KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

COLLEGE OF ENGINEERING

DEPARTMENT OF MATERIALS ENGINEERING

CHARACTERIZATION AND POTENTIAL UTILISATION OF

PALM OIL FUEL ASH (POFA) FROM A LOCAL OIL MILL

BY

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DECLARATION

I hereby declare that this submission is my own work towards the Msc. And that, to the best of my knowledge, it contains neither material previously published by another person nor material which has been accepted for the award of any other degree of the University, except where due acknowledgement has been made in the text.

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ABSTRACT

Solid waste characterisation is fundamental to any proper planning of solid waste management in any area. The aim of the study is to characterize the palm oil fuel ash (POFA) resulting from fuelling a steam boiler for the operation of the mill and explore its potential utilization. Samples from a local mill were characterized using Atomic Absorption Spectrometry, X-ray Fluorescence, X-Ray Diffraction and Toxicity Characteristics Leaching Procedure (TCLP). Leaching tests were also conducted at various pHs.

The results show that the main chemical composition of the palm oil fuel ash were SiO_2 67.4 wt%, Al_2O_3 10.57 wt%, MgO 4.76 wt% and K_2O 4.23 wt%. Leaching tests also revealed the POFA generated by the local oil mill leaches well in acidic media releasing various heavy metals into the aqueous media, though it is not likely to leach out high levels of toxic elements to the environment. An assessment of the usefulness of POFA revealed that mullite formation is accelerated upon the addition of POFA to lithomargic clay from the Awaso bauxite deposit with increasing temperature. POFA can also be used as the main additive in in a glaze recipe for glazing earthenware. Variation of the glaze components results in different finishes.

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CHAPTER ONE

INTRODUCTION

1.1   BACKGROUND

Waste management remains the greatest challenge for many developing nations. Survival of flora and fauna are daily threatened due to the improper disposal of waste while the quest for industrialization continues to pose serious challenges in the area of waste management. The utilization of local waste materials which are abundant and cheap, especially from clean resources have become more pressing than ever. The need for efficient utilization of waste a product is especially critical in the case of oil palm biomass (Bhat and Khalil, 2011). Basel Convention (1992) describes wastes as substances or objects which are disposed of or are intended to be disposed of by the provision of national law. Waste of known characteristics can be made useful where as waste of unknown characteristics can be dangerous either in the short or long term.

According to the Ministry of Food and Agriculture, there were seven major palm oil mills in Ghana by 2011 (mofa.gov) with a total milling capacity of 172 tones/per hour. With a 5% POFA by weight of solid wastes generated from the fuel feed (kernel and shell) for the steam boiler, these oil mills have over the years contributed significantly to the problem of waste (Sata *et al.*, 2004). Each line of production of oil mills is accompanied by some specific waste. After the extraction of oil from the fresh palm fruit, resultant wastes like husk and shell are burnt as boiler fuel in palm oil factory to produce super latent steam which is used in turbine engine for supplying electrical energy for milling operation, domestic or estate use. The burning process generates ash usually referred to as Palm Oil Fuel Ash (POFA) which is generally dealt with as a waste material (Safiuddin *et al.*, 2010; Mahlia *et al.*, 2001).

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POFA has been shown to be a heterogeneous mixture of inorganic particles, varying in shape, size, and composition.

There are catalogue of problems associated with haphazard disposal of the palm oil fuel ash which unfortunately have been the practice of most local oil mills. The lack of a well-tailored waste management strategy to deal with the tons of POFA produced daily by these oil mills continues to raise public concern especially for communities around the mills. Ironically, POFA has been found to demonstrate varied usefulness in construction and concrete industries by numerous researchers (Tay 1990; Hussin and Awal 1996; Awal and Hussin 1997; Sukuntapree *et al.,* 2002) and therefore the current method of disposal by local oil mills raises concern. It is in this light that the characterization of POFA generated by local oil mills to ascertain its impact on the environment and the possible utilization of this waste are of importance.

1.2   LOCAL OIL MILLS

Most local oil mill companies are joint ventures between local and leading multi-national companies in the business of food ingredients. Ghana Oil Palm Development Company, Twifo Oil Palm Plantations Ltd., Ayiem Oil Mills, Norpalm Ghana Ltd., Juabin Oil Mills, Benso Oil Palm Plantations Ltd etc. are some of the major oil mills in Ghana. Some were initially state farms established by the Ghana government until the government decided to sell the farms under the Divestiture Implementation Committee in 1994 (ejisujuaben.ghanadistricts.gov.gh).

These local oil mills companies directly and indirectly employ numerous workers and engage in

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Commercial production of palm oil and palm kernel oil. Local oil mills have been engaged in commercial palm oil production for well over thirty years mostly operating three plants namely Crude Palm Oil Plant, Crude Palm Kennel Oil Plant and Refinery Plant. These plants require high energy for their operation. Reliance on the national grid for power supply proved to be unsustainable leading to the decision to generate power internally to run their operations hence the acquisition of a boiler plant. The unique feature of such boiler is that it is fueled by the palm fiber and shell which are all by-products from the palm oil processing.

1.3   STATEMENT OF THE PROBLEM

Most local companies in developing countries focus on maximizing profit with little regard to the problems created by their operations. A number of palm oil mills in Ghana have no well structured solid waste management strategy to deal with the tons of solid waste generated daily from their operations. Unquantified levels of solid wastes from the mill including POFA are loaded into trucks and used for land filling or just dumped at any available site as intimated by Weerachart *et al.* (2007). This over the years has resulted in heaps of solid wastes spread at land areas near the mill. Little or no use has been made of it (Sumadi and Hussin, 1995). The possibility of groundwater pollution by accumulated POFA leaching into nearby water bodies, soil contamination, the nuisance posed to surrounding communities coupled with the general environmental problems resulting from its haphazard disposal (Tonnayopas *et al.*, 2006) substantiate the need to characterize the palm oil fuel ash (POFA), investigate and propose its effective utilization.

1.4   OBJECTIVES

The objectives of this research are to:

i.   characterize the palm oil fuel ash generated by the oil mill

ii.   investigate and propose potential utilization of the palm oil fuel ash.

1.5   JUSTIFICATION

The continuous expansion of the palm oil industry in the country implies that the quantity of POFA generated is also steadily increasing and thus creating large environmental load (Abdullah *et al.*, 2006). According to Mohanty *et al.* (2005), the increasing tons of waste generated on daily basis when diverted into judicious applications will alleviate environmental problems related to its disposal.

Characterizing the waste generated would therefore enable a sustainable waste management option to be implemented by local palm oil mill companies. It will also ensure that negative impact resulting from the current disposal system is eliminated whilst giving a blueprint for the potential utilization of POFA.

1.6   METHODOLOGY

The methods and procedures employed in this research included;

i.   review of literature collection of waste samples and characterization

ii.   tests on possible areas of application.

1.7   SCOPE

Even though various waste streams are generated by palm oil mills in solid, liquid and gaseous forms, this study is focused on the characterization and potential utilization of palm oil fuel ash (POFA) from a steam boiler. Samples of palm ash from a local oil mill were used for all the tests. Major tests employed in the research were Atomic Absorption Spectrometry for heavy metal analysis, X-ray Fluorescence for chemical analysis, X-Ray Diffraction for mineralogical or phase analysis, Toxicity Characteristics Leaching Procedure for toxicity test and Leaching test. The scope of the study was extended to the assessment of possible utilization of POFA including;

 i.   additive to clay as a miniraliser for mullite formation.

 ii.   additive to a glaze formula as the main ingredient for glazing of earthenware.
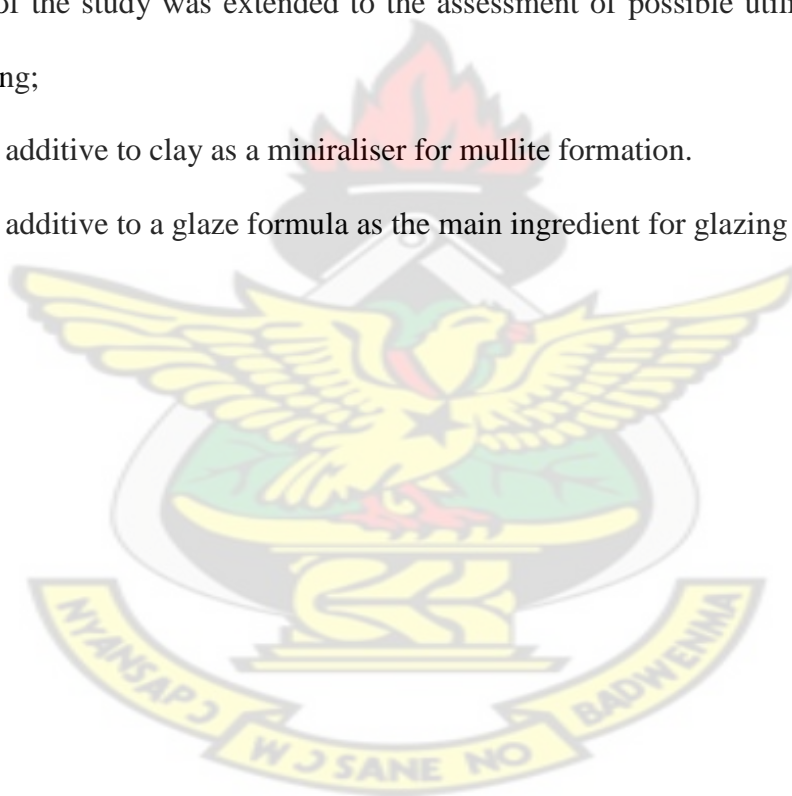
CHAPTER TWO

LITERATURE REVIEW

2.1   PALM OIL MILL PROCESSING

Oil extraction is a complex process, carried out by large mills that may process up to 60 tons of fruit per hour, or by small scale mills in rural villages that produce only about 1tonne   (1000 kg) of oil in an 8 hr shift (Poku, 2002).

The process involves the physical extraction of palm products namely, crude palm oil and palm kernel from the fresh fruit bunch (FFB). The process begins with sterilization of the FFB. The fruit bunches are steamed in pressurised vessels up to 3 bars to arrest the formation of free fatty acids and prepare the fruits for subsequent sub-processes.

The sterilised bunches are then stripped of the fruitlets in a rotating drum thresher. The stripped bunches or empty fruit bunches (EFB) are transported to the plantation for mulching while the fruitlets are conveyed to the press digesters. In the digesters, the fruits are heated using live steam and continuously stirred to loosen the oil-bearing mesocarp from the nuts as well as to break open the oil cells present in the mesocarp. The digested mash is then pressed, extracting the oil by means of screw presses. The pressed cake is then conveyed to the kernel plant where the kernels are recovered (Poku, 2002). The oil from the press is diluted and pumped to vertical clarifier tanks. The clarified oil is then fed to purifiers to remove dirt and moisture before being dried further in the vacuum drier. The clean and dry oil is ready for storage and dispatch.

The sludge from the clarifier sediment is fed into bowl centrifuges for further oil recovery. The recovered oil is recycled to the clarifiers while the water and sludge mixture which is referred to as Palm Oil Mill Effluent (POME) is treated in the

effluent treatment plant (ETP). The press cake is conveyed to the depericarper where the fibre and nuts are separated. Fibre is burnt as fuel in the boiler to generate steam. The nuts are cracked and the shell and kernel are separated by means of a winnower and hydro-cyclone. The clean kernels are dried prior to storage (Hai, 2002). The general flow diagram summarizes palm oil processing in *figure 2.1*.
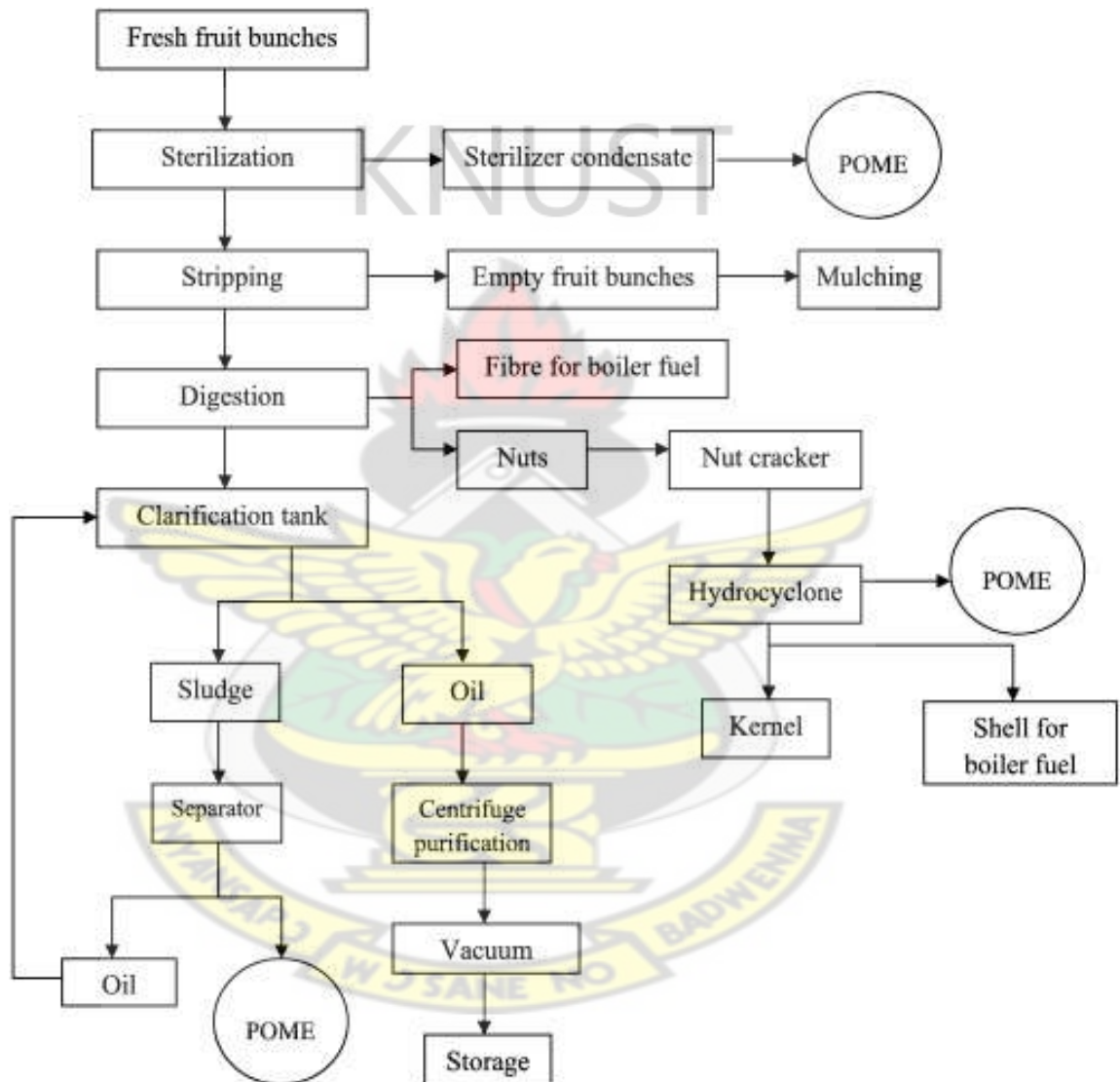
Figure 2.1 Flow chart of the palm oil process (Source: Sivasothy, 2000)

2.1.1   Bunch Reception

Bunch reception is the receiving of fresh palm fruits from the field as bunches or loose fruit. At the mill the FFB is generally discharged from the lorries or trailers, onto a loading ramp for the filling of sterilizer cages, which have a nominal capacity of 2.5 tons. A flow diagram of the palm oil milling process is shown in *figure 2.1* and the unit operations of palm processing are summarized in *table 2.1*. The quality standard achieved is initially dependent on the quality of bunches arriving at the mill (Poku, 2002).

Table 2.1   Summary of unit operations of oil palm processing (Source: Poku, 2002)

	Unit operation	Purpose
1	Fruit fermentation	To loosen fruit base from spikelets and to allow ripening processes to abate
2	Bunch chopping	To facilitate manual removal of fruit
3	Fruit sorting	To remove and sort fruit from spikelets
4	Fruit boiling	To sterilize and stop enzymatic spoilage, coagulate protein and expose microscopic oil cells
5	Fruit digestion	To rupture oil-bearing cells to allow oil flow during extraction while separating fibre from nuts
6	Mash pressing	To release fluid palm oil using applied pressure on ruptured cellular contents
7	Oil purification	To boil mixture of oil and water to remove water-soluble gums and resins in the oil, dry decanted oil by further heating
8	Fibre-nut separation	To separate de-oiled fibre from palm nuts.
9	Second Pressing	To recover residual oil for use as soap stock
10	Nut drying	To sun-dry nuts for later cracking

2.1.2 Threshing

Bunch threshing is the removal of the fruit from bunches. The fresh fruit bunch consists of fruit embedded in spikelets growing on a main stem. Manual threshing is achieved by cutting the fruit-laden spikelets from the bunch stem with an axe or machete and then separating the fruit from the spikelets by hand. In a mechanized system a rotating drum or fixed drum equipped with rotary beater bars detach the fruit from the bunch leaving the spikelets on the stem. The threshed fruits are cooked in water. Whole bunches which include spikelets absorb a lot of water in the cooking process. In larger mills the bunch waste is incinerated and the ash, a rich source of potassium, is returned to the plantation as fertilizer (Poku, 2002).

2.1.3 Sterilisation

Sterilization or cooking means the high-temperature wet-heat treatment of loose fruit. Cooking normally uses hot water; sterilization uses pressurized steam. According to Hamza (2008), the cooking action serves several purposes including:

i. Prevention of further rises in the free fatty acid (FFA) of the oil due to enzymatic reaction.

ii. Facilitation of mechanical stripping.

iii. Preparation of the pericarp for subsequent processing.

iv. Preconditioning of the nuts to minimize kernel breakage.

One of the major sources of waste water in this step is constituted by the steam condensate coming out of the sterilizer (Thani *et al.*, 1999).

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2.1.4   *Digestion*

Digestion is the process of releasing the palm oil in the fruit through the rupture or breaking down of the oil-bearing cells (Poku, 2002). The objective of digestion is to reheat the sterilized fruits and to loosen the pericarp from the nuts and to break the oil cells before passing to the oil extraction unit (Hamza, 2008).

The digester commonly used consists of a steam-heated cylindrical vessel fitted with a central rotating shaft carrying a number of beater (stirring) arms. Through the action of the rotating beater arms the fruit is pounded. Pounding, or digesting the fruit at high temperature, helps to reduce the viscosity of the oil, destroys the outer covering of the fruits (exocarp) and completes the disruption of the oil cells already begun in the sterilization phase (Poku, 2002).

2.1.5   *Pressing*

There are two distinct methods of extracting oil from the digested material. One system uses mechanical presses and is called the 'dry' method. The other called the 'wet' method uses hot water to leach out the oil.

In the 'dry' method the objective of the extraction stage is to squeeze the oil out of a mixture of oil, moisture, fibre and nuts by applying mechanical pressure on the digested mash. There are a large number of different types of presses but the principle of operation is similar for each. The presses may be designed for batch (small amounts of material operated upon for a time period) or continuous operations.

2.1.6   *Clarification and Drying*

The main point of clarification is to separate the oil from its entrained impurities. The fluid coming out of the press is a mixture of palm oil, water, cell debris, fibrous material and 'non-oily solids'. Because of the non-oily solids the mixture is very thick (viscous). Hot water is therefore added to the press output mixture to thin it. The dilution (addition of water) provides a barrier causing the heavy solids to fall to the bottom of the container while the lighter oil droplets flow through the watery mixture to the top when heat is applied to break the oil suspended in water with the aid of gums and resins. Water is added in a ratio of 3:1.

The diluted mixture is passed through a screen to remove coarse fibre. The screened mixture is boiled from one or two hours and then allowed to settle by gravity in the large tank so that the palm oil, being lighter than water, will separate and rise to the top. The clear oil is decanted into a reception tank. This clarified oil still contains traces of water and dirt.

Re-heating the decanted oil in a cooking pot and carefully skimming off the dried oil from any engrained dirt removes any residual moisture. Continuous clarifiers consist of three compartments to treat the crude mixture, dry decanted oil and hold finished oil in an outer shell as a heat exchanger. The wastewater from the clarifier is drained off into nearby sludge pits dug for the purpose. No further treatment of the sludge is undertaken in small mills. The accumulated sludge is often collected in buckets and used to kill weeds in the processing area.

2.1.7 Oil Storage

In large-scale mills the purified and dried oil is transferred to a tank for storage prior to dispatch from the mill. Since the rate of oxidation of the oil increases with the temperature of storage the oil is normally maintained around 50°C, using hot water or low-pressure steam-heating coils, to prevent solidification and fractionation. Iron contamination from the storage tank may occur if the tank is not lined with a suitable protective coating. Small-scale mills simply pack the dried oil in used petroleum oil drums or plastic drums and store the drums at ambient temperature.

2.1.8 Kernel Recovery

The residue from the press consists of a mixture of fibre and palm nuts. The nuts are separated from the fibre by hand in the small-scale operations. The sorted fibre is covered and allowed to heat, using its own internal exothermic reactions, for about two or three days. The fibre is then pressed in spindle presses to recover second grade (technical) oil that is used normally in soap-making. The nuts are usually dried and sold to other operators who process them into palm kernel oil. Large-scale mills use the recovered fibre and nutshells to fire the steam boilers. The super-heated steam is then used to drive turbines to generate electricity for the mill. For this reason it makes economic sense to recover the fibre and to shell the palm nuts. In the large-scale kernel recovery process, the nuts contained in the press cake are separated from the fibre in a depericarper. They are then dried and cracked in centrifugal crackers to release the kernels. The kernels are normally separated from the shells using a combination of winnowing and hydrocyclones. The kernels are then dried in silos to a moisture content of about 7 percent before   packing.

2.1.9 *Palm Oil Refinery*

Refining process is a necessary step for the production of edible oils and fats products. The refining process removes free fatty acids, phosphatides, odouriferous matter and water as well as impurities such as dirt and traces of metals from the CPO. The objective is to produce an edible oil of consistent quality that meets industry's standards and satisfies customer requirements particularly in respect of moisture and impurities, iodine value, peroxide value, melting point, colour and flavour. The refined oil must be tasteless and have a bland flavor.

The objectionable substance or impurities in palm oil maybe biogenic i.e. synthesized by plant themselves but they can be impurities taken up by the plants from their environment (Borner and Schneider, 1999). The impurities possibly acquired during upstream of bleaching process which are extraction, storage or transportation of the crude palm oil from mill to the refinery.

The refining processes ensure the production of high quality finished products. There are 2 basic types of refining technology available for palm oil:

  i.   Chemical (alkaline) refining and
  ii. Physical refining.

The differences between these 2 types are basically based on the type of chemicals used and mode of removing the FFA (Rohani *et al.*, 2006). Various products from oil mill process are summarized in *figure 2.2* by Lorestani (2006).
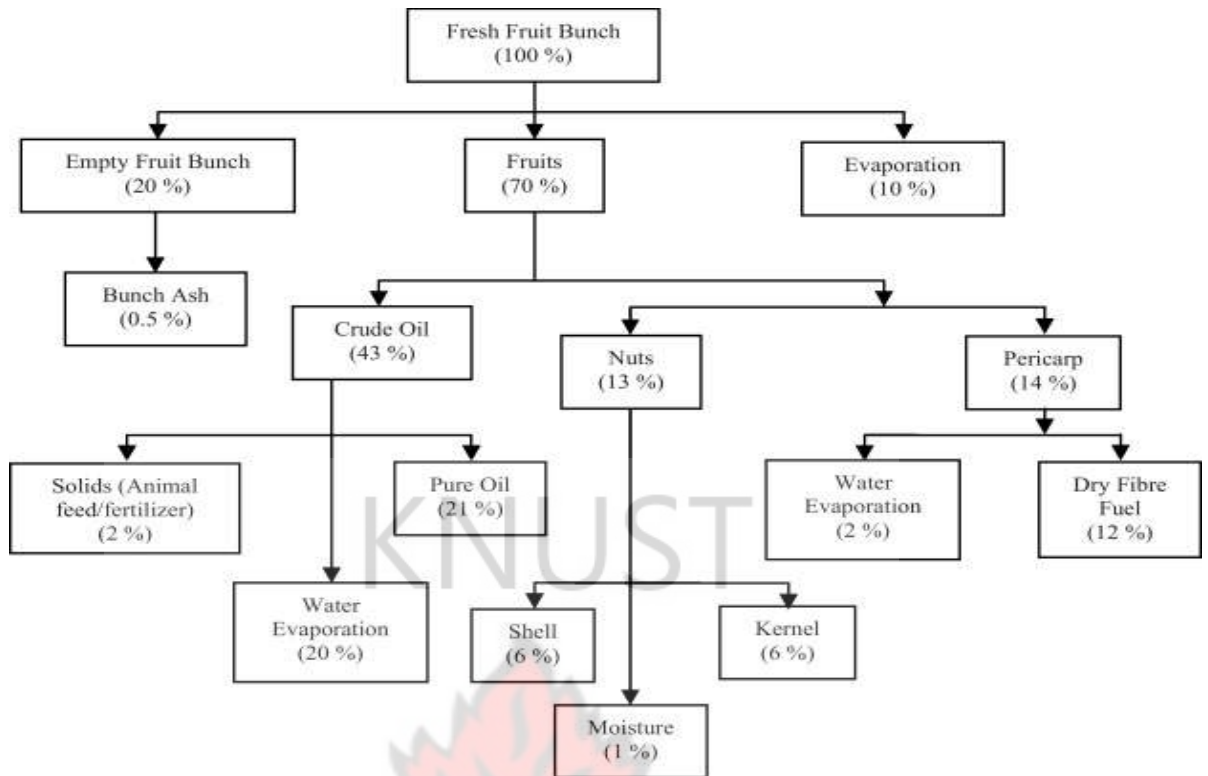
Figure 2.2 Products from oil mill process (Source: Lorestani, 2006)

2.2   WASTES FROM PALM PROCESSING

According to Singh *et al.* (2010), one hectare of oil palm produces 10 to 35 tons of fresh fruit bunches (FFB) per year whilst Kittikun (2000) suggests that each 100 tons of FFB processed yields 20 to 24 tons of crude palm oil and about 4 tons of palm kernels implying that between 72 to 76 percent of the FFB comes out at various stages of the process as waste. According to Prasertsan and Prasertsan (1996), during palm oil processing, more than 70% by weight of the processed fresh fruit bunch (FFB) are left over as oil palm waste where as Pleanjai *et al.,* (2004) points out that fiber, shell, decanter cake and empty fruit bunch account for 30, 6, 3 and 28.5% of the FFB respectively.

Generally, waste products from oil palm processing consist of oil palm trunks (OPT), oil palm fronds (OPF), empty fruit bunches (EFB), palm pressed fibres (PPF) and

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palm kernel shells, less fibrous material such as palm kernel cake and liquid discharge, palm oil mill effluent (POME) (Singh *et al.,* 2010; Aziz and Abdul, 2007). The significant volumes of waste generated pose disposal challenges to oil mills and in many cases they are either used as fuel in the processing plant or dumped at sites near the mill. Schematic diagram of oil extraction and its associated waste streams or by-products according to Mumtaz and David (1976) is shown *figure 2.3*.

2.3 PALM OIL FUEL ASH (POFA)

Tangchirapat *et al.* (2009) looked at the Palm Oil Fuel Ash (POFA) as a by-product from burning process in thermal power plant, where palm nut and fiber of palm are burnt at high temperatures (800 – 1000 ^{0}C). Chindaprasirt *et al.* (2008), also indicate that during combustion at 800 – 1000 °C, oil palm ash tends to be formed and varies considerably according to the burning technique, temperature regime and gasification structures. Awal and Hussin (2010) also looked at POFA as a waste product obtained in the form of ash on burning palm oil husk or fibre and palm kernel shell as fuel in palm oil mill. According to Safiuddin *et al.* (1996), POFA is an agro-waste generated in palm oil industry obtained from the combustion of palm fruit residues.

2.3.1 *Projected Increase in POFA Generation*

For each bunch of the fresh palm fruit, approximately 21% of palm oil, 6 – 7% of palm kernels, 14 – 15% of palm fibers, 6 – 7% of palm shells and 23% of empty fruit bunches can be obtained (Dalimin, 1995). In general oil constitutes only 10% of the palm production, while the rest 90% is the biomass (Yong *et al.*, 2007). For every 100 tons of fresh fruit bunches processed according to Tay (1995), there will be approximately 20 tons of nut shells,7 tons of fibers, and 25 tons of empty bunches

discharged from the mill with about 5% POFA by weight of solid wastes produced after combustion in a steam boiler (Sata *et al.*, 2004).

With a milling capacity of 5 tons per hour in 2007, the local oil mill company now has a milling capacity of 15 tons per hour and projects to increase production to 20 tons per hour in the near future. Increase in production implies more generation of POFA. *Table 2.2* outlines the major oil mills in Ghana and their current capacity of production.

In a conversation on 25th August 2011 the Plant Engineer of the local oil mill confirmed that the local oil mill at peak production produces 234 tons of palm fruits per day (24 hours) with each day comprising 3 shifts of 8 hours each. With fluctuating production levels, an average of 180 tons of palm fruits per day is the capacity of the local oil mill. Fresh fruit bunch of 30-35 are utilized to attain the target of 180 average daily tonnages. 7 tons of palm shells and and 2.5 tons of palm fibre are generated from the daily palm processing which eventually are dried and used to fuel the boiler. With a 5% by weight of POFA generated from the combustion process in the steam boiler (Tay, 1995), about half a ton of POFA is expected on daily basis at current average production capacity. With projected increase in production capacity, POFA levels will continue to rise.

Table 1.2 The major oil mills in Ghana and their current capacity of production

COMPANY	NUCLEUS (HA)	OUTGROWER/ SMALLHOLDER (HA)	TOTAL (HA)	MILLING CAPACITY (TONS/HOUR)
Ghana Oil Palm Development Company Ltd. (GOPDC)	8,000	14,352	22,352	60
Twifo Oil Palm Plantations Ltd. (TOPP)	4,234	1,690	5,924	30
Benso Oil Palm Plantations Ltd. (BOPP)	4666	1,650	6,316	27
NORPALM GH. LTD. (NGL)	4000	-	4000	30
Juabin Oil Mills (JOM)	424	1,100	1,524	15
Ayiem Oil Mills (AOM)	250	-	250	10
Golden Star	-	720	720	-
TOTAL	21,574	19,512	41,086	172

Source: Ministry of food and Agriculture (www.mofa.gov.gh)

2.3.2 Characteristics of POFA

A detailed characterization or analysis of waste is necessary for integrated solid waste management strategies to be successful according to Sakai *et al.* (1996). This has been collaborated by Tchobanoglous *et al.* (1993) who also indicated that knowledge of the sources and types of waste in an area is required in order to design and operate appropriate solid waste management systems. In Cointreau – Levin (1997) perspective, changing volumes of wastes and composition have profound

impact on waste management practices. *Figure 2.3* shows oil extraction, POME generation and associated waste streams according to Mumtaz and David (1976).

Waste characterization begins with an understanding of the industrial processes that generate waste. Enough information about the process will enable proper characterization of the waste. Information such as the physical state of the waste, the volume of waste produced, and the general composition of the waste is necessary for good characterization. Incomplete or mischaracterization of waste can lead to improper waste management or erroneous decisions.

A large amount of solid waste by-products including fibers, nut shells, and empty fruit bunches are generated during the processing of oil-palm fruit for oil extraction. There will be approximately 20 tons of nut shells, 7 tons of fibers, and 25 tons of empty bunches discharged from the mill for every 100 tons of fresh fruit bunches processed according to Tay and Show (1995). During the extraction of oil from oil palm fruit, bunches, fibres and shells are burnt in a steam boiler to produce steam for the turbine engine to generate electricity for use in palm oil mills (Mahlia *et al.*, 2001).
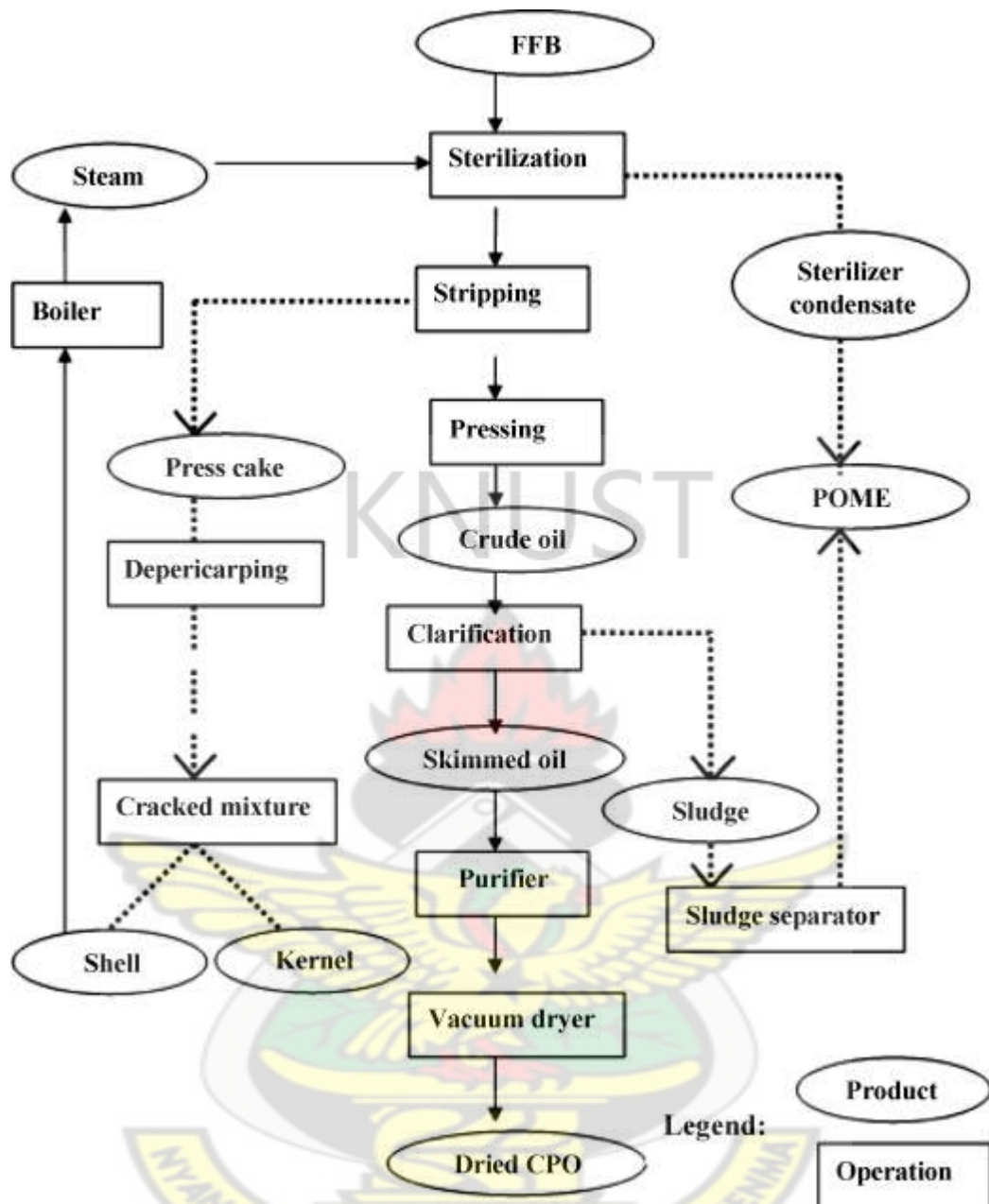
Figure 2.3 Oil extraction, POME generation and associated waste streams are represented by dashed lines (Source: Mumtaz and David, 1976)

After burning, the resulting ash referred to in some literature as palm oil fuel ash, boiler ash, boiler waste ash, oil mill waste ash etc. is generally disposed of in open fields, thus creating environmental and health problems (Tonnayopas *et al.*, 2006). Comprehensive characterization of POFA will depend on its known characteristics which have been extensively looked at by some researchers.

Chindaprasirt *et al.* (2008) indicated that a typical oil palm ash by nature is characterized by a spongy and porous structure with its main form being angular and irregular, though a sizable fraction shows cellular textures. According to Awal and Hussin (1997), POFA particles have a wide range of sizes but are relatively spherical like other fly ashes, greyish in colour but become darker with increasing proportions of unburned carbon. It sometimes varies in tone of colour from whitish grey to darker shade based on the carbon content in it. The physical characteristic of POFA is very much influenced by the operating system in palm oil factory.

Karim *et al.* (2011) also suggested that the major chemical composition of POFA is silicon dioxide (SiO_2), in addition to other constituents like aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3). Tangchirapat *et al.* (2009) also collaborated that the chemical oxides of oil palm ash are silicon dioxide, aluminium oxide, iron oxide, calcium oxide, magnesium oxide, sodium oxide, potassium oxide and sulfur trioxide. In their perspective, varieties of proportion of irrigated area, geographical conditions, fertilizers used, climatic variation, soil chemistry, timeliness of production and agronomic practices in the oil palm growth process are influential in the characteristics of the resulting ash. Awal and Hussin (1997) also labelled POFA as moderately rich in silica content with its chemical composition depending on the operating system in the palm oil mill.

Awal and Hussin (1997), Sumadi and Hussin (1995) among others also researched into the physical and chemical properties of POFA and confirmed that POFA is a pozzolanic material grouped in between Class C and Class F as specified in ASTM C 618-01 (2001).

2.3.3   *Utilization*

Oil palm has demonstrated a wide spectrum of applications with almost every part of its plant useful in one way or the other (Hameed and Sekar, 2009). Currently, oil palm biomass is mostly used for the purpose of compost and fertiliser, mulching mats, plywood and veneer from oil palm trunks, oil palm fibre-filled automotive upholstery parts, dampening sheets for automotive industry using oil palm fibres, moulded particleboard, pulp and paper from empty fruit bunch (EFB), moulded pulp products for food packaging, containers from EFB, medium density boards, furniture, oil palm lumber, activated carbon, and compostable plastic film. Oil palm biomass is also used as fuel for boilers in oil palm mill to produce steam for electricity generation. The usefulness of POFA may differ depending on the fuel type from which the ash is generated. Some of the usefulness of the palm oil fuel ash as is summarized below.

2.3.3.1   *Use As Pozzolana*

POFA has the potential to be used as pozzolanic material in concrete industry as pointed out by Sata *et al.* (2004). Most POFA demonstrates similarities in their chemical composition and mostly satisfy the requirement of pozzolana and may be grouped as a class C or class F pozzolan as specified in America Standard for Testing and Materials ASTM C618 (ASTM, 2001). This class is also suggested by other researchers including Awal and Hussin (1997), Chindaprasirt *et al.* (2007) and Tay and Show (1995).

2.3.3.2 Use As Construction Material

The chemical composition of POFA indicates the presence of high mount of silica and thus considered to possess high potential of serving as a cement replacement (Tangchirapat *et al.*, 2009). Awal and Hussin (1997) have also proven that POFA can potentially be used as partial cement replacement in concrete for production of stronger and more durable construction material. Tay and Show (1995) also buttressed this research. Other researchers have integrated POFA as one of mixing ingredient to produce high-strength concrete (Sata *et al.*, 2004; Budiea et *al.*, 2008) and lightweight concrete (Yahaya, 2003). Awal and Hussin (1997) utilized palm oil fuel ash to reduce the expansion of mortar bars containing tuff as a reactive aggregate and concluded that palm oil fuel ash has the potential in suppressing alkali-silica reaction expansions. Researchers at University Technology Malaysia have produced cement bricks with good strength and adequate dimensional stability using 10% unground POFA by weight of cement. Safiuddin *et al.* (1996) also states that POFA has a good potential for utilization in different types of construction material. Nasly and Yassin (2009) mentioned that POFA can be incorporated in interlocking blocks for use in sustainable housing. Kamaluddin (2008) used POFA as a filler material to produce stone mastic asphalt with enhanced stability, stiffness, and tensile strength.

2.3.3.3 Use As Adsorbent

POFA has also emerged to be an ideal adsorbent in the wastewater treatment processes and as air purifier in cleaning of atmosphere contaminants (Dahlan *et al.*, 2007). The potential use of palm oil fuel ash as an adsorbent for the removal and recovery of heavy metals from aqueous solutions was also assessed by Chu and

Hashim (2002). Oil palm ash was utilized as an absorbent for dry-type flue gas desulfurization. The absorbents were prepared using water hydration method with the addition of other chemicals such as CaO and $CaSO_4$ (Zainudin *et al.*, 2005). Palm ash has also been utilized as adsorbent for the removal of disperse dye from aqueous solution (Isa *et al.* 2004). The use of POFA as low cost adsorbent was also investigated as a replacement of current expensive methods for treating wastewater contaminated by Pb (II) cation (Chowdhur, 2010). Darus (2007) also worked on the removal of basic dye (methylene blue) from aqueous solutions by adsorption on activated carbon prepared from palm oil fibre whilst Hasnain *et al.* (2007) investigated the low cost removal of disperse dyes from aqueous solution using palm ash.

2.3.3.4 *Use as Additive in a Glaze Formula*

Francis (1995) described ash glaze as a layer or coating of a vitreous substance which has been fired to fuse to a ceramic object to color, decorate, strengthen or waterproof it. Glaze is ground minerals in a liquid suspension that will melt when fired at high temperature. The use of glazed ceramics was an ancient technique prevalent in Islamic art and pottery according to Mason (1995). Shamsu (2005) used oil palm biomas successfully as a glaze which he tagged as Eco Oil Palm Ash Glaze. Aside from being cost efficient he indicated that it was aesthetically pleasing compared to the usual commercial glazes. In Shamsu's research, he found the glaze as economical as well as ecological employing 70 - 80% of biomass as a main ingredient in the formula.

Tonnayopas *et al.* (2009) prepared floor tile body recipes using granite fine quarry waste (GFQW) and oil palm fiber ash (OPFA) as raw materials. Ragunathan *et al.*

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(2009) researched into palm composite composed of palm ash and unsaturated polyester with variety of useful applications for fabricating tiles. The composite tiles produced exhibits high strength compared to commercial tile.

Ceramic glazes generally contain silica to form glass, in combination with a mixture of metal oxides such as sodium, potassium and calcium which act as a flux allowing all the glaze to melt at a particular temperature, alumina to stiffen the glaze and prevent it from running off the piece, colorants such as iron oxide, copper carbonate or cobalt carbonate, and sometimes opacifiers such as tin oxide or zirconium oxide.

Rogers (2003) indicated that good glaze can be made by mixing roughly equal parts of wood ash, feldspar, and kaolin. A different chemical composition of ashes causes the glaze to produce different results from batch to batch according to Svoboda (2010).

Normally, ash glazes require high-fire temperatures, usually falling between cone 9 and cone 11 (1265 ºC – 1285 ºC) for 60 ºC/h temperatures. The glaze has glasslike and pooling characteristics which put emphasis on the surface texture of the piece being glazed.

Glaze made up of ash mostly produce dark brown to green finish. Wares with ash glaze mostly resemble the earth in color and texture. As the ash percentage decreases, there is more control on the color and the final glaze color differs from light to dark shades of brown or green.

Local industries which utilize ceramics, such as, tiles, roofing tiles, tableware, sanitary ware, handicrafts and various artistic products always seek to beat down cost of glazing and the development of low cost and efficient palm ash glaze is therefore very essential. Some examples of tiles glazed with fly ash are shown in *figure 2.4*.

Figure 2.4 Examples of glazed tiles from fly ash   (Source: Warrier, 2008)

2.3.3.5   *Use For Mullite Synthesis*

Mullite is the main phase in Alumino-silicate refractories formed by the transformation of Aluminium silicate at high temperature hence making it stable at high temperatures. Whenever there is a source of free silica and alumina in any refractory, mullite is formed upon heating at high temperatures. Generally it is believed that this can happen at as low a temperature as   1200 ^{0}C (Dilip, 2007).

The unique mechanical and thermal properties of mullite make it a good engineering material. In recent times the need to produce high quality mullite for optical, dielectric and structural applications has led to numerous studies on the synthesis and processing of mullite (Schneider   *et al.*, 2008).

Typical applications of mullite include furnace centre tube and liners, heat exchange parts, heat or electrical insulation parts and rollers. Mullite is also widely used in the production of heat resistant materials in heat insulation, ceramics, composites, computer chips etc. (Kanka and Schneider, 1994; Sarikaya *et al.,* 1987)

Mullite crystallization is a common phenomenon involving the thermal transformation of kaolinites (Carty and Udayan, 1998). The amount of SiO_2 in kaolinite is much higher than that in mullite ($3Al_2O_3. 2SiO_2$), the excess SiO_2,

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together with the impurities in kaolinite, forms a glassy phase and cristobalite to accompany the formation of mullite at a temperature higher than 1000 ^{o}C (Brindley and Nakahira, 1959).

The transformation from kaolinite is represented by the reaction

$$2Al_2O_3.2SiO_2.2H_2O \longrightarrow Al_2O_3.2SiO_2+2H_2O$$
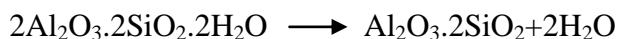
Kaolin-type clays undergo a series of phase transformations upon thermal treatment in air at atmospheric pressure. Endothermic dehydroxylation begins at 550 – 600 °C to produce disordered metakaolin $Al_2Si_2O_7$, but continuous hydroxyl loss is observed up to 900 °C and has been attributed to gradual oxolation of the metakaolin.

$$2 Al_2Si_2O_5(OH)_4 \rightarrow 2 Al_2Si_2O_7 + 4 H_2O.$$
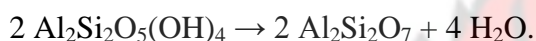
Further heating to 925 – 950 °C converts metakaolin to an aluminium-silicon spinel, $Si_3Al_4O_{12}$, which is sometimes also referred to as a gamma-alumina type structure:

$$2 Al_2Si_2O_7 \rightarrow Si_3Al_4O_{12} + SiO_2.$$
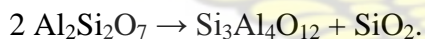
Upon calcination to 1050 °C, the spinel phase ($Si_3Al_4O_{12}$) nucleates and transforms to mullite, $3 Al_2O_3 \cdot 2 SiO_2$, and highly crystalline cristobalite, SiO_2:

$$3 Si_3Al_4O_{12} \rightarrow 2 Si_2Al_6O_{13} + 5 SiO_2.$$
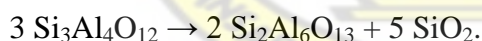
It has a melting point of 1850 ^{0}C. It has normally about 56-79% of Al_2O_3. All monolithics have source of either reactive or calcined alumina, silica fume and other sources of silica and alumina in the matrix. Monolithics are very complex with many sources of corundum and mullite and hence it is very difficult to know when and how much mullite is being formed at any given temperature (Dilip, 2007).

Different transition metal oxides have been shown to have favourable mineralizing effect on the formation of mullite ceramics from the precursor materials.

Ferriera da Silva (1998) observed that presence of manganese ion can induce mullitization at lower temperature from Al_2O_3-SiO_2 gel. Martisius and Giraitis (2003) observed that copper oxide as an additive can decrease the transformation temperature of kaolinite to mullite by 200 °C. According to Spokauskas and Kicas (1979) and Segnit and Gelb (1972), copper oxide reacts with kaolinite at 800 °C by forming a quartz-type phase. At a higher temperature it decomposes with amorphous SiO_2 and quartz crystallizing to cristobalite and finally leading to the formation of mullite. Spokauskas and Kicas (1979) again observed that copper oxide is one of the most effective additives for reducing the temperature for the conversion of kaolinite to mullite. The effect of copper oxide addition results in an exothermal reduction of the transformation temperature by some 50 – 70 °C.

Kong *et al.* (2003) observed that V_2O_5 accelerated mullite phase formation, while Nb_2O_5 and Ta_2O_5 inhibited the mullitization. Baudin and Moya (1984) observed that addition of TiO_2 under the solubility limit enhanced the initial sintering and grain size in mullite whereas an amount in excess of that limit inhibit sintering and drastically increased the total porosity and mean pore size. Nass and Tkalcec (1995) investigated the influence of chromium on homogeneity of gels and on mullite formation at 980 °C and observed that difference in chromium content affected the crystallization path of mullite. Mitra *et al.* (2001) observed that Cr_2O_3 played a positive role in the formation of mullite at elevated temperatures from the aluminosilicate gel precursor.

2.3.3.6 Other Uses

Palm waste ash typically has a high pH and may be beneficial as a liming agent (Sander and Andre'n, 1997; Zhang *et al.*, 2002).

Poku (2002) has suggested that Boiler ash can be recycled as fertilizer and factory floor cleaning agent. He indicated that the potash in the ashes reacts with the oil to form a weak potash soap that is washed away with water.

2.4 THE LOCAL OIL MILL

2.4.1 Processing Plant

The oil mill company operates four processing plants at the site. These include:

  i.   Crude Palm Oil (CPO) Plant

  ii.   Crude Palm Kennel Oil (CPKO) Plant

  iii. Refinery Plant

These three plants are powered through internally generated power from a steam boiler plant. The boiler in turn is fueled by by-products of the processing plants.

The oil mill company like other oil mills produces crude palm oil and kernels, as primary products and biomass as secondary product. Capacity of mills varies between 60-100 tons of fresh fruit bunch per hour. The local oil mill has many operation units comprising sterilization, stripping, digestion and pressing, clarification, purification, drying and storage. The palm kernel processing line includes steps such as nut or fibre separation, nut conditioning and cracking, cracked mixture separation, kernel drying and storage.

2.4.2 The Steam Boiler Plant At the Mill

In a conversation with the Plant Engineer of the local oil mill on the 25th of September, 2011, he indicated that the steam boiler plant at the mill commissioned in

2005 generates super latent steam to turn turbines to generate electricity to power all the operations of the mill. The power generating capacity of the turbine is 424 KW. The plant at the site is designed to have water tubes in the furnace and fire tubes in the boiler drum. The water tubes in the furnace are heated to convert the water to steam. Temperature increase in the furnace increases the steam pressure from 15bar to 20 bar for the turbine. Steam from the boiler is channeled through pipelines to drive turbines. A separator along the pipeline path separates dry steam from moisture leaving only dry steam required to turn the turbines. Pressure from dry steam of the separator normally averages 19 bar. The dry steam pressure of about 19 bar impacts the turbine impeller thereby rotating it at high energy speed of 10,000 to 11,000 rpm. A speed reduction gear box steps it down to 1500 rpm. The process generates a frequency of 50Hz, power factor of 0.8 and a voltage of 415V. From the power generated by the steam boiler, the various plants on site are powered.

2.4.3 Waste Management By Local Oil Mills

Wastes generated from oil mill operations may either be in the solid, liquid or gaseous form.

2.4.3.1 Solid Waste

Solid waste streams from oil palm processing consist of empty fruit bunches (EFB), mesocarp fruit fibres (MFF) and palm kernel shells (PKS) (Hanida and Abdul, 2007). The MFF and some of the PKS are used as fuel to generate steam and electricity for the processing plant. Excess PKS are either used for road hardeningor where demand exists, they are sold to third parties.The EFBs are either incinerated or appliedto the fieldPart of the untreated EFB are used for mulching in the plantation while the remaining EFB are incinerated. The resultant ash from the

boiler fuel are also loaded into trucks and are used for landfilling with the excess dumped at locations near the mill (*appendices B.1 and B.2*). Indiscriminate dumping of the waste results in undesirable scenes characterized by excessive piles of EFB near the mills (*appendices B.1 and B.2*). The ash recovered from the incinerated EFB is also sold or used as fertilizer in the palm plantation. Palm oil mill sludges (POMS) consisting of suspended solids and dissolved solids left after POME treatment also has adverse impact on the environment.

2.4.3.2 *Liquid Wastes*

The liquid waste generated from the extraction of palm oil through wet process comes mainly from oil room after seperation by the separator or decanter. This liquid waste combined with the wastes from sterilizer condensate and cooling water is called palm oil mill effluent (POME). Palm oil mill effluent is a thick brownish liquid that contains high solids, oil and grease, Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) values. Palm oil mill effluent is generated mainly from oil extraction, washing and cleaning processes.

Agamuthu (1995), points out that the extraction of crude palm oil from FFB requires huge amounts of water and Ma (1999) estimated that 5 - 7.5 tons of water is required to produce 1 tonne of crude palm oil with more than 50% of the water ending up as palm oil mill effluent (POME). Liquid effluents are digested in open tanks until they are suitable for discharging into watercourse (*appendices B.5 and B.6*).

The oil mill company discharges liquid effluent through open drains into nearby watercourses (*appendice B.3 and B.4*) after digestion in open tanks. A situation that has rendered such water bodies unsuitable for human consumption. *Figure 2.5* shows an effluent treatment system at the local oil mill.

Figure 2.5 Palm oil mill effluent treatment system at the local oil mill.

2.4.4   Challenges Posed By Waste Management By Local Oil Mills

The current waste handling by local mills poses serious challenges to both plant and animal lives. Incineration of EFB causes the loss of oil content in EFB and loss of potential renewable energy source. The current liquid waste treatment also causes methane emission into the atmosphere hence contributing to green house gas and eventually the loss of potentially renewable energy source. In addition, the liquid waste treatment requires quite large area as the dump site. Though POME is considered non toxic, it is identified as a major source of aquatic pollution as it depletes dissolved oxygen when discharged untreated into water bodies (Khalid and Mustafa, 1992). Biogas containing methane generated during POME digestion is currently not being captured or utilized and it just escapes into atmosphere. Methane gas is one among other green house gases which can cause ozone depletion. During POME digestion odour released into surrounding air reduces the air quality in the surrounding area. Large quantity of POME production each year

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implies increase in the amount of POMS. These sludges results in bad odors and is considered as a source of surface and ground pollution.

Disposal of EFB into oil palm plantation (*appendix B.7*) without recovering remnant oil in the EFB contributes to oil spills whilst incineration of EFB means wasting renewable energy source and heat which actually could be provided for the boiler. Though the application of shells for road hardening has no impact on the environment, current practice is actually wasting potential renewable energy source.

2.5   CHARACTERIZATION OF POFA

2.5.1   *Chemical Analysis of Palm Oil Fuel Ash (POFA)*

2.5.1.1   *X-ray fluorescence (XRF)*

POFA was analyzed for its chemical composition with X-ray Fluorescence Spectrometry (PHILIPS PW2400) at the Geological Survey Department in Accra to determine oxides and trace elements as heavy metals. Samples of the < 90 micrometer sieved palm ash were submitted for the chemical analysis. Four (4g) of the sample was weighed with an electronic mass balance, homogenized using two polymer balls and then pressed into pellets under 5 tons of load using the press machine. The pellets were analyzed in the Phillips XRF spectrometer.

X-ray fluorescence (XRF) is the emission of characteristic secondary (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals, glass, ceramics and building materials, and for research in geochemistry, forensic science and archaeology. The relative ease and low cost of sample preparation, and the stability and ease of use of

x-ray spectrometers make this one of the most widely used methods for analysis of major and trace elements. The XRF method depends on fundamental principles of interactions between electron beams and x-rays with samples. When materials are excited with high-energy, short wavelength radiation (e.g. X-rays), they can become ionized. If the energy of the radiation is sufficient to dislodge a tightly-held inner electron, the atom becomes unstable and an outer electron replaces the missing inner electron. When this happens, energy is released due to the decreased binding energy of the inner electron orbital compared with an outer one. The emitted radiation is of lower energy than the primary incident X-rays and is termed fluorescent radiation. Because the energy of the emitted photon is characteristic of a transition between specific electron orbitals in a particular element, the resulting fluorescent X-rays can be used to detect the abundances of elements that are present in the sample. XRF-(PHILIPS PW2400) shown in *figure 2.6* was employed in the analysis.

Figure 2.6 XRF-(PHILIPS PW2400)

2.5.1.2 *Atomic Absorption Spectroscopy (AAS)*

Atomic-absorption (AA) spectroscopy uses the absorption of light to measure the concentration of gas-phase atoms. Since samples are usually liquids or solids, the analyte atoms or ions must be vaporized in a flame or graphite furnace. The atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. The analyte concentration is determined from the amount of absorption. Concentration measurements are usually determined from a working curve after calibrating the instrument with standards of known concentration.

In their elemental form, metals will absorb ultraviolet light when they are excited by heat. Each metal has a characteristic wavelength that will be absorbed. The AAS instrument looks for a particular metal by focusing a beam of ultra violet light at a specific wavelength through a flame and into a detector. The sample of interest is aspirated into the flame. If that metal is present in the sample, it will absorb some of the light, thus reducing its intensity. The instrument measures the change in intensity. A computer data system converts the change in intensity into an absorbance. As concentration goes up, absorbance goes up. A calibration curve is constructed by running standards of various concentrations on the AAS and observing the absorbance. Samples are then tested and measured against this curve. *Figure 2.7* shows a 210VGP Atomic Absorption Spectrophotometer.

Figure 2.7 210VGP Atomic Absorption Spectrophotometer

2.5.2 *Mineralogical / Phase Analysis*

X-ray diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and provision of information on unit cell dimensions. In X-ray powder diffraction, the analyzed material is finely grounded and homogenized. XRD provides direct information on the mineralogical composition of the waste ash as each crystalline compound produces a unique diffraction pattern. Phase identifications are made by comparing the diffraction pattern of the mixture to a database of pure phase reference patterns published by the International Center for Diffraction Data.

The powder which is made up of small crystals is irradiated with a monochromatic beam of X-ray. The beam is diffracted at angles determined by the spacing of the planes in the crystals and the type and arrangement of atoms. A scanning detector or a computer records the diffracted beams as a pattern. The intensity and position of the diffractions are then interpreted by comparing to reference spectra using a computerized database. The intensity of an individual phase diffraction pattern in a mixture is proportional to its concentration. Therefore, phase concentrations can be estimated through the use of an internal standard and calibration that relates the peak

intensity ratio of each phase and internal standard to their mass fraction ratio. *Figure 2.8* shows a typical XRD Analyzer (Siemens D5000).

Figure 2.8 D5000, Siemens XRD analyzer

2.5.3 *Toxicity Characteristic Leaching Procedure (TCLP)*

Kim (2002) and Hesbach *et al.* (2001) state that various leaching methods including acid digestion, TCLP, Multiple Extraction Procedure *(*MEP*),* Equilibrium Leach Test *(*ELT*)*, etc., to remove soluble components from solid matrix have been cited in literature.

Multiple Extraction Procedure (MEP) is designed to simulate the leaching from repetitive precipitation of acid rain on an improperly designed sanitary landfill (Testing methods, Canada, 1986). Equilibrium leach test (ELT) is meant for the evaluation of the maximum leachate concentration under mild conditions (Prudent *et al.*, 1996). Toxicity Characteristics Leaching Procedure (TCLP) developed by the United States of Environmental Protection Agency (USEPA) is widely used to classify hazardous solid wastes and evaluate the worst leaching conditions in a landfill environment (USEPA, 1992). The TCLP tests consist of using a buffered organic acid solution to extract chemicals from solid wastes. This test was designed to simulate leaching in landfills.

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TCLP test is used to determine the toxicity of contaminants of hazardous wastes or soils which determines the mobility of organic and inorganic analytes in the wastes. In this test, waste samples are crushed to particle sizes less than 9.5 mm and extracted with an acetic acid solution with pH either 2.88 or 4.93 depending on the alkalinity of the waste.

The current regulatory benchmark test designed to identify wastes likely to leach hazardous concentrations of toxins is the toxicity characteristic leaching procedure (TCLP). If extract concentrations of certain elements or organic compounds exceed regulatory limits the waste is classified as hazardous. U.S. EPA Toxicity Characteristic Leaching Procedure (TCLP), Test Method 1311 is used to generate leachate under controlled conditions to determine if a waste is hazardous due to its characteristics.

If a total analysis of a waste demonstrates that individual analytes of concern are not present in the waste or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the test need not be run.

Although the TCLP test was designed to determine if a waste is hazardous, the importance of its use for waste characterization is to understand the parameters to be considered in properly managing the wastes.

If a waste is 100 percent solid, as defined by the TCLP method, then the results of the total compositional analysis may be divided by twenty to convert the total results into the maximum leachable concentration. This factor is derived from the 20:1 liquid to solid ratio employed in the TCLP. This is a conservative approach to estimating leachate concentrations and does not factor in environmental influences, such as rainfall.

For wastes containing greater than or equal to 0.5 percent solids, the liquid, if present, is separated from the solid phase and stored for later analysis. The solids must then be reduced to particle size, if necessary. The solids are extracted with an acetate buffer solution. A liquid-to-solid ratio of 20:1 by weight is used for an extraction period of 18 ± 2 hours. After extraction, the solids are filtered from the liquid through a glass fiber filter and the liquid extract is combined with any original liquid fraction of the wastes. Analyses are then conducted on the liquid filtrate or leachate to determine the constituent concentrations.

If the TCLP liquid extract contains any constituents at concentrations equal to or greater than the regulated limit, the waste is considered to be a hazardous waste, unless in special situations exempted or excluded.

Yin *et al.* (2008) employed toxicity characteristic leaching procedure (TCLP) Method 1311 to assess the toxicity of the palm waste ash in terms of leachable heavy metals. Lottermoser (1985) states that toxic effects of solid wastes are known to be greatly influenced by their heavy metal contents whilst Bishop (1990) outlines the eight regulated elements as As, Ba, Cd, Cr, Hg, Pb, Se, and Ag. *Table 2.3* outlines the contaminants and their regulatory standards.

Table 2.3 Regulatory Standards for maximum concentration of contaminants

Contaminant	Regulatory Level, (mg/l)	Contaminant	Regulatory Level, (mg/l)
Arsenic	5	Lead	5
Barium	100	Mercury	0.2
Cadmium	1	Selenium	1
Chromium	5	Silver	5

Source: (USEPA, 1992)

CHAPTER THREE

MATERIALS AND METHODS

3.1   MATERIALS

3.1.1   Palm Oil Fuel Ash

Palm oil fuel ash (POFA) was obtained from a local oil mill. This included POFA slag which is a caked form of POFA. The sample collection was done at the foot of the flue tower where all the ashes are deposited from the burning chambers of the boiler. A large quantity of the ash and slag were collected into polyethylene bags by grab sampling. The ash was first washed with distilled water and then air-dried. The waste ash used in the study was dried at 105 °C for one hour before the tests.

3.1.2   Lithomagic Clay

Lithomagic clay from Awaso bauxite deposit was wet sieved through 90μm to separate the gibbsitic fraction (G) from the kaolinitic fraction (K) according to the work of Momade and Gawu (2004).

3.1.3   Silica

This was obtained from the Ceramic Department of the College of Art, KNUST

3.1.4   Whiting (CaCO₃)

$CaCO_3$ was obtained from the Ceramic Department of the College of Art, KNUST

3.1.5   Kaolin

This was obtained from the Ceramic Department of the College of Art, KNUST

3.1.6   0.1M H₂SO4 and 0.1M NaOH

This was prepared at the Materials Laboratory of the Materials Engineering department, KNUST

3.1.7　Deionised water

This was obtained from the Materials Laboratory of the Materials Engineering Department, KNUST

3.2　METHODOLGY

3.2.1　Material Preparation

POFA slag was ground in an abrasion machine with steel balls of diameter 9.5mm. The ashes were sieved using the 0.125 and 0.090 metric millimeter sieves in order to remove bigger size ash particles and foreign materials. Particle size ranges of less than 0.090, 0.090 to 0.125 and greater than 0.125 metric mm of the palm ash and slag were obtained and representative sample taken for chemical and phase analysis.

3.2.2　Material Characterization

Analytical methods employed for characterization of palm waste ash included Atomic Absorption Spectrometry, X-Ray Diffractometry, X-Ray Fluorescence and Toxicity Characteristic Leaching Procedure (TCLP). Chemical compositions of raw materials were determined by X-ray fluorescence and Atomic Absorption Spectrometry, phase compositions were obtained by X-ray diffraction and Toxicity test was done with the help of Toxicity Characteristics Leaching Procedure (TCLP).

3.2.2.1　X-Ray Fluorescence (XRF)

POFA was analyzed for its chemical composition with X-Ray Fluorescence Spectrometry (PHILIPS PW2400) at the Geological Survey Department in Accra to determine oxides and trace elements as heavy metals. Samples of the < 90 micrometer sieved palm ash were submitted for the chemical analysis. Four (4g) of

the sample was weighed with an electronic mass balance, homogenized using two polymer balls and then pressed into pellets under 5 tonnes of load using the press machine. The pellets were analyzed in the Phillips XRF spectrometer.

3.2.2.2 *Atomic Absorption Spectroscopy (AAS)*

Atomic Absorption Spectrometer equipped with a digital readout was used for the determination of four heavy metals comprising iron (Fe), manganese (Mn) copper (Cu) and lead (Pb) of leachates.

Atomic absorption spectroscopy (AAS) determines the presence of metals in liquid samples. Metals include Fe, Cu, Al, Pb, Ca, Zn, Cd, etc. It also measures the concentrations of metals in the samples. Typical concentrations range in the low mg/l range.

3.2.2.3 *Mineralogical / Phase Analysis Of POFA*

Firstly, a sample of kaolinite was pulverized into powder and pressed into sample holders for x-ray diffraction analysis. Approximately 5g of raw kaolinite sample and another 5g of kaolinite to which an impurity of 0.2g palm waste ash have been added were heated through temperature ranges of 900ºC, 1100ºC, 1200ºC and 1300ºC for 2 hours. The heated samples were ground to reduce particle sizes to less than 10 μm and homogenized using a mortar and pestle to improve the sample packing characteristics before analyzing with X-Ray Diffractometer.

X-ray diffraction analysis was done in a model D5000 Siemens XRD analyzer shown in *figure 3.3*, using copper K-$\propto$ radiation, with 2Ө from $3^{°}$ to $65^{°}$, with $0.05^{°}$/s steps, to identify the crystalline phase components of fired samples. X-ray patterns were interpreted with DiffracPlus software, using ICDD (JCDS) – PDF2 files, version 2001.

3.2.2.4 Toxicity Characteristic Leaching Procedure (TCLP)

50g dried sample of POFA under investigation was weighed and placed in a 500 ml beaker containing a magnetic stirrer bar. The particle size of the crushed sample was kept less than 9.5 mm according to the requirement of the TCLP procedure (USEPA, 1992). It was then extracted for 18 hours with an amount of extraction liquid equal to 20 times the weight of the solid phase. The extraction liquid employed was chosen on the basis of waste alkalinity (Extraction Fluid 1: CH_3COOH, pH= 4.93 +/- 0.05 for sample pH < 5 and Extraction Fluid 2: CH_3COOH, pH = 2.88 +/- 0.05 for sample pH > 5). The pH of the filtrate was measured. The leachates were maintained highly acidic by adding nitric acid to avoid any change in concentration and stored at 48 °C for metal analysis.

Subsequent to completion of the 18-hour extraction, the leachates were filtered with Whatman glass fiber filter paper (0.45 mm) and analyzed for heavy metal content using Buck Scientific Model 210VGP atomic ion spectrophotometer.

3.2.3 Solubility Test / Leaching Test

To investigate the leaching behavior of the POFA on contact with different media and environment for some specific heavy metals, a pre-washed sample of POFA was acid-treated. 5g of the pre-washed ash using distilled water was mixed with 100 ml of a solution 0.1M H_2SO_4 at room temperature and agitated using a magnetic stirrer and varied through a pH range of 2, 4, 8 and 10. The solution was kept at room temperature and the samples withdrawn from the shaker at pre-determined time intervals (0, 15, 30 and 60 minutes) using a pipette for each pH value. The effect of pH was studied by adjusting the pH (2, 4, 8 and 10) of test solution using 0.1M H_2SO_4 (lowering pH) and 0.1 M NaOH solutions (raising pH).

The 0.1M H_2SO_4 solution was prepared by dissolving 5.4 ml of concentrated H_2SO_4 in 1000 liters of deionised water and 100ml of that added to the 5g waste ash sample. A liquid-to-solid ratio of 20:1 was used to determine 0.1M H_2SO_4 extractable and distilled water extractable metals. The amount of Fe, Pb, Mg and Mn leached were analyzed with Atomic Absorption Spectrometer. Pipetted samples were filtered through Whatman (No. 1) filter paper to exclude the adsorbent particles and other suspended particles.

3.2.4   POFA as a Mineralizer in the Formation of Alumino-silicate Refractories

An initial test was conducted with kaolinite and gibbsite samples to determine the optimum soaking time. The sample mixtures were heated to 1300 ^{o}C and soaked at different times as outlined in *table 3.1*. The results of the above were analyzed and subsequent sample mixtures were heated to 1300 ^{0}C.

The temperature of 1300 ^{o}C was chosen in accordance with literature which suggests that mullite begins to form at about 1250 ^{0}C (Kingery, 1976). The heat-treated samples were then taken out and placed in the desiccators to prevent the absorption of moisture into the sample which may have the potential of changing the chemical properties. The samples per their label were placed in a mortar and grounded to a particle size of 5 - 10 µm after cooling and prepared for XRD analysis. Different amounts of POFA were added to various proportions of blended kaolinite and gibbsite as shown in *table 3.2* and soaked for 2 hours except the blend with 0.5g POFA which was soaked for 5 hours at 1300 ^{0}C.

Table 3.1   Proportions of kaolinite and gibbsite fractions in pure forms

Proportion for pure samples / Batch (5g)	Soaking time (in hrs) at 1300^0C
90%K-10%G	1
90%K-10%G	2
90%K-10%G	3
80%K-20%G	2
50%K-50%G	2
30%K-70%G	2
20%K-80%G	2

Table 3.2: Proportions of samples with POFA addition

Proportion of samples (5g) with POFA	Soaking time (hrs) at 1300 ^{o}C
90%K-10%G + 0.1g POFA	2
90%K-10%G + 0.2g POFA	2
90%K-10%G + 0.5g POFA	5
30%K-70%G + 0.1g POFA	2

Also 5g of five different raw sample of kaolinite fraction of lithormagic clay from Awaso bauxite deposit were first heated at temperatures of 900 ºC, 1000 ºC, 1100 ºC, 1200 ºC and   1300 ºC for 2 hours. Another batch of 5g samples of kaolinitic fraction to which an impurity of 0.2g of waste ash has been added and carefully homogenized were also heat treated at similar temperatures indicated above also for 2 hours.

Cooled fractions of the material were then prepared for XRD analysis. The heated samples were ground to reduce particle sizes to less than 10 μm and homogenized using mortar and pestle to improve the sample packing characteristics.

3.2.4   POFA as an Admixture in Glaze Recipe

2g of raw sample of the POFA (< 90 μm fraction) were measured and placed on fired clay slabs to determine melting point. The samples were fired at 1150 ^{0}C, 1250 ^{0}C, 1300 ^{0}C and 1350 ^{0}C temperature ranges. Changes observed upon heat treatment were noted. Subsequently, all glazed pieces were treated at 1350 ^{0}C.

Seven different samples of 100g of glaze recipes of various fractions of POFA, slag, kaolin, whiting (CaCO$_3$) and silica (SiO$_2$) were mixed and water added to form a paste or slurry with appropriate consistency. Test pieces (fired clay slabs) were dipped in the various glaze recipe, allowed to cool for a while before firing to a temperature of   1350 ℃. Fired cylindrical clay test pieces were also glazed with the prepared recipe and fired at 1350 ^{0}C. *Table 3.3* shows the composition of the various batches used for the preparation of the glaze recipe.

Table 3.3:   Initial components of POFA glaze recipes

Samples	POFA (g)	POFA slag (g)	Kaolin (g)	Whiting (CaCO$_3$) (g)	Silica (SiO$_2$) (g)
1	50	-	20	15	15
2	50	20	15	15	-
3	20	50	-	10	20
4	30	40	-	10	20
5	25	25	-	30	20
6	25	25	20	-	30
7	25	25	10	20	20

0.1g of a colorant MgO was further added to each batch, glazed on cylindrical test pieces and also fired at 1350 ºC.

The amounts of the various components were varied to investigate the different effect produced. This was carried out by reducing the kaolin component by 50% and silica component by 20% and uniformly distributing the reduced fraction to other components for each glaze recipe thereby maintaining the overall 100g weight. The new weights are shown in *table 3.4*.

Figure 3.1 portrays test pieces glazed with recipes containing POFA prepared for firing.

Table 3.4 Varied components of POFA glaze recipe (final batches)

Samples	POFA (g)	POFA slag (g)	Kaolin (g)	Whiting (CaCO$_3$) (g)	Silica (SiO$_2$) (g)
1	56.5	-	10.0	21.5	12.0
2	52.5	22.5	7.5	17.5	-
3	21.3	51.3	-	11.3	16.0
4	31.3	41.3	-	11.3	16.0
5	26.3	26.3	-	31.3	16.0
6	33.0	33.0	10.0	-	24.0
7	28.0	28.0	5.0	23.0	16.0

Figure 3.1 Prepared glazed test pieces ready for firing

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1   MATERIAL CHARACTERISATION

4.1.1   Chemical Analysis Of POFA

The results of the XRF analysis of POFA are presented in *Table 4.1* for the major elements whilst those of the minor elements are presented in *table 4.2* all in ascending order of magnitude.

Table 4.1   Major elements of POFA

Oxide	Composition, %	Oxide	Composition, %
SiO_2	67.40	Na_2O	1.42
Al_2O_3	10.57	SO_3	0.32
MgO	4.76	TiO_2	0.21
K_2O	4.23	MnO	0.06
CaO	2.88	Cl	0.02
P_2O_5	2.60	L.O.I	3.30
Fe_2O_3	2.27	Total	100.04

Table 4.2 Minor elements of POFA

Element	Composition, ppm	Element	Composition, ppm
Rb	243.3	Hf	8.7
Cs	240.9	Ba	7.4
Cu	165.8	Ga	6.9
As	148.8	Ce	5.3
Zr	93.8	Nb	4.8
Cr	75.9	Y	3.5
Zn	44.1	Th	3.3
Ta	27.6	Sn	3.1
V	25.3	U	2.1
Ni	24.5	Mo	1.4
Co	14.9	Bi	0.6
La	10.1	Pb	0.6

From the chemical constituents given in *tables 4.1* and *4.2,* the POFA used in this study could be classified as a Class F fly ash with 80.24 wt% being $SiO_2 + Al_2O_3 + Fe_2O_3$, 0.32 wt% SO_3 and 3.3 wt% loss on ignition (LOI), meeting the requirement as natural pozollan as required by ASTM C618 (ASTM, 2001) and in conformity with earlier studies by Awal and Hussin (1997), Chindaprasirt (2007) and Tay (1990).

However CaO content of this palm oil fuel ash (POFA) was rather low at 2.2 wt% but in accordance with earlier suggestion by Nagataki (1994) that fly ash from Class F should have calcium oxide less than 5%. The main chemical composition of the POFA was SiO_2 67.4 wt%, Al_2O_3 10.57 wt%, MgO 4.76 wt% and K_2O 4.23 wt%.

The Ca, K, Na, Mg and Fe content of the ash help improve molecular network by breaking the Si-O, Al-O bonds in quartz, silicates and aluminum salts to form new silicates and aluminosilicates. Hence, they are help in the reduction of energy consumption in making of fired construction materials, such as glazed tile, ceramic brick, ceramic glass etc. Among the minor elemental component of palm waste ash are some hazardous heavy metals like Pb, Cr and As which may harm the environment if leached out of the ash. Metals such as manganese (Mn), mercury (Hg), lead (Pb), cadmium (Cd), arsenic (As), copper (Cu) are known to be significantly toxic due to their non-biodegradability and toxicity (Ghaly *et al.*, 2008). POFA is also associated with volatile components, organic matter and decomposition of carbonates (CaO). Loss in weight according to Mehtal *et al.* (1978) represents the quantity of unburned carbon present in the material and is often a good indication of how it will affect the air content. The high alkaline earth and alkaline oxide content (CaO and K_2O), indicates the flux potential of the POFA as ceramic additive. Fe_2O_3, MgO, K_2O and Na_2O, which constitute molecular network improvers like CaO, can reduce energy consumption by enhancing the destruction of Si-O and Al-O, and finally forming new crystal phases or melting into glass phases.

4.1.2 *Toxicity Test By TCLP*

The toxicity of POFA was analyzed by the Toxicity Characteristic Leaching Procedure (TCLP) test specifically for arsenic and concentrations of Zn, Fe and Pb determined from extract. Regulated heavy elements present in the POFA from the XRF scan were Barium, Arsenic Chromium, Lead and Selenium. The initial TCLP test according to ASTM Method 1311 stipulates that if a waste is 100 percent solid, as defined by the TCLP method, then the results of the total compositional analysis

may be divided by twenty to convert the total results into the maximum leachable concentration. All the regulated elements present in the POFA passed the initial TCLP test except Arsenic hence a full scale TCLP test for Arsenic.

Arsenic has attracted considerable attention due to the fact that it is mobile throughout a wide pH range. The leachability of arsenic varies widely depending on the nature of the ash. Arsenic releases from acidic fly ash increase with pH, whereas in alkaline fly ash this trend is reversed (van der Hoek *et al.*, 1994). Its response to different leaching procedures is also notably variable (Izquierdo *et al.*, 2008).

The TCLP results revealed an arsenic level of 3.969 mg/l which is an indication that the ash is not hazardous as it fell below the regulated level of 5 mg/l according to EPA Test Method 1311 (USEPA, 1992). It is however a substantial figure and periodic monitoring is necessary to ensure the arsenic levels do not exceed the regulated limit.

According to Akinbile *et al.* (2012), the presence of arsenic is probably due to the application of herbicides and insecticides used in the fields which deposited it or were later absorbed by the plants *table 4.3* outlines the concentrations of Zn, Fe and Pb in TCLP extract.

Table 4.3 Concentrations of Zn, Fe and Pb from TCLP extract.

Element	Zn	Fe	Pb
Concentration (mg/l)	0.13	0.02	0.59

Studies on the POFA extract showed that some tested metals in the TCLP extract were either not detectable or significantly below the regulatory limits. It can be

deduced that POFA is not hazardous and can be disposed off in a secured landfill. Earlier suggestions by Izquierdo *et al.* (2011) and Soco and Kalembkiewicz (2007) that the leachability of Zn in alkaline ash varies widely, commonly 0.02 - 0.2 mg/l and in all cases below 1 mg/l buttressed the 0.13mg/l Zn concentration in the POFA.

4.1.4 Leaching/ Solubility Test

The results of varying pH (2, 4, 8 and 10) of test solutions 0.1M H_2SO_4 and 0.1 M NaOH at various leaching times (15, 30 and 60 minutes) is presented in *table A.1* (*appendix A*).

Graphs of concentration (mg/l) against time (min) for some selected heavy metals from the leachates are presented in *figure 4.1* to *4.4*.
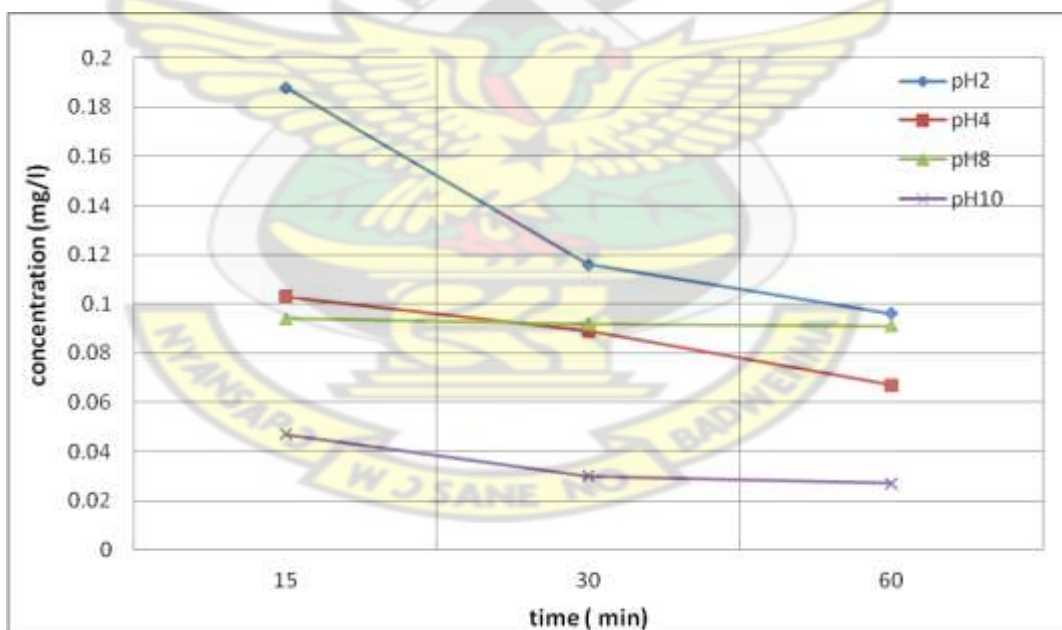

Figure 4.1 Graph of concentration (mg/l) against time (min) for Fe
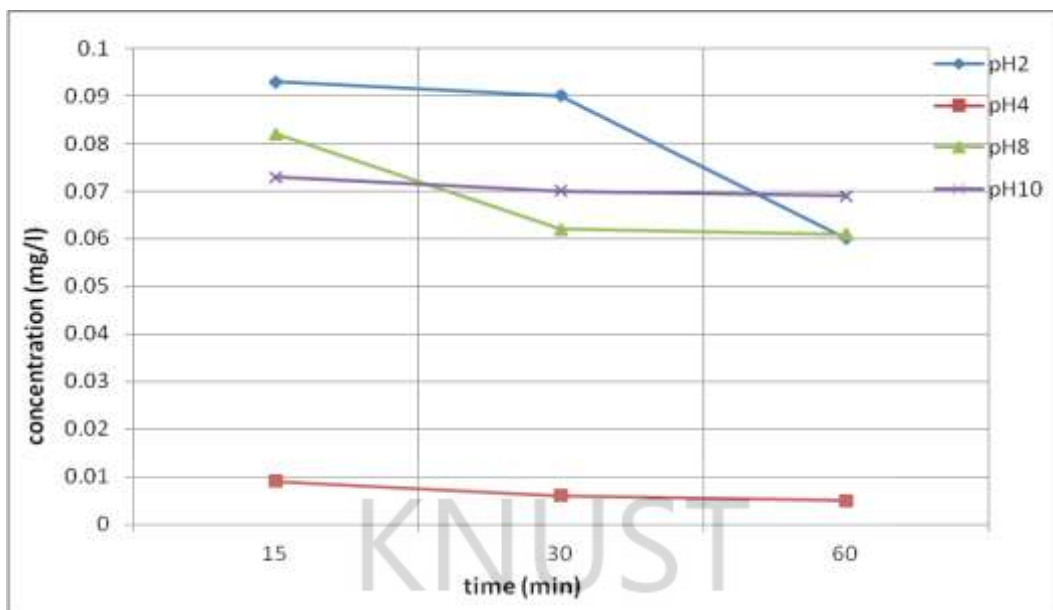
52

Figure 4.2 Graph of concentration (mg/l) against time (min) for Mn
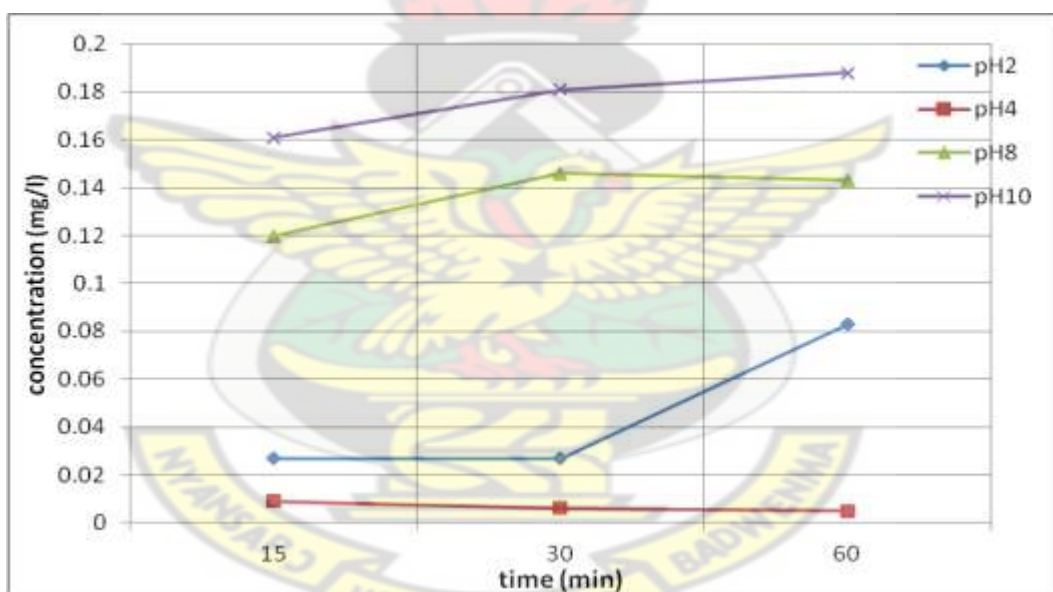

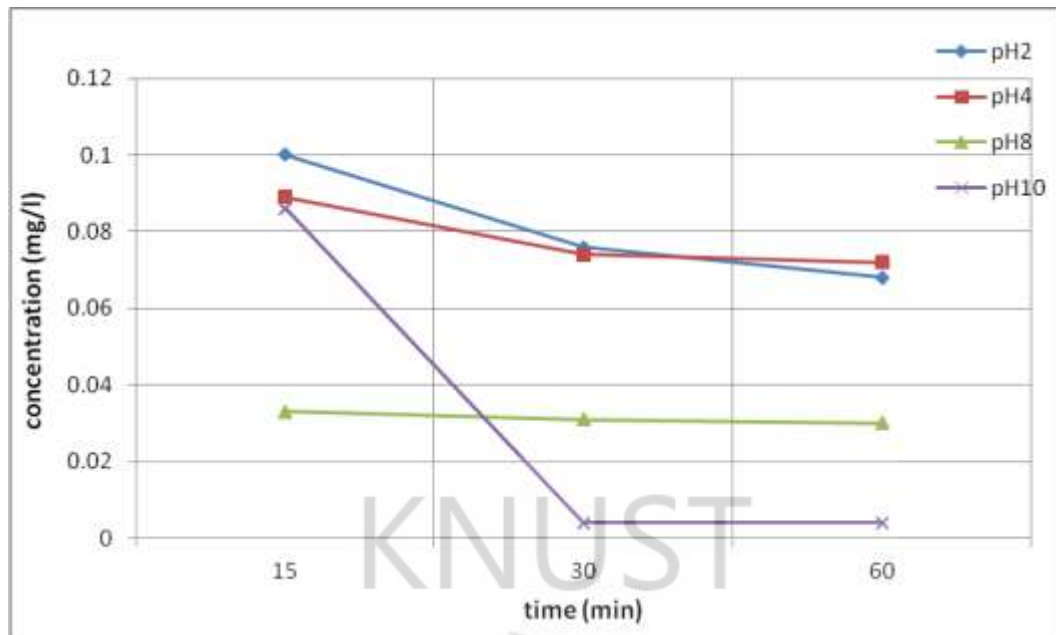*Figure 4.3 Graph of concentration (mg/l) against time (min) for Cu*

Figure 4.4 Graph of concentration (mg/l) against time (min) for Pb

It is known that the solubility of metals and their compounds is a function of pH. The solubility test revealed that for pHs 2, 8 and 10, the extraction rate for Fe, Mn and Pb generally decreased with increasing pH (for *figures 4.1, 4.2 and 4.4.*) with pH4 deviating from this trend. This is in accordance with Gould *et al.* (1989) who stated that metal solubility generally decreases with increasing pH due to the precipitation of metal ions as insoluble hydroxides at high pH values. Leaching results generally conformed to earlier suggestion by Izquierdo *et al.* (2008) that Cu, Fe, Mn and Pb attain minimum solubility in the pH 7-10 region. These elements can be regarded as being of low concern in alkaline ash under environmental conditions. They are pH dependent with low leacheability not correlated to their concentration in the ash (Izquierdo *et al*., 2008). The metal concentrations in the acidic leachate were generally low because the ash contains enough basicity to neutralize the acid extracting fluid in the palm waste ash.

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The case of increasing solubility of Cu with increasing pH (*figure 4.3*) is not understood. This may have to be investigated.

Generally leaching was high in the acidic pH ranges compared to the basic regions. From *figures 4.1, 4.2* and *4.4*, increasing times also showed a reduction in leaching. Dissolution was higher in the first fifteen minutes and steadily reduced with time. After 60 minutes the leachate values for the four metals were all observed to be less than 1%. Thus, progressive leaching of all the metals yielded values far below the limit imposed in the guidelines of environmental waste disposal (USEPA, 1993).

Based on the results, it was found that high mobilization of heavy metals (Fe, Mn and Pb) takes place better under acidic conditions probably due to the instability of the mineral phases that contain these metals under acidic conditions with the exception of Cu.

4.2   UTILIZATION OF POFA

4.2.1   *Phase Analysis By X-Ray Diffraction*

Sakai *et al.* (1996) has indicated that the mineralogical compositions of ashes tend to be very complex in nature due to the complex formation processes (vapourization, melting, crystallization, vitrification, condensation and precipitation) during combustion of waste. Foo and Hameed (2009) buttressed that the ash composition can be expected to fluctuate due to variation in the proportions of irrigated area, geographical conditions, fertilizer used, climatic variations, and timeliness of production, soil chemistry and agronomic practices in the palm growth process.
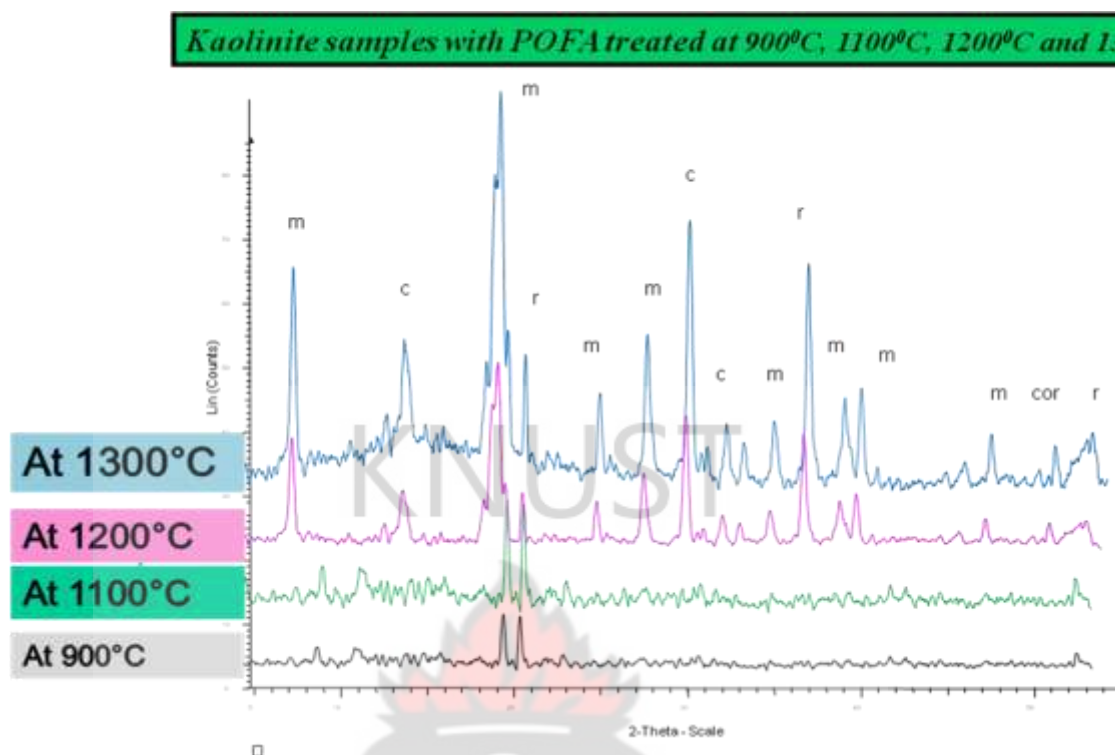
mullite-m   cristobalite-b   r-rutile   cor-corundum

Figure 4.5 Kaolinite samples with POFA treated at 900^0C, 1100^0C, 1200^0C and
1300^0C

XRD analysis as shown in *figure 4.5 and 4.6* revealed that the addition of POFA coupled with rise in temperature enhanced mullite formation. Mullite formation is intensified upon the addition of POFA in *figure 4.5*. Mullite with other transitional phases is observed from 1200 ℃ confirming earlier suggestions by Dilip (2007). POFA with rise in temperature enhanced mullite formation. The presence of silica in the form cristobalite is a product of the transformation of kaolinite to mullite. The intensification of the transformation of kaolinite to mullite accounts for the significant presence of Cristobalite.

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4.3 UTILISATION AS MINERALIZING ADDITIVE

4.3.1 Effect of POFA Addition on Mullite Formation

The combined x-ray diffractograms of lithomargic clay from Awaso bauxite deposit (kaolinite and gibbsite plus varying amount POFA treated at 1300 ^{0}C is presented in *figure 4.6*.

The relative peak intensities of the mullite and corundum peaks were determined and tabulated in *table A.2.* (*appendix A*) These values were used to plot *figure 4.6.*
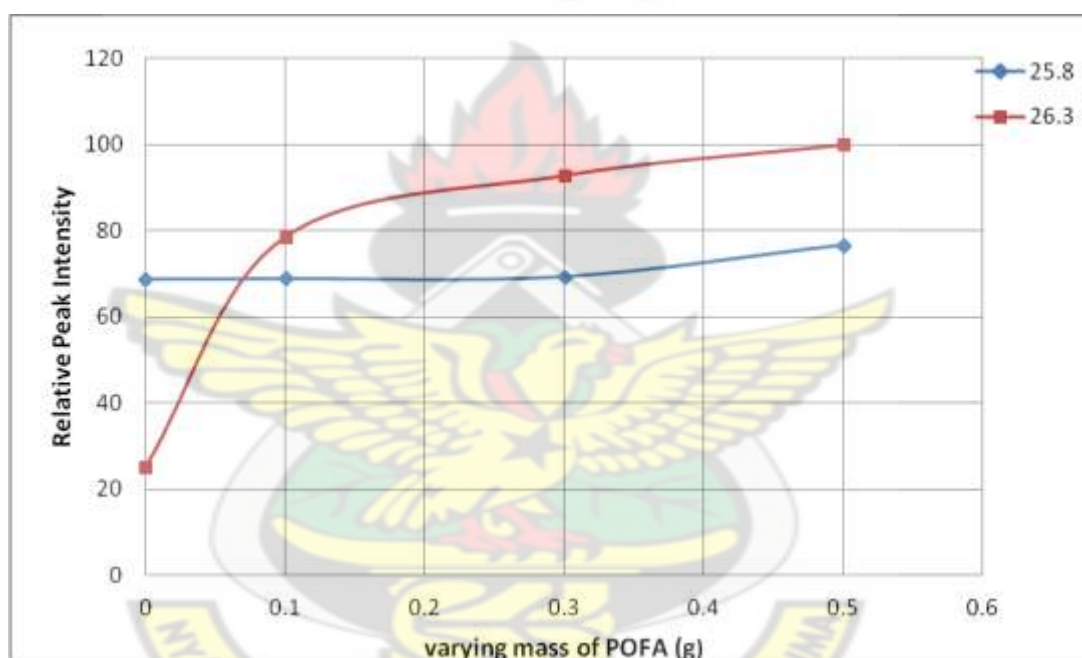

Figure 4.6 Effect of POFA (varying mass) on mullite formation

The graph of the relative intensity of the mullite (*figure 4.6*) showed mullite formation increasing with increasing amount of POFA impurity. It is known that alkali and alkali earth oxides acts as mineralisers for mullite formation. These oxides are found in the ash in varying quantities. With increase in the amount of ash, the amount of the mineralisers increases, therefore aiding the formation of mullite. The interesting observation however, was that the mullite peak at 26.3^0 intensifies more

than that at 25.8^0. The formation of corundum is as a result of the transformation of gibbsite in the sample.

4.3.2   *Utilization of POFA as Additive in Glaze Formula*

The results of varied POFA glaze recipes after firing at 1300 ºC are presented in *table 4.5.*

Table 4.5 POFA glaze recipes with variation of components

CODE	GLAZE RECIPE	DESCRIPTION	FINISHING	
			SLAB PIECE	CYLINDRICAL PIECE
MF1	POFA (g) 56.5 POFA slag (g) - Kaolin (g) 10.0 Whiting (CaCO$_3$)g 21.5 Silica(SiO$_2$) 12.0	Natural sandy brown colour		
MF2	POFA (g) 52.5 POFA slag (g) 22.5 Kaolin (g) 7.5 Whiting (CaCO$_3$)g 17.5 Silica(SiO$_2$) -	Textured light burnt-sugar brown colour		
MF3	POFA (g) 21.3 POFA slag (g) 51.3 Kaolin (g) - Whiting (CaCO$_3$)g 11.3 Silica(SiO$_2$) 16.3	reddish-brown colour		

Con't Table 4.5 POFA glaze recipes with variation of components

MF4	POFA (g) 31.3 POFA slag (g) 41.3 Kaolin (g) - Whiting (CaCO$_3$)g 11.3 Silica(SiO$_2$) 16.0	light textured brown colour	
MF5	POFA (g) 26.3 POFA slag (g) 26.3 Kaolin (g) - Whiting (CaCO$_3$)g 31.3 Silica (SiO$_2$) 16.0	ashy natural earth colour	
MF6	POFA(g) 33.0 POFA slag (g) 33.0 Kaolin (g) 10.0 Whiting (CaCO$_3$)g - Silica (SiO$_2$) 24.0	ashy natural earth colour	
MF7	POFA(g) 28.0 POFA slag (g) 28.0 Kaolin(g) 23.0 Whiting (CaCO$_3$)g 5.0 Silica (SiO$_2$) 16.0	glassy Light amber finish	

The entire glaze melted from 1250 ºC but a fine melt was observed at 1350 ºC forming a glassy appearance but with different finishes as presented *table 4.5* depending on the composition of the glaze. The finishes observed ranged from reddish burnt brown sugar colour to light reddish sandy colour among others depending on the ash composition.

The significant amount of Fe_2O_3 in raw palm waste (2.27%) is responsible for the reddish colour of the fired specimens. Increased POFA substitute led to a more burnt sugar brown or reddish finish. The results show that the POFA is capable of producing an attractive glaze finishes with acceptable characteristics and hence a good material for glazing ceramic products.

POFA is abundant and can be obtained without incurring much cost whilst the process of making it is simple. Again equipment used to produce palm ash glaze is simple and cheap. The usage of 50-80% of POFA as the main ingredient may reduce the costs of glaze production.

CHAPTER FIVE

## CONCLUSION AND RECOMMENDATIONS

5.1   CONCLUSION

The main conclusions that can be drawn from this experimental study may be summarized as follows:

- The Palm Oil Fuel Ash (POFA) examined in this study is not likely to leach high concentrations of toxic elements when disposed of in a secured landfill. The significant level of Arsenic however warrants periodic monitoring to keep it within range.

- Generally leaching was high in the acidic media as compared to the basic media. The deviation at pH4 and the behavior of Cu are not understood. After 60 minutes the leachate values for the four metals were all observed to be less than 1%. Thus, progressive leaching of all the metals yielded values far below the limit imposed in the guidelines of environmental waste disposal.

- Mullite formation is accelerated with increasing temperature and POFA addition to lithormagic clay from Awaso bauxite deposit.

- POFA can potentially be used as the main additive or ingredient in a glaze formula with variation of the components capable of producing an attractive glaze with acceptable characteristics.

5.2   RECOMMENDATIONS

- Similar study exploring further utilization of the POFA from local oil mills should be conducted to bring to fore the usefulness of palm waste ash from the oil mill company.

- Further critical and specific study on the toxicity of the POFA in various media and quality of the drinking water of areas around the mill would be necessary to establish an emphatic statement about the effect of POFA on the environment.

- POFA can be used for glazing ceramic products and therefore local oil mill companies and ceramic material manufacturers should be conscientised.

- The behavior of Cu and deviation at pH4 should be investigated.
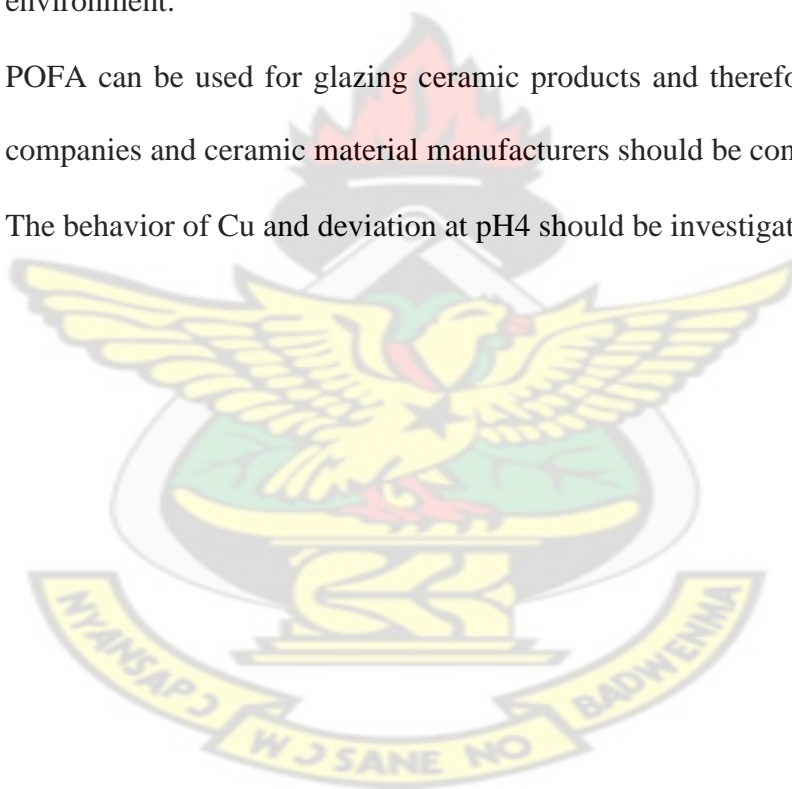
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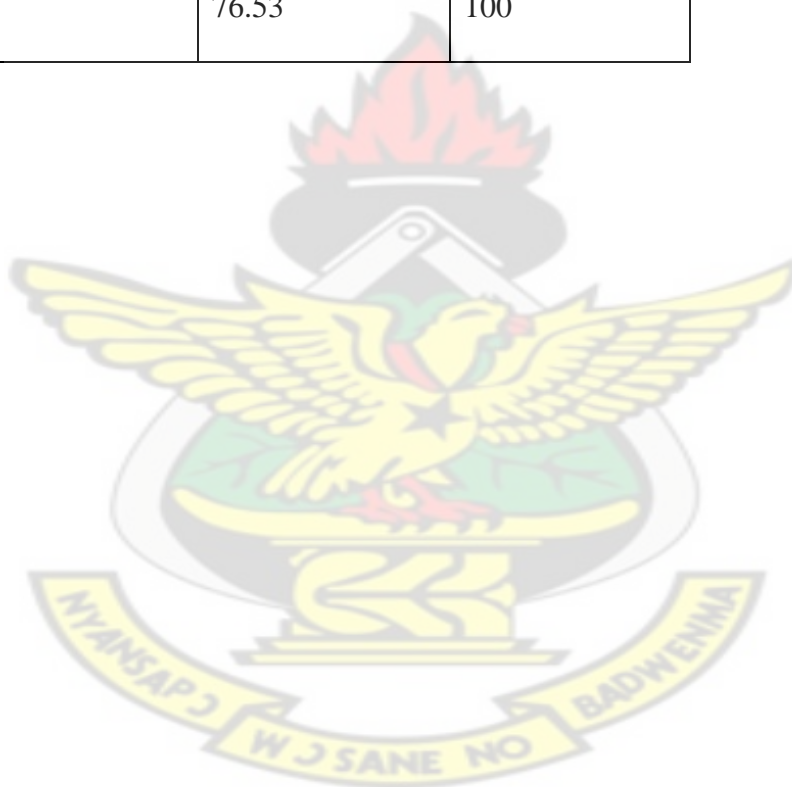www.mofa.gov.gh/site/?page_id=8819 [accessed August 12, 2011]
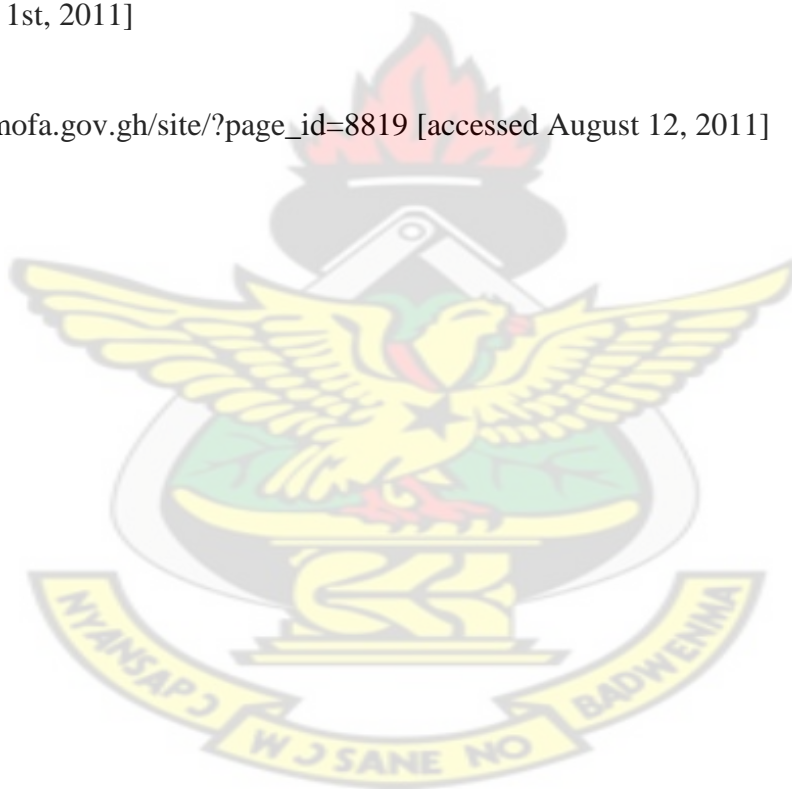
APPENDICES

APPENDIX A - TABLES

Table A.1: Concentrations of Fe, Mn, Cu and Pb in Leachates at Various pHs   And Leaching Times.

Media	Time, (min)	Fe, Concentration (mg/l)	Mn Concentration (mg/l)	Cu Concentration (mg/l)	Pb Concentration (mg/l)
pH2	15	0.188	0.093	0.027	0.100
	30	0.116	0.090	0.027	0.076
	60	0.096	0.060	0.083	0.068
pH4	15	0.103	0.009	0.103	0.089
	30	0.089	0.006	0.095	0.074
	60	0.067	0.005	0.103	0.072
pH8	15	0.094	0.082	0.120	0.033
	30	0.092	0.062	0.146	0.031
	60	0.091	0.061	0.143	0.030
pH10	15	0.047	0.073	0.161	0.086
	30	0.030	0.070	0.181	0.004
	60	0.027	0.069	0.188	0.004

Table A.2:   Relative Peak Intensities Showing the Effect of POFA on Mullite Formation

Amount of POFA in mixture, g	Relative Peak Intensities	
	Mullite at $2\Theta = 25.8^0$	Mullite at $2\Theta = 26.3^0$
0	68.80	25.2
0.1	68.93	78.57
0.3	69.39	92.86
0.5	76.53	100

APPENDIX - B

PHOTOS OF WASTE DISPOSAL PRACTICES AT THE LOCAL OIL MILL

Plate B.1: Palm oil fuel ash littered outside the local oil mill

Plate B.2: Solid wastes littered at sites near the oil mil

Plate B.3: palm oil mill effluent flowing through ground channel at the mill

Plate B.4: Palm effluent flows to join a river course

Plate B.5: Palm Oil Mill Effluent digestion tank at the local oil mill in a bad shape

Plate B.6: Palm Oil Mill Effluent digestion tanks at a local oil mill

Plate B.7: POME runs through vegetations at sites near the local oil mill