$ is used to access the exposure due to gamma radiation from building materials. The external radiation hazard index (H_{ex}) was calculated using equation (3.7) (Samad et al., 2012; Antovic, Svrkota, & Antovic, 2012);

$$H_{ex} = \frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \tag{3.7}$$

Where; A_{Ra}, A_{Th} and A_K have the same meaning as in equation (3.6).

Equation (3.7) assumes the conservative model that the buildings are of infinitely thick walls without windows and doors (Al-Trabulsy et al., 2011).

ii) Internal Hazard Index $\left(H_{in}\right)$

The internal hazard index $\left(H_{in}\right)$ is used to assess the exposure level due to radon inhalation originating from building materials. This parameter was calculated using equation (3.8) (Al-Trabulsy et al., 2011).

$$H_{in} = \frac{A_{Ra}}{185} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \tag{3.8}$$

c) Indoor Absorbed Gamma Dose Rate (D_{in}) and Annual Indoor Effective Dose (E_{in}) from Cement

The absorbed dose rate in indoor air due to gamma-ray emission from the radionuclides (Ra-226, Th-232 and K-40) in the cement was evaluated using the standard room model for the dose conversion coefficients. In this case, the dimensions of the room were assumed to be 4 m × 5m × 2.8 m while the thickness of walls, floor and ceiling and density of the structures are 20 cm and 2350 kg m^{-3} (concrete), respectively (European Commission, 1999). Hence, the absorbed dose rate in indoor was calculated using equation (3.9a).

$$D_{in} = 0.92A_{Ra} + 1.1A_{Th} + 0.08A_K \qquad (3.9a)$$

Where; A_{Ra}, A_{Th} and A_K have the same meaning as in equation (3.6). Equation (3.9a) is valid for a building where all the structures (floor, ceiling and walls) are contributing to irradiation. However, for buildings where not all structures are contributing to irradiation, the following equations (European Commission, 1999) were used to determine the indoor absorbed dose rate in the respective structures.

Floor and walls only (wooden ceiling):

$$D_{in} = 0.67A_{Ra} + 0.78A_{Th} + 0.057A_K \qquad (3.9b)$$

Floor only (wooden house with concrete floor):

$$D_{in} = 0.24A_{Ra} + 0.28A_{Th} + 0.020A_K \qquad (3.9c)$$

Superficial material: tile or stone on all walls (thickness 3cm, density 2600 kgm^{-3}):

$$D_{in} = 0.12A_{Ra} + 0.14A_{Th} + 0.0096A_K \qquad (3.9d)$$

According to (UNSCEAR, 2000), the world average (populated-weighted) indoor absorbed gamma dose rate, D_{in}, is 84 nGyh^{-1}

The annual indoor effective dose for each of the above building structures was estimated using equation (3.10).

$$E_{in}\,(Sv) = D_{in} \times 24 \times 365 \times 0.7 \times 0.8 \qquad (3.10)$$

Where; 0.7 is the conversion coefficient in Sv Gy^{-1} from absorbed dose in air to effective dose and 0.8 is the indoor occupancy factor (UNSCEAR, 2000). Thus, with D_{in} = 84 nGyh^{-1}, then the annual indoor effective dose is 0.41 mSv.

d) Radon Emanation Coefficient (η), Surface Exhalation Rate/flux density (E_x), Radon Concentration (C_{Rn}) and Inhalation Effective Dose $(E_{in(Rn)})$ from Crystal Cement

(i) Radon emanation coefficient (η)

The radon emanation coefficient is defined as the fraction of radon atoms generated that escape the solid phase in which they are formed and become free to migrate through the bulk medium (IAEA, 2013). The radon emanation coefficient from cement was calculated from equation (3.11) (White & Rood, 2001)

$$\eta = \frac{N}{N_0 + N} \tag{3.11}$$

Where;

N_0 is the net count rate of Rn-222 at the time of sealing the sample container (Marinelli) and N is is the net count rate of Rn-222 at secular equilibrium.

(ii) Radon surface exhalation rate or flux density (E_x)

Radon surface exhalation rate or flux density describes the release of radon over a specific area (IAEA, 2013). The radon flux density was calculated from equation (3.12) (Rizzo et al., 2001).

$$E_x\,(\mathrm{Bq/m^2\,h}) = \frac{1}{2} C_{Ra}\, \lambda_{Ra}\, \rho \eta d \tag{3.12}$$

Where;

C_{Ra} (Bq/kg) is the concentration of Ra-226 ;

λ_{Ra} (h^{-1}) is the radon decay constant (7.554 x10^{-3} h^{-1});

ρ (kg/m^3) is the material density;

η is the emanation coefficient and

d (m) is the wall thickness

(iii) Radon concentration (C_{Rn}) and annual inhalation effective dose $(E_{in(Rn)})$

The theoretical indoor radon concentration was calculated from equation (3.13) (Rizzo et al., 2001).

$$C_{Rn} = \frac{E_x\ S}{\varphi} = \frac{E_x \times S}{K \times V} \tag{3.13}$$

Where;

S (m^2) is the total surface area of structures contributing to irradiation i.e walls, floor and ceiling and φ (m^3 h^{-1}) is the air ventilation flux which is the product of volume (V) of the room and air exchange rate (K). In this study K was taken as 1h^{-1} as suggested by (UNSCEAR, 2000) while S was taken as 100 m^2 instead of 96 m^2 as calculated from the standard room model dimensions mentioned in subsection 3.4.3.2 (c). This was because the model on which equations (3.12) and (3.13) were derived, suggested that S/V=1.8 m^{-1} (OECD, 1979).

The annual inhalation effective dose $(E_{in(Rn)})$ was then calculated from equation (3.14) (Faanu et al., 2011).

$$E_{in(Rn)} = C_{Rn} \times DCF_{Rn} \times F_{Rn} \times T \tag{3.14}$$

Where;

DCF_{Rn} is the dose per unit intake of radon through inhalation (DCF_{Rn}= 9 nSv (Bq h $m^{-3})^{-1}$ (UNSCEAR, 2000),

F_{Rn} is the indoor equilibrium factor for Rn-222 (F_{Rn} =0.4) (IAEA, 2011) and

T is the annual occupancy rate of 7000 hours (IAEA, 2011).

(e) Outdoor Absorbed Gamma Dose Rate (D_{out}) and Annual Outdoor Effective Dose from Soil Around the Cement Factory

In order to determine radiological significance from the activities of the cement factory to the nearby places around the factory, the absorbed dose rate in outdoor (D_{out}) from the soils around the factory was determined using equation (3.16) (Antovic et al., 2012). Similarly, the corresponding annual effective dose from each soil sample was computed using equation (3.15) (Samad et al., 2012, and Kessaratikoon & Awaekechi, 2008).

$$D_{out}\ (nGy/h) = 0.462A_{Ra} + 0.604A_{Th} + 0.042A_{K} \qquad (3.15)$$

Where A_{Ra}, A_{Th} and A_K have the same meaning as in equation (3.6).

$$E_{out}\ (Sv) = D_{out} \times 24 \times 365 \times 0.7 \times 0.2 \qquad (3.16)$$

Where, the factor 0.7 is as earlier defined while 0.2 is the outdoor occupancy factor reported by UNSCEAR (2000).

3.5 Instrumentation of the Atomic Absorption Spectroscopy (AAS) System

Plate 3.5 shows the Varian AA-240FS First Sequential Atomic Absorption Spectrometer. It consists of three major chambers in addition to the monitor and the compressor. These major components are the lamp, spray and atomizing chambers labelled a, b and c respectively on the diagram.

Plate 3.5: Set up of AAS equipment

The lamp chamber consists of a multi-cathode chamber that can accommodate four lamps at ago. The spray chamber houses the burner head, spray block as well as the nebulizer. The atomizing chamber consists of the monochromator and detector lenses. The function of the compressor labelled d in the plate is to supply compressed air that aids the flame during the burning process as well as creating pressure in the capillary tube that introduces the analyte into the system.

3.5.1 Calibration of the AAS Equipment and Sample Measurement

a) Calibration of the AAS Equipment

Calibration of the instrument was done by aspiring into the flame samples of reference standard solutions containing known concentration of each element to be determined and then measuring absorption of each solution. After each reading, the instrument was made to read zero percentage precision by aspiring into the flame with distilled water. This was done to completely remove trapped elemental ions from the previous reading that could give false readings. For each element, the measured absorbance was plotted against the concentration. In this study, the reference standards were from fluka analytical Sigma Aldrich Chemie GmbH, product of Switzerland.

b) Sample Measurement by AAS

A Varian AA-240FS First Sequential Atomic Absorption Spectrometer was used to determine the concentration levels Pb, Cr, Cd, Hg and Arsenic in soil samples. This was done by aspiring into the flame solutions of prepared samples for atomization. Replicate analyses were carried out for each element in a sample to ascertain reproducibility and quality assurance. Additionally, after every five real sample measurements for all the elements of interest, both the standard and blank were re-read to detect any drift in the instrument as early as possible. It should be noted that Arsenic because of its low-wavelength primary resonance lines, a different equipment was used for generating its hydride before being atomized in the AAS equipment. The equipment is the Vapour Generation Accessory (VGA) that makes use of a gas-liquid separator to separate the gaseous hydrides from the liquid reagents prior to introduction into the atom cell. Additionally, cold vapour generation was used for mercury as it is the only analyte that has an appreciable atomic vapour pressure at room temperature (Evans et al., 1998). The elemental concentration was displayed in mg/L on the monitor of the AAS equipment. Hence, this concentration was converted into mg/kg by use of equation (3.17).

$$C_E\,(\text{mg/kg}) = \frac{C_e \times D.F \times V}{M_s} \tag{3.17}$$

Where;

C_E is the required elemental concentration in mg/kg;

C_e is the elemental concentration displayed on the monitor in mg/L;

D.F is the dilution Factor;

V is the Nominal volume in mL and

M_s is the mass of the sample in g

3.5.2 Heavy Metal Analysis by AAS

Pollution is defined as the introduction by man into the environment of substances or energy forms liable to cause hazards to human health, harm to living resources and Ecological systems, damage to structures or amenity or interference with legitimate uses of the environment (Ibrahim, 2004). There are several methods used to assess soil and sediment quality for decision making and spatial planning. However, in this study, two types of pollution indices i.e., single indices and integrated indices in an algorithm point of view (Qingjie et al., 2008) were considered.

a) Single Indices

These are indicators used to calculate only one metal contamination (Qingjie et al., 2008) and they include among others, pollution index, index of geo-accumulation and ecological risk factor.

i) Pollution Index (P_{ij})

The pollution index is used to get real quantitative information of key pollution elements in an area (Hong-gui et al., 2012). The following expression was used to calculate P_{ij} (Hong-gui et al., 2012).

$$P_{ij} = \frac{C_{ij}}{S_j} \tag{3.18}$$

Where, P_{ij} is the pollution index of the heavy metal *j* in the *i*-th functional area soil, C_{ij} is the measured elemental concentration value of heavy metal *j* in the *i*-th functional area soil, and S_j is the background contamination value of heavy metal *j*. In this study, the background elemental concentration values were taken as the World-soil average values (table 3.2). The grading standard of the single factor is shown in Table 3.1.

Table 3.1: Grading standard for single pollution index (Hong-gui et al., 2012)

Sub- index	$P_{ij} < 1$	$1 \leq P_{ij} < 2$	$2 \leq P_{ij} < 3$	$3 \leq P_{ij}$
Quality grade	Clean	Potential pollution	Slight pollution	Heavy pollution

ii) Geo–Accumulation Index (I_{geo})

An index of geo-accumulation (I*geo*) is used to determine and define metal contamination in sediments by comparing current concentrations with pre-industrial levels (Qingjie,et al., 2008). The I_{geo} value of heavy metals was calculated using equation (3.19) (Likuku et al., 2013; Addo et al., 2012; Ahiamadjie et al., 2011; Qingjie et al., 2008).

$$I_{geo} = \log_2\left[\frac{C_i}{1.5C_{ri}}\right] \tag{3.19}$$

Where, C_i is the measured concentration of the examined metal *i* in the sediment, and C_{ri} is the geochemical background concentration or reference value of the metal *i*. In this study, the pre-industrial reference values (Table 3.2) were used for the determination of

I_{geo}. The factor 1.5 is used because of possible variations in background values for a given metal in the environment as well as very small anthropogenic influences.

Table 3.2: Pre-industrial reference level, World-soil average background values (mg/kg) and toxic- response factor

Element	**Hg**	**Cd**	**As**	**Pb**	**Cr**	**Reference**
World-soil Average (mg/kg)	0.07	0.41	6.83	27	59.5	(Kabata & Alina, 2011)
Pre-industrial reference level (mg/kg)	0.25	1.0	15	70	90	(Hakanson, 1980)
Toxic-response factor	40	30	10	5	2	(Hakanson, 1980)

Table 3.3: Classification for the geo-accumulation index (Buccolieri et al., 2006).

I_{geo} value	Class	Quality of sediment
≤ 0	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly to extremely polluted
> 5	6	Extremely polluted

iii) Ecological Risk Factor (E_r^i)

An ecological risk factor E_r^i expresses quantitatively the potential ecological risk of a given contaminant (Qingjie et al., 2008). The ecological risk factor was computed using equation (3.20) (Ogunkunle & Fatoba, 2013).

$$E_r^i = T_r^i . P_{ij} \tag{3.20}$$

Where, T_r^i is the toxic-response factor for a given substance, and P_{ij} is the contamination factor or single pollution index. The T_r^i values are given in Table 3.2.

The following classification was then used to categorize the ecological risk as suggested by Qingjie et al., (2008).

E_r^i<40, low potential ecological risk; 40≤ E_r^i<80, moderate potential ecological risk; 80≤E_r^i<160, considerable potential ecological risk; 160≤E_r^i<320, high potential ecological risk; and E_r^i≥320, very high ecological risk.

b) Integrated Indices

Much as the single index method can be used to evaluate the pollution of heavy metals in a given area, it cannot express accurately the comprehensive impact caused by each kind of heavy metals (Hong-gui et al., 2012). This is because different reference values such as the pre-industrial reference level, the average crust level, the background level, baseline, national criteria, threshold pollution value, etc., are not uniform. Therefore, using different reference values will lead to discrepancy in assessment (Qingjie et al., 2008), hence, the need to use Nemero index comprehensive evaluation method. This evaluation method can reflect the degree of soil pollution caused by various pollutants (heavy metals). The comprehensive pollution index was computed using equation (3.21) (Hong-gui et al., 2012; Qingjie et al., (2008).

$$P_i = \sqrt{\frac{\left(P_{ij\max}\right)^2 + \left(P_{ijave}\right)^2}{2}} \tag{3.21}$$

Where, P_i is the compressive pollution index of the *i*-th functional area, and $P_{ij\max}$ is the corresponding maximum value in the single-factor pollution index, and P_{ijave} is the corresponding average value in the single-factor pollution index. The soil pollution grading standards on the Neremo pollution index is shown in table 3.4.

Table 3.4: Grade standard of the Nemero index method

Grade	I	II	III	IV	V
P_i	$P_i < 0.7$	$0.7 < P_i \leq 1$	$1 < P_i \leq 2$	$2 < P_i \leq 3$	$P_i > 3$
Pollution grade	clean	Warning limit	Slight pollution	Moderate pollution	Heavy pollution

From equation (3.21), it is observed that the final value of P_i heavily depends on the value of $P_{ij\max}$. Therefore, if one index is much higher than the rest in a given functional area, the calculated value of P_i will be high and thus this type of evaluation becomes unreasonable. Additionally, the Nemero index does not consider the weight factor and treats every pollution factor equally. Hence, any high value of pollution index will cause the composite value higher and yet different pollution factors have different influences on environmental toxicity, degradation, and removal. Hong-gui et al., (2012) solved this problem by carrying out a correction through analyzing the weight factor. In this case, $P'_{ij\max}$ as expressed in equation (3.22) should be used instead of $P_{ij\max}$ in equation (3.21).

$$P'_{ij\max} = \frac{P_{ij\max} + P_{iw}}{2} \tag{3.22}$$

Where P_{iw} is the top pollution factor of weight in all the pollution factors in the *i*-th functional area $\left(\frac{C_{ij}}{S_j}\right)$.

Pollution factor weights (w_j) are calculated according to different pollutants with varying degrees of harm to the environment and human body. According to the background value S_j of each pollution factor, the maximum concentration value ($C_{ij\,max}$) is selected to compare with each S_j and R_j $\left(R_j = \frac{C_{ij\,\max}}{S_j}\right)$ is defined as the relative importance ratio of heavy metal *j*. Thus,

$$w_j = \frac{R_j}{\sum_{j=1}^{n} R_j} \tag{3.23}$$

CHAPTER FOUR

Results and Discussion

4.1 High Purity Germanium Detector Characterization

4.1.1 Energy Calibration

Figure 4.1 shows the graphical representation of energy versus channel number for the mixed radionuclide standard. Using the linear fit, both Pearson's *r* and Adjusted R-square values were unity. This shows that there was a high degree of linear dependence between the energy and the channel number. Hence, radionuclide identification in terms of energy from all the samples was done with highest degree of accuracy.

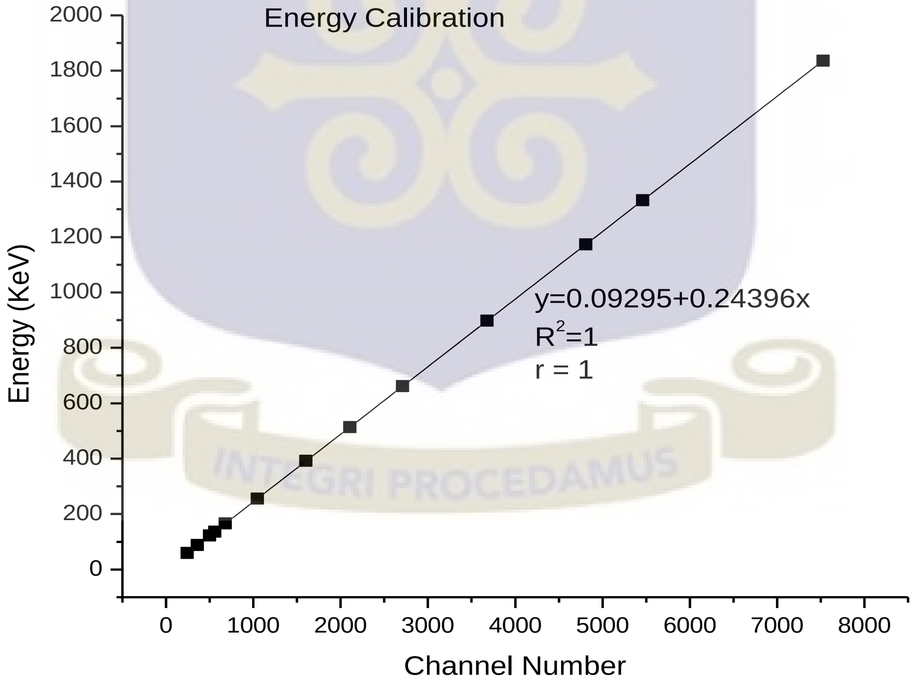

Figure 4.1: Energy Calibration curve for the radionuclide mixed standard

4.1.2 Efficiency Calibration

Figure 4.2 shows the curve from which an equation was used to determine the absolute efficiencies at different gamma lines of interest such as Pb-214, Bi-214, Ac-228, Bi-212 among others. This procedure was necessary because the dimensions of germanium detectors are not standardized to any degree, and it is very difficult to determine precisely their active volume. Furthermore, long-term changes in charge collection efficiency and/or window thickness can lead to rifts in the detector efficiency over periods of time (Knoll, 2010). Hence, it was important to carry out efficiency calibration rather than adopting the published measurements or calculations for detectors of similar size. This calibration procedure takes into account any error in assumed detector dimensions and applies both to the calibration and actual measurements.

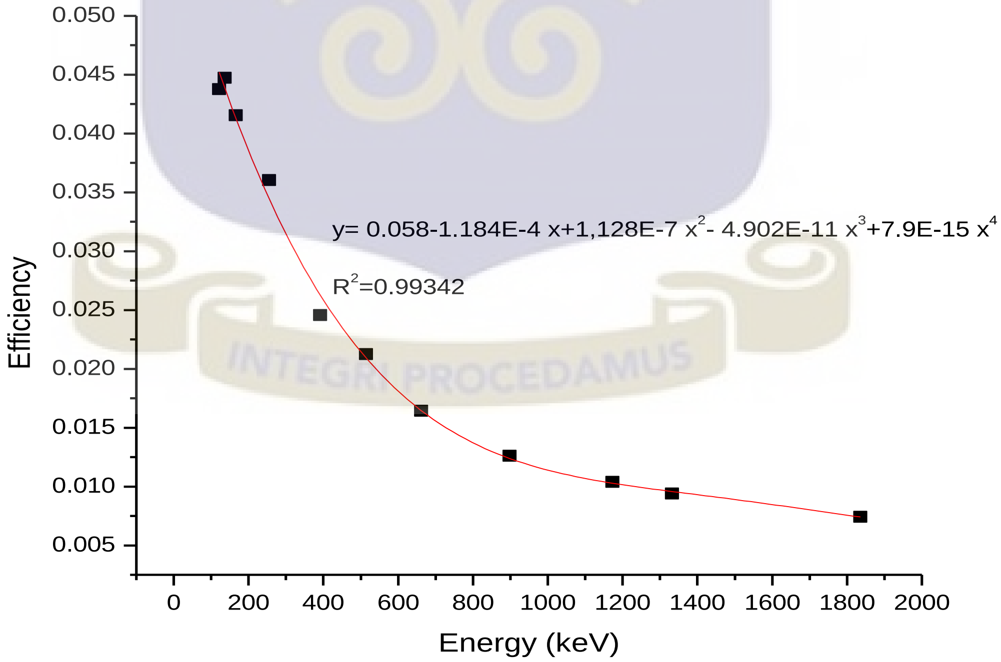

Figure 4.2: Efficiency calibration curve for the mixed radionuclide standard

4.1.3 Minimum Detectable Activity (MDA)

Following the spectrum analysis for the background counts, the results of the average MDA for the U-238, Th-232 and K-40 peaks are presented in Table 4.1.

Table 4.1: Minimum Detectable Activities of Ra-226 (U-238), Th-232 and K-40

Radionuclide	**MDA (Bq/kg)**
U-238	0.234±0.024
Th-232	0.173±0.014
K-40	1.74±0.000

4.2 Activity concentrations of Ra-226, Th-232 and K-40 in the samples

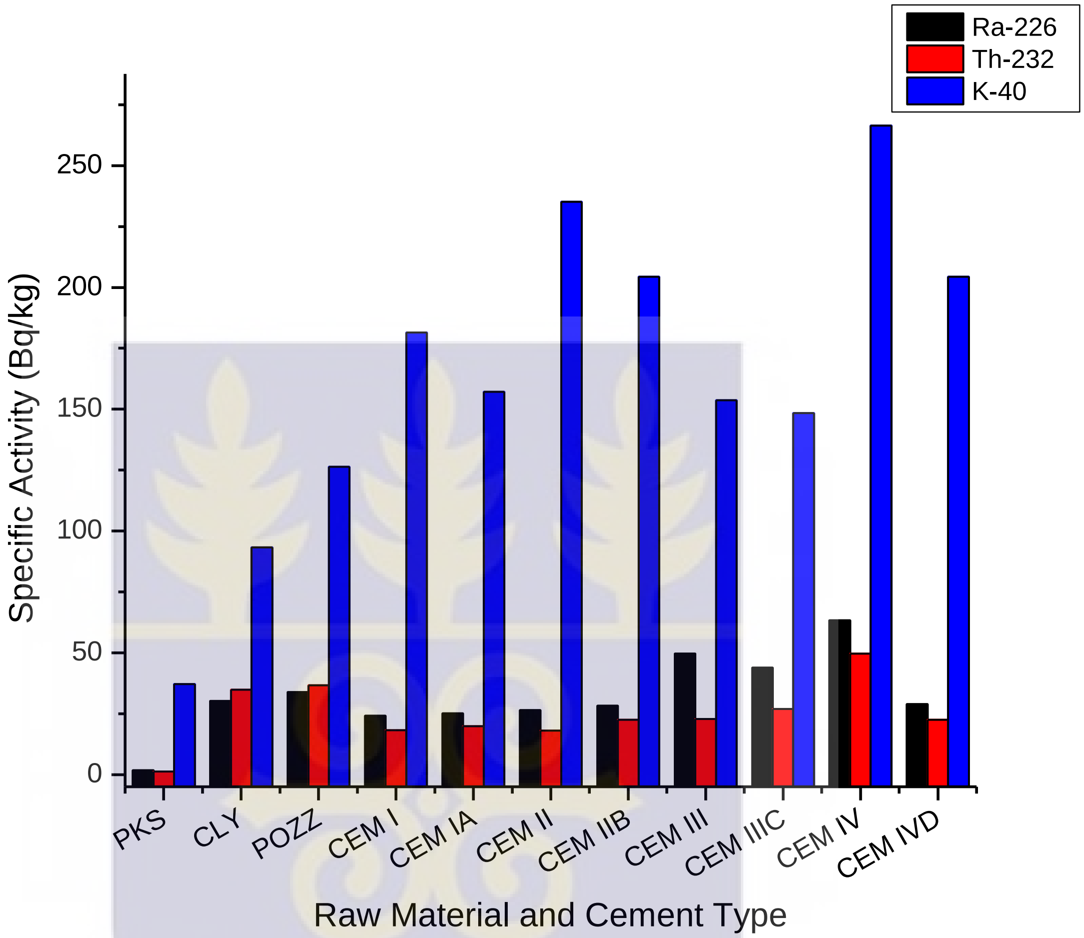

Figure 4.3: Distribution of Ra-226, Th-232 and K-40 radionuclides in Crystal cement and its raw materials.*PKS; CLY; POZZ[10]

Figure 4.3 is a graphical representation of Table 4.2 and shows that the specific activity concentrations of Ra-226, Th-232 and K-40 in PKS were the lowest compared to the rest. Similarly, the concentrations of Ra-226, Th-232 and K-40 in CEM IV were the highest as compared to all cement types and other raw materials before mixing. Additionally, the concentration of K-40 in raw materials (PKS, raw clay and clay Pozzolana) was lower than in all cement types (both mixed and un-mixed). It is also observed that mixing raw clay and PKS increases the radionuclide activity concentrations in the processed product (clay Pozzolana). It was difficult to estimate the contribution of each radionuclide content from PKS and raw clay to the total concentrations in clay Pozzolana since no measured

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[10] *PKS-Palm kernel Shell; CLY-Clay; POZZ-Pozzolana

quantities of each are taken care of at the factory. This is because the role of PKS is only to provide fuel for calcinating clay to the required temperature. Though, the contribution from PKS is small compared to that of raw clay, using large quantities of PKS may subsequently lead to increased levels of radionuclide contents in clay Pozzolana. Table 4.2 shows the numerical activity concentration values in all samples before and after mixing. Cement types labelled CEM IV represent unmixed cement types while CEM IA-IVD represent the respective mixed types.

Table 4.2: Mean Specific Activity (Bq/kg) of Ra-226, Th-232 and K-40 in the samples

Sample ID*	A_{Ra}	A_{Th}	A_K	**D_{in} (A) $nGyh^{-1}$**
PKS	1.68 ± 0.15	1.31 ± 0.02	37.08 ± 4.09	5.96±2.41
CLY	30.30 ± 1.60	34.82 ± 1.97	93.28 ± 9.83	73.64±2.74
POZZ	33.84 ± 0.27	36.67 ± 4.05	126.32 ± 13.30	81.58±4.59
CEM I	24.15 ± 1.28	18.25 ± 0.90	181.52 ± 19.00	56.81±2.17
CEM IA	25.05 ± 1.21	19.91 ± 0.23	157.10 ± 16.40	57.52±1.74
CEM II	26.47 ± 0.78	18.06 ± 2.13	235.08 ± 24.60	63.02±3.14
CEM IIB	28.32 ± 0.47	22.47 ± 1.77	204.43 ± 21.40	67.12±2.63
CEM III	49.67 ± 3.06	22.78 ± 1.74	153.65 ± 16.10	83.05±3.64
CEM IIIC	43.81 ± 2.90	26.89 ± 2.08	148.33 ± 15.60	81.75±3.72
CEM IV	63.24 ± 0.24	49.59 ± 2.21	266.35 ± 26.35	134.03±3.30
CEM IVD	28.94 ± 1.90	22.46 ± 1.75	204.43 ±21.40	67.68±3.11

*PKS: Palm Kernel Shell; CLY: Clay; POZZ: Pozzolana (Mixture of PKS and CLY); CEM I: Portland Limestone cement (GHACEM); CEM II: Portland Limestone cement (Diamond); CEM III: Ordinary Portland cement (Dangote); CEM IV: Ordinary Portland cement (WP-China); CEM IA, IIB, IIIC, and IVD: Crystal cement types

Considering the effect of mixing clay Pozzolana with Ordinary Portland cement on each radionuclide, both reduction and enhancement in activity concentrations were observed in the mixed cement samples. Table 4.2 generally shows that there was a reduction in the activity concentration of K-40 in all mixed cement types. It is also worth to note that the activity concentration values of K-40 in CEM IA, CEM IIB, CEM IIIC and CEM IVD remained higher than in clay Pozzolana. This shows that the major contribution of K-40 concentration in mixed cement was from un-mixed cement rather than from clay Pozzolana. The reduction in the activity concentration was further observed for Ra-226 in

CEM IIIC and CEM IVD while the only reduction in Th-232 activity concentration was observed in CEM IVD. The most significant reduction in activity concentrations of Ra-226, Th-232 and K-40 was only observed in CEM IVD.

Apart from the above mentioned reductions in activity concentration of Ra-226, Th-232 and K-40, enhancement in activity concentrations of two radionuclides i.e., Ra-226 and Th-232 was also observed. There was an increase in activity concentration of Ra-226 in CEM IA and CEM IIB while activity concentration enhancement of Th-232 was observed in CEM IA, CEM IIB and CEM IIIC.

Comparing the mean specific activity concentrations of Ra-226, Th-232 and K-40 with the world reported values, was observed that in both reduction and enhancement cases, these mean specific values remained with the world reported ranged of 7-180, 7-240 and 24-850 Bq/kg respectively (International Atomic Energy Agency, 2003).

In general, for un-mixed cement types (CEM I-IV) where the activity concentrations of Ra-226 and Th-232 were lower than in clay Pozzolana, there was an increase (enhancement) in the activity concentration of these radionuclides in the mixed cement (CEM IA-IVD). However, in the un-mixed cement types where the activity concentration of Ra-226 and Th-232 were higher than in clay Pozzolana, there was a reduction in the activity concentrations of these radionuclides in the mixed cement. Therefore, mixing clay Pozzolana with radionuclide concentrations lower than those in Ordinary Portland Cement lowers the activity concentrations in the mixed cement and is thus, recommended for reducing radiation exposure.

Considering the contribution of individual radionuclide activity concentration to the total indoor absorbed gamma dose rate, Table 4.2, shows that although there was increase in activity concentration of Ra-226 and Th-232 in CEM IA, this enhancement may be considered insignificant when the indoor absorbed gamma dose rates in CEM I and CEM IA are compared (0.47% increase). However, the same increase in the activity concentrations of these radionuclides in CEM IIB was significant as there was an increase of 5.43% in indoor absorbed gamma dose rate from CEM II to CEM IIB. Similarly, the reduction in activity concentrations of Ra-226 and K-40 observed from CEM III to CEM IIC did not result in any significant reduction to the indoor absorbed gamma dose rate in CEM IIIC (reduction of 1.38%). However, the reduction in activity concentrations of Ra-226, Th-232 and K-40 observed from CEM IV to CEM IVD resulted in a 48.45% reduction to the indoor absorbed gamma dose rate in CEM IV.

This study did not consider the effect of mixing more than one type of Ordinary Portland Cement (OPC) on activity concentrations in the mixed brand. However, it can be deduced that mixing more than one type of OPC might alter the activity concentrations in the mixed type depending on the mixing ratios.

4.3 Radiological Health Risk from use of Crystal Cement

The effect of mixing clay Pozzolana with Ordinary Portland cement on the various radiological parameters is discussed in the following subsections.

4.3.1 Annual Indoor Effective Dose

Figure 4.4 compares the calculated values of indoor effective dose with World Average reported values. It is the graphical representation of Table 4.3 (Appendix IV) and shows that the amount of exposure depends on the type of building structure ie., the annual indoor effective dose is highest in a structure where all the floor, ceiling and walls are contributing to irradiation and lowest where the structure is made of superficial material only (tile or stone on all walls). Since the highest risk is from building where all the described structures are contributing to irradiation, only the value of the indoor annual effective dose from such a building ie., $E_{in}(A)$ will be referred to in any discussion.

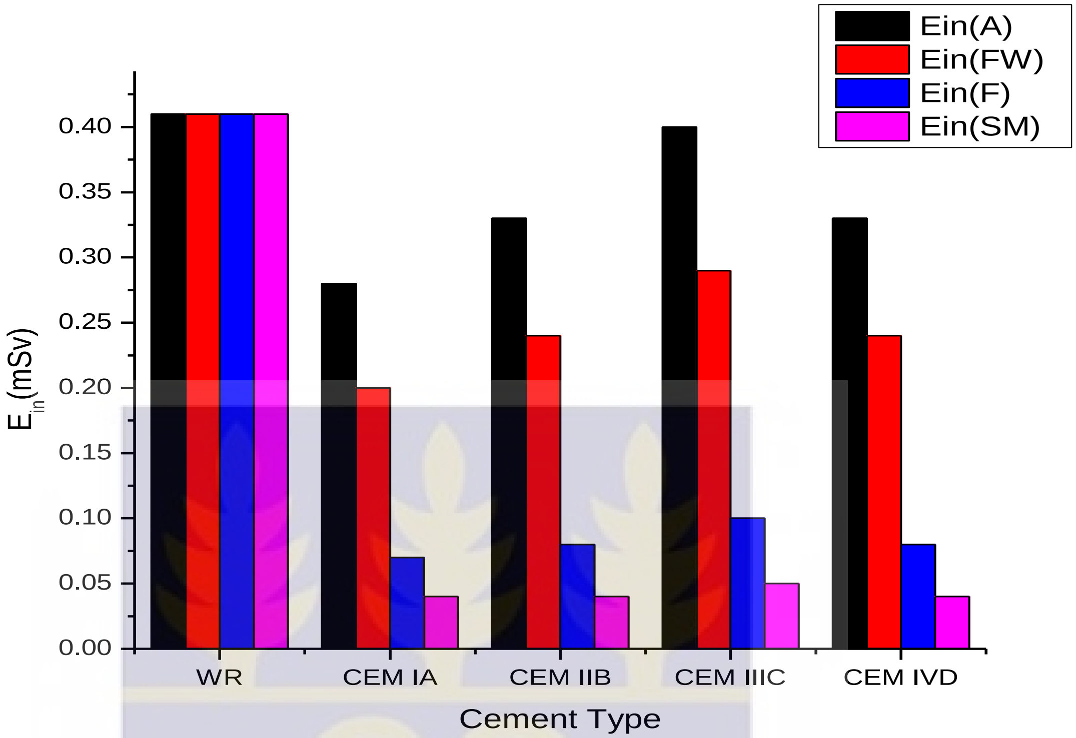

Figure 4.4: Indoor Annual effective Dose in crystal cement types and respective building structure. *Ein (A); Ein (FW); Ein (F); Ein (SM)[11]

The highest estimated indoor annual effective dose was 0.40±0.02 mSv recorded in CEM IIIC while the lowest was 0.28±0.01 mSv recorded in CEM IA.

It is observed from Figure 4.4 that the estimated indoor annual effective dose in all building structures from all crystal cement types was lower than World reported average of 0.41 mSV/y (UNSCEAR, 2000).

Another important point to note is that there was no significant change in the estimated annual effective dose between the mixed and un-mixed cement except in CEM IV where

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[11] Ein-Indoor effective dose, A-All (Floor, wall and ceiling), FW-Floor and Walls, F-Floor only, SM-superficial Material, WR-Word Reported

estimated annual indoor effective dose from CEM IV was 0.66 mSv higher than the World Reported Average. However, after mixing CEM IV with clay Pozzolana, it reduced to 0.33mSv/y. Therefore, CEM IVD in its un-mixed state seems to have high long term radiation effects (stochastic) from low level exposure as compared to other cement types. Hence, the process of mixing it with clay Pozzolana, reduces these possible radiation effects.

Although, there was generally an enhancement in radionuclide content from either Ra-226 or Th-232 in CEM IA, CEM IIB and CEM IIIC , use of these cement types is considered safe since annual indoor effective dose is lower than the upper limit of radiation dose arising from building materials of 1.5 mSv/y (Al-Trabulsy et al., 2011). However, it should be noted that the estimation of doses was based on a standard room model and since the dose varies inversely proportional to distance from the source, doses arising from buildings with smaller room dimensions may be higher.

4.3.2 Radium Equivalent

Figure 4.5 (extract of Table 4.4 Appendix IV) clearly shows that the radium equivalent in all crystal cement types are lower than the recommended value of 370 Bq/kg (UNSCEAR, 2000). The lowest was recorded in CEM IIB while the highest was recorded in CEM IIIC. Since the radium equivalent value from all crystal cement types is lower than the recommended, then crystal cement is safe for use as a building material.

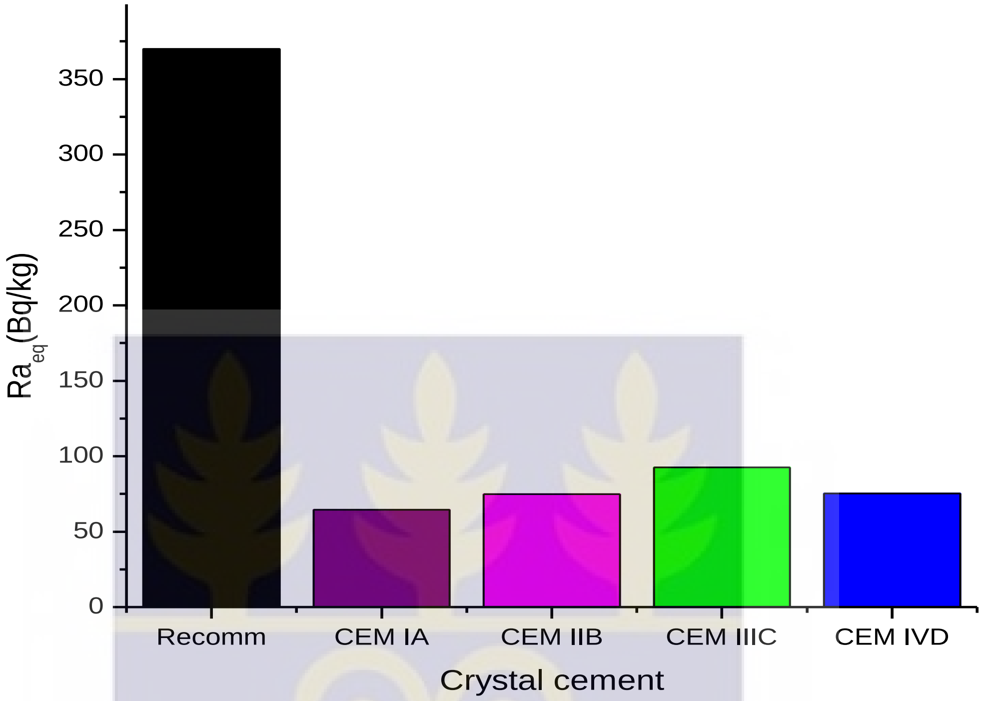

Figure 4.5: Radium Equivalent in Crystal Cement

4.3.4 External and Internal Hazard Indices

Figure 4.6 compares the calculated values and recommended values of external and internal hazard indices in crystal cement with the recommended. It generally shows that the internal hazard index which assesses the level of exposure due to radon inhalation originating from building materials is more than the external hazard index that assesses the exposure arising from gamma emitting radionuclides in cement. However, the estimated hazard indices are lower than the recommended value of 1 (European Commission, 1999). Thus, the use of crystal cement as a building material is considered safe.

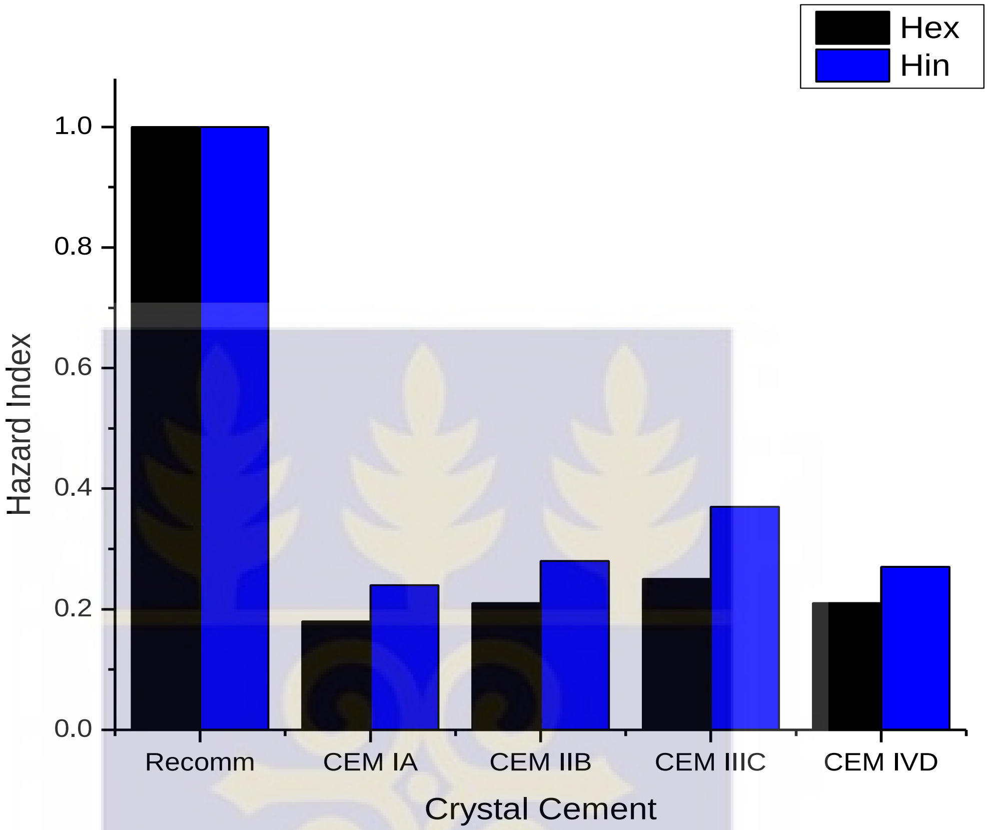

Figure 4.6: Hazard indices in Crystal Cement:[12]

4.3.3 Radon Annual Inhalation Effective Dose

Table 4.5 shows that the average radon emanation coefficient from all the cement types was 0.50 while the indoor radon concentration ranged between 42.31 Bq m^{-3} recorded in CEM IA to 73.02 Bq m^{-3} recorded in CEM IIIC. The order of decreasing indoor radon concentration was CEM IIIC>CEM IVD>CEM IIB>CEM IA.

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[12] *Hex- external hazard index, Hin –internal hazard index, Recomm- Recommended value of hazard indices[12]; CEM IA, CEM IIB, CEM IIIC, CEM IVD-mixed cement

Table 4.5: Indoor Radon Concentration and Annual Inhalation Dose

Cement type	Ra-226 concentration (Bq kg^{-1})	Emanation coefficient	Radon flux density (Bq m^{-2} h^{-1})	Indoor Radon concentration (Bq m^{-3})	Annual effective dose (mSv)
CEM IA	25.05±1.12	0.51	23.69	42.31	1.07
CEM IIB	28.31±0.47	0.50	25.55	45.63	1.15
CEM IIIC	43.81±2.90	0.50	41.45	73.02	1.87
CEM IVD	28.94±1.90	0.51	27.92	49.86	1.26

The correlation between the concentrations of Radium-226 and Radon-222 is shown in Figure 4.7.

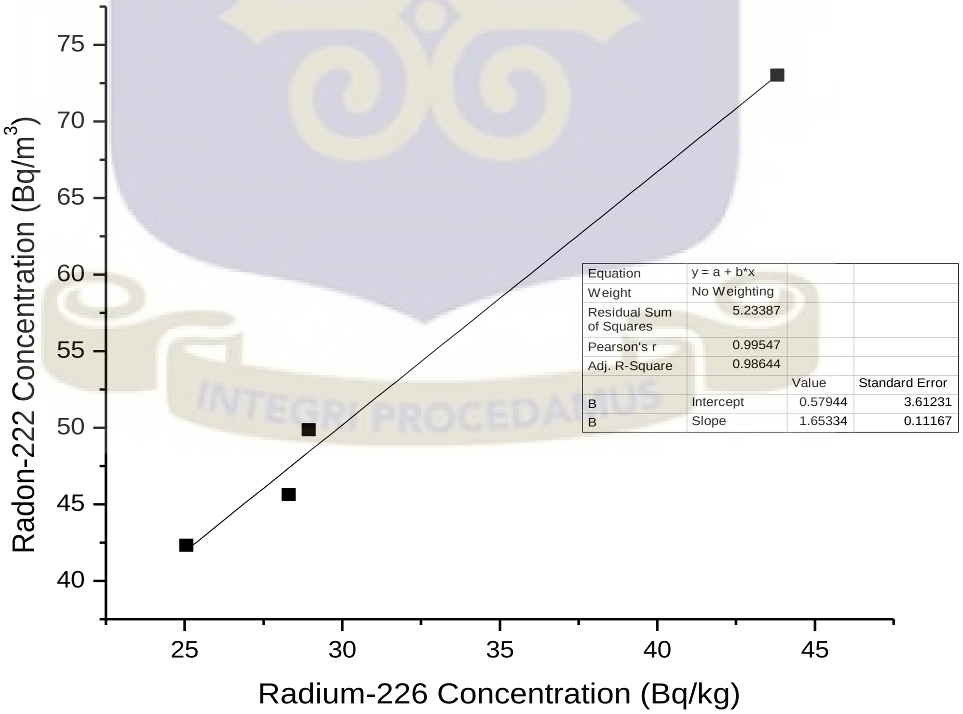

Figure 4.7: Comparison of Radium and Radon Concentrations

The high correlation coefficient (r = 0.99547) could be attributed to the amount of Radium-226 concentration in each cement type as well as the respective porosities of the cement samples (Varshney et al., 2010).

According to (IAEA, 2011), the indoor concentration of Rn-222 for dwellings and other buildings with high occupancy factors for members of the public should not exceed 300 Bq m^{-3} that corresponds to an annual effective dose of the order of 10 mSv. From Table 4.5, the indoor radon concentrations and the annual inhalation doses were lower than 300 Bq m^{-3} and 10 mSv respectively. This further confirms that use of crystal cement as a building material is considered safe.

4.4 Environmental Impact of Natural Radionuclides (Ra-226, Th-232 and K-40) from Manufacture of Crystal Cement

4.4.1 Comparison of Activity Concentrations of Ra-226, Th-232 and K-40 in soils with world Population-Weighted Averages (PWA)

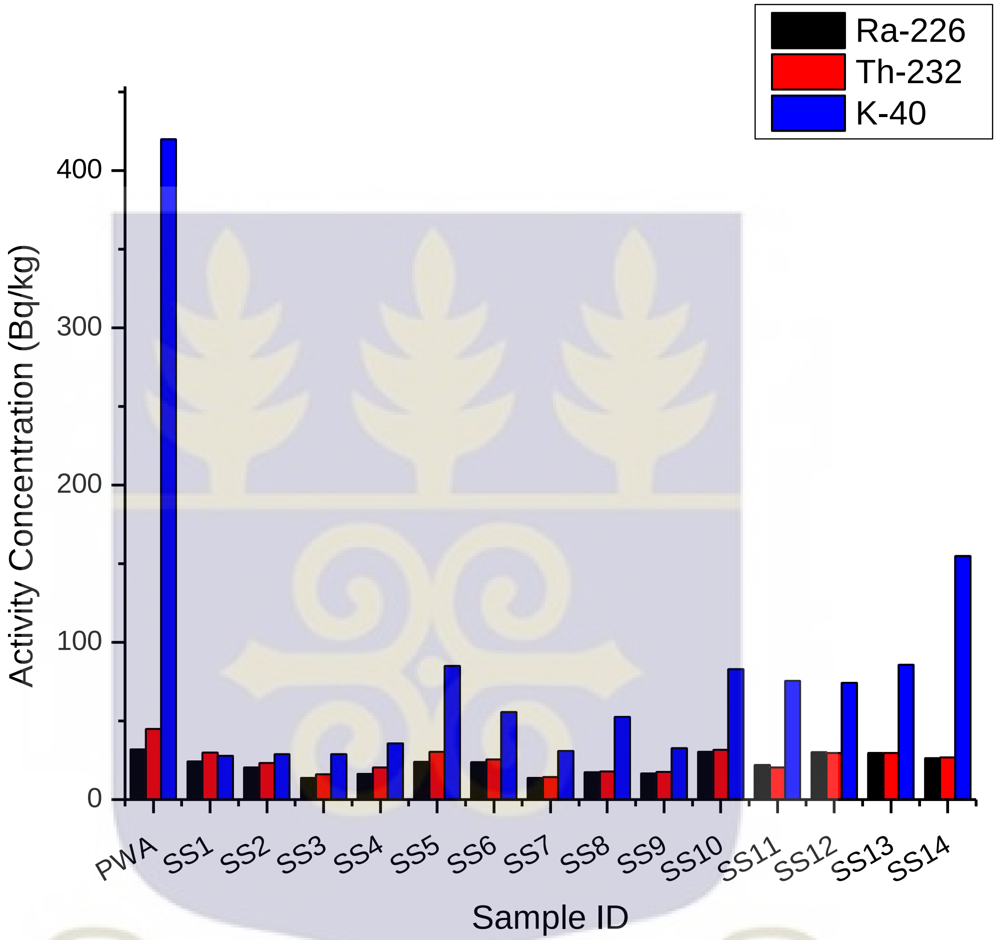

Figure 4.8: Distribution of Ra-226, Th-232 and K-40 in Soil Samples

Figure 4.8 is an extract of Table 4.6 and it compares the concentration of Ra-226, Th-232 and K-40 from soil samples with world Population- Weighted Average. From the figure, it is clear that the concentration of K-40 in all soil samples was higher than for Ra-226 and Th-232 except in SS1. The concentration of K-40 was highest in SS14 and lowest in SS1. Generally the figure shows that the activity concentrations of Ra-226, Th-232 and K-40 were all lower than the world Population-weighted Averages. From Table 4.6

(Appendix IV), the average activity concentrations of Ra-226, Th-232 and K-40 in the soils were 22.03±5.82 Bq/kg, 23.81±6.00 Bq/kg and 60.77±35.62 Bq/kg respectively. These values of Ra-226, Th-232 and K-40 are below the world Population-Weighted Averages of 32, 45 and 420 Bq/kg respectively (UNSCEAR, 2000).

4.4.2 Outdoor Absorbed Gamma Dose Rate and Outdoor Annual Effective Dose

Considering the annual outdoor absorbed gamma dose rates, from Table 4.6 (Appendix IV), the annual outdoor absorbed gamma dose rate ranged between 16.34±0.66 $nGyh^{-1}$(in SS7) to 36.68±0.53 $nGyh^{-1}$ (in SS10) with an average of 27.11±7.16 $nGyh^{-1}$. Hence all the values of the annual outdoor absorbed gamma dose rate were below the world average outdoor absorbed gamma dose rate of 59 $nGyh^{-1}$(UNSCEAR, 2000). Consequently, the annual outdoor effective dose for all sampling points was less than the annual world reported average of 0.07mSv (UNSCEAR, 2000). This is further demonstrated in Figure 4.9.

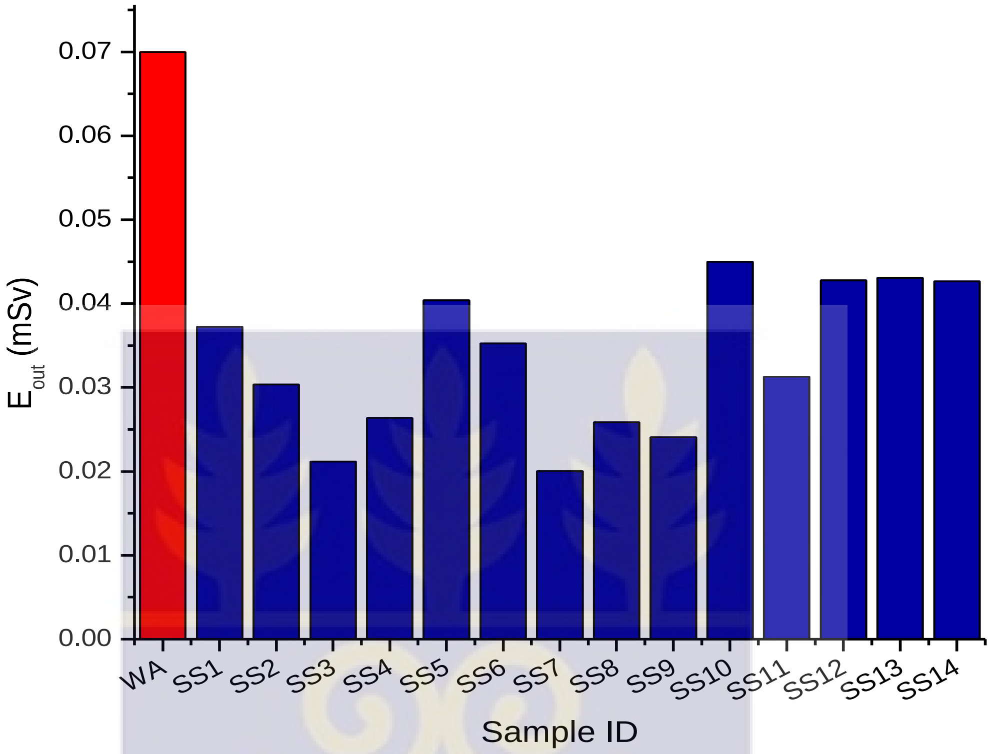

Figure 4.9: Annual outdoor effective dose from soil samples: *E_{out}, WA[13]

The lowest Annual outdoor effective dose was reported in SS7 (0.020±1.073E-5 mSv) while the highest was reported in SS10 (0.045±1.944E-5 mSv). Owing to the fact that the samples were collected once and no similar studies had been carried out, it is difficult to establish whether the activities of the factory had elevated the individual radionuclide concentrations in the soils. However, what is clear is that there are no radiological health risks from the soils around the factory. Therefore, as per this study, there is no evidence to suggest that by the time of sample collection, the natural radioactivity content of soils around the factory had been altered to significantly pose health risks.

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[13] E_{out}-Annual outdoor Effective Dose, WA –World Reported average annual outdoor Effective Dose

4.4.3 Variation of Outdoor Absorbed Gamma Dose Rate with Distance from the Factory

From Table 4.6, the calculated annual outdoor effective dose is lower than the world reported average. However, the results do not indicate whether there were no natural radionuclides dispersed into the environment and settling on the soils around the factory by either dry or wet disposition of the radionuclides contained in the emitted dust. To solve this problem, a graph of outdoor absorbed gamma dose rate versus distance from the factory (Figure 4.10) was plotted.

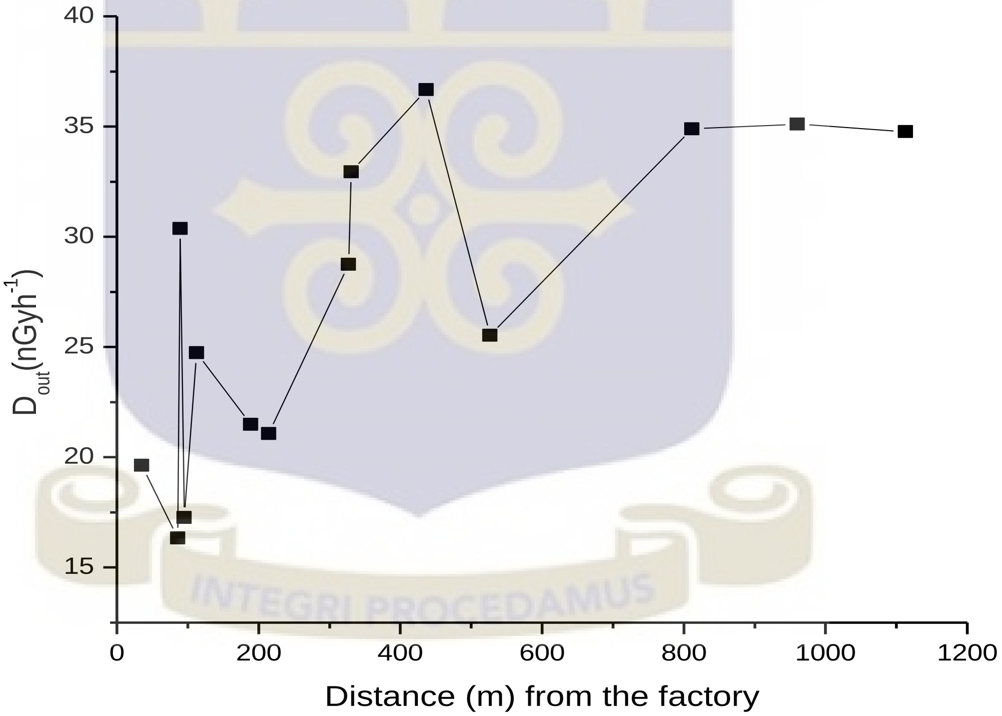


Figure 4.10: Variation of outdoor absorbed gamma dose rate with Distance from the Factory

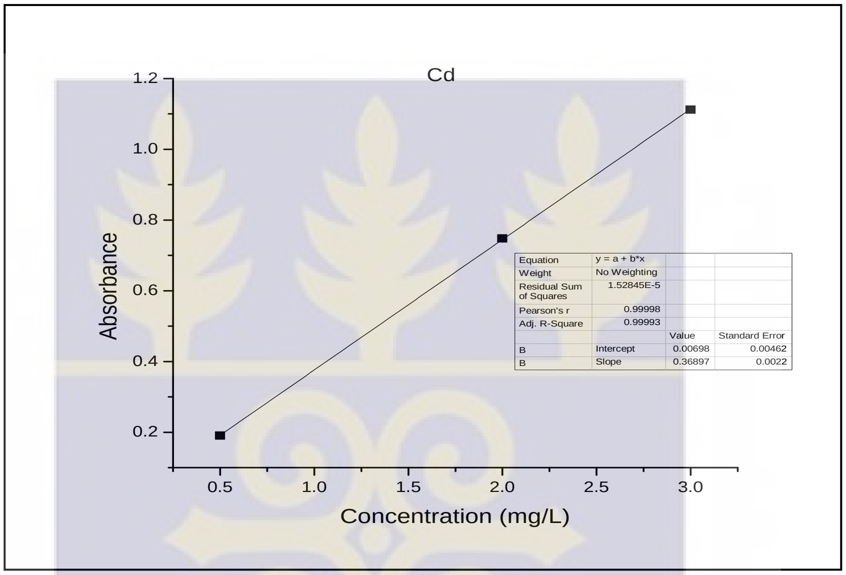
The soils within and around the factory can be radiologically enhanced by the dust emitted from the production processes. Adukpo et al., (2011) investigated the concentration of NORMs in soils and water around Diamond cement factory and found out that concentration of radionuclides in soils closer to the factory were higher than those far away. Therefore, assuming constant rate of dust emission and homogeneous horizontal meteological conditions over the soil sampling area, it was expected that the soils near the factory would have greater radionuclide concentrations than those far away, if there was to be any soil pollution from emitted dust. However, Figure 4.10 shows that doses calculated from the soils samples collected near the factory were found to be lower than those far away.

Although, the factory had been in operation for four years, this study did not find any uniform relation between distance from the source and the outdoor absorbed gamma dose rate. This shows that the concentrations of natural radionuclides (Ra-226, Th-232 and K-40) in the soils collected around the factory were due to their natural occurrences than any anthropogenic activity especially from the activities of the factory under study. Hence, the operation of the facility could not have disturbed the geological structure of the soils nearer the facility. It has been reported that companies which operate at large scale for many years increase the activity levels of the surroundings due to geological destructions by the machinery used (Avwiri, 2006). Therefore, the short duration of the operation of the factory under study may not have caused any significant disturbance of the surrounding environment.

4.5 Environmental Impact of Trace Elements from Manufacture of Crystal Cement

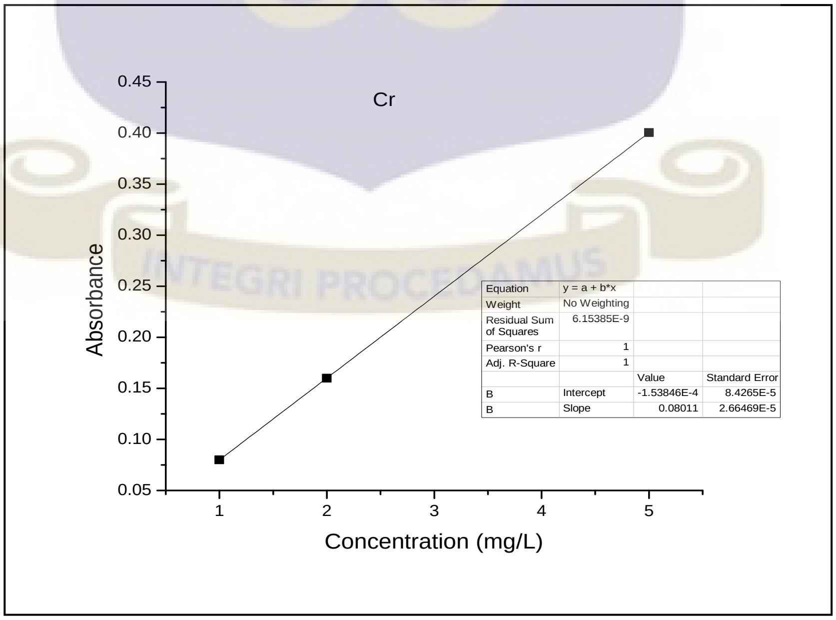
4.5.1 Calibration of the Atomic Absorption Spectrophotometer

Spectroscopic techniques require calibration with standards of known analyte concentration. Figures 4.11 (a), (b), (c), (d) and (e) show the calibration curves for the elements under study.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	1.52845E-5		
Pearson's r	0.99998		
Adj. R-Square	0.99993		
		Value	Standard Error
B	Intercept	0.00698	0.00462
B	Slope	0.36897	0.0022

Figure 4.11 (a)



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	6.15385E-9		
Pearson's r	1		
Adj. R-Square	1		
		Value	Standard Error
B	Intercept	-1.53846E-4	8.4265E-5
B	Slope	0.08011	2.66469E-5

Figure 4.11 (b)

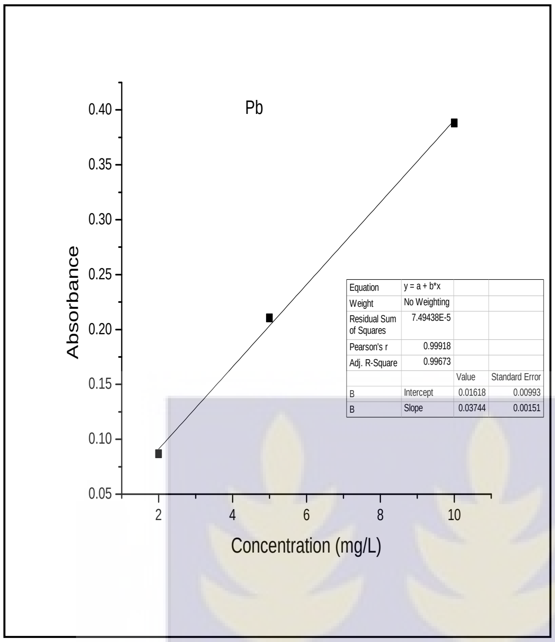


Figure 4.11 (c)

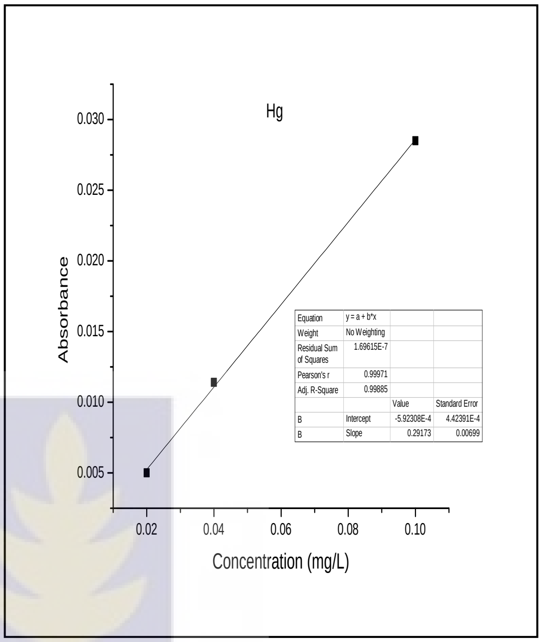


Figure 4.11 (d)

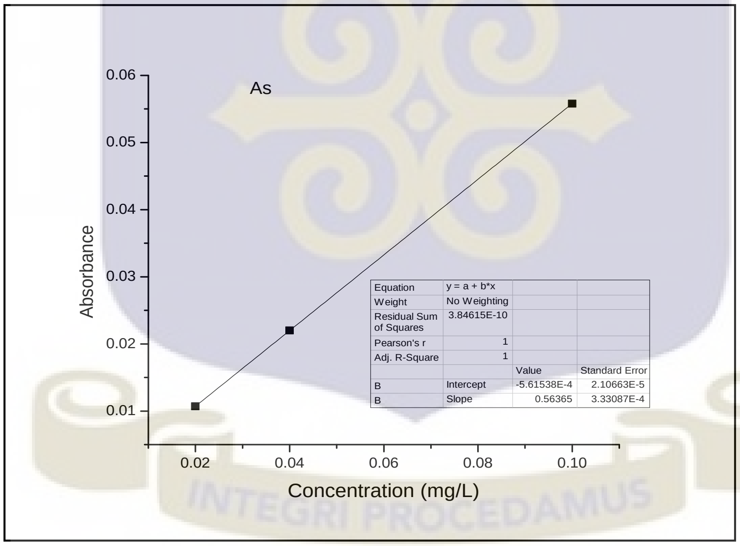


Figure 4.11 (e)

Figure 4.11 (a)-(e): Calibration curves of standards of Cr, Cd, Pb, Hg and As

4.5.2 Validation of AAS Instrumentation

Table 4.7 shows results obtained by analyzing the Estuarine Sediment standard Reference material -SRM 1646a (Appendix III) and International Soil Exchange 2011 Sample 4-114 ISE4

Table 4.7: Analysis of SRM 1646a and 114 ISE4 by AAS in mg/kg

	SRM 1646a			114 ISE4		
Element	Certified Value	Measured Value	Maximum Percentage recovery (%)	Measured Value	Certified Value	Percentage recovery (%)
Pb	11.7±1.2	12.1±0.6	98.4	299.395	299.800	99.9
Cd	0.148±0.007	0.151±0.007	101.9	8.558	8.567	99.9
Cr	40.9±1.9	39.8±2.0	97.7	270.978	271.400	99.8
As	6.23±0.21	6.06±0.30	98.7	45.968	46.180	99.5
Hg	0.040	0.031±0.001	80.0	3.129	3.925	79.7

4.5.3 Evaluation of Heavy Metals by Single Indices

In evaluating the single and integrated indices, the average elemental concentration values of respective heavy metals from all the sampling points were used instead of independent values from each sampling points. This was because the average values gave a representative picture of the functional area (agricultural area) since 12 out of the 14 samples were collected from garden fields. Table 4.9 is an extract of Table 4.8 (Appendix V) and it shows the mean elemental concentrations of heavy metals and single indices.

Table 4.9: Mean elemental concentrations and single indices

	Concentration (mg/kg)		Pollution Index	Ecological Risk	Geo-Accumulation Index
Heavy metal	Range	Mean ±SD	P_{ij}	E_r^i	I_{geo}
Pb	0.55-3.80	1.66±1.11	0.06	0.30	-5.98
Cd	0.15-0.25	0.20±0.04	0.49	14.70	-2.91
Cr	0.95-14.50	4.03±3.50	0.07	0.14	-5.06
Hg	0.02-0.03	0.02±0.00	0.35	14.00	-3.91
As	0.30-1.90	0.97±0.49	0.14	1.40	-4.53

Table 4.9 shows the mean concentrations of heavy metals in soils around the factory as well as single indices related to pollution. The mean concentrations decrease in the order of Cr >Pb>As>Cd>Hg. The table also shows that the pollution index of all the heavy metals was less than unity indicating clean environment according to Hong-gui et al., (2012).

Considering the possible ecological risk owing to the activities of the factory, Table 4.9 shows that the range of ecological risk factors for the heavy metals was 0.14 -14.70. According to the grading by Qingjie et al., (2008), an ecological risk factor of less than 40 indicates low potential ecological risk. Hence, as per results of this study, the activities of the factory do not indicate any ecological risk to the environment.

The calculated mean values of I_{geo} in garden soils (Table 4.9) ranged from -5.98 to -2.91. This range falls under class zero. According to the classification by Buccolieri et al., (2006) Table 3.3, the soils around the factory are still unpolluted.

4.5.4 Evaluation of Heavy Metals by Integrated Indices

Although the values of pollution indices in Table 4.9 show that for each heavy metal, the pollution grade is clean, they do not give a comprehensive impact of each heavy metal but rather stress elemental concentrations that seem to be high and this might lead to wrong conclusions. Hence, there is need to cater for those heavy metals whose pollution index values are considered high relative to the rest. From Table 4.8, the maximum pollution index $P_{ij\,\max}$ is 0.49 while the calculated average value $P_{ij\,ave}$ is 0.222. In this case, the corresponding calculated comprehensive pollution index P_i according to equation (3.21) is 0.380. This comprehensive pollution index is less than 0.7 and according to the grading by Hong-gui et al., (2012) Table 3.4, this value of pollution factor indicates that the agricultural area is clean.

Much as the single and comprehensive pollution factors still indicate that the agricultural area is clean, individual pollutants (heavy metals) affect the environment differently in terms of toxicity, degradation and removal (Hong-gui et al., 2012). Thus, there is need to consider the weight factor of each pollutant.

From Table 4.9, the maximum/highest mean concentration ($C_{ij\,\max}$) is from Cr i.e. 4.032±3.50 mg/kg. When this value is compared with the background values for each heavy metal, then the computed pollution factor weights ω_j for each heavy metal are shown in Table 4.10.

Table 4.10: Pollution weight factor of each heavy metal

Heavy metal element (mg/kg)	Pb	Cd	Cr	As	Hg
S_j	27	0.41	59.5	6.83	0.07
R_j	0.149	9.834	0.068	0.590	57.6
ω_j	0.002	0.144	0.001	0.009	0.844

From table 4.10 it is seen that the weight value ω_j of Hg is the highest. Thus, the pollution factor weight P_{iw} of Hg is taken as the pollution index of Hg i.e., 0.35. Considering this highest pollution factor weight, the improved maximum comprehensive pollution index according to equation (3.22) is $P'_{ij\max}$ = 0.42. Hence, the improved comprehensive pollution index is 0.54. From Table 3.4, this value is still less than 0.7 and therefore, the functional (agricultural) area is clean.

The factory uses the dry method to manufacture clay Pozzolana. Therefore, for any soil pollution to occur, it must be mainly from the dust emitted during the various manufacture processes as well as during mixing of clay Pozzolana with ordinary Portland cement. However, Table 4.8 shows that clay Pozzolana contained all the studied heavy metals while some of these heavy metals were not detected in a number of soil samples collected, possibly because they were below the detection limits or non-existent. The factory had been in operation for four years by the time of sample collection and therefore heavy metal accumulation in nearby soils might not have had any significant effect to alter the physicochemical characteristics of the soil. It should be noted that there is a natural presence of heavy metals in soils resulting from weathering and other pedogenic processes acting in the rock fragments of the parent material (Ade-Ademilua

& Umebese, 2007). Hence, even in the absence of significant inputs from external sources, these heavy metals exist in the soils with varying amounts from one location to another. The comparison of estimated dust elemental concentrations with soil concentrations is shown in Table 4.11.

Table 4.11: Comparison of elemental concentrations in clay Pozzolana and soil samples

	Mean heavy metal concentration (mg/kg)				
Sample ID	Pb	Cr	Cd	Hg	As
Pozzo	0.85±0.04	5.35±0.27	0.30±0.01	0.10±0.01	1.00±0.05
Soil	1.66±1.11	4.03±3.50	0.20±0.04	0.02±0.00	0.975±0.49

Table 4.11 indicates that the elemental concentrations of dust from clay Pozzzolana are comparable with those in the soil. This is not surprising because the major component of clay Pozzolana is clay which is mined in the nearby soils where the soil samples were collected. Therefore, the closeness of these values further suggest that there is no evidence to suggest any enhancement in elemental concentrations of the soils around except for Cr in soils around the facility as explained below.

The production of cement is a potential source of chromium emissions because chromium can be a component of both the process feed materials and the fuels that are burned in cement process kilns and dryers. However, the primary chromium emission sources in cement production are the rotary kilns and grinding mills (EPA, 1984). The concentrations of Cr in SS1, SS2, SS3, SS7 and SS9 are higher than the rest. These samples were collected in close proximity of the factory. Hence, the relatively high Cr concentrations in these samples compared to the rest of sampling points could be attributed to the above mentioned sources.

CHAPTER FIVE

Conclusion and Recommendations

5.1 Conclusion

The effect on activity concentrations from mixing clay Pozzolana with Portland cement has been studied. Results show that in some cement types there was an enhancement while in others; there was a reduction in activity concentration. The resultant effect of either enhancement or reduction in activity concentration of individual radionuclides (Ra-226, Th-232 and K-40) on the indoor absorbed gamma dose rate was insignificant in CEM IA (0.47% increase from CEM I) and CEM IIIC (1.38% decrease from CEM III). However, a significant increase in indoor absorbed gamma dose rate was observed from CEM II to CEM IIB by 5.45% while a significant reduction in the indoor absorbed gamma dose rate was reported from CEM IV to CEM IVD by 48.48%. In both significant and insignificant cases however, the estimated annual effective dose was lower than the world reported average value of 0.41mSv as well as less than 1 mSv/year which is considered as the limit for public exposure. The highest estimated indoor radon concentration from use of crystal cement was 73.03 Bq/m^3 reported in CEM IIIC. This value is four times lower than 300 Bq/m^3 considered as the action level in dwellings and other buildings for members of the public.

Furthermore, the effect of factory activities on the surrounding environment has been studied. The annual outdoor effective dose from soils within and around the factory ranged from 0.02±1.07E-05 to 0.04 ±1.94E-05 mSv. Thus, all the values in this range were lower than the world reported average of 0.07 mSv per year. Additionally, estimated pollution parameters i.e., pollution index, ecological risk factor, geo-accumulation index and comprehensive pollution index were less than 1, 40, 0 and 0.7 respectively that are considered as no possible pollution or clean environment.

Therefore, the use of Crystal cement as a building material is considered safe and there was no evidence to suggest any possible changes in the geochemical structure of the surrounding environment. However, with prolonged operation of the factory, there may be effects.

5.2 Recommendations

The following are the recommendations made to various government agencies involved in protection of public and workers against any form of exposure to hazardous substances/materials as well as those concerned with preserving the environment.

5.2.1 The Ministry of Employment and Labour Relations-Ghana

The inhalation of mineral dust can cause severe health problems that include silicosis, fibrosis and lung cancer resulting from chronic inhalation of mineral dusts. This study neither considered dermal nor internal exposure of workers from dust generated as a result of different processes involved in production of clay Pozzolana and subsequently crystal cement. Hence, further study on the elemental contents of dust needs to be done to estimate the possible health hazards associated with processing of clay. In particular, the amount of Respirabe Crystalline Silica (SiO_2) in clay Pozzolana, needs to be investigated since it is associated with all the three types of silicosis, i.e, chronic, accelerated and acute.

5.2.2 The Environmental Protection Agency (EPA)-Ghana

Soil samples around the factory were collected once. Hence, prolonged studies with samples collected at specified intervals need to be done to estimate the effect of factory activities on the environment.

5.2.3 The Radiation Protection Institute (RPI) and Ghana Standards Authority (GSA)

The indoor absorbed gamma dose rate calculated in CEM IV was 134.05 nGyh^{-1}. This dose is equivalent to an annual effective dose of 0.66 mSv. Much as this effective dose is less than the recommended value of 1 mSv per year for occupational exposure, it may be high in buildings with smaller rooms. This is because the calculations were based on standard room model of dimensions 4m x 5m x 2.8m, thickness of walls, floor and ceiling of 20m and density of structure of 2350 kg m^{-3}. Hence, for smaller rooms because of Inverse Square law between dose and distance from the source, the value of indoor absorbed gamma dose rate and subsequently annual effective dose may be higher than the recommended. Thus, the two organizations above should work together to develop separate model to cater for different dimensions of the rooms. This would then enable estimation of amount of exposures from use of CEM IV as well as other cement types to determine their suitability as building materials in terms of radiation exposure.

Results have also insinuated that mixing more than one type of Ordinary Portland Cement might alter the radionuclide activity concentrations in the mixed type. Therefore, RPI should investigate this effect by considering many cement types and different mixing ratios. This is because there might be the tendency by some builders and construction workers to mix more than one type of cement with other building materials on the same construction site.

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Appendix I

a) U-238 decay series

	Half-life	Mode of decay[a]	Gamma energy (keV)[b]
^{238}U	4.468 × 10^9 a	Alpha	
^{234}Th	24.10 d	Beta	63.29 (4.8%), 92.38–92.8 (5.6%)
^{234m}Pa	1.17 min	Beta	1001.03 (0.837%)
^{234}U	245 700 a	Alpha	
^{230}Th	75 380 a	Alpha	
^{226}Ra	1600 a	Alpha	186.211 (3.59%)
^{222}Rn	3.8235 d	Alpha	
^{218}Po	3.10 min	Alpha	
^{214}Pb	26.8 min	Beta	351.932 (37.6%)
^{214}Bi	19.9 min	Beta	609.312 (46.1%), 1764.491 (15.30%)
^{214}Po	164.3 μs	Alpha	
^{210}Pb	22.20 a	Beta	46.539 (4.25%)
^{210}Bi	5.012 d	Beta	
^{210}Po	138.376 d	Alpha	
^{206}Pb	Stable	—	

[a] Only major modes of decay are shown.
[b] Only major gamma emissions of interest are shown.

b) Thorium-232 decay series

	Half-life	Mode of decay[a]	Gamma energy (keV)[b]
^{232}Th	1.405 × 10^{10} a	Alpha	
^{228}Ra	5.75 a	Beta	
^{228}Ac	6.15 h	Beta	911.204 (25.8%), 968.971 (15.8%)
^{228}Th	1.912 a	Alpha	
^{224}Ra	3.66 d	Alpha	240.986 (4.10%)
^{220}Rn	55.6 s	Alpha	
^{216}Po	0.145 s	Alpha	
^{212}Pb	10.64 h	Beta	238.632 (43.6%)
^{212}Bi	60.55 min	Beta 64.06% Alpha 35.94%	727.330 (6.67%)
^{212}Po	0.299 μs	Alpha	
^{208}Tl	3.053 min	Beta	583.191 (84.5%), 2614.533 (99.16%)
^{208}Pb	Stable	—	

[a] Only major modes of decay are shown.
[b] Only major gamma emissions of interest are shown.

Adapted from: (International Atomic Energy Agency, 2013)

Appendix II

CZECH METROLOGY INSTITUTE
INSPECTORATE FOR IONIZING RADIATION

Radiová 1, 102 00 Praha 10

CERTIFICATE

Cert. No: 9031 - OL - 146/14 Type: MBSS 2 Prod. No: 050214-1425039

Radionuclide	Half life days	Activity kBq	Combined standard uncertainty, %
Am-241	157800	4,694	1,1
Cd-109	462,6	14,54	1,4
Ce-139	137,5	1,355	1,1
Co-57	271,26	1,156	1,1
Co-60	1925,4	2,697	1,1
Cs-137	11019	2,689	1,3
Sn-113	115,1	4,000	2,2
Sr-85	64,78	4,570	1,5
Y-88	106,6	5,323	1,2

Mass: 980,0 g Density: 0,98 g/cm^3 Volume: 1000 cm^3

Radionuclide inpurities: gamma < 0,1 %

Reference date: 20.3.2014 Homogeneity better than: 1 %

Description:

Radioactive material is homogeneously dispersed in silicone resin. Composition of the matrix: C - 0,324 H - 0,0816 O - 0,216 Si - 0,379 (mass ratio).

Measuring method:

Preparation issues from standard ER solutions whose activities were determined by suitable absolute method. Final control is based on gamma spectrometry on HPGe detector.

Note:

As the criterion of homogeneity standard deviation of the acivity value of 1 cm^3 element was chosen (n=10). The volume is calculated from the mass and the density.

Date of the cetificate issue: 25.2.2014 Validity: 3 years

Customer:

CANBERRA-PACKARD CENTRAL EUROPE
Wienersiedlung 6
A-2432 Schwadorf
Austria

Ing. Jiří Šuráň, MBA
director

Control: RNDr. Richard Bluďovský, CSc., RNDr. Pavel Dryák, CSc.

Tel.: +420 266 020 497 Fax: +420 266 020 466

Appendix III

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1646a

Estuarine Sediment

This Standard Reference Material (SRM) is intended primarily for calibrating instrumentation and evaluating the reliability of analytical methods for the determination of major, minor, and trace elements in estuarine sediments and similar matrices. One unit of SRM 1646a contains 70 g of material.

Certified Values and Uncertainties: The certified values for the constituent elements are shown in Table 1. They are based on results obtained either by definitive methods or by two or more independent, reliable analytical methods. The results of two or more independent analytical methods were weighted according to the algorithm of Paule and Mandel [1]. The expanded uncertainties, whose level of confidence is approximately 95 %, include random and systematic sources of uncertainty from within each analytical method, material variability, which was detected for lead, and a systematic component of uncertainty between analytical methods [2]. All values are based on a minimum sample size of 500 mg of the material dried as indicated under ("Instructions for Drying").

Noncertified Values: Noncertified values are given in Table 2. Noncertified values are provided for information only because only one independent method was used, or there was insufficient agreement between the methods.

NOTICE AND WARNING TO USERS

Expiration of Certification: The certification is valid for five years from the date of shipment from NIST. Should any of the certified values change before the expiration of the certification, purchasers will be notified by NIST. Registration, see attached sheet, will facilitate notification.

Stability: This material is considered to be stable; however, its stability has not been rigorously assessed. NIST will monitor this material and will report any substantive changes in certification to the purchaser.

Use: The material should be kept in its original bottle and mixed well before each use. A minimum sample of 500 mg of the dried material (see "Instructions for Drying") is required for any analytical determination that is to be related to a certified value of this certificate.

Instructions for Drying: Except for volatile elements (e.g., arsenic, mercury, and selenium), elements should be determined on samples that have been dried at 110 °C for 2 h.

Volatile elements should be determined on undried samples. However, because the certified values are reported on a dry weight basis, the volatile elements determined on undried samples will have to be adjusted for the difference in moisture content.

The overall direction and coordination of the technical measurements leading to certification were performed by R.R. Greenberg of the NIST Analytical Chemistry Division.

Statistical consultation was provided by S.B. Schiller of the NIST Statistical Engineering Division.

Willie E. May, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 20 February 2004
See Certificate Revision History on Last Page

John Rumble, Jr., Chief
Measurement Services Division

Appendix III cont'

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by J.S. Kane and B.S. MacDonald of the NIST Measurement Services Division.

Source and Preparation of Material: The material for this SRM was collected under the direction of M. Unger, Virginia Institute of Marine Sciences, Gloucester Point, VA. It was dredged from the Chesapeake Bay at a location of 37° 11.1' min N, 76° 17.11' min W. The material was freeze-dried at Hanover Foods, Inc., Lancaster, PA, and transferred to the U.S. Geological Survey (USGS) in Denver, CO. The material was lightly deagglomerated and sieved through a 1 mm screen to remove coarse contaminants. The < 1 mm material was then ball milled to pass a (75 µm) 200 mesh and then blended in a single batch using a 10 ft^3 blender. The blended material was radiation sterilized at COBE Laboratories, Lakewood, CO, and then bottled.

Homogeneity Assessment: Prior to bottling, a preliminary evaluation of homogeneity was performed by the USGS using ten 50 g samples obtained from various locations in the blender. These homogeneity measurements were made by wavelength dispersive X-ray fluorescence (WDXRF) and inductively coupled plasma optical emission spectrometry (ICPOES) analyses. Final homogeneity evaluations of the bottled samples were made by WDXRF at the USGS, and by instrumental neutron activation analysis (INAA) at NIST. Except for lead, nickel, and antimony, a satisfactory level of homogeneity was observed for the certified elements, that is, no large sample-to-sample variations were observed over those expected from the analytical measurements. Some heterogeneity was observed for nickel and antimony, and because of the degree of heterogeneity observed for nickel and antimony, the concentrations of these elements have not been certified.

Table 1. Certified Values

Element	Mass Fraction, (%)	Element	Mass Fraction, (mg/kg)
Aluminum	2.297 ± 0.018	Arsenic	6.23 ± 0.21
Calcium	0.519 ± 0.020	Cadmium	0.148 ± 0.007
Iron	2.008 ± 0.039	Chromium	40.9 ± 1.9
Magnesium	0.388 ± 0.009	Copper	10.01 ± 0.34
Phosphorus	0.027 ± 0.001	Lead	11.7 ± 1.2
Potassium	0.864 ± 0.016	Manganese	234.5 ± 2.8
Silicon	40.00 ± 0.16	Selenium	0.193 ± 0.028
Sodium	0.741 ± 0.017	Vanadium	44.84 ± 0.76
Sulfur	0.352 ± 0.004	Zinc	48.9 ± 1.6
Titanium	0.456 ± 0.021		

Table 2. Noncertified Values

Element	Mass Fraction, (mg/kg)	Element	Mass Fraction, (mg/kg)
Antimony	0.3	Neodymium	15
Barium	210	Nickel	23
Beryllium	<1	Rubidium	38
Cerium	34	Scandium	5
Cobalt	5	Silver	<0.3
Gallium	5	Strontium	68
Lanthanum	17	Thallium	<0.5
Lithium	18	Thorium	5.8
Mercury	0.04	Tin	1
Molybdenum	1.8	Uranium	2.0

Appendix IV

Table 4.3: Indoor Absorbed Gamma Dose rate (nGyh^{-1}) and Annual Indoor Effective Dose (mSv) in Pozzolana and Crystal Cement

Sample ID*	D_{in} (A)	E_{in} (A)	D_{in} (FW)	E_{in} (FW)	D_{in} (F)	E_{in} (F)	D_{in} (SM)	E_{in} (SM)
POZZ	81.58±4.59	0.40±0.02	58.48±3.25	0.29±0.02	20.92±1.17	0.10±0.01	10.41±0.58	0.05±0.00
CEM IA	57.52±1.74	0.28±0.01	41.27±1.25	0.20±0.01	14.73±0.44	0.07±0.00	7.30±0.22	0.04±0.00
CEM IIB	67.12±2.63	0.33±0.01	48.15±1.87	0.24±0.01	17.18±0.67	0.08±0.00	8.51±0.33	0.04±0.00
CEM IIIC	81.75±3.72	0.40±0.02	58.78±2.68	0.29±0.01	21.01±0.96	0.10±0.00	10.45±0.48	0.05±0.00
CEM IVD	67.68±3.11	0.33±0.01	48.56±2.23	0.24±0.01	17.32±0.79	0.08±0.00	8.58±0.39	0.04±0.00

Table 4.4: Radium Equivalent (Bq/kg) and hazard indices from clay Pozzolana and crystal cement

Sample ID	Ra_{eq}	H_{ex}	H_{in}
POZZ	95.12±5.87	0.26±0.02	0.35±0.02
CEM IA	64.53±1.70	0.18±0.00	0.24±0.01
CEM IIB	74.76±2.98	0.21±0.01	0.28±0.01
CEM IIIC	92.64±4.29	0.25±0.01	0.37±0.02
CEM IVD	75.37±3.48	0.21±0.01	0.27±0.01

Table 4.6: Specific activity of ^{232}Th, ^{40}K and ^{226}Ra (Bq/kg)with corresponding annual values of outdoor absorbed gama dose rate D_{out} (nGyh^{-1}) and effective dose E_{out} (mSv)

Sample ID	A_{Ra-226}	A_{Th-232}	A_{K-40}	**Distance from stack (m)**	D_{out}	E_{out}
SS1	24.18±3.16	29.86±0.94	27.80±3.09	89.48	30.37±1.56	0.037±4.745E-05
SS2	20.47±1.19	23.30±0.72	28.71±3.14	112.40	24.74±0.71	0.030±1.770E-05
SS3	13.90±0.34	15.95±0.65	28.88±3.14	95.09	17.26±0.44	0.021±7.619E-05
SS4	16.45±1.21	20.51±0.46	35.84±3.87	189.10	21.49±0.65	0.026±1.388E-05
SS5	23.86±0.87	30.37±0.50	84.93±8.97	331.00	32.96±0.63	0.040±2.070E-05
SS6	23.68±1.96	25.63±0.63	55.69±5.95	326.60	28.76±1.01	0.035±2.913E-05
SS7	13.75±0.12	14.40±1.06	30.76±3.33	86.01	16.34±0.66	0.020±1.073E-05
SS8	17.41±1.46	17.91±0.97	52.54±5.52	214.60	21.07±0.92	0.026±1.947E-05
SS9	16.60±0.40	17.54±1.10	32.62±3.87	35.25	19.63±0.71	0.024±1.391E-05
SS10	30.42±0.61	31.69±0.42	82.83±8.76	436.70	36.68±0.53	0.045±1.944E-05
SS11	21.83±0.86	20.31±0.27	75.47±7.90	526.70	25.52±0.54	0.031±1.384E-05
SS12	30.23±1.08	29.49±0.27	74.11±7.84	811.40	34.89±0.62	0.043±2.167E-05
SS13	29.48±0.13	29.62±2.16	85.62±9.03	960.00	35.11±1.36	0.043±4,781E-05
SS14	26.16±1.36	26.79±0.80	154.96±16.20	1113.00	34.77±1.05	0.043±3.640E-05
AV±SD	**22.03±5.82**	**23.81±6.00**	**60.769±35.62**		**27.11±7.16**	**0.033±0.01**

Appendix V

Table 4.8: Soil sample coordinate locations, respective distances from Factory Chimney/stack and mean concentration

Sample ID	Description	Coordinates	Distance from the factory (metres)	Heavy metal mean concentration (mg/kg)				
				Pb	Cd	Cr	Hg	As
SSI	Compound	5.363153°N 0.742370°W	89.48	1.65±0.08	< DL	14.50±0.72	0.02±0.001	1.90±0.10
SS2	Cassava garden	5.363479°N 0.742015°W	112.40	0.70±0.03	< DL	6.75±0.34	0.02±0.001	1.50±0.08
SS3	Tomato garden	5.363174°N 0.741452°W	95.09	1.40±0.07	< DL	4.05±0.20	< DL	1.30±0.07
SS4	Ground nuts & maize garden	5.363951°N 0.741099°W	189.10	< DL	< DL	2.30±0.11	< DL	1.000.05
SS5	Sugar cane plantation	5.365178°N 0.740697°W	331.00	3.80±0.19	< DL	3.60±0.18	< DL	1.55±0.08
SS6	Maize plantation	5.365295°N 0.741130°W	326.60	0.55±0.03	< DL	3.45±0.17	< DL	1.05±0.05
SS7	Okro garden	5.362417°N 0.741166°W	86.01	< DL	< DL	5.15±026	0.03±0.001	0.80±0.04
SS8	Cleared field for ploughing	5.361411°N 0.740321°W	214.60	< DL	< DL	1.90±0.09	< DL	0.90±0.05
SS9	Compound	5.362562°N 0.741636°W	35.25	< DL	< DL	6.20±0.31	0.03±0.001	1.35±0.07
SS10	Plantain plantation	5.358972°N 0.740149°W	436.7	2.30±0.11	ND	2.30±0.11	< DL	0.55±0.03
SS11	Cassava garden	5.358706°N 0.739054°W	526.7	< DL	0.20±0.01	0.95±0.05	< DL	0.3±0.02
SS12	Cassava, plantain & garden egg garden	5.355931°N 0.738691°W	811.40	< DL	0.20±0.01	1.60±0.08	< DL	0.5±0.03
SS13	Cassava garden	5.354620°N 0.738334°W	960.00	1.20±0.06	0.15±0.01	1.65±0.08	< DL	0.40±0.02
SS14	Okro garden	5.353272°N 0.737974°W	1113.00	< DL	0.25±0.01	2.05±0.10	< DL	0.55±0.03
pozzo				0.85±0.04	0.30±0.01	5.35±0.27	0.1±0.01	1.00±0.05

*< DL –Less than the Detection Limit.

Note: the Detection Limit for Pb , Cd, Cr, Hg and As were taken as, 0.01 mg/L, 0.002mg/L, 0.005mg/L, 0.001mg/L and 0.002mg/L respectively.