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CHEMICAL ANALYSIS OF SOME SELECTED CEMENTS (HABESHA, DERIBA, DANEGOTIE, EAST AND MOSSEBO) IN ETHIOPIA

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COLLEGE OF SCIENCE POST GRADUATPROGRAM

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Wisdom at the source of the Blue Nile

CHEMICAL ANALYSIS OF SOME SELECTED CEMENTS (HABESHA, DERIBA, DANEGOTIE, EAST AND MOSSEBO) IN ETHIOPIA

BY

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August, 2018

Bahir Dar, Ethiopia

Chemical Analysis of some Selected Cements, (Habesha, Deriba, Danegotie, East and Mossebo) in Ethiopia

A Thesis Submitted To the Department Of Chemistry Presented In Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemistry (Analytical Chemistry)

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Advisor Tihitinna Asmellash (PhD)

August, 2018

Bahir Dar, Ethiopia

LETTER OF APPROVAL

BAHIR DAR UNIVERSITY

Wisdom at the source of the Blue Nile

The thesis entitled “Chemical Analysis of some Selected Cements (Habesha, Deriba, Danegotie, East and Mossebo) in Ethiopia” presented by Abraraw Birhanu has been accepted as the partial fulfillment for the degree of Master of sciences in chemistry (analytical chemistry).

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DECLARATION

This is to certify that this thesis entitled “Chemical Analysis of some Selected Cements (Habesha, Deriba, Danegotie, East, and Mossebo)in Ethiopia in partial fulfillment of the requirements for the degree of Master of sciences in analytical chemistry to the post Graduate program of college of science, Bahir Dar University is an authentic work conducted by Abraraw Birhanu under the supervision of Tihitna Asmelash (PhD).

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TABLE OF CONTENTS

Contents **Page**

DECLARATION i

TABLE OF CONTENTS ii

LIST OF TABLES iv

LIST OF FIGURES v

ACKNOWLEDGEMENT vi

ACRONYM/ABBREVIATION vii

ABSTRACT viii

1. INTRODUCTION 1
   - 1.1 Background of the study 1
   - 1.2. Statement of the problem 3
   - 1.3 Objectives 4
     - 1.3.1 General objective 4
     - 1.3.2. Specific objectives 4
   - 1.4. Significant of the study 4

2. LITERATURE REVIEW 5
   - 2.1. Cement 5
   - 2.2. Type of cements 7
     - 2.2.1 Natural Pozzolana 7
     - 2.2.2. Expansive cement 7
     - 2.2.3. High-alumina cement 8
     - 2.2.4 Portland cement 8
   - 2.3. Clinker phases of Portland cement 12
     - 2.3.1. Alite (C_3S) 12
     - 2.3.2. Belite (C_2S) 13
     - 2.3.3. Aluminate (C_3A) 13
     - 2.3.4. Ferrite (C_4AF) 13
   - 2.4. Parameter of Portland cement 13
     - 2.4.1. Chemical Parameters 13
       - 2.4.1.1. Insoluble residue (IR) 14
       - 2.4.1.2 Loss of ignition (LOI) 14
       - 2.4.1.3 Free CaO 14
       - 2.4.1.4 SO_3 14

2.4.1.5 SiO_2 14
2.4.1.6 Fe_2O_3 14
2.5. Heavy metal Exposures for cement production 14
2.6 methods for the determination of heavy metals 17
2.6 1. Atomic absorption spectrometry (AAS) 17
2.6.2. Inductively coupled plasma/optical emission spectrometry (ICP-OES) 18
3. METHODOLOGY 19
3.1. Sample Collection 19
3.2. Instrument and Equipment 19
3.3Chemicals and Reagents 19
3.4. Experimental method for chemical analysis 19
3.4.1 Determination of Insoluble Residue (IR) 19
3.4.2 Determination of Loss on Ignition (LOI) 20
3.4.3 Determination of SiO_2 21
3.4.4 Determination of iron oxide (Fe_2O_3) 21
3.4.5 Determination of free-lime (CaO) 21
3.4.6 Determination of sulphur trioxide (SO_3) 22
3.5. Determination of Heavy Metals Concentration 22
3.6. Standard solution preparation 23
4. RESULT AND DISCUSIONS 24
4.1 Determination of detection limits and limits of quantization 24
4.1.1 Detection limits 24
4.1.2. Limits of quantization 24
4.1.3. Spiking solution preparation 25
4.2 Calibration curve 25
4.3 Statistical Analysis 28
4.4. The comparison of the level of metals in five Different Cement Samples 28
4.5 Percentage composition oxides 32
4.5.1 Comparison of Chemical Parameter in each Portland cement brand 33
5. CONCLUSIONS 36
6. RECOMMENDATION 37
REFERENCES 38

LIST OF TABLES

Page

Table 2. 1 Summary of chemical data for a selection of Portland cement 10
Table 2. 2 ASTM Specification of the chemical and mineralogical composition of Portland cement 12
Table 2. 3 The BUWALvalves of Regulatory requirements for concentrations of metals in cement clinker and product.. 17
Table 4. 1 Method Detection and Quantitation Limits, (DLM =3σblank and MQL = 10σblank, in ml/L) for each cement samples.. 24
Table 4. 2 Stock solutions, Concentration of spike and UN spike in metal cement sample in mg/L and % of recoveries... 25
Table 4.3 working standards and correlation coefficient of the Calibration curves for determination of metal using ICP-OES 26
Table 4. 4 Concentration (mg/Kg) of heavy metal in cement samples and their ANOVA analysis 28
Table 4. 5 The concentration of heavy metals in cement from previous studies in mg/Kg 32
Table 4. 6 Amounts of chemical constituents by % and their ANOVA analysis.................... 32

LIST OF FIGURES

Page

Figure 1 Calibration curve for determination of metals (a) Zn, (b) Cr, (c), Ni, (d) Cu, and (e) Cd 27
Figure 2 (a-e), Trends of metal concentrations according to the source of Portland cements........ 30
Figure 3 Variation of Fe2O3 (a), SiO2 (b), LOI (c), SO3 (d), Free CaO (e) and (IR) (f) 35

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ACRONYM/ABBREVIATION

C2S	Dicalcium silicate
C3A	Tricalcium Aluminate
C4AF	TetracalciumAlumferrite
IR	Insoluble residue
LOI	Loss of ignition
ASA	Acidic sodium acetate extractable
AHH	Acidic hydroxylamine hydrochloride extractable
SB	Sulfide bound
R	Residual
AAS	Atomic absorption spectrometry
AES/AFS	Atomic emission fluorescence spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
ANOVA	analysis of variance
SO_3	Sulfur tri oxide

ABSTRACT

The characterization and classification of cement is based on the determination of its chemical composition. Therefore, the major purpose of this study was to determine chemical properties of five different brands of cement (Habesha, Deriba, East, Mossebo and Danegotie) in Ethiopia using standard methods such as the American Society for Testing and Materials (ASTM) and British Standards Institution (BSI) . The results of the analysis indicated that Free CaO, SiO_2, LOI andFe_2O_3 in all samples are within the acceptable limits. Even though the IR and SO_3 results for East, Deriba and Habesha are inside the recommended limit, the two cement samples from Mossebo and Danegotie showed results above the recommended limit. The results revealed there are significant differences in chemical analysis of some cements.

The concentration of heavy metals (Cd, Ni, Cr, Ni and Zn) in the Portland cement were analyzed using ICP OES. The results of heavy metals in cement showed different trained Cr> Zn> Ni >Cu, Ni > Cr >Zn>Cu, Cr > Ni>Zn >Cu, Cr > Ni > Cu>Zn and Cr> Ni > Cu >Zn for Habesha, East, Danegotie, Deriba and Mossebo respectively. Even though cadmium was not detected in all samples, high concentration of Cr and Ni was observed in Mossebo and Deriba sample. In addition the statistical analysis revealed that except Zn all measured metals showed a significance difference.

Key words

Cement, Clinker, Hazardous wastes, Heavy metal

1. INTRODUCTION

1.1 Background of the study

Cement is among the most important and necessary materials in the world, which is the second most highly consumed product after water .Without it, the construction industry that utilizes huge tonnages of concrete annually would struggle to survive [1]. It is known that some developed countries depend on the construction industry as one of the main pillars for the growth of their economies. In developing economies, the construction industry provides many jobs for people in both the formal and the informal sectors. Any shortfall that stagnates, the construction industry usually leads to serious economic slump, bridges and tunnels [2].

One of the most important considerations to make before embarking on the construction of a building is the cement that would be used; the common type of cement used across the world is Portland cement. The primary reason for its global use is its composition and essential characteristics in the setting and hardening of the concrete, durability when dry, fire-proof nature, effective protection of iron or timber structures, ability to prevent corrosion, its use in ships, tanks and bunkers [3]. Cements used in construction can be characterized as being either hydraulic or non-hydraulic, depending upon the ability of the cement to set in the presence of water. Non-hydraulic cement will not set in wet conditions or underwater; rather, it sets as it dries and reacts with carbon dioxide in the air. It can be attacked by some aggressive chemicals after setting .*Whereas* Hydraulic cements (e.g., Portland cement) set and become adhesive due to a chemical reaction between the dry ingredients and water. The chemical reaction results in mineral hydrates that are not very water-soluble and so are quite durable in water and safe from chemical attack. This allows setting in wet condition or underwater and further protects the hardened material from chemical attack. The chemical process for hydraulic cement found by used volcanic ash [4].

About 90 - 95% of Portland cement is composed of the four main cement minerals, tricalciumsilicate (C_3S), dicalciumsilicate (C_2S), tricalcium aluminate (C_3A) and tetra calcium aluminoferrite (C_4AF) with each of them playing different roles in the hydration process that converts the dry cement into hardened cement paste [5].

About 10.0 – 5.0% of the remaining compositions are calcium sulphate, alkali sulphates, unreacted calcium oxide, magnesium oxide and other minor constituents left over during the clinkering and grinding steps [6].This is an indication that qualities of cement may differ based on the production origin. However, the quality of cement is very important to its application which made the product useful in mortars, plasters, screeds and grouts as a material which can be squeezed into gaps to consolidate the structures. In addition, lime saturation factor (LSF), silica ratio (SR) and aluminum ratio (AR) are important factors for chemical control in cement [7].

The use of poor quality cement in structural and constructional works may cause loss of lives and properties. So, quality assurance of Portlandcement has become an important and critical factor. The cement to be used in construction must have certain qualities in order to play its part effectively in structure. When these properties lie within a certain specified range of standard values, the engineer is confident that in most of the cases the cement performance will be satisfactory. In addition, based on these properties it is possible to compare the quality of cement from different sources. A number of tests are performed in the laboratories of cement industries to ensure that the cement is of the desired quality and it conforms to the requirement of the relevant standards [8].

The raw materials used in the manufacture of cement consist mainly of lime, silica, alumina and iron oxide. These compounds interact with one another in the kiln to form a series of more complex products, and apart from a small residue of uncombined lime, which has not had sufficient time to react; a state of chemical equilibrium is reached. Chemical components in cement are combined to from different potential compounds [9]. Cement industry has been in operation for many decades and has contributed to Economy greatly [10] Despite the remarkable achievements recorded in the use of cement, it studies have shown that it is associated with some environmental problems such as emission of air pollutants in form of dust, gases, noise and vibration during the process of manufacture . Cement is also associated with heavy metals as evident in many studies conducted [11]. Heavy metals are known to pose serious health problems to humans, affect plant growth and general damage to ecosystem the cement may be directly exposed to human population, particularly to cement plant workers, construction workers as well as the community living nearby the cement plants and construction sites. The presence of heavy metals in the cement may pose a risk to human health by incidental ingestion, inhalation of suspended cement and dermal absorption. Incidental ingestion involves hand-to mouth transfer during outdoor activities such as mouthing, contacting dirty hands, eating dropped food, or consuming cement directly [12].

1.2. Statement of the problem

The breakdown of cement monopoly which allowed the entrance of other brands of cement is currently creating a major problem for builders in making the best and preferred choice of cement for their constructional work. The performance of Portland cement in concrete or mortar formation is very well influenced by chemical compositions among other factors. Many engineers usually have little information on the chemical compositions of cement in making decisions for the choice of commercially available (Danegotie, Habesha, Deriba, Mossebo and East) Portland cement in Ethiopia. This could be an important key for the selection of best performing cement.

Cement kiln co-processing of hazardous waste in Cement Company produces Portland cement in a rotary kiln in which hazardous waste, both solid and semisolid, these solid and semisolid hazardous wastes being co-processed were mainly derived from soil contaminated with heavy metals or organic matters, water treatment sludge and industrial wastes. However, (Cu, Ni, Cr, Cd, and Zn metals in wastes might be discharged through different streams during co-processing of hazardous wastes in cement kilns. Based on mass balance of metals, during burning of cement in the kiln, most metals in waste materials were transported into clinkers in cement. The cement may be directly exposed to human population [13].

1.3 Objectives

1.3.1 General objective

The general objective of this study was to determine chemical properties in five different brands of cement (Habesha, Deriba, East, Mossebo and Danegotie) in Ethiopia.

1.3.2. Specific objectives

- To determine some major oxides (Fe_2O_3 SiO_2 ,SO_3 and Free lime)
- To determine levels of heavy metals in the cement samples(Cd, Ni, Cr, Cu and Zn)
- To determine the extent of variation that exists between the commercially available cement and standard literature

1.4. Significant of the study

It is important that the Ethiopian cement conforms to the set of internationally required standards. In practice, cement structure durability, i.e., resistance to aggressive agents is determined largely by concrete permeability and it is influenced by the efficiency with which cement hydration products fill the void between the grains of aggregates. Poor conformity of structures to established guidelines leads to the development of their degradation. This has necessitated investigations into the basic raw materials compositions, the finished products and other factors that could ensure longer service life for cement-based structures. Therefore, with the present socio-economic development and the envisaged technological advancement, the increased demand for cement cannot be overemphasized. It has become necessary, therefore, to characterize the available cement and effectively determine the area of optimal application. And also to analyzed concentrations of metals in cement clinker, produced during co-processing of hazardous waste procedure in the cement kiln of the Ethiopia Cement Company.

2. LITERATURE REVIEW

2.1. Cement

Cement is an inorganic, non-metallic substance with hydraulic binding properties, and is used as a bonding agent in building materials. It is a fine powder; usually gray is color that consists of a mixture of the hydraulic cement minerals to which one or more forms of calcium sulfate have been added [14]. Mixed with water it forms a paste, which hardens due to formation of cement mineral hydrates. Cement is the binding agent in concrete, which is a combination of cement mineral aggregates and water. Concrete is a key building material for a variety of applications cement industry is made up of either Portland cement plants that produce clinker and grind it to make finished cement, or clinker grinding plants that intergrind clinker obtained elsewhere, with various additives. Clinker is produced through a controlled high-temperature burn in a kiln of a measured blend of calcareous rocks (usually limestone) and lesser quantities of siliceous, aluminous, and ferrous materials. The kiln feed blend (also called raw meal or raw mix) is adjusted depending on the chemical composition of the raw materials and the type of cement desired [15].The most common construction material used in building industry.

Cement is a basic component of concrete used for building and civil engineering construction. Therefore concrete (i.e. cement) is one of the World's most significant manufactured materials. Because of its abundance in the world market, understanding the environmental implications of concrete and cement manufacturing are becoming increasingly important [16]. The most common raw materials used for cement production are limestone, chalk and clay. The major component of the raw materials, the limestone or chalk, is usually extracted from a quarry adjacent to or very close to the plant. Limestone provides the required calcium oxide and some of the other oxides, while clay, shale and other materials provide most of the silicon, aluminum and iron oxides required for the manufacture of cement [17].

Cement production starts with the extraction of the raw materials and their subsequent pre-crushing in the quarry located in the vicinity of cement works. With the ratio of raw materials being specified exactly, a mixture is produced, if necessary, by adding correction materials, such as sand, iron ore and clay. Apart from natural raw materials, waste materials containing lime, aluminates, silicate, and iron are used as raw materials substitute. This mixture of raw materials is milled to raw meal and, at the same time, dried with the residual heat of the kiln of gases. In the downstream electrostatic precipitator, the raw meal is separated and subsequently transported to the raw meal silos. Via the pre-heater, the dust-like raw meal is fed into the rotary kiln. By means of the burning process at 1250 to 1599 ◦C, clinker granules are formed. The energy required is supplied by the combustion of coal in a burner at the end of the rotary kiln (primary combustion) and partly also at the beginning of the rotary kiln (secondary combustion). The hot flue gases generated by combustion, flow through the rotary kiln and pre-heater in opposite direction to the solids. The clinker leaving the rotary kiln has to be cooled down [18].

The production of cement involves the consumption of large quantities of raw materials, energy, and heat. Cement production also results in the release of a significant amount of solid waste materials and gaseous emissions. The manufacturing process is very complex; involving the cement manufacturing industry is under close scrutiny these days because of the large volumes of CO_2 emitted. Actually this industrial sector is thought to represent 5–7% of the total CO_2 anthropogenic emissions [19].The cement industry has made significant progress in reducing CO_2 emissions through improvements in process and efficiency, but further improvements are limited because CO_2 production is inherent to the basic process of calcinating limestone [20].

Life cycle assessment (LCA) is used to evaluate the impact of processes or products on the environment. The inclusion of every stage of the process or product's life cycle is fundamental to this analysis. In the case of products, every stage from the production of the raw materials to the end of their useful lives and their use and maintenance should be included. Thus, all significant environment impacts in their life cycle can be addressed. For cement, a cradle to grave assessment is especially difficult because cement has so many end uses, and each use has a unique, often complex life-cycle [21].

The cement manufacturing process is required energy inputs and heat. Coal fly ash slag or pozzolans may be blended with the raw material. The addition of these optional materials will result in lower emissions. The clinker burning process is the most important part of the process in terms of the key environmental issues for cement manufacture: Most of the balance is lost from the process as carbon dioxide emissions to air in the calcinations reaction ($CaCO_3 \rightarrow CaO + CO_2$) [22]. The amount of clinker needed to produce a given amount of cement can be reduced by the use of supplementary cementitious materials such as coal fly ash, slag, and natural pozzolans (e.g., rice husk ash and volcanic ashes). The addition of these materials into concrete not only reduces the amount of material land filled (in case of industrials byproducts), but also reduces the amount of clinker required per ton of cement produced. Therefore cement substitutes may offer reduction in environmental impacts and material costs of construction [23].

2.2. Type of cements

2.2.1 Natural Pozzolana

Natural pozzolana exhibited a significant retarding effect when used in combination with Coleanite ore waste. The replacement of Portland cement by 10–15% of natural pozzolana in the presence of fixed quantity of colemanite ore waste improves the bending strength of the specimens compared with control specimens after 60 days of curing age. Rice husk ash has been used as a highly reactive pozzolanic material to improve the microstructure of the interfacial transition zone between the cement paste and the aggregate in high-performance concrete. Mechanical studies had shown the blending efficiency of cement varies with addition rice husk ash. Porosity, pore-size distribution, surface area and drying shrinkage are determined for silica fume. Portland cement blends, paste blends a discontinuous pore structure is formed after as little as seven days of curing due to reaction of $Ca\ (OH)_2$ with silica fume. The pores are not too large as those in mortar owing to the lack of interface effects. The development of the strength, heat, porosity, bound water, and calcium hydroxide content was measured. Higher strengths were observed after 14 days, whereas in cement replacement higher strength was observed after 91days [24].

2.2.2. Expansive cement

The expansive cement consists of a Portland cement component and a calcium-sulfoaluminate anhydrite component. Chemical composition of the components, fineness of the sulfoaluminate component, proportions of the two components in the total cementing material, ratio of water to total cementing material, richness of mix, conditions of curing, and degree of restraint are the factors influencing the magnitude and rate of the expansive reaction. Concrete

Exhibits free expansions up to 6 percent or more. Predetermined characteristics within a practical range can be obtained by proper mix proportioning and curing, with compositions, proportions, and fineness of components fixed [25]

2.2.3. High-alumina cement

Calcium aluminate cements have a radically different chemistry to Portland cements. Due principally to their higher cost, they do not compete directly with Portland cements [26]. Nevertheless, concretes based on these cements have very high performance in specific applications. High-alumina refractory castables with compositions in the systems $CaO–Al_2O_3$ and $CaO–Al_2O_3–SiO_2$, the effect of accelerators, and in particular lithium salts and citric acid solutions, on the setting time of high alumina cement has been studied using calorimeter, solution analysis and X-ray diffraction techniques [27].

2.2.4 Portland cement

Portland cement is the most commonly utilized cement in almost every part of the world. The understanding of the embodiment of cement could lead to a more sustainable concrete and mortar design. It chemically reacts with water to attain setting and hardening properties when used in the construction of buildings, roads, bridges, and other structures. The production of Portland cement is made by the calcinations of a mixture of a calcareous and an argillaceous material at a temperature around 1450°C [28]. Calcareous substances are of calcium oxide origin usually found in limestone, chalk, or oyster shells whereas argillaceous substances are of silicate and aluminates origin predominantly found in clays, shale, and slags [29].

The calcination process between well-proportioned argillaceous and calcareous substances leads to the production of clinker. Portland cement is obtained when the produced clinker is mixed together with a Predefined ratio of gypsum and milled together in a ball mill. The chemical composition of Portland cement involves both major and minor oxides [30]. The major oxides include CaO, SiO_2, Al_2O_3, and Fe_2O_3whereas the minor oxides also include MgO, SO_3, and some alkali oxides (K_2O andNa_2O) and sometimes the inclusion of other compounds, P_2O_5, Cl, TiO_2, MnO_3, and so forth. Each of the oxides performs unique work during cement hydration. However, each content of the oxide must be in the right quantity during proportioning of raw materials provided the required oxide composition of Portland cement and a deviation from standard specifications of the oxide composition may lead to unsoundness and sometimes failure of concrete structures Many experienced authors have shown that cement oxides which fall very close to the average values are more suitable to maintain concrete integrity [31].

During cement hydration CaO in conjunction with SiO_2, Al_2O_3, and Fe_2O_3leads to hardening of Portland cement due to the formation of calcium alumino silicates and alumino ferrite hydrate. With Portland cement, an increased presence of MgO (greater than 2%) may be detrimental to the soundness of cement, especially at late ages. High percentage of SO_3 tends to cause unsoundness of cement. For the Americans in their standard, limits $SO_3$to 4% and 5% whilst the Indian standard limits $SO_3$to 2.75%. Alkalis at higher levels and in the presence of moisture gives rise to reactions with certain types of aggregates to produce gel which expands and gives rise to cracking in mortars and concretes. Sometimes Loss on Ignition (LOI) is classified as a component of chemical composition n. LOI indicates the amount of unburnt carbon in the material. However, in some instances it may not necessarily be a measure or indication of carbon content. It may be burning away of residual calcite, bound water molecules, and clay materials [32]. High LOI content may be detrimental to concrete and mortar. It is also known that a high value of LOI results in increased water requirement and dosage of super plasticizer usage in mortar and concrete [33].

Table 2. 1 Summary of chemical data for a selection of Portland cement [34]

Types of oxide	Component in %
CaO	60-67
Fe_2O_3	1-5
Al_2O_3	4-9
SiO_2	18-25
SO_3	1-3
Free lime	0.03-3.68
Tricalcium silicate ($3CaO.SiO_2$) (C_3S)	30-65
Dicalcium silicate ($2CaO.SiO_2$) (C_2S)	15-45
Tricalcium Aluminate ($3CaO.AlO_2$) (C_3A)	5-15
TetracalciumAlumferrite ($4CaO.Al_2O_2Fe_2O_3$) (C_4AF)	5-15
IR	<0.75
LOI	<3.00

Nowadays, the Portland cement is the main cement type used all over the world and its production is the largest in amount if compared to the other products produced [35].The Portland cement is composed of clinker and additions. The clinker is the main component and it is present in all types of Portland cement. The additions can vary from each cement type to another and they mainly define the different cement types. The clinker, base component of the Portland cement, is obtained from the grinding, homogenization and subsequent burn in high temperatures (1450ºC) inside a rotary cement kiln starting from a powdered mixture called raw, originating from the following raw materials: limestone, clay, sand, iron ore, etc.

The main chemical elements that constitute the clinker are the lime (CaO) and the silica (SiO_2) that react between themselves forming lime silica, which is the main active component of the cement. However, other materials can be used on the cement Portland production. However, the introduction of secondary materials must be subject to the desired final product quality, which is the most important control parameter in the cement Portland production. Moreover, when industrial residues are used as secondary fuels in the rotary kilns, the generated ashes replace some of the components of the raw materials, and therefore these ashes must be made compatible with the remaining raw materials, in order to be absorbed in high percentage in the clinker matrix. Clinker represents the most important constituent of the Portland cement produced by the addition of gypsum or other inter-ground additives (limestone, coal fly ash etc.) and subsequent crushing. The dust-containing off-gas from the kiln is cooled down in the off-gas cooler subjected to subsequent de-dusting in the bag filter.

The separated dust, and the trace elements contained in it are partly returned to the cement production process during cement milling and partly added to the raw meal again. These operations considerably influence the temperatures and material flows between the meal, kiln system, and bag filter of the plant. Part of the filter dust is removed and, hence, does not enter the raw meal. Thus, the trace element cycle is relieved. The discharged material, however, usually enters the cement as an inter-ground additive [36].Ability to calculate compositions of cements in terms of the amounts of the main compounds present provided a valuable new tool for explaining, or predicting, differences in engineering performance among Portland cements. The ability to calculate the amounts of the major compounds in a clinker or cement had important implications [37].

Table 2. 2 ASTM Specification of the chemical and mineralogical composition of Portland cement [38]

Chemical Name	Common Name	Chemical Notation	Abrevete dNotation
Calcium oxide	Lime	CaO	C
Silicon dioxide	Silica	SiO_2	S
Aluminum oxide	Lumina	Al_2O_3	A
Ferric Oxide	Iron	Fe_2O_3	F
Magnesium oxide	Magnesia	MgO	M
Sulphur trioxide	Sulphuricon hyrite	SO_3	S^-
Alkaline Oxides	Alkalis	$K_2 O$ & $Na_2 O$	K+N
Tricalcium silicate	Alite	$3C aOSiO_2$	C_3S
Dicalcium silicate	Belite	$2CaOS iO_2$	C_2S
Tricalcium aluminate	Belite	$3CaOAI_2 O_3$	C_3A
Tetracalcium alimino ferite	Celite	$4CaOAl_2O_3$ $Fe_2 O_3$	C_4AF
Pentaclcium trialuminate	Celite	$5CaO Al_2O_3$	C_4AF
Calciumsulphate dihyrate	Gypsum	$CaSO_4 .2H_2O$	CSH_2

2.3. Clinker phases of Portland cement

2.3.1. Alite (C_3S)

Portland cement contains between 50-70% C_3S (Ca_3SiO_5), which makes it the most common component in Portland cement. The hydration reaction of C_3S lasts several months but most of it reacts within the first 24 h, with a peak around 10-15 h [39]. Its hydration rate compared to beliteis very high; therefore it plays a more important role in the early stages of cement hardening.

The high reaction rate depends on lower thermodynamic stability and holes in the molecule structure which makes it easier for the water to react [40].

2.3.2. Belite (C_2S)

Portland cement contains about 15-30% C_2S (Ca_2SiO_4). C_2S occurs most often in 4 different polymorphic states: α (a hexagonal phase), α’ (an orthorhombic phase), γ (an orthorhombic phase) and β (a monoclinic phase) which is called larnite. The most common phase in cement clinkers is β-belite. The reaction rate of β-belite is very slow compared with the one of alite.Therefore is it not very important for the early strengthening phase in cement. On the other hand, it is important for the strength of the final hardened cement [41].

2.3.3. Aluminate (C_3A)

C_3A has a cubic structure and its chemical formula is written Ca_3AlO_6. C_3A is one of the main components in Portland cement; about 5-10% of ordinary Portland cement is C_3A. Its reaction with water is very exothermic and occurs immediately. This leads to a phenomenon called flash-setting, meaning that the cement hardens to quick, which is prevented by adding calcium sulphate (gypsum) [41].

2.3.4. Ferrite (C_4AF)

C4AF exists in May possible compositions and that is why its molecular formula is written Ca_2 (AlxFe1-x) $_2O_5$, where x varies from 0 to 0.7 [42]. Portland cement contains about 5-15 % C_4AF. The hydration reaction of C_4AF is very similar with the one of aluminate and forms AFm and AFt phase.

2.4. Parameter of Portland cement

2.4.1. Chemical Parameters

Chemical Parameters of Cement chemical composition was done using XRF analyzer; this machine uses polarized energy dispersion. All reagents used were of analytical grade [43]. By using analysis specified in [44, 45]. And based on British Standards [46] .Have been followed for chemical analysis of Portland cement. Amount of total SiO_2, Fe_2O_3, lime content, SO_3, IR, free lime and LOI were determined [47].

2.4.1.1. Insoluble residue (IR)

This is a non-cementing material, which eventually exists in Portland cement. This residue material affects the properties of cement, especially its compressive strength. To control the non-cementing material in Portland cement, specified by allows the IR content to a maximum limit of 0.75%.[3] .

2.4.1.2 Loss of ignition (LOI)

A high LOI indicates pre-hydration and carbonation, which may be caused by improper and prolonged storage or adulteration of Portland cement during transport or transfer. All the cement samples were found to be competent with regard to maximum LOI limit of 3.0% as specified by [3].

2.4.1.3 Free CaO

If appreciable lime is left uncombined; it may cause expansion and cracking of the mortar or concrete [47].

2.4.1.4 SO_3

The maximum allowable SO_3-content in the cement to prevent sulfate expansion is established according to the various cement standards, between 1.5 and 2.5 % SO_3. At the lowest limit imposed by cement standard specification, it could be possible that there is no sufficient scope left for an extensive sulfatizing of the alkalies [48].

2.4.1.5 SiO_2

This type of chemical content is an index for fineness or coerciveness and it determine the grind ability of the cement clinker, level of water intake and strength of concrete [49].

2.4.1.6 Fe_2O_3

Is one of the parameters responsible for cement colouration; all the cement samples were found to be competent with regard to maximum Fe_2O_3 limit of 6.0% as specified by [50].

2.5. Heavy metal Exposures for cement production

Trace elements are naturally present in the biological world in acceptable quantities but increase of these metals through an anthropogenic contribution has the last century been known to harmed humans and environments [51]. Cement industry has been operated in Ethiopia for many decades and contributed to economic greatly. Despite the remarkable achievement recorded in the use of cement, it is associated with some environmental problem such as emission of air pollutants in form of dust, gases, noise and vibration during the process of manufacture [52]. Cement is also associated with heavy metals as evident many studies conducted [53]. Heavy metals are known to pose serious health problems to humans affect, plant growth and general damage to ecosystem [54]. It is recognized that the cements commonly used in the building industry, especially the blended cements manufactured with mineral additions such as slag's or coal fly ashes, are often characterized by a significant presence of heavy metals of particular environmental concern [55].

However, the use of mineral additions in blended cement formulations is an effective way of reducing the Portland cement clinker consumption and then reducing the related CO_2 emission [56]. In addition metals are leached into water in contact with concrete surfaces by direct dissolution of surface phases and/or diffusion through the pore solution to the concrete surface. The solubility of heavy metals depends on their bonding in the hydration products as well as their ability to form aqueous complexes and precipitate solubility-controlling phases. Consequently, the evolution of environmental risk cannot be used on the total amount of trace metals contained in concrete alone but requires better understanding of the mechanisms involved in leaching. In addition to this leaching is affected by the actual environmental condition at the surface of concrete structural components [57], these include exposition to CO_2or various aggressive environment. Exposure of concrete structural components to the external sulphates leads to deterioration owing to the formation of the expansive phases ettringite and gypsum whereas portlandite. AFM phase and C-S-H tend to dissolve [58].

It is likely that external sulphates affect the solubility of trace metals and thus their leaching behavior [59]. Co-processing of hazardous wastes in cement kilns has been widely implemented in developed countries for several decades. The technology offers a beneficial alternative towards the disposal of certain hazardous wastes due to the process that provides energy and material recovery simultaneously while the cement is being produced. Generally, a properly controlled co-processing process will conserve the natural resources by reducing the consumption of conventional fuel and natural raw material, decreasing greenhouse gas emissions and eliminating the need for waste disposal to land fills and also as an approach to decrease the environ mental impacts as well as to reduce the economic costs [60] . This option is also in line with the principles of waste management hierarchy that promotes reusing, recycling or reutilization of wastes processing will replace a portion of natural raw materials used with hazardous wastes. The burning process will produce clinker, a hard intermediate product, which is then cooled and blended. The blending of the ground clinker with a specific amount of gypsum will produce Portland cement, and the addition of other additives such as flay ash from the power plant, granulated blast furnace slag and others will produce blended cement [61].Hazardous wastes used as an alternative raw material or fuel may contain various heavy metals and other trace elements at a wide range of concentration compared to natural raw material and conventional fuel. This has raised a concern as to where the heavy metals will end up either it is transferred into the clinker or Cement products or it is emitted into the environment [13].

The cement may be directly exposed to human population, particularly to cement plant workers, construction workers as well as the community living nearby the cement plants and construction sites. The presence of heavy metals in the cement may pose a risk to human health by incidental ingestion, inhalation of suspended cement and dermal absorption. Incidental ingestion involves hand-to- mouth transfer during outdoor activities such as mouthing, contacting dirty hands, eating dropped food, or consuming cement directly [12].

This includes the impacts from exposure to heavy metals in various environmental aspects such as in surface soil, sediment, indoor dust and municipal solid waste. However, the potential health risk due to the presence of metals in cement products has not been widely investigated. Therefore, in this study, the concentration of heavy metals (i.e. Cd, Ni, Cr, Cu and Zn) in the Portland cements produced from natural raw material and co-processing with hazardous waste was investigated. These metals are the most common heavy metal elements that have been found increasing in cement products [13].

These solid and semisolid hazardous wastes being co-processed were mainly derived from soil contaminated with heavy metals or organic matters, water treatment sludge and industrial wastes. However, metals in wastes might be discharged through different streams during co-processing of hazardous wastes in cement kilns. Based on mass balance of metals, during burning of cement in the kiln, most metals in waste materials were trans- ported into clinkers in cement [62].It is necessary to evaluate and analyze leaching of metals from cement products in different environments. Sequential extraction of metals from cement with determination of metal speciation is valuable for forecasting mobility and leaching of metals from cement or concrete products when they are placed into various environments [63].

Specifications of metals usually includes characterization by fractionation of total concentrations into exchangeable (ES), acidic sodium acetate extractable (ASA), acidic hydroxylamine hydrochloride extractable (AHH), sulfide bound (SB) and residual (R) forms according to modified.Tessier sequential extraction procedures. Metals in exchangeable forms are most leachable, whereas those in residual forms are more recalcitrant. Therefore, investigation of metal speciation and leaching behavior is an important way to determine risks to the environment [64].In this study, concentrations of metals in cement clinker, produced during co-processing of hazardous waste procedure in the cement kiln of the Ethiopia Cement Company, will be analyzed.

Table 2. 3 The BUWALvalves of Regulatory requirements for concentrations of metals in cement clinker and product [65]

Element	Cement clinker(mg.kg-1)
Cd	1.5
Cr	150
Ni	100
Zn	500
Cu	100

2.6 methods for the determination of heavy metals

Many instrumental analytical methods may be employed to measure the concentration level of heavy metals in various samples. The most predominant techniques are atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES),

2.6 1. Atomic absorption spectrometry (AAS)

AAS is a quantitative method of metal analysis suitable for the determination of approximately70 elements. This method measures the concentration of the element by passing light in specific wave length emitted by a radiation source of a particular element through cloud of atoms from a sample. Atoms will absorb light from an energy source known as hollow cathode lamp (HCL).The reduction in the amount of light intensity reaching the detector is seen as a measure for the concentration of particular element in the original sample .A typical AA spectrometer consists of energy (light) source, sample compartment (atomizer) ,monochromatic, detector, and a data process system .The radiation source is usually a hollow cathode lamp (HCL) or electrode less discharge lamp (EDL), while different atomizers are used in various AAS techniques such as flame, a graphite furnace, or a quartz tube. The Monochromatic is eliminating scattered light of other wavelengths by a number of lenses and mirrors to focus the radiation and the detector is typically a photomultiplier tube that converts the light signal to an electrical signal proportional to the light intensity [66].

2.6.2. Inductively coupled plasma/optical emission spectrometry (ICP-OES)

Inductively coupled plasma/optical emission spectrometry (ICP/OES) is a spectroscopic technique suitable for trace elements analysis in several types of samples. The technique is based on the unprompted emission of photons from atoms and ions that have been excited in a radiofrequency discharge. Samples are usually introduced into the plasma in liquid form; thus, solid samples require acid digestion prior to injection, while gas and liquid samples may be injected directly into the instrument. The sample solution is converted to an aerosol then sends into the centre of the plasma which maintains high atomization temperature of around 10,000 K. As the plasma free atoms in the gaseous state are generated and adequate energy is often available to convert the atoms to ions then promote the ions to excited states. The ionic excited state species may then return to the ground state via emission of photons. Specific wavelength of the photons can be used to identify the elements and the number of photons is directly proportional to the concentration of the element in the sample. A variety of sample introduction methods are used in this technique such as nebulization, hydride generation for certain elements, electro thermal vaporization and laser ablation [67].

3. METHODOLOGY

3.1. Sample Collection

2 Kg of each type of cement (Habesha, Deriba, East, Mossebo and Danegotie) were collected from Bihar Dar market in May 2018.The procedures were conducted at Bihar Dar University in the Chemistry Department Research Laboratories.

3.2. Instrument and Equipment

The instruments used in this study includes: , furnace, hot plate, Electronic balance, oven and ICP-OES (petkin Elmer ICP –OES optima 8000).

3.3Chemicals and Reagents

All Chemical used in this study were analytical grade and include; Cement sample; 35.4%ofHCl (LOBA Chemie), 98% of NaOH (Blulux Laboratories (p) Ltd.-121001), 69.7% of HNO_3(RANCHEM), 99% of glycol (Blulux Laboratories (p) Ltd.-121005) , 33.7%of per chloric acid (UNI-CHE), red methyl(Ranchem Industry Trading), Whatman no. 42 filter paper, 99% of NH_4Cl(LOBA Chemie Laboratory REAGENTS and FINE CHEMICALS), 99.5%of EDTA (Blulux Laboratories (p) Ltd.- 121001), 2g of dry sand, NH_3,salicylicacid and bromophenol indicator, $BaCl_2$ and standard solution(Cd, Cr, Zn,Ni and Cu).

3.4. Experimental method for chemical analysis

The experimental methods carried for chemical analysis were adopted from literature with some modification [68, 69]

3.4.1 Determination of Insoluble Residue (IR)

1.0 g of each of the cement sample (Habesha, Deriba, East, Mossebo and Dagotie) were weighed into 250 ml beakers and dissolved by adding exactly 5 ml of concentrated HCl and diluted to 100 ml with warm distilled water then stirred well with a glass rod before the mixture was heat on a hot plate to boiling. The mixture was then filtered using a Whatman no. 42 filter paper, then washed with hot distilled water about four times in a beaker. The filter paper with the residue was transferred into a 250 ml beaker and 100 ml of 0.10M NaOH solution, add 3 - 5 drops of methyl red indicator. The mixture was boiled on a hot plate again, with drop-wise addition of 4 - 5 drops of concentrated HCl until the colour changed to pink.

The mixture was filter again using a Whatman no. 42 filter paper, after which the filter paper was washed four times with 0.2M NH_4Cl solution. Then the mixture was removed all the precipitate adhering during washed [68].An empty crucible was ignited for 5 min in a furnace set at 950°C; then allowed to cool in adesiccator to ambient room temperature and weighed as W1. The filter paper with its residue was then transfer into the crucible and ignited in the furnace at temperature 950°C for 30 min .The crucible and its content were then removed and allowed to cool to ambient room temperature inside adesiccator, and then weighed as W2. The percentage Insoluble Residue (IR) was calculated using (Eq. 1)

$$\%IR = (W2-W1)/w100 \qquad (1)$$

Where:

W1 = weight of empty crucible;

W2= weight of sample + crucible;

W = weight of sample taken.

3.4.2 Determination of Loss on Ignition (LOI)

3.0 g of each the cement sample (Mossebo, Deriba, East, Habesha and Dagotie) were transferred into a pre-weighed dried platinum crucible; then each of the crucibles with the sample were ignited to above 900°C in a furnace for about 30 min. The crucible was then removed, cooled and weighed [68]. The percentage loss on ignition (LOI) was calculated using (Eq .2)

$$LOI = ((w2 - w1)/w \times 100 \qquad (2)$$

Where:

W1 = weight of empty crucible;

W2= weight of sample + crucible;

W = weight of sample taken.

3.4.3 Determination of SiO_2

Each cement sample (Habesha, Deriba, East, Mossebo and Danegotie) of mass 10 g in 100 ml beaker containing 1 g of NH_4Cl was mixed thoroughly, before adding 10 ml of concentrated HCl. After heated each mixture to 60°C for 30 min, 5 ml of hot distilled water was added and heatedand diluted to the mark with distilled water. The mixture allowed to cooled to ambient temperature The filter paper with its residue were then placed on a dried pre-weighed platinum crucible and ignited in the furnace for 30 min at temperatures above 900°C before it was removed, cooled and weighed [68]. The percentage SiO_2 was calculated using (Eq .3)

$$\% \, SiO_2 = [(W1 - W2)/w100] \qquad (3)$$

Where: W1 = weight of sample before ignition,
W2 = weight of sample after ignition.
W = weight of sample taken

3.4.4 Determination of iron oxide (Fe_2O_3)

20 ml of the filtrate obtained from the SiO_2 determination of each cement sample, 3 - 5 drops of bromophenol was added, follow by another 3 - 5 drops of NH_3 solution until the colour change to pale blue. Then 20 ml of 0.10M HCl was added followed by 15 ml of buffer solution and 3 - 5 drops of salicylic acid. The solution was warmed to 40 – 60°C before it was titrated against 0.5M EDTA. And the endpoint signaled with a pink to clear yellow colour [69].The percentage of $Fe_2O_3$was calculated using (Eq.4)

$$\% \, Fe_2O_3 = VF \qquad (4)$$

Where: V = Volume (ml) of 0.5M EDTA used; F = factor of dilute EDTA = 03671

3.4.5 Determination of free-lime (CaO)

10 g of each cement sample were pouring in to a 500 ml flask follow by the addition of 2 g of dry sand and 40 ml of glycol, the mixture was corked with the stopper. The mixture was shaked vigorously and the flask place in an oven set at 70°C for 30 min, and further shaken every 5 min. and the solution filtered by sanction through a dry filter paper. Then 3 drops of bromophenol blue

indicator was added to the filtrated and titrated with 0.10M HCl until colour change [69]. The Free-lime was calculated using the relationship in (Eq .5)

$$(\% \text{ FL} = \text{factor vol (HCl)} \qquad (5)$$

Where %FL = Percentage free lime the factor is given as 0.35

3.4.6 Determination of sulphur trioxide (SO_3)

To 10 g of Habesha, Deriba,East, Mossebo and Danegotie cement each weighed into a 100 ml beaker, 10 ml of warm distilled water was added followed by 5 ml of concentrated HCl .stirred thoroughly. After the mixture was heated on a hot plate to boiling point, and filtered and also added 20 ml of (10%) $BaCl_2$solution again the solution was allowed to cooled and precipitated for about 2 h, before filtering the mixture through afilter paper again. An empty crucible was ignited for 5 min in the furnace set at 900°C and then allowed to cool in desiccators to ambient temperature and weighed as W1. The filter paper transferred from the funnel into the crucible and ignited in the furnace at 900°C for complete ignition before cooling the sample to ambient temperature in the desiccators and weighed as W2 [69]. The percentage sulphur trioxide was calculated using (Eqn .6)

$$\% \ SO_3 = 0.343(w2-w1)/w100 \qquad (6)$$

Where:

W1 = weight of empty crucible;

W2= weight of sample + crucible;

W = weight of sample taken.

3.5. Determination of Heavy Metals Concentration

0.5gof the cement sample were taken and digested on hot plate .after preparer optimization of the digestion procedure .parameters such as digestion time, temperature and regent volume were optimize prior to digestion based on the digestion procedure developed .Initially ,series of procedure involving some changes in reagent volume, temperature and as digestion time were tested. The optimized procedure was selected depending upon clarity of digests, minimum digestion, time, reagent volume and required temperature. Based up on these criteria the optimize digestion procedure chosen as follows; The cement samples were digested by the aqua regia and chloric acid digestion method 0.5 g of each sample of Portland cements was accurately weighed and added to 14ml of the aqua regia and chloric acid solution consisting of a 5ml(35.4% hydrochloric acid), 4ml(69.7% nitric acid). The mixture was transferred to the hood for 2h. Cooled 10 minutes then added 5ml (35.7% of chloric acid). The mixture was again transferred to the hood for 1hheated gradually at 100- 200℃ to eliminate losses of traces by abrupt boiling. After the reaction of the sample and mixture acids, the mixture was cooled 15minuteat room temperature. The samples were then filtered using the Whatman No. 42 filtration paper, subsequently added with distilled water up to 50 ml prior to analysis. Heavy metal (Cd, Ni, Cr, Cu and Zn) were determined by Inductively Coupled Plasma- Optical Emission Spectrometer, ICP-OES.

3.6. Standard solution preparation

Standards solution of each element were prepared serially from solution of known concentrations from the original Standards solution the required amount were taken by applying the dilution law and calibration curve was made by using instrument response and known concentration of the analyte. The standard curve should be covered the entire range expected concentrations. Stock solution of1 ml (1000µL) Cr, Cd, Ni, Cu and Zn were used to prepare an intermediate solution of each metal. In order to prepare 10ppm intermediate solution in 100ml volumetric flask. Then 6 serial dilution with (0.002ppm,0.02ppm,0.2ppm,1ppm,2ppm and 4ppm) concentration were prepared in 50ml volumetric flask from intermediate solution for calibration curve by using dilution formula($C_1V_1=C_2V_2$).

4. RESULT AND DISCUSIONS

4.1 Determination of detection limits and limits of quantization

4.1.1 Detection limits

Detection limit is the lowest concentration level that can be determined to be statistically different from an analyte blank or the minimum concentration that can be detected by the analytical method with a given certainty [70]. For a measurement, detection limit can be properly estimated from the standard deviation of several blank determinations. There are numerous ways of determining detection limits of a given measurement. A general accepted definition of detection Limit is the concentration that gives a signal three times the standard deviation of the blank or background signal [71].

4.1.2. Limits of quantization

Limit of quantization (or limit of determination) is the lowest concentration of the analyte that can be measured in the sample matrix at an acceptable level of precision and accuracy. An acceptable level of precision is typically 10 to 20 % of relative standard deviation depending upon the concentration level measured. However, in the absence of specified precision, the limit of quantification is the same as the concentration that gives a signal 10 times the standard deviation of the blank .Limit of quantization is the lowest limit for precise quantitative measurements [70].

Table 4. 1 Method Detection and Quantitation Limits, (DLM =3σblank and MQL = 10σblank, in ml/L) for each cement samples

Metal	Method detection limit	Method quantitation limit	Instrumental detection limit
Zn	0.075	0.25	0.0059
Cr	0.057	0.19	0.0071
Cu	0.027	0.09	0.0097
Ni	0.018	0.06	0.015
Cd	0.015	0.05	0.0027

4.1.3. Spiking solution preparation

0.5 gram of sample Danegotie was weighted using analytical balance and transferred in to two 50 ml beakers C&D which are labeled as spike.10µl Zn, 10 µl Cu, 30µl Cr and 30µl Ni were measured by using micro pupate from 1000 µl stock solutions of (Zn, Cu, Ni, and Cr) respectively and added into beaker C. solution consisting of a 5ml (35.4% hydrochloric acid), 4ml (69.7% nitric acid). The mixture was transferred to the hood for 2h. Cooled 10 minutes then added 5ml (35.7% of chloric acid). The mixture was again transferred to the hood for 1h heated gradually at 100- 200 C ^{0} after that the color less liquid was cooled for 15 min and filtered on 50ml volumetric flask using Whatman filter paper. Finally the samples were diluted by distilled water until the mark of the flask and submit ICP OES analysis.

The recoveries of metals in the spiked cement samples were 83.6 % to 106.5%.The results are given in Table 3.3; generally good recoveries were obtained for all metals, like Cr, Ni, Cu and Zn.

Table 4. 2 Stock solutions, Concentration of spike and UN spike in metal cement sample in mg/L and % of recoveries

Metal	Zn	Cr	Cu	Ni
Stock solution	0.2	0.6	0.6	0.2
Concentration of spike metal	0.382	0.857	0.895	0.538
Concentration of un spike metal	0.20	0.32	0.682	0.036
%Recovery	91%	89.5%	106.5%	83.6%

4.2 Calibration curve

The qualities of result obtained from ICP-OES for metal analysis are highly affected by Calibration and standard solution preparation procedures. The Calibration curve was performed by using six series of working standards. The working standard solutions of each metal were prepared freshly by diluting the intermediate standard solutions (10ml/L).The concentration of the intermediate standards, working standard and the value of correlation coefficient of the Calibration graph for each selected metal are listed in table4.1: below.

Table 4.3 working standards and correlation coefficient of the Calibration curves for determination of metal using ICP-OES

Element	Standard solution in ml/L	Correlation coefficient{R^2}	y= B*x +A
Zn	0.002,0.02,0.2,1, 2,4	0.9997	y=12408x+2764
Cr	0.002,0.02,0.2,1,2,4	0.9995	y=78924x-17966
Cu	0.002,0.02,0.2,1,2,4	0.9995	y=92613x-8821
Ni	0.002,0.02,0.2,1,2,4	0.9998	y=24698x-2543
Cd	0.002,0.02,0.2,1,2,4	0.9996	y=45644x-1656

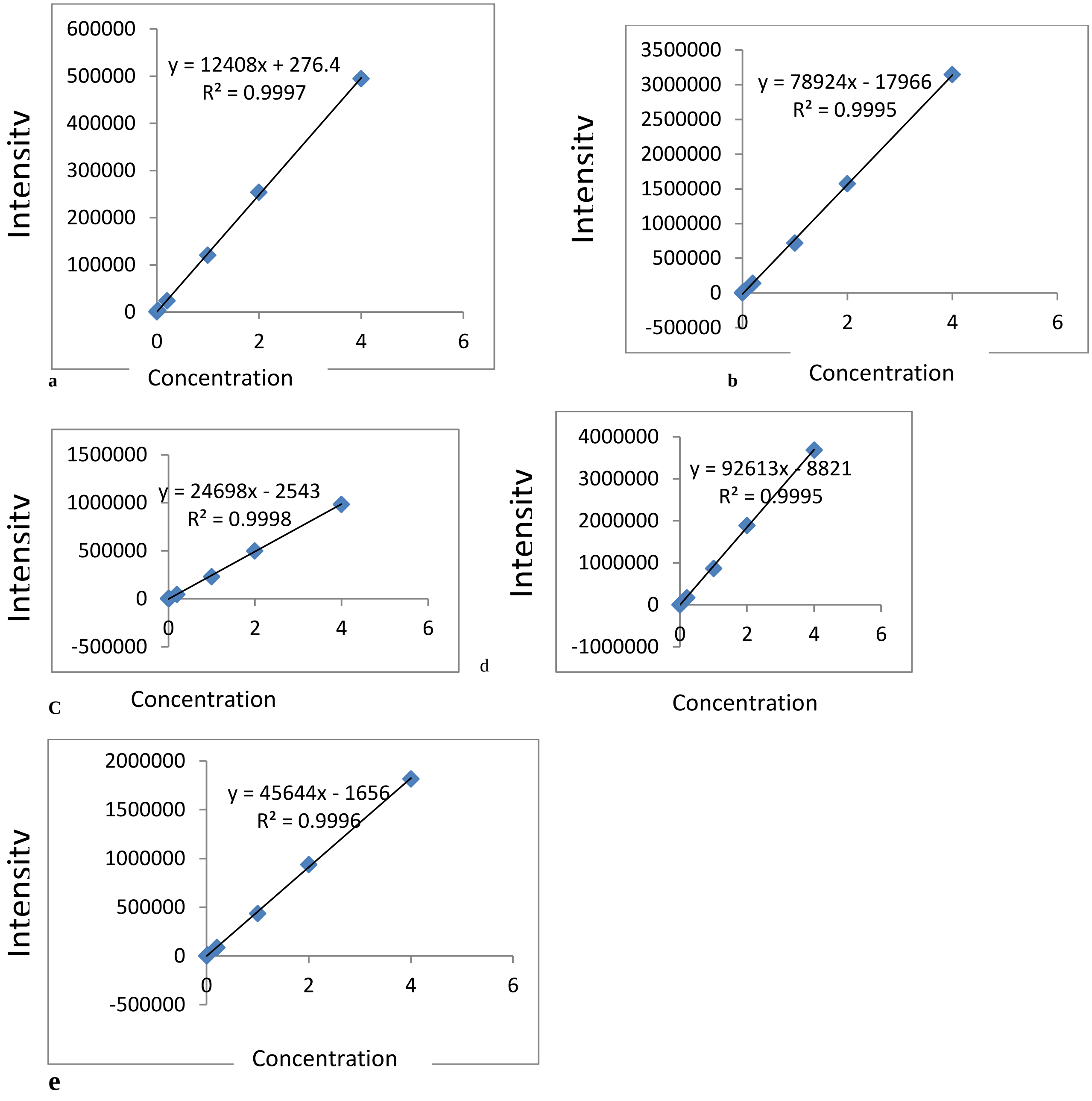


Figure 1 Calibration curve for determination of metals (a) Zn, (b) Cr, (c), Ni, (d) Cu, and (e) Cd

4.3 Statistical Analysis

Data analysis was performed by using statistical soft ware packages SPSS. Each data set consisted of matrix, in which the columns represented the individual cement sample. One –way analysis of variance (ANOVA) was used to test for the presence of significant difference in the mean concentration of metal and percentage composition of chemical parameter of cement. Differences were considered significant when $p<0.05$ and no statically significant Differences $p> 0.05$. Whenever constructed to display the differentiation among cement sample extracted and analyzed in triplicate, and average values were used for statistical calculations.

4.4. The comparison of the level of metals in five Different Cement Samples

Table 4. 4 Concentration (mg/Kg) of heavy metal in cement samples and their ANOVA analysis

Metal	East	Danegotie	Deriba	Hbesha	Mossebo
	Mean ± sd	Mean ± sd	Mean ± sd	Mean ± sd	Mean ± sd
Zn	21 ± 1^{a}	20 ± 3^{a}	9 ± 8^{a}	15 ± 8^{a}	2 ± 1^{a}
Cr	70 ± 9^{c}	120 ± 11^{c}	1202 ± 216^{b}	26 ± 2^{c}	1880 ± 287^{a}
Cu	6 ± 00^{b}	6 ± 1^{b}	19 ± 2^{a}	3 ± 1^{b}	22 ± 1^{a}
Ni	76 ± 1^{c}	56 ± 4^{c}	520 ± 91^{b}	11 ± 1^{c}	799 ± 115^{a}
Cd	ND	ND	ND	ND	ND

Where values of the arrow followed by the same letter indicates no significance difference ($p > 0.05$) and different letters are significantly different ($p<0.05$).and ND =not detected.

Zinc: Even though the results obtained for Zn was low in Mossebo cement, the statistical analysis indicate no significant difference ($p>0.05$).Therefore, it can be conclude that all the five cement have the same grade regarding Zn metal. As shown in table 4.2 and figure 2 the concentration of Zn range from 2-21mg/Kg, compared to previous studies done in different countries (table.4.4) and clinker product [65] the concentration is low.

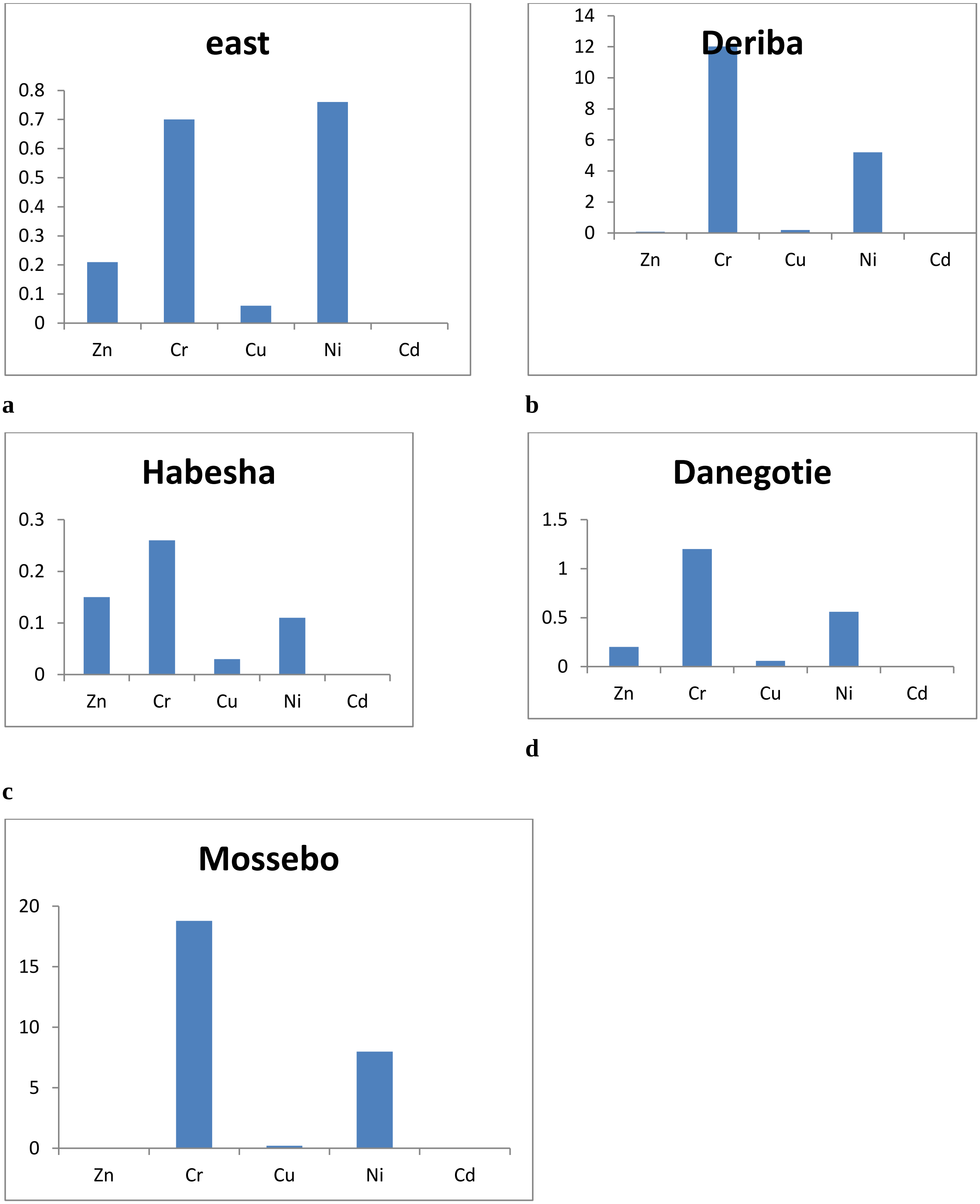
Chromium: The results of Cr concentration show no significant difference between East, Danegotie and Hbesha. However, Deriba and Mossebo cement have highest concentration of Cr and the statistical analysis also show significant difference ($p < 0.05$).As shown in the figure 2 Cr concentration range from 26 (Habesha Cement) to 1880 mg/Kg (Mossebo Cement) which is higher than the concentration reported from other studies, i.e. between 0.6-597.5mg/Kg[73-76] and in the clinker [65].The source for Cr may be from waste utilization as a raw material in cement plant. Since Cr are known as human carcinogens and associated with allergic dermatitis in humans [77], countries set standards for chromium less than 150mg/Kg to protect the environment.

Nickel: High concentration of nickel found in all cement compared to previous studies .Though, the three cement, (East, Dangote and Habesha) are within the standard set for cement clinker [65].

Copper: Cu in the five sample were investigated as indicate in the table data for East, Danegotie and Hbesha have no significant difference ($p>0.05^{)}$ between each other. But, Deriba and Mossebo cement is statistically highest from the other three cement samples. Total Cu present in the range 3-22mg/Kg which are higher than the concentration reported from other studies [73-76]. But lower than its clinker concentration. Cu is an element essential to humans. However, in high doses, especially when exceeding the reference dose, it can cause liver and kidney damage, anemia, stomach and intestinal irritation [74]

Cadmium: Cd was not detected in all samples.

According to a study on the distribution of heavy metals in the production of cement tends to accumulate in cement dust which is then collected by the bag filters or other air pollution control equipment installed by the cement plant instead of being deposited in the clinker due to its nature as a volatile. Cement plant and construction workers can be considered to have a long-term exposure and are likely to develop chronic kidney diseases. It has also been reported to have a significant effect on the respiratory tract, which has been the major focus of most studies on cement plant workers [74].



a

b

c

d

e

Figure 2 (a-e), Trends of metal concentrations according to the source of Portland cements

Figure 2 show all metal analysis results in individual cement the bar designates metal distribution were Cr > Zn>Ni>Cu for Habesha and East in the order of Ni> Cr >Cu> Zn. Whereas, Deriba, Mossebo and Dagotie was found to be in similar trends for which Cr and Zn were the highest and the lowest concentrations, respectively. The concentrations of Ni, Cr, Cu and Zn in these types of cement were found to be variable according to the sources of cement. This indicates that the sources of raw material, fuel and type of hazardous wastes used by each plant may determine the metal concentrations in their cement product [72].

Table 4. 5 The concentration of heavy metals in cement from previous studies in mg/Kg

Heavy metal	Present study	South Korea [73]	Nigeria [74]	Nigeria [75]	USA [76]
Cd	ND	0.4–3.0	0.6	2.3–3.10	0.1
Ni	11-799	5.8–60.3	17.3	3.7–8.0	47.5
Cr	26-1880	7.8–20.9	91.7	0.6–2.6	597.5
Cu	3-22	1.4–130.5	7.0	No data	23.77
Zn	2-21	10.6–554.0	422.4	No data	474.6

4.5 Percentage composition oxides

Table 4. 6 Amounts of chemical constituents by % and their ANOVA analysis

Parameter	Cement									
	East		Danegotie		Deriba		Habesha		Mossebo	
	Mean ± sd	Range	Mean ± sd	Range	Mean ± sd	Range	Mean ± sd	Range	Mean ± sd	Range
Fe_2O_3	2.64±0.05^b	2.58 – 2.67	1.98 ± 0.11^c	1.86 – 2.07	2.93 ± 0.27^b	2.64 – 3.17	4.91 ± 0.23^a	4.67 – 5.13	1.5 ± 0.03^d	1.48-1.54
SiO_2	19.79±0.34^c	19.45-20.13	20.44 ±1.07^{bc}	19.21-21.13	23.77±1.15^a	22.46-24.62	25.04±1.68^a	23.08-26.06	23.29± 0.88^{ab}	22.31-24.09
SO_3	1.32±0.38^a	0.89-1.64	3.52±0.49^c	2.96-3.87	1.42±0.05^a	1.38-1.48	2.31±0.13^b	2.18-2.43	3.68±0.2^c	3.46-.86
Free CaO	4.27± 0.08^a	4.18-4.35	2.66±0.23^b	2.42-2.88	2.66±.03^b	2.62-2.68	2.38±0.05^b	2.33-2.42	0.28± 0.03^c	0.25-.31
LOI	2.76± 0.05^b	2.71-2.80	3.61± 0.16^a	3.44-3.76	1.71± 0.04^c	1.68-1.76	1.74±0.06^c	1.68-1.79	1.56±0.08^c	1.49-1.65
IR	0.72± 0.04^a	0.67-0.75	0.76± 0.02^a	0.74-0.79	0.79± 0.09^a	0.68-.87	0.78± 0.08^a	0.69-.84	0.75± 0.02^a	0.73-.78

Where values of the arrow followed by the same letter indicates no significance difference ($p > 0.05$) and different letters are significantly different ($p<0.05$).

4.5.1 Comparison of Chemical Parameter in each Portland cement brand

The percentage of iron oxide both in East and Deriba have no significant difference ($p>0.05$) between each other. But Danegotie, Habesha and Mossebo cement is statistically have significant difference ($p<0.05$), Habesha and Mossebo cements have the highest and the lowest percentage of iron oxide respectively. Iron oxide in the cements sample (Mossebo, Danegotie, East, Deriba and Habesha), were 1.5, 1.98, 2.64, 2.93 and 4.91% respectively (table4.6). Generally, the values obtained in the studies were below the maximum requirement of 5.0% iron oxide content in common cement as recommended by [34].The $Fe_2O_3$is one of the parameters responsible for cement coloration which explains when Habesha Cement is darker grey than all the cements.

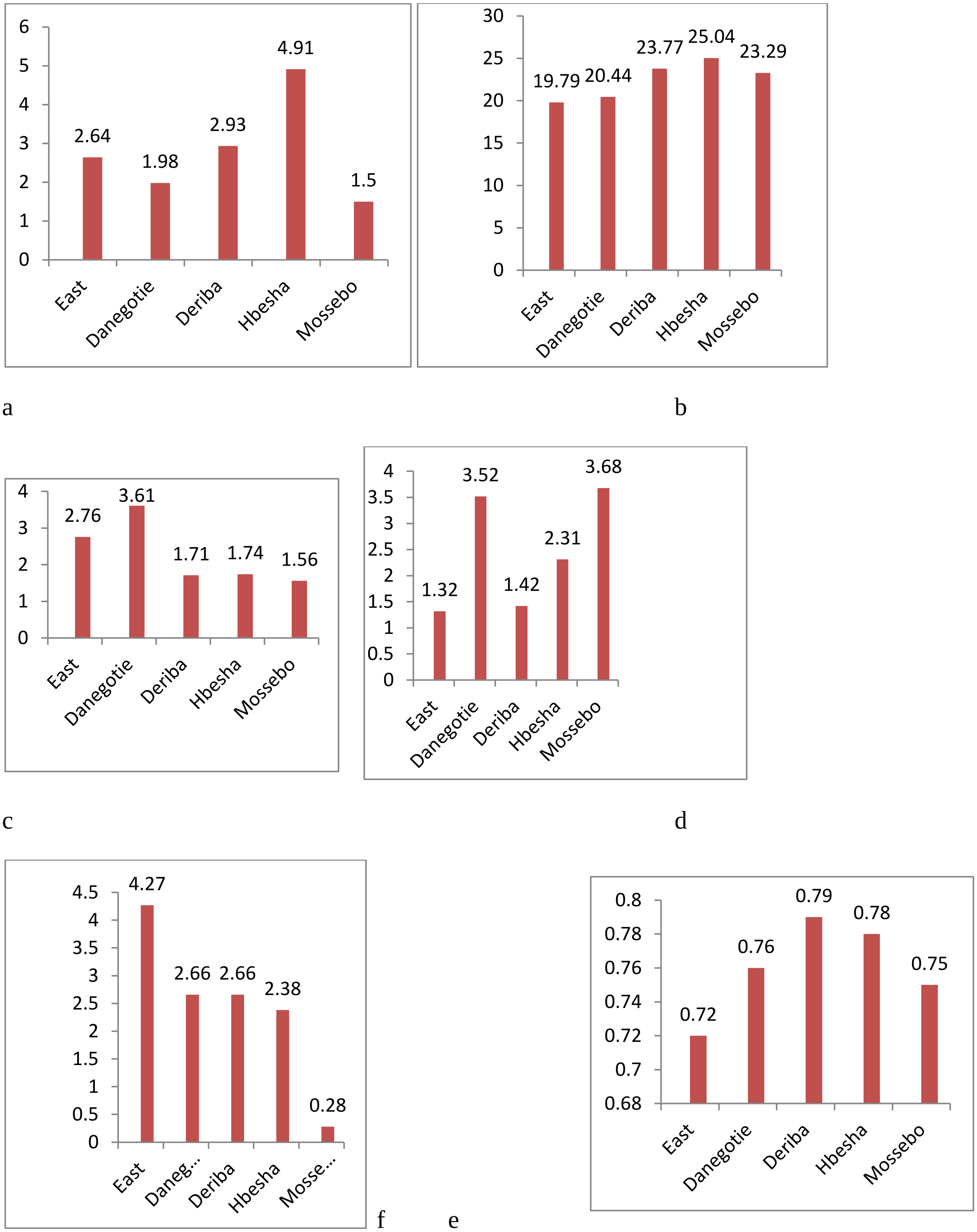
The percentage ofSiO_2 in East and Danegotie have no significant difference ($p>0.05$) between each other. But in Deriba, Habesha and Mossebo cement it is statistically highest from the other two cement samples. And also the three cement sample(Deriba, Habesha and Mossebo) have no significant difference ($p>0.05$)in their percentage ofSiO_2.Silicon oxide in the samples cements(East, Danegotie, Mossebo Deriba and Habesha) were 19.79, 20.44, 23.29, 23.77, and 25.04respectively.Following from table all the samples with exception of Habesha cement are within the range [34].

The percentage of free CaO in Deriba, Danegotie and Habesha have no significant difference ($p>0.05$) between each other. But East and Mossebo cement have statistically significant difference ($p<0.05$). East and Mossebo cement have the highest and the lowest percentage of free CaO respectively. The amount of Free CaO in Portland cement was within the range 0.03% to 3.68 %. It has been observed that Deriba, Mossebo, Dangote and Habesha cements are within specified limit. But East cement slightly deviates from the specification. High free lime content results in expansion due to formation of $Ca(OH)_2$. East cement is therefore unsound due to the higher content of free CaO. Amount of free lime were found to vary in between 0.28 to 4.27% among the different brands of cements that is shown in (figure e).

Composition of sulphur trioxide SO_3; From the study, the percentage sulphur trioxide in the cement samples East, Deriba, Hbesha, Danegotie and Mossebo 1.32, 1.42, 2.31, 3.52and 3.68% respectively (table 4.6). Mossebo also had the highest value of SO_3 and East the least SO3 content which also favours formation of C_3S mineral compound which is responsible for initial set and early strength ,The lower the SO_3 value the better[78].

Percentage of the Loss on Ignition There is no significant difference among Deriba, Mossebo and Habesha in the percentage of LOI ($p>0.05$).But the percentage of LOI is statistically higher in East and Danegotie than other three cement samples. Furthermore, East and Danegotie have also significant difference ($p<0.05$)in their percentage of LOI. Danegotie cement has the highest percentage of LOI from other cement samples. Loss on ignition in the cement samples studied Mossebo, Deriba, Habesha, East Danegotie are 1.56, 1.71, 1.74, 2.76, and 3.61% respectively as shown in table 4.6 The values of all the samples with exception of Danegotie cement are below the [34] maximum limit of 3.00%. The value in Danegotie cement implies that the cement products are poor in mineral content and high in combustible materials (79].

The percentage of IR in all Deriba, Mossebo, Habesha, East and Danegotie has no significant difference ($p>0.05$). The variation in chemical composition may be attributed to the differences in the proportioning of raw materials and the nature of production used to produce Portland cement. Insoluble residue content of the cement samples East, Mossebo, Danegotie, Habesha, and Deriba studied are 0.72, 075, 0.76, 0.78 and 0.79% respectively. All the samples with exception of East and Mossebo above the maximum limit and specified by [34]. Insoluble residue is a non-cementing material, which eventually exists in Portland cement. This residue material affects the properties of cement, especially its compressive strength. To control the non-cementing material in Portland cement, addition of the IR affects the compressive strength of cement mortar during the early age, but it is reduced as the cement mortar getting older.



a

b

c

d

f

e

Figure 3 Variation of Fe2O3 (a), SiO2 (b), LOI (c), SO3 (d), Free CaO (e) and (IR) (f)

5. CONCLUSIONS

The results of this study showed all cement brands have Free CaO, SiO_2, LOI and Fe_2O_3 contents within the acceptable limits with the exception of East with Free CaO, Habesha with SiO_2, and LOI with Danegotie content being above the required standard. The IR result from Danegotie, Deriba and Habesha and SO_3 compositions of Danegotie and Mossebo reveled above the recommended limit. However, the ANOVAs output indicated that each brand of commercial Portland cement has individual variations with respect to chemical composition. This could be due to the differences that exist with individual factory proportioning of raw materials for Portland cement production.

The concentration of heavy metals in cement produced from Habesha was in the order of Cr > Zn> Ni >Cu. And for East it was in the order of Ni > Cr >Cu> Zn. While, the presence of heavy metals in cement produced from co-processing activity as represented by cements Deriba, Mossebo and Danegotie were found to be in similar trends for which Cr and Zn were the highest and the lowest concentrations respectively. But Cd is not detected in all cement samples. In all the sample cements, % IR and concentration of Zn show no statistically significant difference each other ($p > 0.05$) . The ANOVAs output indicated that each brand of commercial Portland cement has individual variations with respect to chemical Composition. This is due to the differences that exist with individual factory proportioning of raw materials for Portland cement production. The concentration of Cd and Ni in cement samples showed high, which indicates the need of waste treatment before discharging waste from this factories.

6. RECOMMENDATION

- Further investigation is needed to study other parameters of cement to develop and to control the quality of cement product during manufacturing of cement.

- Government should set National standard for cement.

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