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CENTER FOR ENVIRONMENTAL SCIENCE

MASTER THESIS

CHARACTERIZATION AND RECYCLING OF TEXTILE SLUDGE THROUGH ENERGY EFFICIENT BRICK PRODUCTION, THE CASE OF HAWASSA INDUSTRIAL PARK

BY

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Declaration

This is to certify that the thesis prepared by Dawit Alemu Beshah "Characterization and Recycling of Textile Sludge Through Energy Efficient Brick Production, The Case Of Hawassa Industrial Park " which is submitted to Center for Environmental Science, College Natural and Computational Sciences, Addis Ababa University in partial fulfillment of the requirements for the degree of master of science in Environmental Science, complies with the regulations of the university and meets the accepted standards with respect to originality and quality.

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CHARACTERIZATION AND RECYCLING OF TEXTILE SLUDGE THROUGH ENERGY EFFICIENT BRICK PRODUCTION, THE CASE OF HAWASSA INDUSTRIAL PARK

ABSTRACT

Textile industry sludge from zero liquid discharge treatment plant of industrial parks in Ethiopia faces environmental problem with no safe disposal options. One potential opportunity for the disposal of sludge is by incorporating it in clay bricks, such application can be practiced in a large scale in the country's brick-manufacturing industry. Clay bricks were prepared with different proportions of sludge (10, 20, 30 and 40% by weight) in laboratory conditions and its properties such as strength, water absorption, and weight loss on ignition were investigated. Results indicated that increasing the sludge content in bricks resulted in a decrease in compressive strength. However, the compressive strength was increased with the increase of firing temperature. The compressive strength of textile sludge bricks was reduced significantly from 30.42 to 2MPa when textile sludge content increased from 0% to 40% fired at 1200 ^oC. Moreover, it was estimated that an energy saving of 38% was achieved with 10% textile sludge incorporated bricks during firing; this is due to the heating value of the textile sludge. Toxic characteristics leaching procedure test results indicated that the leaching behavior of targeted heavy metals has been found to be insignificant ($P<0.01$). The recommended proportion of sludge in brick making can be 10% (by dry weight) and fired between 900 °C and 1200 °C for producing good quality bricks. This study indicated that textile sludge can be sustainably stabilized and recycled in clay bricks and large-scale application of this technique can be advised for Ethiopia where both the industrial parks and brick industries benefits mutually.

Key Words*: Textile Sludge, Fired Clay Bricks, Stabilization, Energy Efficient, Zero liquid discharge*

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
ASTM	American Standard of Testing and Materials
BOD	Biological Oxygen Demand
CETP	Central Effluent Treatment Plant
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
ETP	Effluent Treatment Plant
ECAE	Ethiopian Conformity Assessment Enterprise
GFAAS	Graphite furnace Atomic Absorption Spectro photometer
OMC	Optimum Moisture Content
TS	Textile Sludge
TCLP	Toxicity Characteristics Leaching Procedure
TDS	Total Dissolved Solid
UNEP	United Nations Environment Program
UNIDO	United Nations Industrial Development Organizations
USEPA	United States Environmental Protection Agency
ZHE	Zero Headspace Extractor
ZLD	Zero Liquid Discharge

CHAPTER ONE

1. INTRODUCTION

1.1 Background

The Ethiopian textile industry has grown-up on an average of 51% over the last 5 years and more than 65 international textile and apparel projects have been licensed for foreign investors. Ethiopia has fronted textile sector as one of the key priority sectors for the generation of employment and to improve foreign currency earnings. As of 2017, the sector represents 6% of the country's total export value with the ambition to grow to 22% in 2020. One of the main pollution problems worldwide is the textile industry due to dye-containing wastewater, 10-25% of textile dyes are lost during the dyeing process, and 2-20% is directly discharged as aqueous effluents in different environmental components. Without adequate treatment these waste containing dyes can remain in the environment for a long period of time (Delelegn 2018).

Most industries in Ethiopia accumulate or dispose untreated sludge on unsecure open landfills which aggravate pollution. Raw sludge coming from textile effluent treatment plant may contain heavy metals that are very active to circulate on environment. This poses a health concern to the public because of the known health problems that may arise from accumulation of physical and chemical pollutants toxicity and physical injuries in the body. In addition, leaching of pollutants in textile sludge may lead to environmental pollution and public health risks. Unlike wastewater and air emission standards to air, land and water, disposal of sludge has not got attention in Ethiopia. Untreated sludge disposal and accumulation in an open area has been a big issue in terms of human and animal health.

No or a little report in Ethiopia is available about the presence and content of physical and chemical residues from wastewater treatment plant sludge and its recovery option (Delelegn 2018). Accumulation of toxic metals in agricultural land during wastewater irrigation and sludge disposal may not only result in soil contamination, but also affect food quality and safety (Baawain, Al-jabri, and Choudri 2014). The thermal treatment of sludge involves incineration, gasification, and pyrolysis as a means of disposal, whilst also recovering energy from waste. These are costly and may contribute to air pollution and the residues of the process still have to be disposed of, but this is more easily achieved than with untreated sludge (Juel 2017). A technique to treat or stabilize hazardous waste is by solidification in construction materials such as brick or concrete which has been applied in several instances for the cases of sewage and textile sludge and arsenic-rich filter materials (Patel 2012).

Stabilization usually refers to a techniques that reduce the toxicity of a waste by converting the toxic substance into less soluble or mobile form , while solidification refers to physical phenomenon that solidifies the waste, forming a solid material, and does not necessarily involve a chemical interaction between the contaminants and the solidifying additives (R. Swaminathan 1998). The solidified product may be disposed off to a secured landfill site or it can be recycled as construction materials if it meets the specific strength requirement and can be shown to leach toxic pollutants within acceptable limits (Rouf 2003). Several studies have shown that textile industry sludge can be effectively stabilized in construction materials such as fired clay bricks (Ravikrishnan and Senthilselvan 2014). Here in this study, experiments are demonstrated to show that textile industry sludge can be stabilized in clay bricks. IPDC has made a strategic plan (2015-2019) to build 14 industrial parks throughout the country. It can be estimated that 30240 tons of partially dried sludge will be generated each year by all the industrial park if they become operational. Large and small scale brick manufacturing industry in Ethiopia are using nonrenewable energy sources for firing of the clay bricks. Considering the brick manufacturing industry of Ethiopia as a potential opportunity for recycling of textile industry sludge can be a viable option for commercial application because of the mineralogical property and calorific value of the sludge. This study was focused in Hawassa textile and apparel industrial park which is located in the city of Hawassa 275 km from Addis Ababa.

1.2 Statement of the problem

Textile industries in Ethiopia disposed-off raw sludge on open landfills which results in environmental pollution. The sludge discharged from textile effluent treatment plant may contain unsafe levels of heavy metals that are very active to circulate on environment. Often factories, especially in textile and garment sector, get clustered in huge industrial park, which are equipped with common effluent treatment plant. The centralized wastewater treatment system are often well designed and in good operation condition. Currently the solid remaining of the wastewater treatment process (dewatered excess sludge, left over from ZLD plant) often get filled in to plastic bags and stored on the premises of ZLD. No report is available about the presence and content of physical and chemical residues from wastewater treatment plant sludge and its recovery option. This poses a health concern to the public because of the known health problems that may arise from accumulation of physical and chemical pollutants toxicity and physical injuries in the body. Therefore, there is a need to carry out a research on the sustainable manageability of textile sludge from Zero Liquid Discharge (ZLD) treatment plant using stabilization. Moreover, to a large extent the textile and garments get produced from the park is for international market (Europe, North America). Such global companies set high standard in regard to environment protection.

1.3. Objective of the study

1.3.1. General objective of the study

The main objective of this study was to examine the manageability of textile industry wastewater treatment plant sludge as a constituent of clay bricks.

1.3.2. Specific objectives

- To collect and prepare clay and textile sludge samples
- To characterize the physico-chemical properties of textile sludge and clay
- To assess the effect of partial substitution of sludge with clay on the strength, water absorption, loss on ignition and toxicity leaching properties of bricks
- To propose an optimum clay-sludge mix proportion that can be used for brick manufacturing towards environment friendly recycling of textile sludge.

1.4 Scope of the study

The scope of this research is to investigate the possibility of clay brick production from textile sludge. The scope of the research is limited to textile sludge characterization, production of brick by substitution of the sludge and measuring the strength, water absorption and loss on ignition of the bricks. This study does not consider other sources of rather than textile sludge from zero liquid discharge wastewater treatment plan

CHAPTER TWO

2. LITERATURE REVIEW

This chapter presents the environmental impact of textile wastewater, treatment technology of textile wastewater, textile sludge management and disposal practices, brick manufacturing technology and previous studies on stabilization of sludge through fired clay bricks.

2.1 Environmental impact of textile wastewater

Industry Parks Development Corporation (IPDC) is constructing Environmental friendly industrial parks in different regions of the country along with its infrastructure to build cleaner and resource-efficient production technologies. To reduce pollution and water resource depletion due to the existence of industry parks, Wastewaters must be treated to the level of acceptable standards to discharge or re use. Sludge from industrial wastewater treatment plants is a serious environmental issue because it can affect human and animals' health, and also environmental quality. A single research done in Ethiopia, Bole lemi industrial park shows that physical and chemical pollutants in the sludge have public health interests (Delelegn 2018) .

Manufacturing process of textile products are majorly a wet process. It consumes large amount of water for its processes. There are different techniques used for the disposal of textile sludge the most common are land-filling, incineration and gasification. The land-filling is now an issue, mainly because of highly-polluting emissions, the low recovery of energy and the limited capacity of available land-fill site. Hazardous waste can be stabilized through solidification in construction materials such as brick or concrete which has been applied in several instances for the cases of sewage and textile sludge and arsenic-rich filter materials, the use of sludge as construction material not only converts waste in to use full products but also eliminates disposal problems. Natural resources like clay are also conserved. Good aspect of using sludge as an additive to bricks makes immobilization of heavy metals in the fired matrix, oxidizing organic matter and destroying any pathogens during firing process and reducing frost damage (Patel 2012).

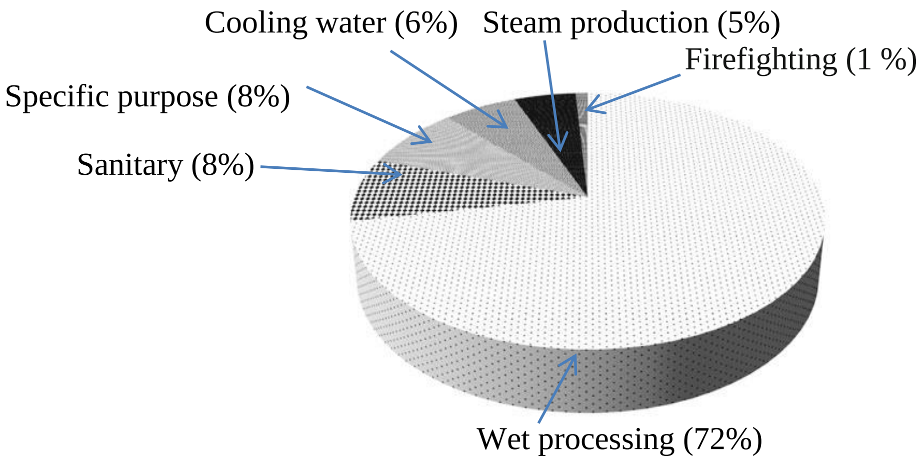
Stabilization usually refers to a techniques that reduce the toxicity of a waste by converting the toxic substance into less soluble or mobile form , while solidification refers to physical phenomenon that solidifies the waste, forming a solid material, and does not necessarily involve a chemical interaction between the contaminants and the solidifying additives (R. Swaminathan 1998).

The solidified product may be disposed-off to a secured landfill site or it can be recycled as construction materials if it meets the specific strength requirement and can be shown to leach toxic pollutants within acceptable limits (Mahbub 2014). Several studies have shown that sludge can be effectively stabilized in construction materials such as bricks and ceramic tiles(Basegio et al. 2009).

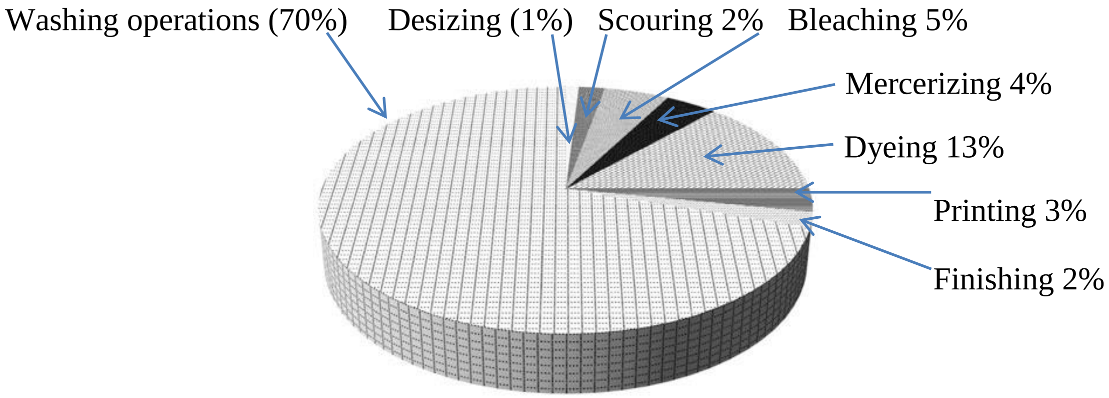
Most industries in Ethiopia accumulate or dispose untreated sludge on unsecure open landfills which aggravate pollution. Untreated sludge from textile effluent treatment plant may contain physical and heavy metals that are very active to circulate on environment. This poses a health concern to the public because of the known health problems that may arise from accumulation of physical and chemical pollutants toxicity and physical injuries in the body (Delelegn 2018). The presence of inorganic and physical pollutants in textile sludge also may lead to environmental pollution and public health risks. An industry that consumes 50 m^3 of water per hour can generate 1-10 ton of sludge per day in wet basis. Advanced conventional Effluent treatment plant can produce 1.5 kg of dried sludge from 1000 liter of treated textile wastewater. Hawasa industrial park zero liquid discharge treatment plant has a capacity of treating 11 million litter of wastewater per day with this capacity it can be estimated that 16 ton of sludge is produced per day.

2.2 Treatment of textile wastewater

The difference in the use of raw materials, chemicals, processes and technologies applied to the processes cause complex and dynamic structure of environmental impact of textile industry. The concentrations of pollutants in textile wastewater vary depending upon the wastewater management practices and amount of water used in the production (Tüfekci, Sivri, and Toroz, 2007).Therefore, it is of overriding significance to implement an appropriate treatment processes. Currently, various physical, chemical and biological treatment methods are used. Biological and chemical methods involve the destruction of pollutants, while physical methods usually transfer the pollutant from one phase to another (Kumar, Bharti Ajay Dwivedi, Sanjay K, 2017). Since textile effluents are complex, several factors such as dye type, wastewater composition, dose and costs of required chemicals, operation costs (energy and material), environmental fate and handling costs of generated waste products determine the technical and economic feasibility of each treatment option (Van Der Zee 2002). The quantity of water required for textile wet processing is huge (120–150 l/kg) and varies from industry to industry depending on the type of fabric processed, the quality and quantity of fabric, processing sequence, and the source of water. Other major uses of water in the textile industry are shown in Figure 1.



a) Water used at various intermediate process



b) Water used at various manufacturing steps.

Figure 1. Water consumption Pattern of Textile industries (Shashank Singh Kalra, 2011)

2.2.1 Physical treatments

i) Adsorption

Adsorption is one of the most effective and proven treatment with potential application in textile wastewater treatment. This process involves the transfer of soluble organic dyes from wastewater to the surface of solid, highly porous, particles (the adsorbent). The adsorbent has great capacity for each soluble dyes to be removed, and when is ‘spent’ must be replaced by fresh material (the ‘spent’ adsorbent must be either regenerated or incinerated). Activated carbon is the main used adsorbent and also other commercial inorganic adsorbents(Carmen and Daniel 2012).

ii) Irradiation

Irradiation is effective process for destroying organic contaminants, and as well disinfecting harmful microorganism using gamma rays or electron beams (e.g., source for irradiation can be a monochromatic UV lamps working under 253.7 nm. Irradiation treatment of effluent from sewage treatment plant reduced COD, TOC and color up to 64%, 34% and 88% respectively(Carmen and Daniel 2012).

iii) Membrane processes

The reduction of water consumption implies sustainable development. Industrial wastewater treatment process which is integrated with in-plant water circuits rather than subsequent treatment is effective method of circulating water and reducing consumption of water. Membrane processes are pressurized processes, capable to clarify, concentrate, and most important, separate dye discontinuously from effluent. This process can restrict organic contaminants and microorganisms presented in wastewater.

2.2.2 Chemical treatment

i) Oxidative processes

Oxidation facilitates the treatment of pollutants by chemical oxidation agents other than oxygen/air or bacteria to similar but less harmful or hazardous compounds and/or to short-chained and easily biodegradable organic components (aromatic rings cleavage of dye molecules). dye and color can be removal effectively by using powerful oxidizing agents such as chlorines, ozone, Fenton reagents, UV/peroxide, UV/ozone.

ii) Coagulation-flocculation and precipitation

Coagulation-flocculation represents a physicochemical textile wastewater treatment method which is typically applied prior to sedimentation or filtration to enhance removal of the unwanted dyes. Coagulation is a process used to neutralize charges and form (slightly) larger particles. The actual coagulation process results from a lowered zeta potential at the surface of the particles and the association of those particles to form agglomerates (Al-alawy 2014). Next, following coagulation, flocculation (a gentle stirring or agitation stage) increases the particle size into masses large enough to settle or to be trapped in/on a filter(Jagaba et al. 2016).

Coagulation-flocculation methods have been successfully applied for removal of water-insoluble sulfur and disperse dyes. Coagulation-flocculation not only removes color, but also reduces COD to varying extent and hereby increases the biodegradability of the textile wastewater depending on the coagulant used. However, there are also a number of drawbacks associated with this method. Firstly, recycling of the (expensive) chemicals during the process is not feasible. Secondly, highly water-soluble dyes are able to resist coagulation and require higher amounts of coagulants, thus resulting in higher costs(Jagaba et al. 2016). Thirdly, colored sludge is generated which requires further disposal. Additionally, flocculation behavior is greatly influenced by the charge on the system in which it is used (implicating increased electricity costs), as demonstrated by previous research using polyelectrolytes and polyelectrolyte-surfactant complexes.

iii) Electrocoagulation

Electrocoagulation is an innovative electrochemical treatment method for dye and colour removal (EC) that has as main goal to form flocs of metal hydroxides within the effluent to be cleaned by electro-dissolution of soluble anodes. EC includes important processes as electrolytic reactions at electrodes, formation of coagulants in aqueous effluent and adsorption of soluble or colloidal pollutants on coagulants, and removal by sedimentation and flotation. This method is effective even at high pH for colour and COD removals being strongly influenced by the current density and duration of reaction.

iv). Ionic exchange

Because of the general opinion that ion exchangers cannot accommodate a wide range of dyes, the ion exchange process has not been widely used for treatment of dye-containing effluents, mainly. It occurs mainly based on the interaction of ionic species from wastewater with an adsorptive solid material, being distinguished from the conventional adsorption by nature and morphology of adsorptive material or the inorganic structure containing functional groups capable of ionic exchange. The mechanisms of ionic exchange process are well known, and two principal aspects must be mentioned: (1) ionic exchange can be modeling as well as adsorption onto activated coal; (2) the ion exchangers can be regenerated without modifying the equilibrium condition (e.g., by passing of a salt solution containing original active groups under ion exchanger layer)(W. S. Castagna, C. J. Miller Pieper 2009). In the case of wastewater treatment, the effluent is passed over the ion exchanger resin until the available exchange sites are saturated (both cationic and anionic dyes are removed).

The ionic exchange is a reversible process, and the regenerated ion exchanger can be reused. The essential characteristic of ionic exchange that makes distinction of adsorption is the fact that the replace of ions takes place in stoichiometric proportion. The effluent treatment by ionic exchange process contributes to the diminishing of energetic consumption and recovery of valuable components under diverse forms, simultaneously with the wastewater treatment. In practice, the ion exchangers are used in combination with other wastewater treatments. The main advantages of ion exchange are removal of soluble dyes, no loss of adsorbent at regeneration, and reclamation of solvent after use. The important disadvantages of this process is the cost, organic solvents are expensive, and ion exchange treatment is not efficient for disperse dyes(Kansara et al. 2016).

2.2.3 Biological treatments

Biological processes of treatments are considered as self-purification phenomena existing in natural environment. Types of biological treatments are aerobic or anaerobic or combined anaerobic/aerobic conditions. The decisive parameters for removal efficiency in biological system are processing, quality, adaptability of microorganisms and the reactor type. Since microorganisms do not use coloured constituents as a source of food, dyes themselves are not biologically degradable. Aerobic microorganisms are the most currently used method of biodegradation which involves utilization of molecular oxygen as reducing equivalent acceptor during the respiration process. Research data indicates that certain dyes are liable to anaerobic color removal, and also that an anaerobic process followed by an aerobic process may result in a significant advancement of biological decolourization treatment in future.

A waste treatment plant which treats dye-containing effluents has high potential capacity to produce toxic biodegradation products. To prevent this risk, anaerobic with aerobic sequential process systems seem to be an efficient procedure. Most azo dye metabolites are quickly degraded by oxidation of the substituents under aerobic conditions. Treatment of poorly degradable amines can be successfully achieved by adaptation of microorganisms. The main benefit of biological treatment in relative to certain physico-chemical treatments is that more than 70% of organic matter expressed by COD may be converted to bio solids (Tisma et al. 2012)

2.2.4 Zero liquid discharge

Zero Liquid Discharge (ZLD) is an ambitious wastewater management strategy to purify wastewater by subjecting it to a chain of treatments so that 80-90% of wastewater is recovered and recycled within the industry. A ZLD system involves a range of advanced wastewater treatment technologies to recycle recovery and re-use of the ‘treated’ wastewater and thereby ensure there is no discharge of wastewater to the environment. A typical ZLD system comprises of pre-treatment, reverse osmosis, evaporator & crystallizer. ZLD thus prevents the risk of environmental pollution associated with wastewater discharge and maximizes the efficiency of water usage, thereby striking the balance between exploitation of freshwater resources and preservation of aquatic environment.

Until now, ZLD was generally characterized by energy intensive. Despite the main goal of ZLD to reduce water pollution and improve water sustainability, application of ZLD also results in unintended environmental impacts. Some of the factors which have environmental impacts are: solid waste disposed in landfills may result in leaching of chemicals into groundwater (Anon 2017).

2.5 Wastewater treatment plant sludge

Sludge is semi-solid slurry and can be produced as textile sludge from textile wastewater treatment processes. Sewage sludge can be produced from wastewater treatment processes or as a settled suspension obtained from conventional drinking water treatment and numerous other industrial processes. The term is also sometimes used as a generic term for solids separated from suspension in a liquid; this 'soupy' material usually contains significant quantities of 'interstitial' water (between the solid particles).Industrial wastewater solids are also referred to as sludge, whether generated from biological or physical-chemical processes. Surface water plants also generate sludge made up of solids removed from the raw water. Textile sludge is a heavy metal rich solid waste which can disposed‒off by landfilling, incineration or can be reused as soil coordinator if heavy metal content can be reduce. In comparison with sanitary sludge, textile sludge has greater inorganic matter content, greater heavy metal content, and greater sulfur compound content(Shashank Singh Kalra.etal 2011).

2.5.1 Textile sludge management and disposal practices

There is certainly no universal solution for sludge utilization/application. Each ETP produces sludge of specific characteristics and different regions and countries have quite different regulations regarding sludge utilization. Therefore, prior to any ETP construction, a detailed assessment of options should be prepared and the most suitable application proposed. A number of solutions for utilization and safe disposal of textile sludge have been proposed, practiced, tested, and applied at pilot and industrial scale. These are landfill, composting, anaerobic digestion, thermal treatment, pyrolysis, and solidification and stabilization process.

i) Landfilling

Utilization or safe disposal of sludge generated by textile effluent treatment plants poses a challenge worldwide; landfill disposal should be considered only in case when no other viable option is possible. Unfortunately, in developing countries properly designed and constructed landfills are not available. The main drawback of landfilling of sludge is that a new landfill area must be used. In many countries it will not be allowed to use landfills for deposition of sludge with an organic content above 5%. In general, sludge disposal on landfill gets less and less acceptance.

ii) Composting

Composting is a controlled biological process that uses natural aerobic processes to increase the rate of biological decomposition of organic materials. It is carried out by successive microbial populations that break down organic materials into carbon dioxide, water, minerals and stabilized organic matter. Carbon dioxide and water are released into the atmosphere, while minerals and organic matter are converted into a potentially reusable soil-like material called compost. The loss of water and carbon dioxide typically reduces the volume of remaining material by 25–60%. Compost can be used as a soil amendment in a variety of agricultural, horticultural or landscaping applications, as long as appropriate measures are taken to eliminate contaminants and impurities from the finished product. The release of organic acids may decrease the pH and production of ammonia from nitrogenous compounds may raise the pH. At higher pH levels, more ammonia gas is generated and may be lost to the atmosphere. A pH value between 6.5 and 8.5 is optimal for compost microorganisms. As bacteria and fungi digest organic matter, they release organic acids(Renkow and Rubin 1998).

The important physical parameters requiring consideration include size of constituents, density and moisture content. Smaller size of the constituents aids in faster decomposition of the waste. Wastes of high density reflect a high proportion of biodegradable organic matter and moisture. Low density wastes, on the other hand, indicate a high proportion of paper, plastics and other combustibles. Moisture content indicates water contents of the waste, which is the percentage of the wet weight material to dry material. Microorganisms can only use organic molecules if they are dissolved in water, so the compost pile should have a moisture content of 60–80% of water holding capacity. If the moisture content falls below 40% of water holding capacity the microbial activity will slow down or become dormant. If the moisture content exceeds 80% of water holding capacity, aeration is hindered, nutrients are leached out, decomposition slows, and the odor from anaerobic decomposition is emitted (Gautam, et al 2010) .

A study on composting of sludge and heavy metal characterization and the influence of changing the physico-chemical properties of the medium throughout the composting on the concentrations, bioavailability or chemical forms of Cr, Cu, Zn, Pb and Cd in sludge, showed the stability and maturity of end product. Total metal content in the final compost were much lower than the limit values of composts to be used as good soil fertilizer.

iii) Incineration

Incineration is the process of direct burning of wastes in the presence of excess air (oxygen) at temperatures of about 800 ^{o}C and above, liberating heat energy, inert gases and ash. It is a waste treatment process that involves the combustion of organic substances contained in waste materials. The ash is mostly formed by the inorganic constituents of the waste, and may take the form of solid lumps or particulates carried by the flue gas. The flue gases must be cleaned of gaseous and particulate pollutants before they are dispersed into the atmosphere. Net energy yield depends upon the density and composition of the waste; relative percentage of moisture and inert materials, which add to the heat loss, ignition temperature, size and shape of the constituents, design of the combustion system. In practice, about 65% to 80% of the energy content of the organic matter can be recovered as heat energy, which can be utilized either for direct thermal applications or for producing power via steam turbine generators (with typical conversion efficiency of about 30%).

The combustion temperatures of conventional incinerators fuelled only by wastes are about 760 ^{o}C in the furnace and in excess of 870 ^{o}C in the secondary combustion chamber. These temperatures are needed to avoid odor from incomplete combustion but are insufficient to burn or even melt glass. To avoid the deficiencies of conventional incinerators, some modern incinerators utilize higher temperatures of up to 1650 ^{o}C using supplementary fuel. These reduce waste volume by 97% and convert metal and glass to ash. Ash is the weight of residue after combustion in an open crucible. By resource recovery facilities, several solid residuals are produced including bottom ash and fly ash. Bottom ash is the unburned and non-burnable portion. It can contain considerable amounts of metals and glass as well as unburned organics.

Fly ash is composed of the micron and submicron particulates that have been collected by the air pollution control system, it must be handled very carefully to avoid fugitive dust emissions, which may be harmful to workers and the surrounding environment. Wastes burned solely for volume reduction may not need any auxiliary fuel except for start- up.

When the objective is steam production, supplementary fuel may have to be used with the pulverized refuse, because of the variable energy content of the waste or in the event that the quantity of waste available is insufficient. While incineration is extensively used as an important method of waste disposal, it is associated with some polluting discharges which are of environmental concern, although in varying degrees of severity. These can fortunately be effectively controlled by installing suitable pollution control devices and by suitable furnace construction and control of the combustion process. The lower calorific value must on average be at least 7MJ/kg, and must never fall below 6MJ/kg in any season. Higher calorific value indicates the combustion of waste with a lesser amount of auxiliary fuel support. The amount of energy generated at a waste to energy facility depends primarily on the calorific value of the waste. To facilitate self-combustion of waste, the calorific value of the waste should be at least 5MJ/kg and approximately 6MJ/kg for power generation.

Use of incineration produces relative small volumes of ashes and the constructed landfill may at present sludge production last more than 50 years before it is filled-up. This solution may therefore be seen as a long-range solution especially if methods can be developed to recover heavy metals from the ashes. If incineration is used it is recommended to use only small additions of inorganic material as these will significantly increase the volumes of ashes and to avoid oxidation of chromium(III) to chromium(VI) that occurs at high redox potentials and at high pH-values. Two other problems in use of incineration is the poor dewatering properties of the sludge that makes incineration energy consuming and the relative small size of the plant to make incineration cost-effective (Ahamed and Kashif, 2014). One of the most attractive features of the incineration process is that it can be used to reduce the original volume of combustibles by 80 to 95%. The community is willing to absorb the increased treatment cost. Air pollution control remains a major problem in the implementation of incineration of textile sludge.

iv) Pyrolysis / Gasification

Gasification and pyrolysis are similar processes; both decompose organic waste by exposing it to high temperatures. Both processes limit the amount of oxygen present during decomposition; gasification allows a small amount of oxygen, pyrolysis allows none. In other words, gasification and pyrolysis limit or prevent oxidation. The gasification process means treating a carbon-based material with a limited oxygen or steam to produce a gaseous fuel. The gas can either be cleaned and burned in a gas engine, or transformed chemically into methanol that can be used as a synthesis compound. Nowadays, this technology is not used for mass waste but for somewhat homogeneous waste (The Blue Ridge Environmental Defense League 2009).

Pyrolysis is the application of heat in an atmosphere of zero or limited oxygen to a substance in order to induce chemical decomposition and avoid combustion. Organic material is processed within an enclosed chamber where heating releases valuable gas, leaving residual solids and coke, and in some cases, oil. The gas is afterwards combusted to obtain energy. The residual solids can be land filled or vitrified. Like gasification, pyrolysis is a technology sufficiently developed only for homogeneous waste.

Pyrolysis studies revealed that the temperature was effective on the pyrolysis product distribution. The gaseous product yield increased from 17.5 to 21.9% w/w, while the liquid product and char yield slightly decreased (from 26.8 to 24.3% w/w and 55.7 to 53.8% w/w, respectively) with the increase in the pyrolysis temperature from 450 to 600 ^{o}C. The result of pyrolysis gas analysis showed that this gas has a considerable gross calorific value. Therefore, it was suggested that pyrolytic gas from sludge can provide some part of the energy requirements of the pyrolysis process.

v) Anaerobic Digestion (Bio-Methanation)

In anaerobic digestion (AD) process the organic fraction of waste is segregated and fed to a closed container (biogas digester) where, under anaerobic conditions, the organic wastes undergo bio-degradation producing methane-rich biogas and effluent/sludge. The biogas production ranges from $50-150$ m^3/ton of wastes, depending upon the composition of waste. The biogas can be utilized either for cooking/heating applications, or through dual fuel or gas engines or gas/steam turbines for generating motive power or electricity. The sludge from anaerobic digestion, after stabilization, can be used as a soil conditioner, or even sold as manure depending upon its composition, which is determined mainly by the composition of the input waste.

vi) Solidification and Stabilization (S/S)

The main objective of immobilization technology is to convert the hazardous and toxic wastes into an inert, physically stable mass, with very low leachability and sufficient strength to allow for land filling or land reclamation. Immobilization (or chemical stabilization) is a process in which the waste is converted to a more chemically stable or more insoluble or immobile form. Solidification or cementation is a process in which the waste is converted to an insoluble rock like material by mixing with suitable material to form a solid product. Encapsulation is the coating or enclosure of waste with an inert durable material. Micro-encapsulation is applied to the individual particles of a waste, while macro encapsulation is applied to the individual practices of a waste, while macro encapsulation is the encapsulation of a mass of waste in a container (Pavithra 2017).

The most common material used is cementing agents such as cement, lime, fly ash and gypsum mixtures. However, although highly successful in reducing the morbidity of the waste, these methods often lead to a considerable increase in volumes, thus considerably increase the cost of both transportation and disposal. However, new products based on heat treated natural clays have recently become available. These are capable of absorbing liquid wastes and sludge, either organic or inorganic, to produce products that easily pass normal leachability test. Also used are bitumen, polymers such as polythene, and glass materials which are used in the process called vitrification (but this has largely been applied to radioactive wastes). These processes which greatly reduce the mobility of wastes in a landfill play an important role in the disposal of wastes to landfill.

Wastes with relatively high concentration of hazardous materials could be immobilized and therefore disposed as a waste with much lower pollution potential. The use of solidification and stabilization (S/S) process can greatly reduce the effective concentration of waste disposed at a site and thus could be used to limit the amount of macro-encapsulation in specially designed cells of both inorganic (such as arsenic) and organic wastes (such as pesticides) that are contained in sealed drums. The cell is constructed with in an appropriate containment landfill and is designed to minimize the potential leakage of waste from the cell and is of such a size that damage due to earth movements and earthquakes is likely to be minimal.

Macro encapsulation of inorganics always has an important role to play but it is preferable to incinerate organics rather than encapsulate them. Solidification and stabilization of sludge uses additives to reduce the mobility of pollutants. It has gained popularity in recent years following strict regulations on land disposal of waste classified as hazardous. Sludge stabilization is essentially a cost-effective disposal option as compared to landfill disposal for hazardous wastes. S/S typically involves easily available and inexpensive raw materials and simple technologies.

2.6 Manufacturing of bricks

The fundamentals of brick manufacturing have not changed over time. However, technological advancements have made contemporary brick plants substantially more efficient and have improved the overall quality of the products. A more complete knowledge of raw materials and their properties, better control of firing, improved kiln designs and more advanced mechanization have all contributed to advancing the brick industry.

2.6.1 Raw materials

Clay is one of the most abundant natural mineral materials on earth. For brick manufacturing, clay must possess some specific properties and characteristics. Such clays must have plasticity, which permits them to be shaped or molded when mixed with water; they must have sufficient wet and air-dried strength to maintain their shape after forming. Also, when subjected to appropriate temperatures, the clay particles must fuse together.

Clays occur in three principal forms, all of which have similar chemical compositions but different physical characteristics.

Surface clays may be the up thrusts of older deposits or of more recent sedimentary formations. As the name implies, they are found near the surface of the earth. Shales are clays that have been subjected to high pressures until they have nearly hardened into slate. Fire clays are usually mined at deeper levels than other clays and have refractory qualities.

Surface and fire clays have a different physical structure from shales but are similar in chemical composition. All three types of clay are composed of silica and alumina with varying amounts of metallic oxides. Metallic oxides act as fluxes promoting fusion of the particles at lower temperatures. Metallic oxides (particularly those of iron, magnesium and calcium) influence the color of the fired brick. The manufacturer minimizes variations in chemical composition and physical properties by mixing clays from different sources and different locations in the pit. Chemical composition varies within the pit, and the differences are compensated for by varying manufacturing processes. As a result, brick from the same manufacturer will have slightly different properties in subsequent production runs. Further, brick from different manufacturers that have the same appearance may differ in other properties.

2.6.2 Brick manufacturing process

The manufacturing process has six general phases: 1) mining and storage of raw materials, 2) preparing raw materials, 3) forming the brick, 4) drying, 5) firing and cooling and 6) de-hacking and storing finished products. See Figure 2.

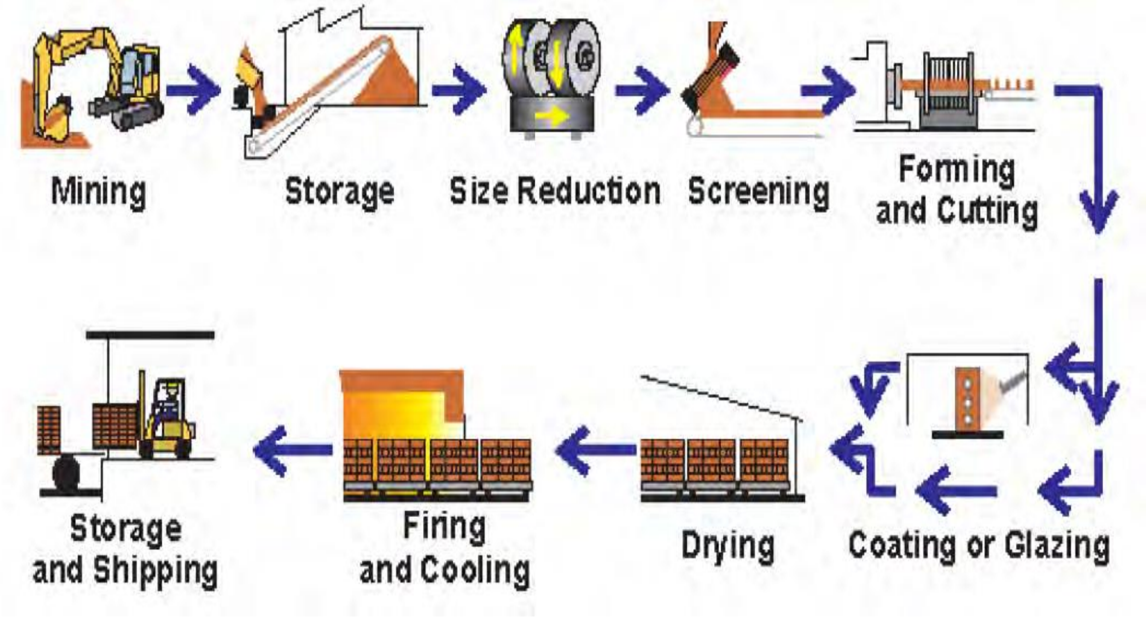


Figure 2. Diagrammatic representation brick manufacturing process (Centennial Park Drive 2006)

i) Mining and Storage

Surface clays, shales and some fire clays are mined in open pits with power equipment. Then the clay or shale mixtures are transported to plant storage areas. Continuous brick production regardless of weather conditions is ensured by storing sufficient quantities of raw materials required for many days of plant operation. Normally, several storage areas (one for each source) are used to facilitate blending of the clays. Blending produces more uniform raw materials, helps control color and allows raw material control for manufacturing a certain brick body.

ii) Size reduction and Screening

To break up large clay lumps and stones, the material is processed through size reduction machines before mixing the raw material. Usually the material is processed through inclined vibrating screens to control particle size.

iii) Forming

Tempering, the first step in the forming process, produces a homogeneous, plastic clay mass. Usually, this is achieved by adding water to the clay in a pug mill a mixing chamber with one or more revolving shafts with blade extensions. After pugging, the plastic clay mass is ready for forming.

iv) Drying

Wet brick from molding or cutting machines contain 7 to 30% moisture, depending upon the forming method. Before the firing process begins, most of this water is evaporated in dryer chambers at temperatures ranging from about 38 ^{o}C to 204 ºC. The extent of drying time, which varies with different clays, usually is between 24 to 48 hours. Although heat may be generated specifically for dryer chambers, it usually is supplied from the exhaust heat of kilns to maximize thermal efficiency. In all cases, heat and humidity must be carefully regulated to avoid cracking in the brick.

v) Firing

Brick are fired between 10 and 40 hours, depending upon kiln type and other variables. There are several types of kilns used by manufacturers. The most common type is a tunnel kiln, followed by periodic kilns. Fuel may be natural gas, coal, sawdust, and methane gas from landfills or a combination of these fuels. In a tunnel kiln brick are loaded onto kiln cars, which pass through various temperature zones as they travel through the tunnel. The heat conditions in each zone are carefully controlled, and the kiln is continuously operated. A periodic kiln is one that is loaded, fired, allowed to cool and unloaded, after which the same steps are repeated. Dried brick are set in periodic kilns according to a prescribed pattern that permits circulation of hot kiln gases. Firing may be divided into five general stages:

1) Final drying (evaporating free water) ; 2) dehydration; 3) oxidation; 4) vitrification; and 5) flashing or reduction firing. All except flashing are associated with rising temperatures in the kiln. Although the actual temperatures will differ with clay or shale, final drying takes place at temperatures up to about 204 ºC, dehydration from about

149 ºC to 982 ºC, oxidation from 538 ºC to 982 ºC and vitrification from 871 ºC to 1316 ºC. Clay, unlike metal, softens slowly and melts or vitrifies gradually when subjected to rising temperatures. Vitrification allows clay to become a hard, solid mass with relatively low absorption.

Melting takes place in three stages:

1) Incipient fusion, when the clay particles become sufficiently soft to stick together in a mass when cooled;

2) Vitrification, when extensive fluxing occurs and the mass becomes tight, solid and nonabsorbent; and

3) Viscous fusion, when the clay mass break down and becomes molten, leading to a deformed shape. The key to the firing process is to control the temperature in the kiln so that incipient fusion and partial vitrification occur but viscous fusion is avoided. The rate of temperature change must be carefully controlled and is dependent on the raw materials, as well as the size and coring of the brick being produced. Kilns are normally equipped with temperature sensors to control firing temperatures in the various stages. Near the end, the brick may be "flashed" to produce color variations (Centennial Park Drive 2006).

vi) Cooling

After the temperature has peaked and is maintained for a prescribed time, the cooling process begins. Cooling time rarely exceeds 10 hours for tunnel kilns and from 5 to 24 hours in periodic kilns. Cooling is an important stage in brick manufacturing because the rate of cooling has a direct effect on color.

2. 7 Previous studies on stabilization of sludge through fired clay bricks

Brick is one of the most common building materials in Ethiopia. Many experiments have been done to incorporate wastes into the production of bricks. Recycling wastes such as rubber, limestone dust, wood sawdust, processed waste tea, fly ash, polystyrene and sludge by incorporating them into building materials is a practical solution for pollution problem (Kadir et al, 2012). The feasibility of incorporation of 3 to 30% textile sludge into bricks sludge were added to clay bricks and fired at 200 °C to 800 °C and the different properties of fired bricks were investigated, the study claimed that all brick sample satisfied the weight loss and shrinkage criteria but only 9% sludge mix met the compressive strength criterion (Baskar et al., 2006).

Another research result represented the effect of incorporation of textile sludge, fly ash, cement and quarry dust to clay brick (Palanisamy 2011). The study showed that with increase in sludge content, there was a decrease in compressive strength of bricks. There was increase in compressive strength with increase in sand, fly ash, cement and quarry dust proportion. Rouf and Hossain used 5%, 15%, 25% and 50% of iron and arsenic sludge in clay bricks with firing temperatures of 950 ^{o}C, 1000 ^{o}C and 1050 ^{o}C. In this study, they claimed that 15 to 25% by weight with 15 to 18% optimum moisture content is the appropriate percentage of sludge mixture to be incorporated. The compressive strength test indicated that the strength of the brick depends significantly on the amount of sludge in the brick and the firing temperature. The results showed that 15% by weight is the optimum amount of sludge with a 1000 ^{o}C firing temperature. However, the strength of the brick can be as high as normal clay bricks with up to 25% sludge at a firing temperature of 1050 ^{o}C (Palanisamy 2011).

Badr El-Din E et al. studied complete substitution of brick clay by water treatment sludge incorporated with rice husk ash. In this study, three different series of sludge to rice husk ash (RHA) proportions were studied, which exclusively involved the addition of sludge with ratios 25, 50, and 75% of the total weight of sludge-RHA mixture. Each brick series was fired at 900, 1000, 1100, and 1200 ^{o}C. From the obtained results, it was concluded that by operating at the temperature commonly practiced in the brick kiln, 75% was the optimum sludge addition to produce brick from sludge-RHA mixture. The produced bricks properties were obviously superior to the clay control-brick and to those available in the Egyptian market(Hegazy et al. 2012).

A research project in Malaysia investigated physical and mechanical properties of sludge bricks such as compressive strength, efflorescence effects, bulk density, water absorption, weight reduction. The results from this study indicates 40% sludge and 60% clay combination gives best value of bricks and superior to local manufactured brick (Krishnan and Giridev 2007).

The use of sludge in construction industry is considered to be the most economic and environmentally sound option. Due to the similar mineralogical composition of clay and water treatment plant sludge, a study which focused on the reuse of sludge in clay-brick production investigated the use of sludge as partial substitute for clay in brick manufacturing. In this study, four different series of sludge and clay proportioning ratios were studied, which exclusively involved the addition of sludge with ratios 50, 60, 70, and 80% of the total weight of sludge-clay mixture. Each series involved the firing of bricks at 950, 1000, 1050, and 1100 ^{o}C. It was concluded that by operating at the temperature commonly practiced in the brick kiln, 50% was the optimum sludge addition to produce brick from sludge-clay mixture (Mohammed O. Ramadan et al. 2008).

Treatability studies of chemical sludge were conducted using solidification/stabilization treatment to examine the possibility of its reuse in construction materials, the use of textile sludge can definitely be explored for structural and nonstructural applications depending upon strength requirement(Patel and Pandey 2009). Hot-dip galvanizing industry is one of the industries which produces numerous pollutants and causes serious environment contamination. Relatively large amounts of toxic metals are found in used raw materials, but their leachability reduces to a negligible level after fixing in bricks and firing at 1020 °C (Arsenovic, Radojevic, and Stankovic, 2012).

A study which examines the potential reuse of textile effluent treatment plant sludge in building materials indicated that up to a maximum of 30%, may be possible in the manufacturing of non-structural building materials (Sabumon 2006). Sludge was partially replaced (0, 5, 10, 15%) with clay soil used in bricks manufacturing, the result was encouraging for dispose - off sludge (Garg et al, 2017).

A composition of clay-sludge was made by introducing 0, 10, 15, 20, 25, 30, 35 and 40% of sludge into clay. Cubic and cylindrical model specimens were made using a manually operated hydraulic press. The samples were placed in muffle furnace at 1050 ^{o}C for 2 hours. The results indicate that up to 15% sludge can be incorporated into clay bricks with a resultant optimal compressive strength. Leachates obtained from crushed brick specimens showed low levels of heavy metals indicative that these were immobilized in the ceramic matrix during the sintering process. Therefore the bricks are environmentally friendly(Valentine 2017).

A study conducted by Kalyan Patre investigated the use of water treatment sludge incorporated with clay. In this study bricks were produced with sewage sludge additions ranging from 20, 25, 30 and 40% by dry weight respectively and compare produce brick with regular brick. Bricks with a sludge content of up to 40% were capable of meeting the relevant technical standards. However, if bricks with more than 30% sludge addition are not recommended for use because they are brittle in nature and easily broken even when handled gently as well as colour is not as per the requirement. Also from this investigation we can solve disposal problem completely and also construct and economical structure with easy designing (Razvi 2016).

Investigation of the effect of Textile mill sludge addition in burnt clay bricks is done. Sludge percentage is varied from zero to thirty-five percent by weight. Firing temperature and firing period are varied to understand the variations in characteristics of burnt bricks. Parameters such as compressive strength, density, water absorption, are studied. Density of bricks, compressive strength and ringing sound was reduced as sludge content in bricks increases whereas water absorption and efflorescence increases.

Higher firing temperature and firing period i.e. 800 ^{o}C and 24 hours give good results in terms of compressive strength with same percentage of sludge as compared to other temperature and firing period combinations. Textile mill sludge up to 15% can be added so as to get compressive strength greater than 3.5 N/mm^2 (Shrikant et al, 2013). Mary Lissy P N and Dr. M S Sreeja studied bricks manufactured from dried sludge collected from textile wastewater treatment plant. The result of the study indicated that the sludge proportion and the firing temperature were the two key factors determining the brick quality. With up to 6.66% sludge added to the bricks, the strength measured at temperatures 500 ^{o}C met the requirements of the National Standards. This study showed that the pulverized sludge could be used as a brick material in reducing the firing temperature for the production of energy efficient bricks. The bonding strength can be further enhanced by controlling operating conditions (Mary Lissy P Sreeja 2014)

CHAPTER THREE

3. MATERIALS AND METHODS

This chapter narrates the working procedure which was followed in this study. The methodology for collection of samples (clay and sludge), analytical procedures to determine characteristics of sludge and sludge–clay mix, preparation and tests for bricks using sludge-clay mixtures and leaching test of bricks are discussed in a sequential manner.

3.1 Collection of sludge samples

Sludge samples were collected from Hawassa Industrial Park during November and January 2018. Hawassa Industrial park is a located 275 km from Addis in proximity to one of Ethiopia's premium holiday destination, Lake Hawassa. The park is 300 hectare Eco-parks, centered on textile and garment products and fully integrated to the city. A Zero Liquid Discharge treatment plant with a capacity of treating 11 million liters of wastewater per day was installed. Polly Aluminum Chloride (PAC) is used as coagulants and poly cation is used as flocculent for chemical treatment purpose. Sludge generated from chemical treatment is transferred to sludge tank. Chemical sludge was collected from the discharge point as shown in Figure 3 at different time and a composite sample was made by mixing each of the collected samples.

a) Sludge collection **b) sludge discharging point**

Figure 3. Sludge collection point

3.2. Collection of clay samples

Clay samples were collected from Ethiopian brick manufacturing Share Company situated at Addis Ababa; the company uses 25% red and 75% white soil as a raw material for the manufacturing of bricks. As shown in Figure 4. the sample was collected from different storage area at varying depth.

a) White clay **b) Red clay**

Figure 4. Clay collection point

3.3. Preparation of the sludge and clay samples

The clay and sludge samples collected were air dried as shown in Figure 5 for more than 14 days at center of environmental science laboratory room number 101. The air dried samples then subjected to GX-65B drying oven for 24 hours and RRH- 200 high grade grinder was used to grind the dried samples. The grinded samples where sieved with 90µ sieve to make ready for analysis as shown Figure 6.

a) Air dried soil **b) Air dried textile sludge**

Figure 5. Sample drying

Figure 6. Oven dried and grinded samples (white soil, sludge, red soil) from left to right

3.4. Characteristics of sludge

The summary of analytical methods adopted in this study of samples has been shown in Table. Physical characteristics like moisture content, presence of organic compound were tested. Wet method was followed in determining moisture content of sludge samples. Sludge samples of 2.5 gm, were taken in triplicate at ambient temperature. Thereafter samples were oven dried at 105 ^{o}C for about 24 hours. After oven drying the sample were placed in a desiccator for half an hour. After half an hour, weights of the samples were taken again. Now the reduced weight was divided with wet weight and moisture content was found in terms of percentage using ASTM, see Table 1.

Table 1. Analytical methods for characterization of sludge and bricks

Parameters	Test method
pH	ASTM 9045D
Ash content	ASTM D 2974-87
Moisture content	ASTM D 2974-87
Organic content	ASTM D 2974-87
Compressive strength	ASTM C 67
Water absorption	ASTM C 67
Weight loss on ignition	Thermal method
Heavy metals	EPA 200.7/ICP
Calorific value	ASTMD5865

Thermography Analysis (TGA) of sludge sample was made using SDT Q600 V20.9 Build 20 instruments which are in a good operating condition, Ramp method was used for the analysis. Scanning EDS was done using JSM-IT300 to identify elemental composition of the sludge. The flow chart followed for the experiments is presented in as follow.

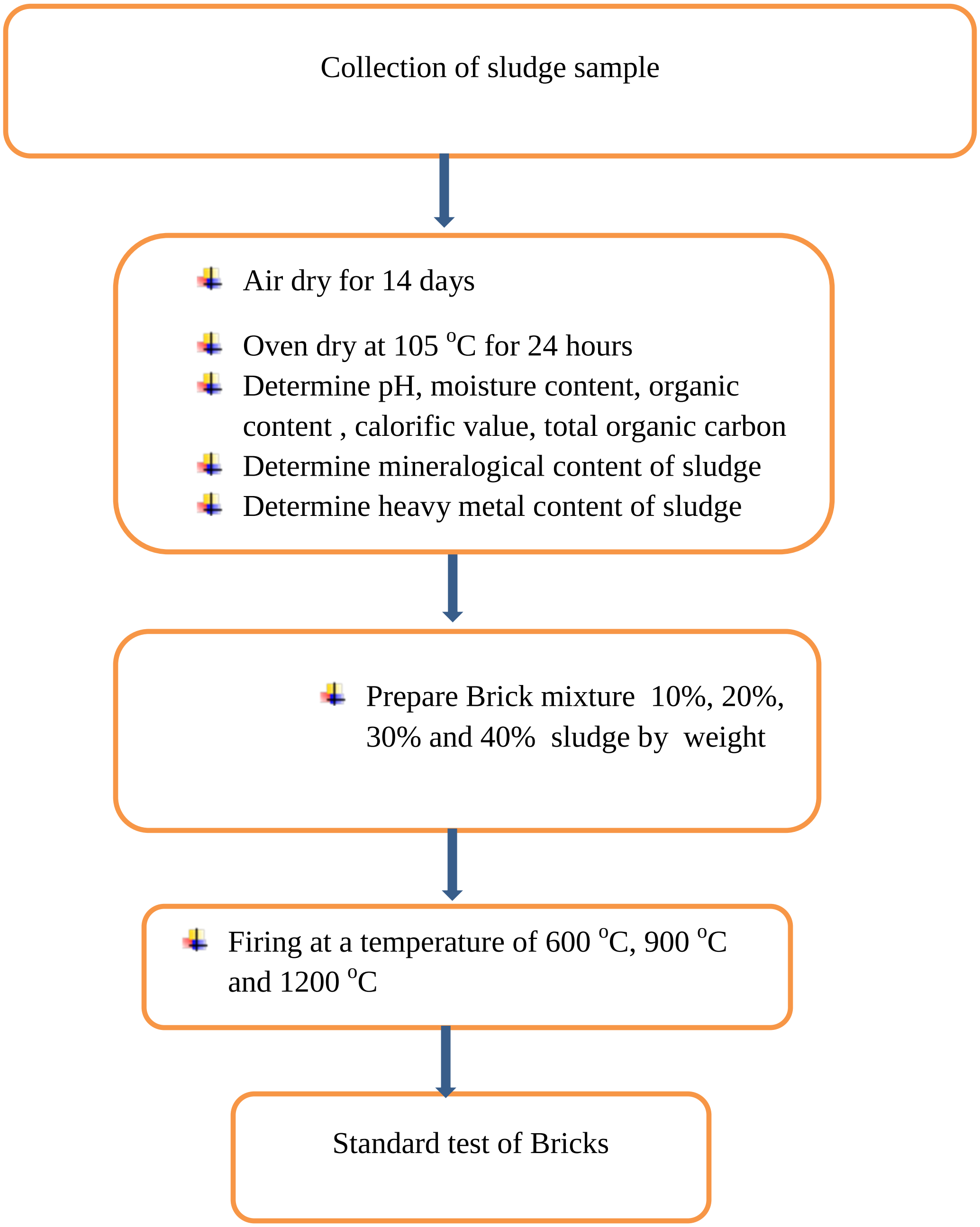


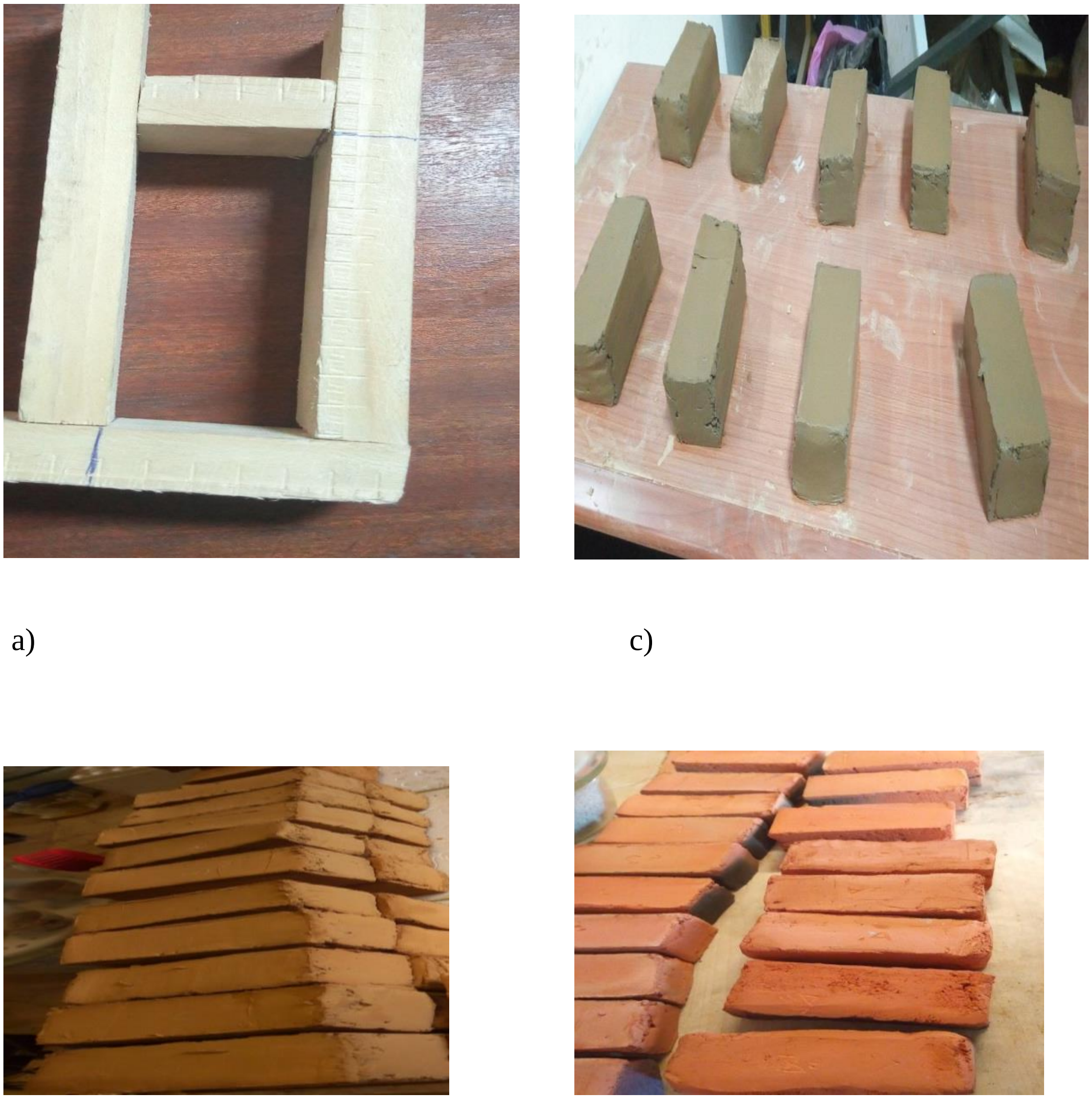
Figure 7. Flow chart of the experiment

3.5 Heavy metal determination

As it is described in the previous section, sludge samples were dried in an oven at 105 °C until constant weight, lightly ground for homogenization and to pass 90µ sieve. For heavy metal analysis, sample preparation was carried out according to EPA 3050B with a slight variation. 5 gm. of dried sample was digested with acid (HNO_3: HCl =1:3 volume ratio) for 24 hours. After adding 350-400 ml distilled water, sample was boiled for 2.5 hours and prepared a 500 ml solution. Then, solution was filtered through 0.45µ pore size filter paper and filtrate was collected to determine the concentration of heavy metals (As, Pb, Cd, Cr, Ni, Cu, Zn and Hg) by using ICP-MS. The analysis was done at ProteKnic Laboratories, Pretoria South Africa.

3.6 Preparation of bricks

Sludge and clay samples were lightly ground with porcelain mortar for homogenization. Total of 135 bricks sample (length 120mm width 50 mm and height 50 mm) of sludge-clay mixture in varying proportion (10, 20, 30 and 40%) were prepared in the laboratory as shown in Figure 10 (b). Three 100% clay samples were prepared as a reference specimen. The sludge-amended clay bricks were molded by wood mold and compacted with hand. Mold for the preparation of brick samples as shown in Figure 10 (a), were prepared with wood. The prepared brick samples were then kept for 24 hours for natural drying and followed by another 24 hours oven drying at 105 ^{o}C. All samples were heated in SX-2.5-10 muffle furnace at the rate of 5 ^{o}C/min up to the design temperatures of 600 ^{o}C, 900 ^{o}C and 1200 ^{o}C, respectively for 6 hours.



a) c)

b) d)

Figure 8. Brick mold and air-dried Brick a) Wooden mold b) Oven dried brick c) Brick during air drying d) Fired bricks using Muffle Furnace

Table 2. Mix proportion of white soil, red soil and sludge

Sample	White soil by		Red soil		Sludge	
	weight	%	weight	%	weight	%
Control	300	75	100	25	0	0
A	292.5	75	97.5	25	39	10
B	240	75	80	25	64	20
C	210	75	70	25	84	30
D	180	75	60	25	96	40

3.7 Standard test of bricks

The suitability of bricks for construction can be decided by making certain test. The main parameters are compressive strength, water absorption, loss on ignition and firing shrinkage. All these test method are described as follows.

3.7.1 Compressive strength of bricks

ASTM C 67 method was used for determining the strength of the bricks. Compressive strength test machine was used to test the bricks sample. The compressive strength was computed using equation.

C= $W/_{A}$, where, C = compressive strength of the specimen W = maximum load A = average of the gross areas of the upper and lower bearing surfaces of the specimen

3.7.2 Water absorption of bricks

ASTM C 67 method was used for testing the water absorption of the sample. Based on this method the samples were oven dried at 105 ^{o}C for 24 hours. After drying, the samples were cooled at room temperature. The dry, cooled specimen was submerged, without preliminary partial immersion, in distilled water at 27 ^{o}C for 24hours. Then the specimen were wiped off the surface water with a damp cloth and taken the weight the specimen within 5min after removing the specimen from the bath. Then, water absorption of the sample is calculated using equation

$$\text{Water Absorption \%} = \frac{100(\mathrm{W_s} - \mathrm{W_d})}{\mathrm{W_d}}$$

Where, W_d = dry weight of the specimen, and W_s = saturated weight of the specimen after submersion in cold water.

3.7.3 Weight loss on ignition

The brick samples were oven dried at 105 ^{o}C for 24 hours. Then these samples were fired at a temperature of 600 ^{o}C, 900 ^{o}C and 1200 ^{o}C. Loss of Ignition (LOI) was determined by measuring the weight loss of the sample between the drying and firing stage.

$$LOI\ \% = \frac{100(W_d - W_f)}{W_d}$$

Where, W_d = Mass of oven dried specimens (g) W_f = Mass of fired specimens (g)

3.8 Firing energy saving

Brick production industries are energy intensive sectors and have a large negative impact on the environment relating to energy use(Christopher Koroneos Dompros and Aris 2007). Savings energy consumption in the brick manufacturing industry by incorporating sludge may lead to a sustainable brick production. The firing energy saved due to incorporating sludge can be calculated using equation the following equation (Mohajerani, Kadir, and Larobina 2016)

$$\text{Energy saved} = \frac{\mathrm{q}m_1-(\mathrm{q}m_2-\mathrm{C_V}.\mathrm{M}_3)100}{\mathrm{q}m_1}$$

Where, q = Specific energy for brick firing, MJ kg $^{-1}$ m_1, = mass of clay in control brick (kg), m_2= mass of sludge brick (kg), M_3= mass of sludge in sludge brick (kg), C_V = calorific value of textile sludge MJ kg^{-1}

The specific firing energy is measured by dividing the firing energy (MJ) with the mass of brick (kg). A survey report on ASEAN countries conducted in 1993–1994 showed that the specific firing energy consumption was between 2 and 3 MJ/kg (Prasetsan, 1995). For this study the specific energy consumption is assumed to be 3 MJ/kg. The calorific value of textile sludge was measured using Bomb calorimeter (Mohajerani et al. 2016).

3.9. Leaching test of bricks

The leachability tests were carried out to ensure the environmental compatibility of these fired bricks to be used as building materials. In this study, Toxicity Characteristics Leaching Procedure (TCLP) test according to USEPA 1311 (1992) was followed. In TCLP test, dried brick samples which are fired at 1200 ^{o}C are ground using grinder and passed through 9.5 mm standard sieve. An acetic acid solution (0.57% v/v) was added to samples at a constant ratio of liquid: solid (20:1). After 18 hours rotating with rotary mixture at 3 ± 2 rpm, the leachate was filtered with 0.45µ pore size filter paper and analyzed for Cu, Ni, Pb and Zn using FLAAS at Geological Survey of Ethiopia. Due to instrument issue the center couldn't do analysis of other heavy metals.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

This chapter deals with the results obtaining from this study. This chapter presents laboratory experiments to determine the characteristics of sludge, engineering properties of sludge-amended bricks.

4.1 Physico chemical characteristics of sludge

The sludge characteristics are shown in Table 3. The pH of sludge was 7.44 and therefore, the sludge can be regarded as neutral. The moisture content of the sludge samples was 21%. The organic contents of sludge were 20.7%.

Table3. Characteristics of the sludge and clay sample

Sample type	pH	Moisture content	Total organic carbon	Net Calorific value	Ash content in %
Red Soil	5.66	7.2%	3.77%	-	-
White Soil	6.96	2.60%	3.60%	-	-
Sludge	7.44	21.4%	20.7%	4.65 MJ/kg	43.3

4.2 Heavy metal content in sludge

EPA 200.7/ ICP method was used to analyze the heavy metal concentration of the sludge. The concentrations of heavy metals in the sludge sample used in this study were: Pb: 10.4; Cd: 0.26; Cr: 27; Cu: 50; Zn: 272; Ni: 11, Co: 3.3, Hg <0.4 and As: 5 mg/kg as shown in Table 4

Table 4. Concentration of heavy metals in sludge and USEPA legislations for sludge utilization (EPA Method 1699)

Heavy metals	Concentration mg/kg	Limit in Ethiopia	USEPA limit
Ni	11	NA	420
Zn	272	NA	7500
Cu	50	NA	4300
Co	3.3	NA	-
Pb	10.4	NA	840
Cr	27	NA	3000
Cd	0.26	NA	0.6
AS	5	NA	75
Hg	<0.4	NA	57

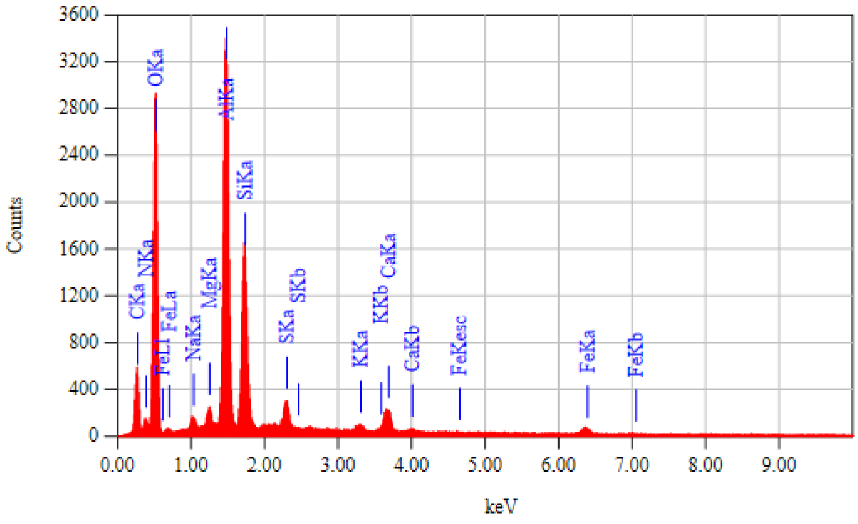
Arranging the metals from higher to lower mean content in this sludge: Zn> Cu > Cr > Ni > Pb > As > Co > Hg > Cd. The total heavy metals content found in the sludge were compared to USEPA (EPA Method 1994) regulatory limits of heavy metal content for sludge utilization.

4.3 Mineralogical content of sludge

The phase and chemical composition of textile sludge and clay was identified using XRD. The chemical composition found as percentage of major oxides as shown in Table 5. This showed that the main components of textile sludge were Al_2O_3 (36.2%), SiO_2 (15%), Fe_2O_3 (12.1%), SO_3 (13.4%), CaO (3.5%) and MgO (2.8%).

Table 5. Chemical composition and phase of sludge and soil

Analytes	**Sludge (%)**	**White clay (%)**	**Red clay (%)**
SiO_2	15	66.5	55.3
CaO	3.5	< 0.01	< 0.01
Al_2O_3	36.2	11.36	16.4
Fe_2O_3	12.1	8.16	9.62
SO_3	13.4	-	-
MgO	2.8	0.16	0.6



Element	Mass %
C	18.9
N	7.85
O	48.7
Na	0.67
Mg	0.79
Al	12.96
Si	6.66
S	1.14
K	0.3
Ca	1.18
Fe	0.84
Total	100

Figure 9. EDS of the sludge sample

From Table 5, We can see that components that are found in clay are also present in textile sludge but in different amount. So clay can be partially replaced by textile sludge as raw material for brick production. The EDS analysis performed to establish the elemental composition of sludge in Figure 11, showed that the main components of sludge where Oxygen, Carbon, Aluminum and Silicon.

4.3 Thermo gravimetric analysis (TGA)

A study on thermo gravimetric analysis provides information on thermal behavior of the materials and hence on optimum condition, 10.75 mg of the sample was analyzed using ramp method. The thermogram obtained by differential scanning calorimeter (DSC) of the studied sludge is presented in Figure 12. The analysis of this thermogram shows the transformation of studied sludge in two processes: endothermic and exothermic between 200 °C and 1200 °C. There may also be a phase transformation between 200, 452.04 and 935.09 °C. Reactions take place at lower temperatures being mainly CO_2 and H_2O, as it expected for mainly total oxidation reactions. Two exothermic peaks are observed between 452.04 and 935.09 °C, which correspond to the combustion. The first peak corresponds to the oxidation of biodegradable matter and the second one will be mainly due to the oxidation organic polymers from the sludge or from dead bacteria. Above 800 °C the mass loss is negligible indicating that no biodegradable matter that burns.

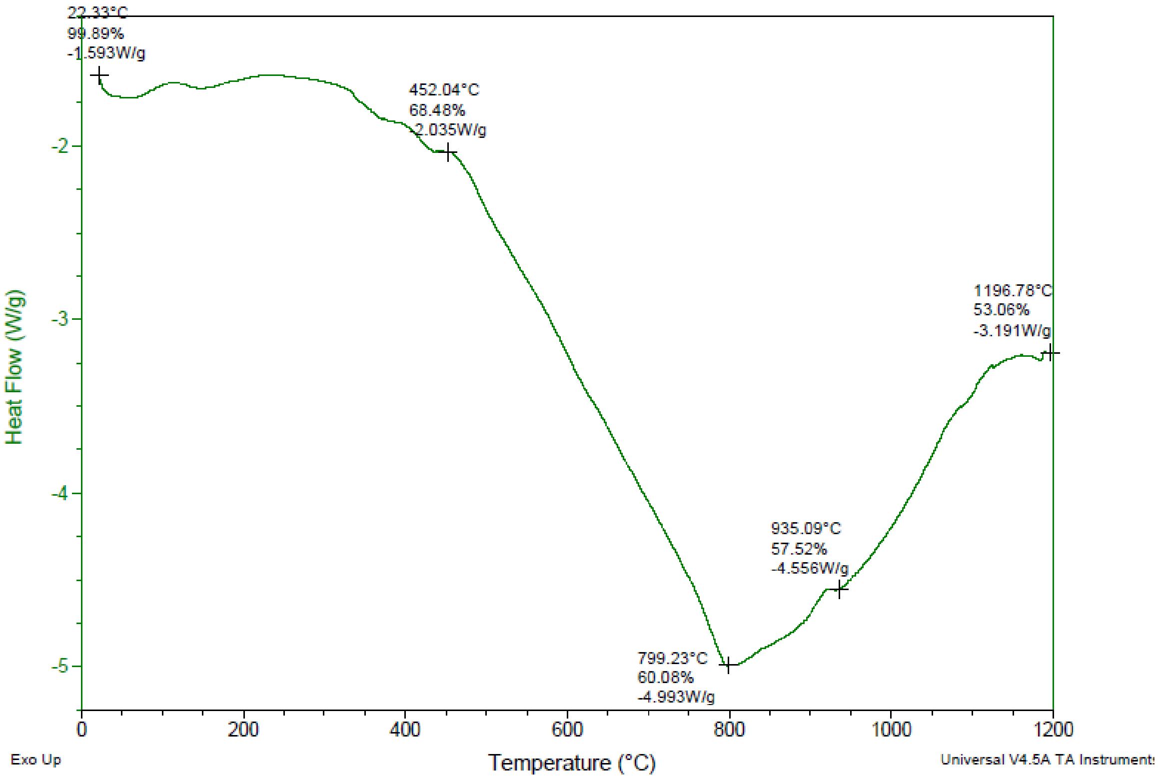


Figure 12**.** DSC-TGA plot of textile sludge sample

4.4 Properties of fired bricks prepared at laboratory

After firing the bricks at different temperature a series of tests include weight loss on ignition, water absorption and compressive strength following standard methods.

4.4.1 Compressive strength of bricks

For confirming the engineering quality of a building material compressive strength test is the key test. The strength of a material is its ability to resist forces at failure. The compressive strength tests of the bricks were shown in Figure 13. The compressive strength of textile sludge incorporated bricks ranged from 2 to 30.42 Mpa .It is also observed that the content of sludge and firing temperature have a significant effect on the compressive strength of bricks. As the sludge substitution increased the compressive strength of the bricks was decreased, sludge content has been inversely proportional to compressive strength. As shown in Table 6 the compressive strength of the 20% sludge substituted brick is comparable with the Ethiopian standard.

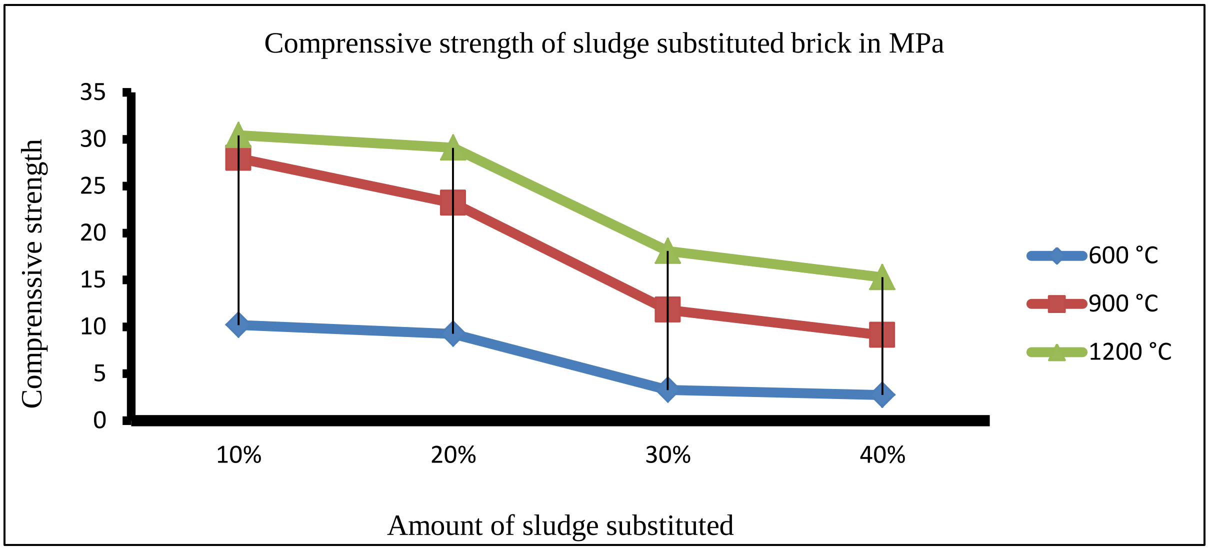


Figure 13. Compressive strength of bricks

Table 6. Ethiopian standard for fired clay bricks (ECAE)

Class	**Minimum compressive strength**		**Water Absorption (%)**	
	Average of 5 Bricks	**Individual Bricks N/mm^2**	**Average of 5 Bricks**	**Individual Bricks**
A	20	17.5	21	23
B	15	12.5	22	24
C	10	7.5	No limit	No limit
D	7.5	5.0	No limit	No limit

4.4.2 Water absorption of bricks

The less water penetrates into the brick, the more durability of the brick and resistance to weathering (Hegazy et al. 2012). Thus, the internal structure of the brick must be compact enough to avoid the intrusion of water. It has been found that the water absorption of the bricks increased with increased sludge addition thereby potentially increasing its susceptibility to weathering action. On the other hand, water absorption was found to decrease when firing temperature was increased. This can be due to the formation of the amorphous phase at high firing temperature. The textile sludge used in these experiments contained high amount of organic content (27%) and it was found that the quantity of absorbed water increased with the increase of textile sludge proportion. In case of bricks containing 10% by w/w. sludge firing at 600 ^{o}C, water absorption was 22% which was reduced to 17.4% when firing temperature increased to 1200 ^{o}C. On the other hand water absorption increased from when textile sludge proportion was increased from 0% to 40% (Figure.14). Similar trends in water absorption with sludge fraction in bricks and other construction materials have been observed in other studies(Tay 1987)

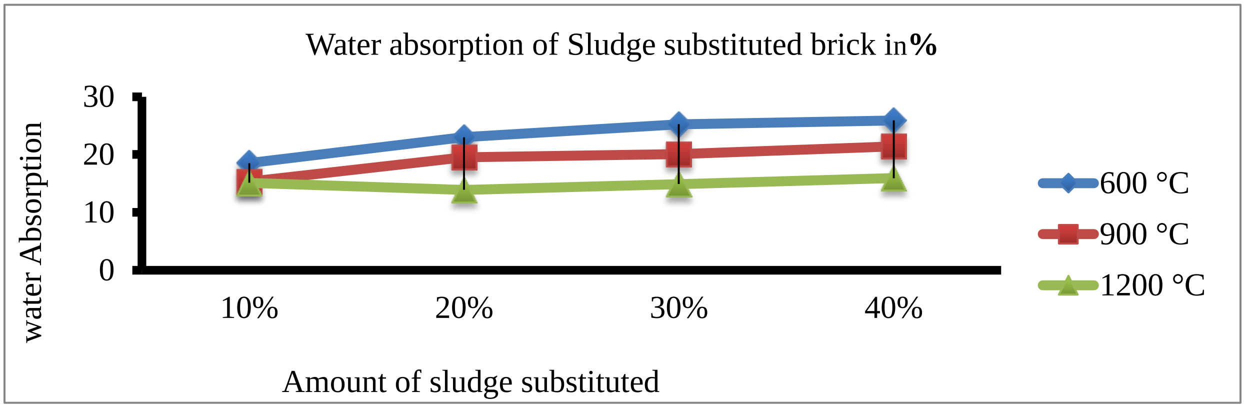


Figure 14. Water absorption at different temperature

4.4.3 Weight loss on ignition

The weight loss on ignition depends on both organic matter content and inorganic substance that are found in both clay and sludge being burnt off during the firing process(Baskar et al., 2006). The effect of sludge content and firing temperature on weight loss of bricks are shown in Figure 15. LOI was found to increase with increased sludge content. For the bricks fired at 1200 °C, the loss on ignition was 21.3% for 30% sludge bricks. The relationship of sludge content was approximately linear with the loss on ignition increasing to 19.3%, 20.2% and 22.4% for the 10, 20 and 40% sludge bricks, respectively. A linear relationship between weight loss through firing and percentage sludge content of the bricks was recorded. As the percentage of sludge used increases, the final weight of the brick reduces. This can be considered a positive result, as by decreasing the overall dead weight of the masonry, a lower strength brick may be required. An overall reduction in weight may also have positive effects on transport costs as these are often calculated by weight. In addition, as the structure is lighter in weight, smaller foundations may be required leading to further overall cost reductions

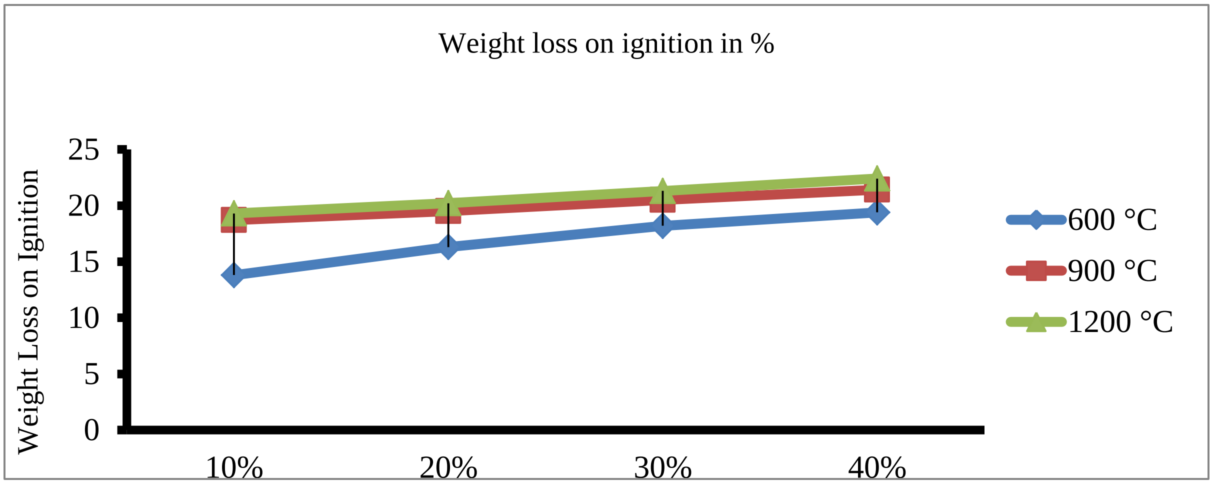


Figure 15. Weight loss on ignition of textile sludge bricks with respect to temperature

This weight loss could be due to the combustion and decomposition of the organic and inorganic matter present in both textile sludge and clay during the firing process. Similar kind of weight loss result in case of sewage sludge, textile sludge and arsenic rich sludge incorporated bricks were found in other studies.

4.5 Firing energy saving

The incorporation of textile sludge in bricks has the potential to reduce the energy required during firing. Currently, energy efficiency and environmental concerns have become as great an issue as quality and cost in the manufacturing sector, due to increased awareness of the effects on the environment (Mohajerani et al. 2016). Calorific value of textile sludge used in this study has been found to be 4.63 MJ/kg which was measured by Bomb Calorimeter .The estimated amount of energy saved during firing of textile sludge bricks was calculated using equation which has been interpreted. The result showed that an estimated of 26% energy would be saved for 10% Textile Sludge bricks and 50% energy saving for 20% textile sludge bricks during firing compared to control bricks. Similar kind of energy saving result was reported for ETP bio solid incorporated bricks and for cigarettes butt incorporated bricks (Mohajerani et al. 2016). Textile sludge used in this study contained about 27% organic content which could facilitate heat input to furnace and reduced the amount of energy required for firing.

4.6 Leaching test of the bricks

The Toxicity Characteristics Leaching Procedure (TCLP) test is designed to identify wastes that are likely to leach hazardous concentrations of particular toxic constituents into the groundwater. During the TCLP test, constituents are extracted from the waste to simulate leaching actions that actually occur in landfills. If the concentration of the toxic constituents exceeds the regulatory limit, the waste is classified as hazardous. The leachate analysis according to USEPA 1311 from sludge amended bricks fired at 1200 ^{o}C temperature showed that Pb did not leach from the sludge amended bricks as their concentrations were far below detectable levels. As shown in Table 7 other metals namely Co, Cu and Zn leached from sludge amended bricks concentration are far below the US-EPA regulatory limits that are 4, 6.8 and 12.2 ppm, respectively.

Table 7. Leaching test of textile brick

	Pb	**Co**	**Cu**	**Zn**
Raw sludge mg/kg	10.4	3.3	50	272
Leached	<0.01	4	6.8	12.2

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATIONS

In developing country like Ethiopia, bricks are used in a large extent for the building construction. To meet the demands of millions and millions of bricks, a large number of brick fields should be established. So, the textile sludge can be useful substitute of soil to some extent for the brick production which will also reduce energy requirement and environmental issue of sludge disposal.

5.1 Conclusion

This study has investigated the effect of incorporating sludge generated from ZLD of Hawassa Industrial Park in fired-clay bricks on their physical and mechanical properties as well as on their environmental aspects. The bricks were manufactured by incorporating 0, 10, 20, 30 and 40% (by dry weight) of textile sludge and fired at 600 ^{o}C, 900 ^{o}C and 1200 ^{o}C with clay for 6hours and relevant engineering properties of the fired clay bricks were assessed.

The major findings of this study are as follows:

The heavy metal content of the sludge is very well below US EPA land application limit standard.

Water absorption increases with the increase of sludge incorporation but decreases with increasing firing temperature. 10, 20, 30 and 40% sludge bricks burnt at 900 and 1200 ^{o}C can be regarded as Grade A category based on ECAE standard requirement for water absorption.

The compressive strength of textile sludge bricks reduced considerably from 30.42 to 2 MPa when textile sludge content increased from 0% to 40% fired at 1200 ^{o}C. On the other hand, compressive strength increased with an increase of firing temperature for all brick samples. The addition of 40% sludge into the mixture reduces compressive strength approximately about 65% compared with the control.

It was estimated that the firing energy of bricks can be saved up to 38% and 50% by incorporating 10% and 20% textile sludge, respectively which may be due to the calorific power of organic content present in the textile sludge.

Sludge addition and higher firing temperature caused higher weight loss in manufactured bricks, which was due to the combustion of organic matter. Based on the results obtained from laboratory condition, bricks with textile sludge content of 10% and 20% by dry weight and fired between 900 ^{o}C and 1200 ^{o}C can produce good quality bricks which can satisfy all the desirable mechanical and physical properties as per ECAE standards.

5.2 Recommendations

- Since there is no standard and guide line for sludge in Ethiopia, Ethiopian government should develop standard and guide line for the management of sludge generated from industrial wastewater treatment plant
- In order to manage sludge generated from textile industrial parks, brick manufacturing industries should be one potential site for recycling of the sludge
- Since the sludge has encouraging heating value compared with clay, it can substitute wood as a source of energy used in brick manufacturing industry

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7. APPENDICES

Appendix A

Result of Fairing of 10% sludge brick at 600 ^{o}C for 6hr

Bricks samples	Weight after oven dry(g)	Weight after ignition in muffle furnace(g)	LOI	Weight after water bath(g)	Water absorption %	Comprehensive strength
A1	364.3	302.1	16.9	380.2	25.8	9.25
A2	368.4	298.3	19	392.6	31.6	11.35
A3	363.5	290.5	20.1	355.8	22.4	7.22
A4	370.7	301.3	18.7	370.3	22.9	13.41
A5	360.6	288.4	20	355.2	23.1	10.23
Average	365.5	296	18.8	370.8	22	10.2

Result of Fairing of 10% sludge brick at 900 ^{o}C for 6hr

Bricks samples	Weight after oven dry(g)	Weight after ignition in muffle furnace(g)	LOI	Weight after water bath(g)	Water absorption(g)	Comprehensive strength (MPa)
A21	366.8	290.2	20.8	350.2	20.6	27.83
A22	369.9	288.1	22.1	339.9	17.9	28.24
A23	379.3	296.5	21.8	352.8	18.9	29.22
A24	372.4	301.32	19	352.4	16.9	26.4
A25	361.2	288.4	20.1	351.7	21.9	28.2
Average	369.9	292.9	20.7	349.4	19.24	27.97

Result of Firing of 10% sludge brick at 1200 ^{o}C for 6 hours

Bricks samples	Weight after oven dry(g)	Weight after ignition in muffle furnace(g)	LOI	Weight after water bath(g)	Water absorption %	Comprehensive strength(MPa)
B1	336.8	259.4	22.9	310.7	20.9	9.66
B2	353.7	271.6	23.1	325.9	20	9.74
B3	354.2	269.1	24.2	320.2	19.7	7.34
B4	360.7	270.5	25	337.5.	25	8.22
B5	362.6	285.9	21.3	355.6	24.4	11.33
Average	353.6	271.3	23.3	262.5	25	9.25

Result of firing of 20% sludge brick at 600 ^{o}C for 6 hours

Bricks samples	Weight after oven dry(g)	Weight after ignition in muffle furnace(g)	LOI	Weight after water bath(g)	Water absorption(g)	Comprehensive strength (MPa)
A31	375.8	280.4	25.3	333.6	19.8	30.63
A32	355.6	266.3	25.11	308.8	15.9	29.33
A33	349.6	273.6	21.7	314.6	14.9	25.21
A34	363.5	266.7	26.6	317.3	18.9	32.37
A35	358.1	271.7	24.2	319.9	17.7	29.41
Average	360.5	271.74	24.6	318.8	17.4	29.3

Result of Fairing of 20% sludge brick at 900 ^{o}C for 6hr

Bricks samples	Weight after oven dry(g)	Weight after ignition in muffle furnace(g)	LOI	Weight after water bath(g)	Water absorption %	Comprehensive strength (MPa)
B21	344.2	254.7	26.1	300.9	18.1	22.94
B22	347.1	260.3	25.3	304.6	17.4	22.35
B23	362.7	282.9	22.4	335.5	19.2	24.21
B24	353.2	371.9	23.5	457.3	20.3	23.33
B25	366.2	267.3	27.5	326.1	22.4	`21.45
Average	354.6	287.4	23.8	344.9	19.5	23.2

Result of Fairing of 20% sludge brick at 1200 ^{o}C for 6 hours

Bricks samples	Weight after oven dry(g)	Weight after ignition in muffle furnace(g)	LOI	Weight after water bath(g)	Water absorption %	Comprehensive strength(MPa)
B31	338.9	250.7	26.3	280.3	12	28.21
B32	343.2	250.53	27.2	282.5	12.7	27.83
B33	350.5	253.4	27.7	296.4	16.9	29.23
B34	355.4	284.32	20	326.9	14.9	40.14
B35	349.4	286.5	18	332.34	12.8	26.75
Average	347.5	265	24.9	303.7	13.9	30.42

Result of Fairing of 30% sludge brick at 600 ^{o}C for 6 hours

Bricks samples	Weight after oven dry(g)	Weight after ignition in muffle furnace(g)	LOI	Weight after water bath(g)	Water absorption %	Comprehensive strength (MPa)
C1	357.9	257.6	28.2	332.3	29.5	2.15
C2	349.9	265.9	24.3	337.6	27.3	4.23
C3	358.3	268.7	25.6	388.5	26.2	2.05
C4	356.4	274.4	23.3	340.2	24.8	3.45
C5	360.1	266.4	26.9	340.9	28.3	4.5
Average	356.52	266.6	25.66	347.9	27.22	3.276

Result of Fairing of 30% sludge brick at 900 ^{o}C for 6 hours

Bricks samples	Weight after oven dry(g)	Weight after ignition in muffle furnace(g)	LOI	Weight after water bath(g)	Water absorption %	Comprehensive strength (MPa)
C21	343.5	274.8	20	313.2	13.9	10.23
C22	335.5	258.3	23	304.2	17.7	8.25
C23	355.3	266.4	25	317.1	19	15.4
C24	356.6	291.8	18.7	329.7	12.9	13.4
C25	358.2	272.2	24	321.1	17.9	`9.8
Average	349.82	272.7	22.14	317.06	16.28	11.82

Result of Fairing of 30% sludge brick at 1200 °C for 6 hours

Bricks samples	Weight after oven dry(g)	Weight after ignition in muffle furnace(g)	LOI	Weight after water bath(g)	Water absorption %	Comprehensive strength
C31	388.7	291.5	25	335.22	14.9	13.22
C32	398.9	287.2	28	327.4	13.9	13.1
C33	375.1	281.3	25	311.8	10.8	10.13
C34	372.4	305.4	17.9	360.37	17.9	12.11
C35	388.9	299.45	23	350.35	16.9	14.2
Average	384.8	292.97	23.78	337.028	14.88	12.552

Result of Fairing of 40% sludge brick at 600 °C for 6hours

Bricks samples	Weight after oven dry(g)	Weight after ignition in muffle furnace(g)	LOI	Weight after water bath(g)	Water absorption %	Comprehensive strength (MPa)
D1	301.4	244.3	18.9	325.9	33.4	2.35
D2	317.7	256.1	19.3	322.7	26	3.43
D3	309.4	237.8	23.1	306.3	28.8	2.15
D4	311.1	255.5	17.8	301.4	14.7	3.45
D5	325.7	230.5	29.2	292.7	26.9	2.25
Average	313.06	244.8	21.66	309.8	25.96	2.726

Result of Fairing of 40% sludge brick at 900 °C for 6 hours

Bricks samples	Weight after oven dry(g)	Weight after ignition in muffle furnace(g)	LOI	Weight after water bath(g)	Water absorption %	Comprehensive strength (MPa)
D21	353.5	265.2	24.9	310.5	17	9.11
D22	345.7	262.4	24	312.2	18.9	7.34
D23	358.3	289.6	19.1	338.7	16.9	11.47
D24	356.4	256.8	27.9	292.6	13.9	8.53
D25	342.9	300.1	22.4	354.3	18	`8.94
Average	351.36	274.82	23.66	321.66	16.94	9.1125

Result of Fairing of 40% sludge brick at 1200^{oC} for 6hr

	Weight after oven dry(g)	Weight after ignition in muffle furnace(g)	LOI	Weight ter water bath(g)	Water absorption %	Comprehensive strength
D31	368.6	272.1	26	307.6	13.1	10.31
D32	358.7	289.8	22.2	329.5	13.9	9.45
D33	365.3	299.2	18	352.8	17.9	9.25
D34	350.4	290.4	17.1	342.2	17.8	8.93
D35	373.9	303.2	18.9	354.5	16.9	12.22
Average	363.38	290.94	24.1	337.32	15.92	10.032

Appendix B

Summarized result of tests

Sludge%	Temperature	LOI	water Absorption	Comprehensive strength
10	600	18.8	22	10.2
10	900	20.7	19.24	27.97
10	1200	24.6	17.4	30.42

Sludge%	Temperature	LOI	water Absorption	Comprehensive strength
20	600	23.3	25	9.25
20	900	23.8	19.5	23.2
20	1200	24.9	13.9	29.3

Sludge%	Temperature	LOI	water Absorption	Comprehensive strength
30	600	25.66	27.22	3.27
30	900	22.14	16.28	11.82
30	1200	23.75	14.88	12.55

Sludge%	Temperature	LOI	water Absorption	Comprehensive strength
40	600	21.66	25.96	2.73
40	900	23.66	16.94	9.11
40	1200	24.1	15.9	10.0

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TEST METHODS:

ANALYSIS	DISCRIPTION
Metal analysis (ICP method)	In-house method based on NIOSH 7300, EPA 200.7 and ISO 15202-3

TEST RESULTS: mg/kg

Report(mg/kg)						
Sample ID	**Li**	**Be**	**B**	**Na**	**Mg**	**Al**
Powder Sample	28	1.4	37	8703	8455	143046
Sample ID	**K**	**Ca**	**Ti**	**V**	**Cr**	**Mn**
Powder Sample	2929	3533	553	31	27	574
Sample ID	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**
Powder Sample	9839	3.3	11	50	272	5.0
Sample ID	**Se**	**Sr**	**Zr**	**Nb**	**Mo**	**Ag**
Powder Sample	31	249	170	6.2	6.3	-
Sample ID	**Cd**	**Sn**	**Sb**	**Te**	**Ba**	**Ta**
Powder Sample	0.26	2.4	2.7	-	68	0.038
Sample ID	**W**	**Tl**	**Pb**	**Bi**	**U**	
Powder Sample	0.53	0.45	10.4	0.006	2.1	

Appendix C