UNIVERSITY OF CAPE COAST

FORMULATION OF TITANIUM DIOXIDE CLIMATE SMART – PORTLAND CEMENT FROM SELECTED KAOLIN DEPOSITS IN THE CENTRAL REGION, GHANA

SAMUEL OBIRI

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BY

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Thesis submitted to Department of Chemistry, School of Physical Sciences, College of Agriculture and Natural Sciences, University of Cape Coast in partial fulfilment of the requirements for the award of Doctor of Philosophy in Analytical Chemistry

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DECLARATION

Candidate's Declaration

I hereby declare that this thesis is the result of my own original research and that no part of it, in whole or in part, has been submitted as a dissertation for another degree at this University or elsewhere.

Candidate's Signature: ……………………………………Date ……………….

Name: ………………………………………………………

Supervisors' Declaration

We hereby declare that the preparation and presentation of this thesis were supervised in accordance with guidelines on supervision of thesis laid down by the University of Cape Coast.

Principal Supervisor's Signature: …………………………Date ………………

Name: ………………………………………………………

Co – Supervisor's Signature: ………………………………Date ……………...

Name: ……………………………………………………..

ABSTRACT

Ordinarily Portland cement and other cementitious materials have played key roles in the construction industry over the years. However, in recent times, exposure of civil structures to toxic contaminants such as NO_x, SO_x, among others have resulted in sulphate attack which affect their structural integrity. Hence the main thrust for this thesis is as follows: (1) to determine chemical composition of major oxides such as TiO_2 concentration in the study area's kaolin samples; (2) to extract the TiO_2 content and used in formulating TiO_2-ordinary Portland cement; and (5) make policy recommendation to relevant stakeholders in the building and construction industries on the use of climate-smart Portland cement. Selective flocculation technique was used to extract TiO_2 and Fe_2O_3 from the kaolin samples. Results from the determination of compressive and flexural strength are tested according to EN 197-1:2005 standards, water of absorption in line with ASTM C1403-15 standards, workability or flow of the mortar according to ASTM C109 standards, and lastly sulphate attack was carried out in line with ASTM C1012 guidelines. The compressive and flexural strength increased considerably when 5% TiO_2 was added to the Portland cement than the control. This means local cement manufacturing companies can extract TiO_2 from kaolin and incorporate it into the formulation of their Portland cement to improve its ability to withstand the changing harsh climate.

KEY WORDS

Climate-smart

Compressive Strength

Flexural

Kaolin

Portland cement

Titanium dioxide

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DEDICATION

To my parents; Very Rev. & Mrs. Daniel K. Obilie, and my children; Daniel Herbert Obiri, Adwoa Oforiwaah Obiri, and Akua Gyesiwaah Obiri

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LIST OF ABBREVIATION

STM	American Standard Testing Methods
BRRI	Building and Road Research Institute
BS EN	British and European Standards
CSIR	Council for Scientific and Industrial Research
OPC	Ordinary Portland cement
PIA	Plagioclase Index of Alteration

CHAPTER ONE

INTRODUCTION

Cement and cementitious materials have played important roles in constructing buildings, roads and bridges. As noted by Feng et al., (2013), cement is used as a binder to hold aggregates such as sand or stones as well as water together to form concrete or mortar. Shi et al., (2010) and Roziere et al., (2009) have both argued that, the binding property of ordinary Portland cement paste have greatly influenced the durability of concrete and other civil structures.

It has been observed recently that mortar and concrete made from ordinary Portland cement are very susceptible to sulphate attacks or acid attacks. Leading to the destruction of the binding strength of the rendered mortar or concrete which makes them brittle and susceptible to cracking or peeling of the rendered mortar pastes from the surface of buildings or civil structure (Rashad, 2014; Rashad, 2013; Sorathiya et al., 2017; Feng et al., 2013).

Hence, this study seeks to modify the inherent property of ordinary Portland cement to improve structural integrity of buildings and other civil works and also affect the long term durability of such structures

1.0 Background to the study

The brittleness and low strength of cement paste is due to pores and movement of water between the cement and sand, while in concrete, which create a layer of water that moves between the cement paste and stones, thus creating cracks within the cement paste or the concrete (Dunuweera and Rajapakse, 2018).

Modification of mortar paste inherent properties of ordinary Portland cement to improve its durability has caught the attention of many scientist and engineers (Nehdi et al., 2004; Shi et al., 2012; Bagheri et al., 2012; Pacheo-Torgal et al., 2012). This has to do with the context of generating crack free concrete or cement paste by adding nanofillers or additives to the ordinary Portland cement.

Nano-sized particles are used to modify properties of ordinary Portland cement to produce crack free cement mortar paste or concrete. Ordinary Portland cement mortar paste or concrete containing nano-sized particles have been shown in literature to possess higher compressive strength, flexural strength, ductility as well as other physical properties such as less shrinkage and less permeability of water molecules that eventually affect the long term durability of civil structures and buildings (Sanchez and Soboley, 2010; Balaguru and Chong, 2006; Birgisson et al., 2010).

According to Dunuweera and Rajapakse (2018) and Feng et al., (2013), the following nano-particles are used to improve durability of ordinary Portland cement. They are; nano-titania (TiO_2), carbon nanotubes, nano-silica (SiO_2), nano-alumina (Al_2O_3), nano-hematite (Fe_2O_3), nano-magnetite (Fe_3O_4), nano-zinc oxide (ZnO), nano-zicronium dioxide (ZrO_2), nano-Cu_2O_3, nano-CuO, nano-$CaCO_3$, as nanotubes or fibers and nano-clay.

He and Shi (2008) argues that adding aforementioned nano-materials to ordinary Portland cement limit the number of pores in cement mortar paste or concrete through the following: (1) the nano-materials act as nano-fillers i.e., filling every void space in the cement paste or the concrete making it an impermeable microstructure as well as a better calcium silicate hydrate (C – S – H) (Shah et al., 2009); (2) as a seed for the growth and formation of hydrated cement products, i.e., acceleration of hydration of cement; and (3) it helps in forming a denser calcium silicate hydrate (C – S – H) structures through parallel packing (Feng et al., 2013).

Titanium dioxide nanoparticles out of the above-mentioned nano-materials in recent times have gained wide attention among material scientists and civil engineers. This is due to the fact that, findings from scientific studies have shown the application of titanium dioxide nano-materials in areas or fields such as; white paint, plastics, papers, inks, medicine, cosmetic products, toothpastes, treatment of contaminated water or environmental remediation, photovoltaic cells, solar cells, photo-catalyst, heterogeneous photoctatlysis as well as generation of photocurrent among others (Kamat, 2012; Fujishiman and Honda, 1972; Wrighton et al., 1976; Chen and Mao, 2007; Hoffman et al., 1995; Fujishima et al., 2000; Herrmann, 2005; Di Paola et al., 2012; Teoh and Scott, 2012).

In the construction industry, adding titanium dioxide nano-materials to cement have also gained wide attention due to its self-cleaning property (Yuranova et al., 2007), air purification (Maggos et al., 2008), and disinfection of buildings in places such as hospitals, restaurants just to mention a few (Linkous et al., 2000). Apart from the self-cleaning, air purification and disinfection properties associated with addition of TiO_2 nano-particles into cement paste and concretes that have received considerable attention in literature, other scholars have studied the effect of adding TiO_2 nano-particles into cement paste or concrete on the compressive strength (Pimenta et al, 2016), flexural strength and workability (Nazari, 2011; Zhang and Li, 2012) and water of absorption (Baoguo et al., 2015). Findings from these studies show that, adding nano-TiO_2 particles to Portland cement does not significantly changes the properties of the cement (i.e., physical and mechanical properties). Rather these scientists suggest that adding nano-TiO_2 particles to Portland cement gives it an extra advantage of self-cleaning, air purification and disinfection properties.

Chen et al., (2007) says that it is possible to use commercially available TiO_2 micro-particles in cement pastes and concretes to achieve the same result obtained when nano-TiO_2 particles were also used, which has also been confirmed by Hanson (2014). According to Shaaban et al., (2020) and Gatto (2014) both argued that micro-sized commercially made TiO_2 as well as any of form of TiO_2 particle when added to ordinary Portland cement to form cement or concrete product, it can exhibit its photocatalytic properties. They further suggested that, nano-sized or micro-sized TiO_2 powder should rather be used to reduce the negative health effects associated with inhaling nano-particles when they are been added to ordinary Portland cement.

Maggos et al., (2008) and Hanson (2014) both argues that, the size of TiO_2 used in the formulation of TiO_2-Portland cement for the construction of buildings and other civil structures does not affect the durability of the building. That is, no notable change in durability properties of buildings observed when either nano or micro-TiO_2 was used as an admixture in making TiO_2-cement. They argue further that pohotocatalytic effects of TiO_2-Portland cement in the removal of environmental contaminants on buildings in comparison does not depend on the size of TiO_2 used as an admixture in Portland cement.

From the work of Maggos et al. (2008) and Hanson (2014), nations that are unable to produce their own micro- or nano-sized TiO_2 or no money to buy already synthesized micro- or nano-sized TiO_2 can extract TiO_2 from kaolin and used it as a substitute to make TiO_2-ordinary Portland cement.

This study was undertaken in the pursuit of a low-cost method of producing TiO_2-climate smart ordinary Portland cement for use in low-income countries, based on the suggestion of Maynard et al., (1969) that in order to use kaolin in the paper coating, paper filing, refractory ceramics and pharmaceutical industries, titanium minerals in them like oxides of titanium must be removed, because the presence of the TiO_2 in the kaolin impairs its white colour required for the aforementioned industries. As a result, TiO_2 content in kaolin, which typically occurs as leucoxene (TiO_2. nH2O), brookite (TiO_2), and anatase (TiO_2) (Luz and Middea, 2004), can be extracted as a by-product.

Hence, the main problem that this study seeks to address is to demonstrate how developing countries like Ghana can formulate TiO_2-ordinary Portland cement and use it to prevent peeling of mortar pastes rendered on buildings and other civil structures from locally available materials like kaolin. It further seeks to assess physical and mechanical properties of TiO_2-ordinary Portland cement used on buildings and other civil structures to prevent the flaking of mortar pastes render on such buildings and civil structures surfaces.

Lucas et al., (2013) have suggested that adding nano-TiO_2 to concrete or mortar pastes changes its mechanical characteristics and microstructure, as such it is able to resist peeling or flaking of the buildings or civil structures. That is, the incorporated TiO_2 is able to improve or modify the mechanical and microstructure during the cement hydration.

Zhang et al., (2015) have noted that the TiO_2 alters pores structures in the cement paste, with the view of reducing the total number of pores in the hardened cement paste. Findings from other scientific studies have collaborated the results of Zhang et al., (2015) that by increasing the TiO_2 content in the cement matrix, the total specific pore volume decreased (Rahim and Nair, 2016; Yang et al., 2015; Ma et al., 2015; Soleymani, 2012). Li et al. (2017) have suggested that addition of nanoTiO_2 into the cement matrix improves the compactness of cementitious composites as well as decreases its porosity from 9.045 to 6.96 percent. Similarly, Salman et al., (2016) also discovered that addition of nano-TiO_2 fill the pores within the cement matrix, thereby reducing the size of calcium silicate hydrate (CSH) crystals. To Salman et al., (2016) as the size of the calcium silicate hydrate (CSH) increases, it results in the development of micro-cracks which eventually leads to flaking or peeling of the rendered mortar paste.

1.1 Problem Statement

Climate change is exerting heavy toll on all facet of human life including infrastructure in the built environment (IPCC, 2004). Ordinary Portland cement widely used in the construction industry strongly adsorb greenhouse gases like CO_2, NO_x, SO_x, volatile organic compounds (VOCs) and particulate matter (PMs) from the atmosphere onto its surface (lee, 2012). Among the greenhouse gases that are strongly adsorbed by ordinary Portland cement from the atmosphere, NO_2 and SO_2 are known major contributors of acid rain, i.e., dissolves in water to give nitric acid (HNO_3) and sulphuric acid (H_2SO_4)

respectively. Due to the hydrophilic nature of ordinary Portland cement, NO_2 and SO_2 acidic gases adsorbed onto surfaces of the built structures absorb moist air or water from the atmosphere which react with the aforementioned acidic gases (as shown in equations 1.0 to 1.3) to attack structures in the environment (Lee, 2012).

$$NO_2 + OH^{\bullet} \rightarrow HNO_3 \quad \ldots \quad (1.0)$$

$$SO_{2(g)} + OH^{\bullet} \rightarrow HOSO_2^{\bullet} \quad \ldots \quad (1.1)$$

$$HOSO_2^{\bullet} + O_2 \rightarrow SO_3 + HO_2^{\bullet} \quad \ldots \quad (1.2)$$

$$SO_{3\,(g)} + H_2O \rightarrow H_2SO_4 \quad \ldots \quad (1.3)$$

The HNO_3 and H_2SO_4 produced in equations (1.0) and (1.3) above react with both hydrated and unhydrated materials in ordinarily Portland cement. This chemical reaction results in decalcification or decomposition of portlandite or calcium hydroxide (CH or $Ca(OH)_2$) at pH$\leq$ 12.5, calcium silicate hydrate (CSH) at pH $\leq$ 9.0 and ettringite at pH $\leq$ 11.0. The decalcification of the hydrated (especially, CH) and unhydrated cement components lead to the formation of soluble calcium products (as shown in equation 1.4 below), eventually increases the porosity and permeability of the rendered mortar paste or concrete as well as loss of both adhesive and cohesive strength of the ordinary Portland cement. The overall effect is the flaking or peeling off of the rendered mortar paste or concrete which lead to deterioration in the durability of the building.

$$2HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2H_2O \quad \ldots \quad (1.4)$$

Furthermore, due to the hygroscopic nature of the calcium salts formed in equation (1.4) above as well as that of hydrated and unhydrated ordinary Portland cementitious materials, it allows movement of moisture by capillary action through the masonry walls leading to flaking of mortar pastes or concrete, thus affecting its durability (Shahidzadeh-Bonn et al., 2008; Atta-ur-Rehman et al., 2018).

Atta-ur-Rehman et al., (2018) and other scientist further argues that moisture or water that moves from the external environment through the masonry walls usually contain sulphate ions, chloride ions, etc which causes the ordinary Portland cement-based materials, masonry walls, or stones to crack or flake due to sulphate attack or salt of crystallization phenomenon (Scherer, 2004; Chatterji and Thaulow, 1997; Thaulow and Sahu, 2004). According to the aforementioned scientists, the severity and nature of the effects associated with sulphate attack or salt of crystallization on cement-based materials, masonry walls or stones are affected by the types of cement used and its composition, such as water/binder ratio, etc.

It is within this context of modifying ordinary Portland cement used in constructing buildings for them to able to withstand the effects of exposure to greenhouse gases and climate change which often lead to acid attack, sulphate attack, salt of crystallization as well as carbonation of such masonry walls or concrete undergoing spalling, cracking or flaking that Chen and Poon (2009) suggested that such modification of ordinary Portland cement is possible with the addition of TiO_2.

According to Fujishima and Zhang (2005), adding titanium dioxide (TiO_2) to ordinary Portland cement has grown in popularity over the last 15-20 years, because of its white colour, it was used to make white cement. Also, the increased interest in the use of titanium dioxide as a climate-smart cementitious material is due to its hydrophobic and hydrophilic properties. That is, it is able to prevent movement of water molecules via capillary action through the pores in the masonry walls or concrete (Husken et al., 2009; Lackhoff et al., 2003; Poon and Cheung, 2007). In the developed countries, the use of nano-TiO_2 climate-smart ordinary Portland cement has been to prevent flaking and spalling of masonry walls or concrete due to its exposure to greenhouse gases.

However, as noted by Shaaban et al., (2020), developing countries who need this type of climate-smart cement are unable to use it due to its high cost of importation and lack of technological capacity to produce it locally using available raw material as substitute. The Intergovernmental Panel on Climate Change (IPCC, 2004) has predicted that, climate change would have significant negative impact on masonry walls and concrete in developing countries such as Ghana who are less emitters of greenhouse gases. This negative impact would manifest itself in an increase incidence of rising damps in buildings in such developing countries. Rising damp contains sulphate ions and other mineral ions, which causes masonry material to disintegrate, resulting in high maintenance costs (Charola, 2013). Absorption of acidic water dissolves soluble salts, resulting in plaster flaking, fungal and mould attack, and reinforcement corrosion (Sena-Kportufe, 2015).

Since, ordinary Portland cement used in Ghana do not contain climate – smart additives such as TiO_2 they are not able to prevent rising damp as well as greenhouse acidic gases like NO_x, SO_x and CO_2 which dissolves in water to attack masonry walls or concrete leading to flaking or spalling (Asamoah et al., 2017). In Ghana, techniques which over the years have been used to address the issue rising damp associated with climate change include but not limited to the use of damp-proof material, cladding of the wall surfaces with tiles as well as painting of the walls with bitumen (Asamoah et al., 2017). These techniques have woefully failed to address the issue of flaking and spalling of masonry walls or concrete structures in Ghana.

Hence, the main problem that this study seeks to address is to demonstrate how developing countries like Ghana can produce climate-smart TiO_2-ordinary Portland cement using locally available materials like kaolin to solve the problem of flaking, spalling and cracking of masonry walls or concrete walls affecting durability of buildings in Ghana.

1.2 Objectives of the study

The main objective of this study is to look for an additive that can modify the physical and mechanical properties of ordinary Portland cement currently in use in Ghana to improve upon their durability to be able to withstand the harsh effects of climate change on buildings and other civil structures.

The specific objectives are as follows:

1. To determine chemical composition of major oxides such as TiO_2 concentration in kaolin deposits from selected deposits in the Central Region, Ghana;
2. To extract the TiO_2 content from the kaolin deposits and used in formulating TiO_2-ordinary Portland cement;
3. To assess mechanical and physical properties such as compressive strength, flexural, water of absorption, workability or flow of mortar made from the formulated cement;
4. To investigate whether the formulated TiO_2 -climate-smart Portland cement can prevent sulphate attack on buildings and other civil structures; and
5. To make policy recommendation to relevant stakeholders in the building and construction industries on the use of climate-smart Portland cement.

1.3 Significance of the Study

Numerous reports from the Intergovernmental Panel on Climate Change (IPCCC) points to the fact that, climate change would have negative effects on buildings and other civil structures constructed from the ordinary Portland cement (IPCC, 2004). Developing countries especially those in sub-saharan Africa who are less emitters of greenhouse gases that causes climate change but are vulnerable to negative effects of climate change. The sectors that will be hardest hit with negative effects of climate change will be buildings and other civil structures.

Hence, it is very important to developing countries like Ghana that are unable to utilise nano-technology due to its cost as well as limited technological advancement to support the production of nano-TiO_2 particles to be used in the formulation of TiO_2-Portland cement to begin looking for an alternative cheap way of producing TiO_2 from locally available raw materials.

This study is significant, because, in spite of the fact that several studies have been conducted to assess the physical and mechanical properties of either nano-sized or micro-sized commercially available TiO_2 powder to formulate TiO_2-Portland cement as well as its self-cleaning, air purification and disinfection or photocatalytic properties (Nazari and Riahi, 2011; Ma et al., 2016; Chen et al., 2012), not much work has been done in extracting TiO_2 powder from local kaolin deposit and using it to formulate TiO_2-Portland cement. As noted by Gazquez etal., (2014), the aforementioned properties of TiO_2-Portland cement make them suitable as climate-smart cementitious material that can be used to address effects of climate change on mortars and concrete.

Findings from this study, which evaluated performance of mortar containing TiO_2 extracted locally from kaolin to prevent flaking or spalling of buildings, can be recommended to developing countries with large kaolin deposits containing TiO_2 to extract it and use the extracted TiO_2 as an additive to make TiO_2-ordinary Portland climate-smart cement in place of commercially available nano- or micro-sized TiO_2.

1.4 Delimitation

Kaolin deposits can be found throughout the entire country. According to the Kesse (1985), these deposits contain titanium dioxide and minerals. However, in this thesis, titanium dioxide was extracted from four known places in the Central Region, Ghana.

1.5 Limitation

Mechanical strength such as compressive strength, flexural and other parameters such as shrinkage, sulphate attack were measured on TiO_2-climate smart Portland cement extracted from kaolin in selected towns in central region.

1.6 Definition of Terms

In this thesis, all terms used have their usual meanings except climate – smart cement, which refers to any cementitious material that has the ability to reduce emission and effects of climate change in the building industry.

1.7 Organisation of the Study

The thesis would be split into five chapters. The following are the contents of each chapter:

- Chapter one set the tone for the thesis. It includes introduction, problem statement, objectives and significance of the study as well as how the thesis is structured;
- Chapter two also include review of relevant literature of previous and current scientific knowledge on the subject matter of this thesis. It begins with short introduction, durability of TiO_2-portland climate – smart cement, uses and benefaction of kaolin, cement and its properties, hydration of cement,

photocatalytic cementitious materials, titanium dioxide as a climate-smart and photocatalytic cementitious material among others;

- Chapter three of the thesis is the methodology section, which discusses the methods used in the determination of chemical constituent of each kaolin deposit, techniques for extracting TiO_2, using the extracted titanium dioxide as an additive in climate-smart ordinary Portland cement, assessment of physical and mechanical characteristics of the titanium dioxide ordinary Portland cement;
- Chapter four of this thesis contains results and discussion section under the following themes; (i) mineralogical composition of kaolin deposits in the study area, (ii) chemical composition of each kaolin deposits in the study area, (iii) chemical characteristics of TiO_2 extracted from kaolin deposits in the study areas, and (iv) assessment of physical and mechanical properties of the titanium dioxide ordinary Portland cement such as flexural, compressive strength, flow or workability of the formulated cement among others; and
- Chapter five summarises key findings and recommendations made from this study as a way of providing an outlook for future work to be carried out by way of improving physical and mechanical properties of cementitious materials in Ghana.

To share the knowledge gained in this study with the larger scientific community and the general public, the results obtained from this thesis would be published in peer-review journals (Publication from this Thesis).

CHAPTER TWO

LITERATURE REVIEW

2.0 Introduction

This chapter review pertinent literature organised under the following headings; durability of TiO_2-ordinary Portland cement as well as mechanisms involved in addressing spalling or flaking of buildings and civil structures; types of cement, compositions and hydration of ordinary Portland cement, role of cement admixtures in improving durability of cement products; TiO_2-ordinary Portland cement as a photocatalytic material in oxidising greenhouse contaminants; and kaolin as a source of TiO_2 for making TiO_2-ordinary Portland cement to improve durability of mortar and concrete.

2.1 Durability of TiO_2-ordinary Portland climate smart cement

2.1.1 The role of Portland cement in contributing to sulphate attack

Ordinary Portland cement has played a critical role in building of houses and others such as bridges, hospitals, etc. However, in recent times, buildings and other civil structures constructed with ordinary Portland cement are found to deteriorate due to exposure to harsh environmental conditions. Atta-ur-Rehman et al., (2018), has noted that, sulphate attack is an example of one of the harsh environmental conditions that affect structural integrity of buildings and other civil structures.

Sulphate attack is a reaction between sulphate ions in run-off water, ground water, soil, sea water or sewers with hydrated or unhydrated alumina products such as calcium hydroxide (CH) or calcium silicate hydrate (CSH) to form ettringite and gypsum. Also, it is a reaction between strong sulphuric acid produced from the dissolution of SO_2 gas deposited on the walls of mortar or concrete and the hydrated or unhydrated products such as portlandite, CSH to form ettringite or gypsum (Yu et al., (2013). That is, the sulphate ion (SO_4^{2-}) from the external environment reacts with calcium alumina monosulphate phase of the hydrated cement to form ettringite.

The ettringite produced from the reaction between the incoming sulphate ion and the calcium silicate hydrate expands very rapidly, thereby reducing strength of concrete or the mortar in the building or the civil structure.

Similarly, the sulphate ion also reacts with portlandite ($Ca(OH)_2$) obtained from hydrating C_2S phase of the Portland cement to produce gypsum (calcium sulphate) according to equation (2.0):

$$Na_2SO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4.2H_2O + 2NaOH \quad \ldots \quad (2.0)$$

The gypsum ($CaSO_4.2H_2O$) produced in equation (2.0) further react with hardened hydrated products in the cement like calcium aluminates, calcium sulfoaluminate (monosulphate- C_4ASH_{12-18}) or tricalcium aluminate (C_3A or $3CaO.Al_2O_3$) and unhydrated phase in cement clinker) to produce ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$).

Yu et al., (2013), further suggested that, as more ettringite are produced in the hardened concrete or mortar, it increases the rate of expansion caused by the ettringite within the hardened concrete or mortar. If the rate of expansion is higher than the strength of the hardened concrete or mortar, it then begins to develop micro-cracks. The micro-crack further develops into major cracks as more ettringite are formed. Also, the developed cracks increases the pores in the hardened concrete or mortar, which eventually increases the passage of the sulphate ions from the surrounding external environment, and hence increases the sulphate attack as well as reducing the strength, softening the concrete or mortar, changing the mass and at the same time increasing spalling or cracking due to increased pore structure in the building or civil structure (as shown in Fig. 2.0).

Fig. 2.0: Spalling of a Building due to Sulphate Attack.

Sulphate attack is controlled by the following factors such as; the type or composition of cement used in the concrete or mortar, the water to binder ratio, usage of other cementitious materials if possible, pore size in the hardened concrete or mortar, etc.

2.1.2 Salt Crystallisation

The product of oxidation of acidic greenhouse gases such as NOx and SO_x on mortar and concrete made from ordinary Portland cementitious materials react together to form different types of salts, which lead to cracking or peeling of rendered mortar or concrete. For instance, nitrates, nitrites and sulphate ions are produced during the photocatalytic oxidation of NOx and SO_x respectively. The oxidised NO_3^- and NO_2^- ions react Ca^{2+} ions in the hydrated cement to give compounds such as $Ca(NO_2)_2$ and $Ca(NO_3)_2$. Similarly, the SO_x

is photocatalytically oxidised to SO_4^{2-} which in the presence of moisture or water dissolves to form a strong acid (e.g., H_2SO_4). The sulphate ion formed (SO_4^{2-}) also react with calcium ions (Ca^{2+}) to give various salts of calcium including ettringite.

These calcium salts (i.e., $Ca(NO_3)_2$, $Ca(NO_2)_2$ and $CaSO_4$) are highly hygroscopic in nature, which means they can absorb moisture or water; that has the potential to affect the durability of the surrounding mortar or concrete. The solubility of the above salts means they can take part in a multiple cycles of dissolution and recrystallization (Shahidzaden-Bonn et al., 2008). Salt crystallization may lead to the destruction of porous materials as a result of formation of such salts.

Salt crystallization is defined as process whereby salt solution filling the pores in mortar paste or concrete materials crystallised due to changes in temperature and other environmental factors. Crystallization causes cracking and spalling damage to materials, masonry, or stone. It occurs due to changes in pressure of the crystallised salt within the pores of the mortar pastes or concrete. That is, if the pressure of the salt formed is greater than both the compressive and flexural strength of the mortar or concrete, a damage occurs to the ordinary Portland cementitious material.

Lee (2012) argues that, different theories have been put forward to explain underlying mechanisms involved in crystallisation of salts within mortars and concretes, but the most widely accepted theory is given by Scherer (2004). According to the theory proposed by Scherer (2004), salt crystallisation occurs as a result of a solute in a salt solution within the pores of a mortar paste or concrete becomes supersaturated, i.e., ready to precipitate or a sudden drop in temperature of the salt solution resulting in undercooling or freezing of the solution, which causes the solute particles to crystallise out in solution within the pores. This process results in changes in pressure between the crystals forming in the solution within the pore and the walls of pores in the mortar paste or concrete.

This pressure difference is known as crystallization pressure. Crystallization pressure can affect a material in three ways (Scherer, 2004). These are; (1) "capillary rise and evaporation," is an occurrence whereby a salt solution rises through porous material via capillary action until such a time that it becomes supersaturated as some of the salt molecules evaporate through the walls of the porous material, and if the crystallization pressure of a material goes above the tensile strength, it precipitates as sub-florescence and causes damage; (2) "cyclic wetting and drying," it occurs during a cyclic of short rains intersperse with equally short dry period where the rainwater supplies ions of salt solution into pores, which quickly dries off causing the solute particles of the salt to crystallise out of solution, thus causing damage to the mortar paste or concrete; and (3) late formation of ettringite or C-S-H growth during cement hydration. It is usually expected that an ettringite is formed as soon as cement begins to hydrate, however, it has somehow be observed some etrringite are formed in the hardened mortar or concrete often referred to as late ettringite or delayed ettringite, which causes a sharp change in the crystallisation pressure resulting in cracking or damage to the mortar paste or concrete.

According to Scherer (2004), crystallisation pressure can be written in equation (2.1) as:

$$P_w = \frac{R_g T}{V_c} \ln\left(\frac{Q^E}{Q^S}\right) = \frac{\gamma_{CL}}{r_p - \delta} \qquad \ldots \qquad (2.1)$$

Where:

P_w is the pressure exerted by the crystal on the surrounding solid matrix, or the crystallization pressure,

R_g is the gas constant, T is the absolute temperature,

V_c is the molar volume of the crystal,

Q^E is the solubility product,

Q^S is the lower solubility 40 product,

γ_{CL} is crystal/liquid interfacial free energy, and

r_p is pore radius, and δ is thickness of the film of solution lying between the crystal and the pore wall.

For very large crystals in the pores of the mortar paste or concrete, the crystallization pressure is expected to reach a maximum value; i.e., for large pore size, $Q^S = K$ and where $Q = Q^E$, equation (2.1), can be re-written as follows;

$$P = \frac{R_g T}{V_C} \ln\left(\frac{Q}{K}\right) \qquad \ldots \qquad (2.2)$$

Where:

P is the general term for a mechanical pressure,

Q is a solubility product, and

K is the equilibrium solubility for a macroscopic crystal

Equation (2.2) is referred to as Correnis equation.

It has been noted that the damage cause to buildings during salt crystallization is as a result of changes in ionic concentrations during the wet and dry cycles, that makes salt solution supersaturated (Shahidzadeh-Boon, et al., 2008; Flatt, 2002). The structure of the precipitated salts (Shajidzadeh-Boon, et al., 2008) within the pores in the mortar paste or concrete material (Scherer, 2004; Coussy, 2006) is closely related to the damage.

Studies have shown that salts such as calcium chloride and sodium chloride used to de-frost ice on roads or pavements during winter usually enters the pores within the concrete or mortar covering the road or pavement leading flaking or spalling (Chatterji and Thaulow, 1997; Valenza and Scherer, 2007a; Valenza and Scherer, 2007b; Thaulow and Sahu, 2004; Idorn, 1997; Haynes et al., 2008; Haynes et al., 2010). For instance, the effect of crystallising sodium sulphate salts like thenardite (Na_2SO_4) and mirabilite ($Na_2SO_4.10H_2O$) on road pavements have been studies by Scherer (2004); while Chatterji and Thaulow (1997) also studied the of crystal growth pressure of sodium thiosulphate pentahydrate ($Na_2S_2O_3.5H_2O$) on road pavements and other materials such as glass test tubes.

Other scientists have studied the effects of nitrates salts, oxalates salts, and acetates salts respectively on masonry and ceramics materials (Linnow et al. 2007; Ottosen et al., 2007; Dei et al., 1998). They conclude that, the aforementioned salts have negative effects on durability of masonry and ceramics materials. For instance, nitrate (NO_3) salts, have been shown to destroy buildings near agricultural lands (Ottosen et al., 2007). Despite the lack of sufficient published literature that discusses the potential for nitrate salts to cause damage in cementitious materials, the work made by Ottosen et al., (2007) advocates that $Ca(NO_3)_2$ might cause damage to cement and concrete products under acidic environment. Thus, it is worthwhile to investigate whether these salts form after oxidation of acidic greenhouse gases such as NO_x, SO_x and CO_2 can affect flaking of buildings via salt crystallization.

2.1.3 Carbonation attack of mortar and concrete

Carbonation occurs when buildings or civil structures containing cementitious materials are exposed to water or moisture and carbon dioxide (CO_2) in the atmosphere. During carbonation process, chemical make-up on the surface of buildings or civil structures changes, due to the alteration of cement-based materials' porosity and interior structure.

Also, hydrated products from reaction of ordinary Portland cement with water like C-S-H, CH, and unhydrated cement phases like C_3S and C_2S further react with CO_2 to produce calcite ($CaCO_3$) as summarised in equation 2.3 to 2.7 below (Papadakis et al., 1991).

$$Ca(OH)_2 \leftrightharpoons Ca^{2+} + 2OH^- \quad \ldots \quad (2.3)$$

$$Ca^{2+} + 2OH^- + CO_2 \rightarrow CaCO_3 + H_2O \quad \ldots \quad (2.4)$$

$$(3CaO.2SiO_2.3H_2O) + 3CO_2 \rightarrow (3CaCO_3.2SiO_2.3H_2O) \quad \ldots \quad (2.5)$$

$$((3Ca).SiO_2) + 3CO_2 + vH_2O \rightarrow SiO_2.vH_2O + 3CaCO_3 \ldots (2.6)$$

$$(2CaO.SiO_2) + 2CO_2 + vH_2O \rightarrow SiO_2.vH_2O + 2CaCO_3 \ldots (2.7)$$

However, carbonation is expected to occur concurrently with nitric acid attack and salt crystallization. Cement carbonation has been shown in experiments to reduce the rate of pollutant degradation (Chen and Poon, 2009;

Lackhoff et al., 2003). Studies have shown that carbonation of mortar pastes or concrete containing photocatalytic cementitious material decreases the ability of the photocatalytic material to degrade environmental contaminants such as atrazine. This is due to the fact that, carbonation on the photocatalytic mortar paste or concrete decreases its specific surface area, sorptivity, and as well as calcite overgrowth on surface of the photocatalytic mortar paste or concrete. While Chen and Poon (2009) investigated rate of photocatalytic degradation of NOx on surfaces of mortar pastes or concrete which has been carbonated, they observed the rate of photocatalytic degradation of NO_x on the surface of the mortar paste or concrete decreases due to the formation of $CaCO_3$ on the surface of the mortar paste or concrete.

2.2 Cement, Types and Uses

Cement is a material that easily binds with aggregates such as sand, stones or gravels and water together. Hence, is mostly used in the construction industries because it set, hardens rapidly and bind aggregates together in buildings, bridges and other civil structures. Dunuweera and Rajapakse (2018), has noted that cement is a powdery material that is made from calcination of clay and limestone above 1400°C in a rotary kiln. The calcine clay and limestone is then ground into fine powder to produce clinker and addition of gypsum to give cement (Schneider et al., 2011).

According to Elimbi et al., (2011), during the calcination process, there is a reaction between the various oxides in the clay and the limestone to form complex mixture. That is, the limestone ($CaCO_3$) reacts with aluminate oxide ($Al_3(SiO_3)_2$ and iron oxide (i.e., Fe_2O_3) during the calcination process at very high temperature to give rise to the following complex mixtures in the clinker;

alite – $(CaO)_3SiO_2$; belite – $(CaO)_2SiO_2$; tricalcium aluminate – $Ca_3(Al_2O_3)$, and ferrite, i.e., tetracalcium alumino ferrate – $Ca_4Al_2O_3Fe_2O_3$ with evolution of large amount of carbon (IV) oxide gas into the atmosphere. In addition to the aforementioned complex mixtures found in cement clinker, it also contains other minor elements such as K, Na, S, Si, Al, Mg and Fe (Dunuweerea and Rajapakse, 2018). Hence, Elimbi et al., (2011) and Dunuweera and Rajapakse (2018), have both suggested that, clinker a major component in Portland cement is known to contain four main oxides such as CaO, Al_2O_3, Fe_2O_3 and SiO_2 and using Bogue formulae, these four oxides can be represented as C, A, F and S. In this regard, Portland cement contain varying composition of each of the four main oxide, thus giving rise to different types of cement. Hence, the different compositions of the clinker in Portland cement has been summarised in Table 2.0 based on Bogue formulae or notation.

Table 2.0: Chemical Composition of Clinker Cement

Compound	Chemical Formula	Chemical Notation	%wt
Alite	$(CaO)_3SiO_2$ or $[3CaO.SiO_2]$	C_3S	55
Belite	$(CaO)_2SiO_4$ or $[2CaO.SiO_2]$	C_2S	20
Brownmillerite	$Ca4Al_2Fe_2O_{10}$ or $[4Ca.Al_2O_3.Fe_2O_3]$	C_4AF	8
Celite	$Ca_3Al_2O_6$ or $[3CaO.Al_2O_3]$	C_3A	10
Sodium Oxide	Na_2O	N	≤ 2
Potassium Oxide	K_2O	K	≤ 2
Gypsum	$CaSO_4.2H_2O$ or $[CaO.SO_3.2H_2O]$	CSH_2	5

Source**:** Dunuweera and Rajapakse (2018)

Variations in cement clinker composition results give rise to different types of cement such as; Portland cement, Siliceous (ASTM C618 Class F), Fly Ash, Calcareous (ASTM C618 Class C) Fly Ash, Slag cement, and Silica Fume (Portland Cement Clinker, 2017; Kosmatka, et al., 2002; Mamiouk and Zanewski, 1999; Holland, 2005). Table 2.1 summarises the different types of cement indicating chemical constituent such as SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, surface specific area (SSA) and specific gravity (SG).

As noted by Dunuweera and Rajapakse (2018), varying the percentage by weight composition of different chemical components in clinker has resulted in the production of over ten varieties of cement for different uses in the construction industry. The use of each of the ten different types of cement as well as the way and manner it is produced has been summarised in Table 2.2.

Table 2.1: Percentage by Weight Composition of Chemical Constituents in Clinker Used to Formulate Different Types of Cement

Component	Portland cement	Siliceous fly ash cement	Calcareous cement	Slag cement	Fume Silica
SiO_2	21.9	52.0	35.0	35.0	85 – 97
Al_2O_3	6.9	23.0	18.0	12.0	0
Fe_2O_3	3.9	11.0	6.0	1.0	0
CaO	63.0	5.0	21.0	40/0	< 1
MgO	2.5	0	0	0	0
SO_3	1.7	0	0	0	0
SSA(m^2g^{-1})	0.37	0.42	0.42	0.40	15 – 30
SG	3.15	2.38	2.65	2.94	2.22

Source: Kosmatka, et al., (2002) and Holland (2005).

Table 2.2: Types of Cement and their Uses

Type of cement	Properties and its uses	Reference
Ordinary Portland Cement (OPC)	Calcination of clay and limestone at a temperature of 1400°C to produce clinker, grind into fine powder and addition of small amount of gypsum. It is an excellent binding material for mortar and concrete of buildings and other civil works	Taylor (1997); Boye (1999)
Rapid Hardening Cement (RHC)	This type of cement contain high amount of lime for early setting and early strength is required.	Medeiros-Junior and Lima (2016); Korsch and Walther (2015); Matschei, et al., (2007)
Quick Setting Cement (QSC)	This type of cement contain reduced amount of gypsum and small amount of aluminium sulphate. It is used in formwork that needs to be completed very quickly such as in running or static water.	Uchida and Fukubayashi (1993)
Low Heat Cement (LHC)	This type of cement is prepared by melting a mixture of CaO, SiO_2 and less amount of Al_2O_3; quenching and grinding the molten mixture into an amorphous material that gives very low heat of hydration. It is used for large constructional works where thermal cracking must be avoided.	Nakatsu, et al., (1996); Novotri'y et al., (2016)
Sulphate Resisting Cement (SRC)	This type of cement contains very low $Ca_3Al_2O_6$ (i.e., below 6%) so as to reduce the formation of ettringite (i.e., $[(CaO)_6(Al_2O_3)(SO_3)]$ or C_6ASH_{32}) – hexacalcium aluminate trisulphate which is formed from a reaction between $Ca(OH)_2$ and $Ca_3Al_2O_6$. Thus weakening the concrete structure. This type of cement is used constructing retaining walls	Yu, et al., (2013)

Source**:** Kosmatka, et al., (2002) and Holland (2005).

2.3 Hydration of ordinary Portland cement

According to Taylor (1997), cement hydration is a chemical reaction between Portland cement and water. The reaction exothermic, i.e., it involves evolution of heat. The hydration process either start immediately water is added to cement or can take place from few hours through days to weeks. This reaction is between the different chemical constituents in cement such as C_2S, C_3S, C_3A, C_4AF, CSH_2 (gypsum) as well as other constituents like Na_2O and K_2O.

As noted by Scrivener et al., (2004), the reaction between water and Portland cement occurs at different speed to form different hydrated products as well as unhydrated products in the cement paste which are responsible for strength development in concrete and mortar. Generally, the authors argue that, each of the different chemical constituent in the cement react differently with water. For example, when water is added to Portland cement, belite constituent, i.e., dicalcim sulphate (C_2S) react with water molecules according to equation (2.7) below:

$$C_2S \quad + \quad H_2O \quad \rightarrow CSH \quad + \; CH \qquad \Delta H = -260J/g \quad \ldots \qquad (2.7)$$

In equation (1), CSH (Calcium silicate hydrate) account for early strength of concrete or mortar anytime cement reacts with water (Rodriguez, et al., 2017). According to Richardson and Gove's (1993), calcium silicate hydrate occupies a very large volume when the cement hydrate. Calcium silicate hydrate is gelatinous and has an amorphous structure. They further suggest that, C/S ratio of Portland cement varies from 1.3 to 2.1 and an average of 1.75.

Similarly, the C_3S constituent in cement also react with water molecules to form both calcium silicate hydrate (CSH) and portlandite (CH) with heat loss

(Taylor, 1997). Bullard et al., (2011), have suggested that, reaction of C_3S constituent in Portland cement with water takes place in four basic steps such as; (1) initial reaction period, (2) period of slow reaction, (3) acceleration period, and (4) deceleration period. According to Taylor (1997), the initial reaction phase of hydration of C_3S is an exothermic process, vigorous and take place within 30 seconds. This initial reaction of C_3S with water as shown in equation (3.2) continues until an equilibrium is reached. The equilibrium state is marked by an increase in the concentration of calcium, silicate and hydroxide ions. Stein (1972) has postulated that, equation (3) summarising activities that goes during the initial reaction phase begins to slow down very rapidly, i.e., step 2.

The mechanism for the slowing down the reaction in step 1 is a subject of intense scientific debate over the years (Bullard et al., 2011), and a lot of hypotheses have been proposed to explain this mechanism.

$$C_3S \quad + \quad 3H_2O \quad \leftrightharpoons \quad 3Ca^{2+} \quad + 2H^+ \quad + SiO_4^{2-} \quad + \quad 4OH^- \quad \ldots$$

(2.9)

It is within this context that, Gartner and Jennings (1987) have argues that C_3S constituents in Portland cement reacts very vigorously with water in the initial stages until the solution is saturated with the formation of C – S – H, thus forming a passivating hydrate layer around the un-hydrated cement grains. While, scientists such as Barret and Menetrier (1980) and Barret et al., (1983) both have suggested that a superficial hydroxylated CSH layer is formed around the unhydrated C_3S in contact with water and dissociation of the C – S – H ions within the superficially hydroxylated layer account for the slowing down of phase of the initial reaction in step 1.

However, other scientists in principle have accepted the hypothesis put forward by Barret and Menetrier (1980) as well as Barret et al., (1983) on how the formation of superficially hydroxylated layer of C – S – H around the unhydrated C_3S and its subsequent dissociation explain the slowing down phase of the initial reaction in step 1, they have offer alternative explanation on possible mechanism for the slowing down reaction in step 2.

This alternative explanation the authors contend that, is partly due to the steady balance between the slow dissolution of C_3S and the initial formation of C – S – H (Garrault and Nonat, 2001; Damidot and Nonat, 1994; Garrault – Gauffinet and Nonat, 1999; Damidot and Nonat, 1990). The aforementioned authors hypothesised that, although the C_3S constituent in the Portland cement dissolves very fast in step 1, their rate of reaction decreases during step 2 as a result of increase in the concentration of both calcium hydroxide and silicates during the dissolution of C_3S.

After the slow down the hydration reaction in step 2, the hydration of the C_3S enters the acceleration phase which is step 3. In this phase, the rate of hydration of C_3S Portland cement, which decreases in step 2, begins to increase as there is a nucleation as well as self-growth CSH crystals on the surface of the C_3S (Gartner et al., 2002). This phase is called the acceleration phase. A lot of theories exist to explain the acceleration phase of C_3S. Notably among them is that, the unhydrated C_3S surface forms a thin metastable layer of the CSH phase that have very high Ca to Si ratio, which reduces the amount of C_3S available for reaction with water molecules, thereby affecting the rate of hydration of the C_3S (Tianqi et al., 2021). However, as noted by Thomas et al., (2011), this metastable layer quickly breaks down leading to the formation nucleation and growth of CSH crystals, which Pommersheim and Clifton (1979) and Thomas (2007) used the reaction – diffusion theory to explain the acceleration phase of the hydration of C_3S.

Other scientists such as Thomas (2007), Thomas et al., (2011) and Thomas et al., (2009) have explained the acceleration phase of C_3S hydration using the precipitation of the CSH gel theory; whilst others like Nicoleau et al., (2016) argues that the acceleration phase of C_3S hydration can be explained by the dissolution theory. This reaction usually takes place between 4 to 8 hours.

The fourth step of the hydration of C_3S is the deceleration phase which occurs between 12 to 24 hours where the rate of hydration reaction slows down again after the rapid increase in the reaction rate in step 3. During this stage, there is a slow diffusion of water molecules across the CSH gel around the unhydrated C_3S grains, which result in further hydrolysis of the C_3S. According to Tianqi et al., (2021), the diffusion control theory can be used to explain the deceleration phase of C_3S.

Hydration of C_3A occurs very quickly in water and releases very large amount of heat. This large amount of heat released is usually referred to as the flash set (Taylor, 1997). In addition to the production of the flash heat, it also produces a poorly crystalline structure called calcium aluminate hydrate. As observed by Tianqi et al., (2021), the poorly crystalline calcium aluminate hydrate is fairly permeable and gradually changes into a more stable calcium aluminate hydrate as the hydration reaction progresses. The general chemical equation governing the hydration of C_3A is shown in equation (3.0) below:

$$C_3A \quad + \quad 6H \rightarrow C_3AH_6 \quad \ldots \quad (3.0)$$

Therefore, in order to control the rate of hydration of C_3A, gypsum is added to the clinker to slow down or modify the initial setting time of the C_3A, and with water present, the gypsum reacts with the C_3A to form ettringite (AFt). The rate for this reaction in equation (3.1) is much slower than the reaction between the C_3A and water in the absence of the gypsum:

$$C_3A \quad + \quad 3C\hat{S}H_2 \quad + \quad 26H \rightarrow C_3A\hat{S}_3H_{32} \quad \ldots \quad (3.1)$$

Corstanje et al., (1973) have observed that if all the gypsum in the C_3A has been used, then the remaining C_3A reacts with ettringite to give monosulphur hydrated calcium sulfoaluminate (AFm). The reaction of C_4AF constituents of cement in water is comparable to that of C_3A, i.e., they both hydrate to give a crystalline structure called calcium aluminate hydrate (as shown in equation (3.2).

$$C_4AF \; + \; 10H \quad \rightarrow \quad C_3AH_6 \; + \; CH \; + FH_3 \quad \ldots \quad (3.2)$$

According to Tianqi et al., (2021), another form of similarity between the hydration of C_3A and C_4AF is that, the C_4AF can also react with the gypsum during initial setting of C_3A to form ettringite, according to the equation (3.3) below:

$$C_4AF \; + \; 3C\hat{S}H_2 \; + \; 30H \rightarrow C_3A\hat{S}_3H_{32} \; + \; CH \; + \; FH_3 \quad \ldots \quad (3.3)$$

Tianqi et al., (2021) further argues that, just like C_3A hydration, when all the gypsum added to the clinker has been used, the C_4AF reacts with the ettringite.

From the above discussions, Bullard et al., (2011) have summed the important steps that hydration of cement takes place into the following:

- There is the dissolution of ions such as Ca^{2+}, SO_4^{2-} from the cement and its subsequent reaction with the water molecules;
- Adsorption of the dissolved ions from the cement onto the solid-liquid interface between solid cement and the water added;
- As more ions are adsorbed on to the solid-liquid interface, it leads to a complexation reaction. That is, each of ion pair begins to form complexes on the solid surfaces of the cement;
- There is a nucleation reaction where the hydrated products such as CSH precipitates on the surfaces of the unreacted solids. This precipitates begins to form centres for new growth. This process occurs as a result of difference in energy, etc.

While, Tianqi et al., (2021) have observed that cement phases such as C_2S, C_3S, C_3A and C_4AF have effect characteristic of cement. The authors have summarised such properties of cement that is affected played by each of the above-named phases in Table 2.3.

Table 2.3: The Role of Cement Phases on Properties of Portland Cement

Characteristics of Portland cement	Cement phases and other chemical constituents			
	C_3A	C_3S	C_2S	C_4AF
Rate of hydration	Rapid	Fast	Slow	-
Heat of hydration (Cal/gram)	207	120	62	100
Setting	Rapid	Quick	Slow	-
Strength				
Early Strength	Not much beyond Day 1	High up to 14 days	Low up to 14 days	-
Late Strength	-	Less late strength	High late strength	-
Resistance to Chemical attack	Poor	Moderate	High	High
Drying Shrinkage	-	-	Low	-

Source**:** Tianqi et al., (2021).

Tianqi et al., (2021), further argues that, in addition to C_3A, C_3S, C_2S and C_4AF phases in cement controlling cement characteristics, other chemical constituents in cement such as MgO, P_2O_5, TiO_2 among others control characteristics of Portland cement. For example, MgO and free lime controls soundness of cement, K_2O and Na_2O is responsible for alkali-silica reactions in cement; while the presence of Cr_2O_3, Mn_2O_3, TiO_2 and P_2O_5 in cement affect strength development and colour of the cement. To Tianqi et al., (2021) gypsum presence in cement is responsible for setting time, development of strength at early age and dry shrinkage.

2.4 Chemical Admixtures in Portland cement

Admixtures are chemical substances or materials that are added to cement to control hydration or alter properties of cement. Cement admixtures have been shown to possess cementitious properties (Jolioeur and Simard, 1998). In recent times, several scientists and engineers have suggested the need to modify properties of cement so as to ensure its durability (Bullard et al., 2011;

Richardson, 2008; Jennings, 2008; Shi et al., 2010; Roziere et al., 2009). These scientists and engineers argues that, addition of cementitious materials as admixtures is able to improve upon the durability as well as other mechanical characteristics of cement mortar or concrete. These properties include compressive strength, ductility, shrinkage and permeability among others (Feng et al., 2013).

Several materials have been identified to show cementitious properties and for that matter could be used as an admixture in modify properties of cement. Feng et al., (2013) have provided a list of materials that could be used as cement admixtures. These materials are; fly ash, steel slag, pozzolanic clays, rice husks, TiO_2, SiO_2, Fe_2O_3, carbon tubes or fillers just to mention a few (Nehdi et al., 2004; Shi et al., 2012; Bagheri et al., 2012).

According to Dunuweera and Rajapakse (2018), the size of the aforementioned admixtures to cement play critical role in the modification of the properties of Portland cement. The usual sizes of admixture cementitious materials added to cement ranges from macro-size to nano-sized particles. To scholars such as Dunuweera and Rajapakse (2018) as well as Feng et al., (2013), nano-sized cementitious materials are usually preferred as admixtures rather than the micro-sized admixtures. The reasons cited by them for their preference for nano-sized admixtures over the micro-sized admixtures are based on the fact that, it reduces the transport property, optimize the micro-structure, and decrease the volume instability of the cementitious material. However, other scientists such as Chen et al., (2007), Shaaban et al., (2020) and Gatto (2014) argued that, the size of the admixtures does not any role in modifying the properties of Portland cement they are added to. That is, addition of micro-sized admixtures to Portland cement does not affect the properties of cement.

2.4.1 The role TiO_2-ordinary Portland cement in resisting acid attack

The role of TiO_2 in Portland cement to prevent sulphate attack of mortars or concrete has been an intense scientific debate in recent times. For instance, scientists such as Chen and Poon (2009) and Jayapsalan et al., (2010) both suggest that adding nano-TiO_2 to ordinary Portland cement mortar contribute significantly decreases pores in hardened mortar paste. This is due to the fact that TiO_2 is an inert material which does not take part in the hydration process but rather fills any void spaces created during the hydration reaction. Also, the inert nature of TiO_2 in Portland cement does not allow a reaction between with the Portland cement phases, water as well as the incoming sulphate ions, hence is able to resist sulphate attack. These scientist further postulate that TiO_2 in Portland cement only provide nucleation sites for the hydration of TiO_2-Portland cement.

Civil structures and buildings are exposed to greenhouse gases (e.g., NO_x, SO_x, CO_2, VOCs, etc). As noted by Lee (2012), acidic greenhouse gases such as NOx and SO_x are strongly adsorbed unto the surface of the buildings or the civil structures, where in the presence of moisture from atmosphere or absorbed water, the adsorbed acidic greenhouse gases dissolve to form acidic solution, which later attacks the mortar or concrete structures.

According to Beddoe and Dorner (2005), the oxidation of strong acidic gases such as NOx and SOx adsorbed on surfaces of buildings and civil structures produce strong acid like HNO_3 and H_2SO_4. The aforementioned acid then reacts with the hydrated and unhydrated cement components which results in decalcification of CSH. Decalcification of hydrated and unhydrated cement components results in the rendered mortar paste or concrete to lose its binding capacity, thereby causing it to flake or spall.

As discussed in equation (1.5) of section 1.1 above, portlandite (CH) is easily attack by nitric or nitrous acid (produced from oxidation and dissolution of NO_x in water) to give calcium nitrate ($Ca(NO_3)_2$ or calcium nitrite $Ca(NO_2)_2$) salts respectively. It is an accepted fact that all nitrates or nitrite salts are soluble in water, hence calcium salts formed from the reaction between CH and the acid dissolves in water to form salt solution, which moves through the rendered mortar or concrete via capillary action and crystallise within the pores to cause cracks and eventual flaking or spalling of the rendered mortar paste or concrete as discussed in section 2.1.3 above.

The extent of damage from acid attack resulting from a reaction between oxidation of acidic greenhouse gases adsorbed on the surfaces of building as well as the water or moisture molecules depends on chemical composition of cement, pH or ionic concentration of acid produced (Beddoe and Dorner, 2005).

It is to address the contribution of the nature and composition of cement to acid attack, that Chen and Poon (2009), suggested that adding TiO_2 to the ordinary Portland cement produces TiO_2-climate smart Portland cement which through

photocatalytic reaction is able to oxidise NO_x and SO_x strong acidic greenhouse gases into NO_3^- and SO_4^{2-} which if allowed to stay on the surface of the walls, will dissolve to give HNO_3 and H_2SO_4 (strong acids). However, due to the hydrophilicity property of the added TiO_2, it is able to wash away the oxidised products such as NO_3^- and SO_4^{2-} in water or rain water. The mechanism involved in this reaction can be summarised in Fig. 2.1 below.

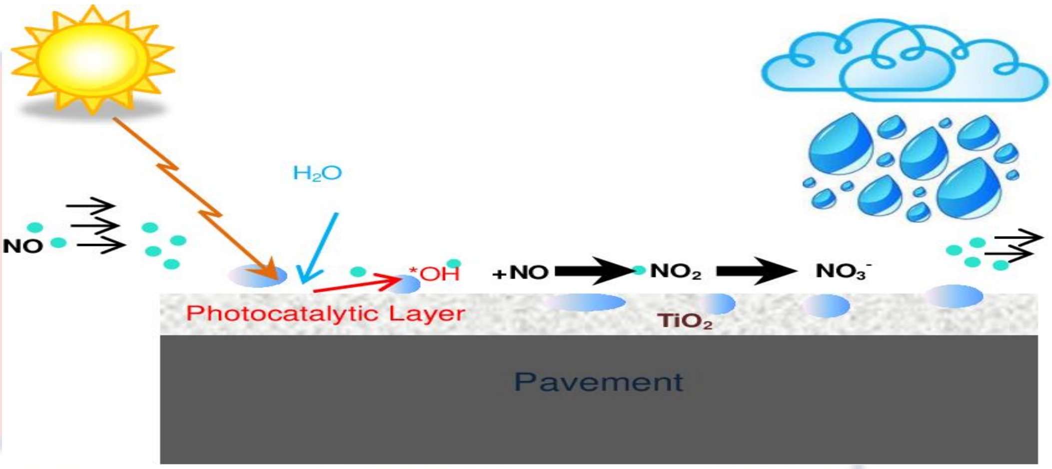

Fig. 2.1: Mechanism of Photocatalytic Degradation of Greenhouse Gases by TiO_2-ordinary Portland Cement.

2.5 Titanium dioxide as a climate-smart cementitious photocatalytic material

Portland cement has played key role as binder of both fine and coarse aggregates in the construction industries for decades. However, in recent times, there is a surge in the search of other materials with cementitious properties to improve properties of ordinary Portland cement used in the construction industry. It is within this context that in section 2.4 above, different materials including nano-sized TiO_2 had been identified by various scientist as materials with cementitious properties few (Nehdi et al., 2004; Shi et al., 2012; Bagheri et al., 2012).

According to Hamidi and Aslani (2019), the use of nano-sized TiO_2 as a photocatalytic cementitious materials in recent times has increased due to the following reasons; (1) it is compatible with other cementitious materials used in the construction industries such as cement without affecting the performance of these cementitious materials (Hanus and Harris, 2013), (2) as a semi-conductor, it has traditionally been used as a pigment in white paints (Chen and Poon, 2009), (3) its ability to self-clean the surfaces of civil structures contaminated with NO_x, PAHs and aldehydes (Addamo et al., 2008; Palmisano et al., 2011; Tsai amd Cheng, 1997).

To Chen and Poon (2009) TiO_2 is a smart photocatalytic cementitious material because its properties are in consonance with that of smart constructional materials, which is summarised as follows: (1) TiO_2 as a smart construction material should be able to make changes in shape so as to response to an external

stimuli; (2) it automatically actuate in responding to an external stimuli; (3) it automatically quantify the amount or extent of the external stimuli; (4) it has self-diagnostic properties; (5) it has the ability to automatically repair any damage; and (6) it automatically clean surfaces exposed to radiation.

Cassar, et al., (2007) defines a photocatalyst as a compound that facilitate the initiation and completion of a redox reaction. That is, the redox reaction occurs when the photocatalyst absorbs a photon of light energy necessary to cause an electron from the valence band to move into conduction band of the semi-conductor. In this case, the valence band acts as the oxidising agent or the electron donor, while the conduction band within the photocatalyst acts as the reducing agent or the electron acceptor. In the periodic table, most of the transition elements are semi-conductors, and as such can be used as photocatalyst. However, of all the oxides of transition elements in the periodic table that can act as photocatalyst, TiO_2 and ZnO are the most widely used.

Mechanistically, TiO_2 as a photocatalytic material, exerts its photocatalytic action in a series of redox reactions summarised as follows:

1. The TiO_2 as a semi-conductor have a conduction band which is devoid of electrons, a valence band which contains electrons and a forbidden band popularly referred to as an energy band gap (E_g);
2. If a photon of energy is absorbed which is the same or greater than energy band gap known as the forbidden band is absorbed by the TiO_2, a cementitious photocatalytic material, it is able to cause electrons from valence band and move it into the conduction band;
3. The electron that moved from the valence band creates a positive hole (h^+), which makes it a strong oxidizing agent; and
4. While the electron in the conduction band creates a negative hole (h^-), thus making it a strong reducing agent.

Cassar (2004) and Palmisano et al., (2011), have used the above processes to describe the photocatalytic action of TiO_2 in degrading H_2O molecules on its surface, as summarised in Fig. 2.2.

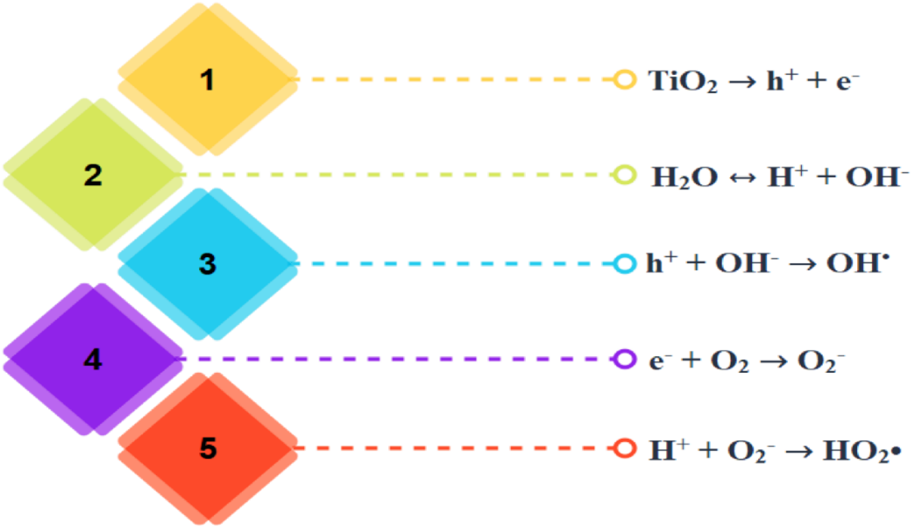

Fig. 2.2: Photocatalytic Reactions of TiO_2 in Degrading H_2O on its Surface.

Scientific studies by several scholars have found out that, photocatalytic degradation of water molecules by TiO_2 is dependent on the following factors (Palmosano et al. 2011; Cassar, 2004; Bellardita et al., 2018):

1. Absorption of appropriate amount or photon of sunlight by the photocatalyst;
2. Quick separation of charge separation after absorption of sunlight to avoid recombination of electron-hole;
3. Separation of redox reaction products from the surface of the photocatalyst;

Fujishma et al., (2000) argues that TiO_2 is most studied photocatalyst among all the metal oxides of the transition elements. Also, the aforementioned factors makes it suitable for use as a self-cleaning cementitious material. In addition, it is widely used because it is very cheap to obtain, chemically stable, non-toxicity, and have excellent as well as efficient photocatalytic activity.

To scholars such as Tsai and Cheng (1997), Vittoriadiamanti and Pedeferri (2013), Bellardiata et al., (2018) and Li et al., (2018), out of the three crystalline structures of TiO_2, i.e., anatase (distorted tetragonal structure), rutile (regular tetragonal structure) and brookite (orthorhombic structure), only anatase is most widely used as photocatalyst in cementitious materials due to the fact that its energy band gap between the valence band and the conduction band is 3.2eV, corresponding to 388nm wavelength and within the near UV region. Hence, the main application of TiO_2 as a photocatalytic cementitious material presented in literature has been summarised in Fig. 2.1.

2.6 Applications of TiO_2 cementious material

2.6.1 TiO_2 cementitious material as self-cleaning agent

Self-cleaning of civil structures by addition of TiO_2 a cementitious material to cement has in recent times being the subject of intense scientific investigation. For example, Liu et al., (2014) have suggested that self-cleaning of civil structures containing TiO_2 can take place either photocatalytic action (as shown in Figs. 2.3 and 2.4) or superhydrophilicity.

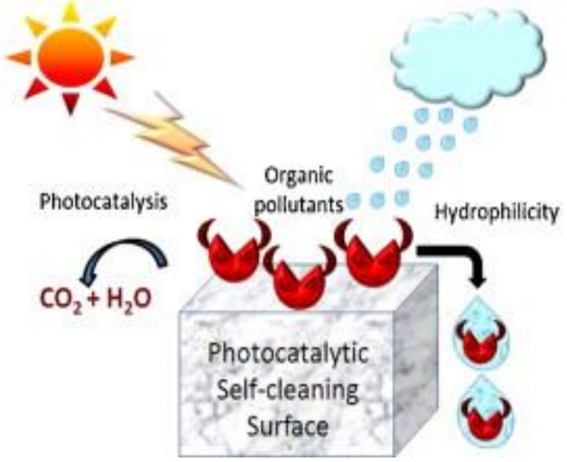

Fig. 2.3: Photocatalytic Induced Self-cleaning by TiO_2 in Civil Structures.

While Liu et al., (2014), have suggested that superhydrophilicity an inherent property of TiO_2 is responsible for self-cleaning of concrete or mortars made from TiO_2-ordinary Portland cement. The mechanism for removal dirt and other contaminants on surfaces of civil structures due to superhydrophilicity has been summarised in Fig. 2.4 below.

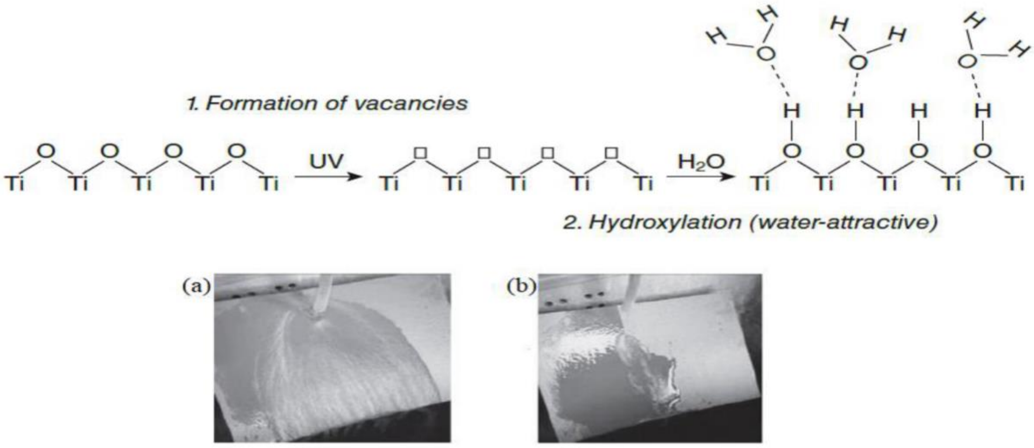

Fig. 2.4: Photo-induced Superhydrophilicity Mechanism of TiO_2 and its Practical Application. (a) A Plastic Covered with TiO_2 Sheet (b) A Plastic Container without TiO_2 Sheets

As shown in Fig. 2.4 above, superhydrophilicity ensure the presence of hydroxyl radicals which degrade any dirt particle on the civil structure. Banerjee, et al., (2015) have concluded that, self-cleaning action of TiO_2 in civil structures is through the simultaneous photocatalytic and superhydrophilicity action of TiO_2 cementitious materials.

2.6.2 TiO_2 cementitious material as an anti-microbial agent

Growth of microbes such as algae, bacteria, fungi and viruses on surfaces of buildings and other civil structures have been shown in several studies to affect the aesthetic beauty of such structures (Hegyi et al., 2021; Wang et al., 2017; Anibal et al., 2013). Protection of buildings against foul attack of microorganism on aesthetic properties as well as structural integrity of buildings have been achieved through the use of chemical pants.

However, in recent time, addition of titanium dioxide to cement pastes and mortar has been shown to an antimicrobial effect. This follows a work done by Matsunaga et al., (1988), that demonstrate the mechanism for photocatalytic action of TiO_2 on cytotoxicity of microorganisms such as *S.cerevisiae* (yeast), *Lactobacillus acidophilus* and *E.coli* (bacteria), and *Chlorella* vulgaris (green algae).

According to Matsunaga et al., (1988), the destruction of microorganism by TiO_2 is due to its photocatalytic action. The mechanism for the cytotoxic destruction of the microorganism begins when electrons in the valence band of TiO_2 absorbs a photon of energy and moves to the conduction band. This results in photo-generated electrons (e^-) and holes (h^+), which oxidises oxygen and water to form anionic radicals such as O^{2-} and $OH^{\bullet}$. The reaction between highly reactive free radicals such as; O^{2-}, $OH^{\bullet}$ and h^+ and microorganism on the surface of the rendered mortar or concrete resulting in the destruction of the microorganism as shown in Fig. 2.5 below.

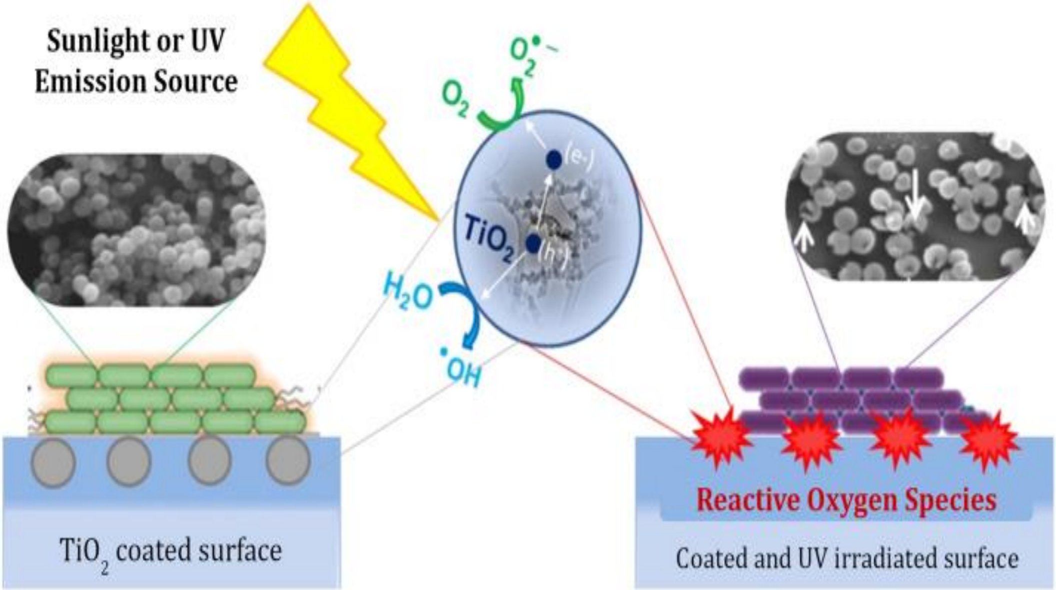

Fig. 2.5: Destruction of Microorganisms on TiO_2 ordinary Portland Cement Building Surfaces

According to Matsunaga et al., (1988), the underlying chemical equations for Fig. 2.5 have been summarised as follows:

$$TiO_2 + hv \rightarrow TiO_2 \left(e^-_{cb} + h^+_{vb}\right) \quad \ldots \quad (3.4)$$

$$O_2 + e^-_{cb} \rightarrow O^{2-} \quad \ldots \quad (3.5)$$

$$H_2O + h^+_{vb} \rightarrow OH^{\bullet} + H^+ \quad \ldots \quad (3.6)$$

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2 \quad \ldots \quad (3.7)$$

$$O^{2-} + H_2O_2 \rightarrow OH^{\bullet} + OH^- + O_2 \quad \ldots. \quad (3.8)$$

$$OH^{\bullet} + Organic + O_2 \rightarrow CO_2 + H_2O \ldots. \quad (3.9)$$

2.6.3 TiO_2 cementitious cement as an agent for purifying air

According to Chen and Poon (2009), the presence of NO_x, SO_x and other volatile organic compounds (VOCs) pollutes the environment and are also responsible for global climate change, i.e., greenhouse gases and their inhalation affect human health. Also, deposition of the aforementioned gases on buildings or other civil structures affect their aesthetic and structural integrity.

As a photocatalytic cementitious material, the TiO_2-ordinary Portland cement degrade the NO_x deposited on its surface and convert it into harmless NO_3^-. The mechanism foe this reaction has been summarised in equations (4.0) to (4.3) and Fig. 2.6 below.

$$H_2O + h^+_{vb} \rightarrow HO_2^{\bullet} \quad \ldots \quad (4.0)$$

$$NO + HO_2^{\bullet} \rightarrow NO_2 + OH^{\bullet} \quad \ldots \quad (4.1)$$

$$NO + OH^{\bullet} \rightarrow NO_2 + H^+ \quad \ldots \quad (4.2)$$

$$NO_2 + OH^{\bullet} \rightarrow NO_3^- + H^+ \quad \ldots \quad (4.3)$$

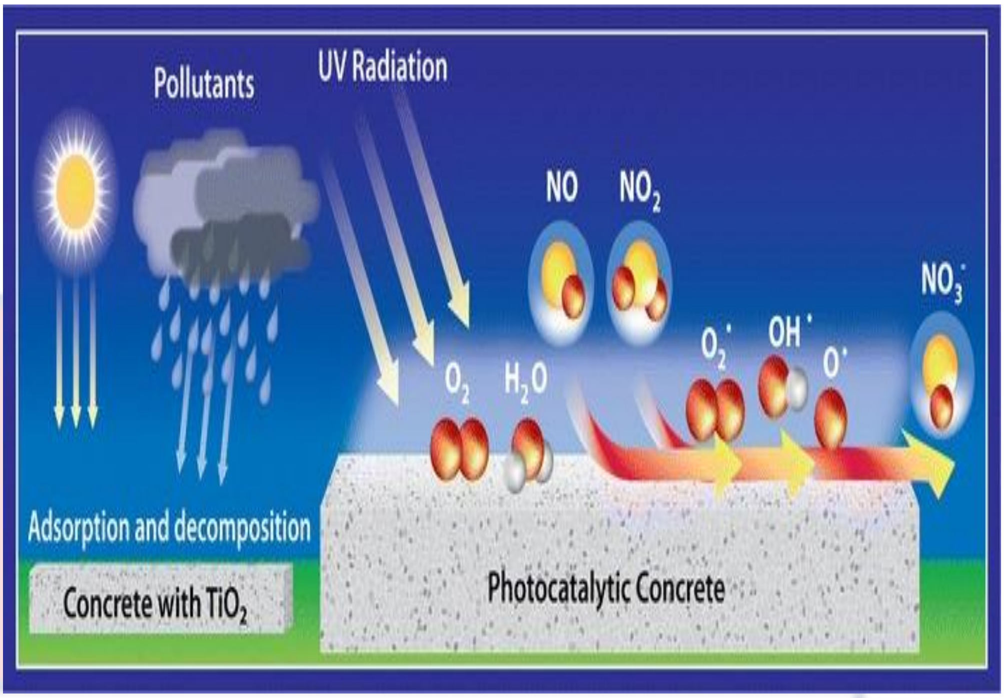

Fig. 2.6: Removal of NO_x on TiO_2-portland Cement Photocatalytic Concrete.

2.6.4 Mechanical and physical properties of TiO_2 cementitious material

1. Microstructural properties of TiO_2-Ordinary Portland Cement

Mechanical properties of cementitious material is affected by its adhesive and cohesive properties. Which is also dependent on its hydrated products and microstructure of hardened mortar or concrete cement composites (Li et al., 2018). Also, the amount of hydrated product formed in the cement composite determines the mechanical properties of the cementitious materials.

According to Nazari and Riahi (2011), addition of nano-sized particles such as TiO_2 to ordinary Portland cement improve the rate of hydration and the formation of CSH gel within cement paste microstructure that improves its mechanical properties. Nazari and Riahi (2011) further explained that, addition of 5% nano-sized TiO_2 to ordinarily Portland cement paste increased the amount of portlandite (CH) or $Ca(OH)_2$ by 50.1% as compared to the control at day 28;

while at the same time decreasing the ratio of ${C_2S}/{C_3S}$ by 17.7% within the 28 days period.

Foli et al., (2012) investigated performance of adding either nano-sized titania particles or micro-sized titania particles on the microstructure of ordinarily Portland cement mortar paste or concrete, and found that micro-sized titanium dioxide aggregates are smaller and have larger pore size as well as being better dispersed in the hydrated solution than the nano-titanium dioxide aggregates as shown in Fig. 2.7.

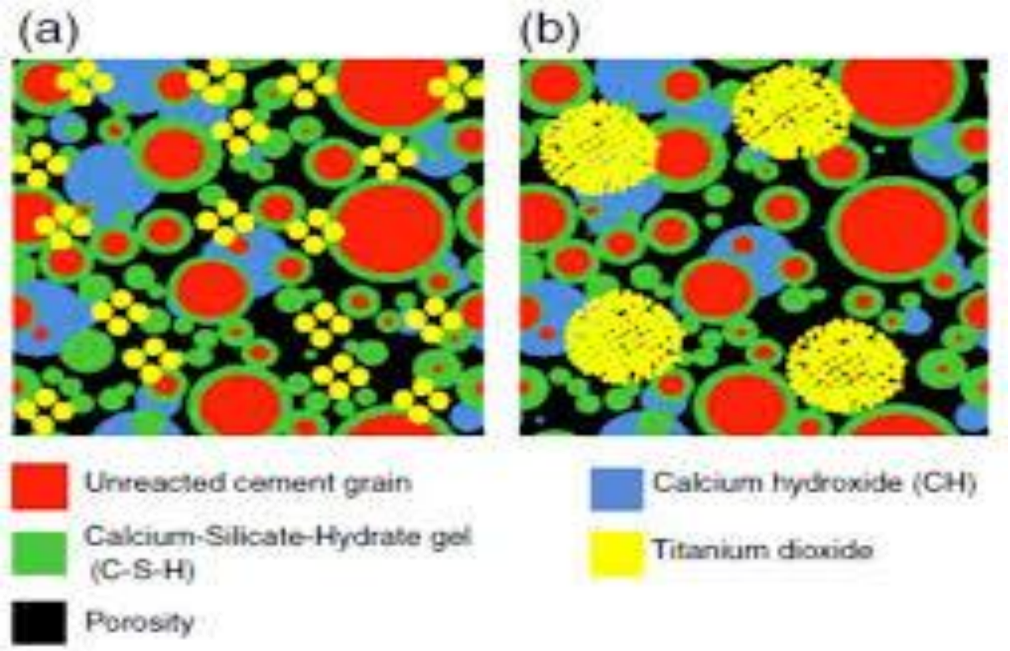

Fig. 2.7: Micro-structure of Mortar Paste or Concrete Containing (a) Micro-sized (b) Nano-sized Titanium Dioxide.

On the issue of whether the addition of nano-sized or micro-sized titanium dioxide to cement paste affect the microstructure of the hardened cement paste, scientists such as Salman et al., (2016) and Kurihara and Maruyama (2016), have all asserted that, addition of nano-sized titanium dioxide to cement paste affect significantly the microstructural composition of the hardened cement composite. That is, addition of nano-sized titanium dioxide to ordinarily Portland cement paste decreases the size of portlandite (CH) or the pore size of the hardened cement paste and thereby reduces the ability of rhodamine B (diameter ≤ 1.6 nm) to enter nano-TiO_2 clusters with difficulty as compared to micro-sized titanium dioxide hardened cement pastes (Foli et al., 2012).

2. Hydration of TiO_2-Odrinary Portland cement

As noted by Hamidi and Aslani (2019), pozzolanic activity of TiO_2 in ordinary Portland cement and how it affects hydration of TiO_2-Ordinary Portland Cement has been a subject of an intense debate among scientist. For example, scientists such as Yang et al., (2015), Li et al., (2017), Soleymani (2012), Salmani et al., (2016), Aslani (2015), Kurihara and Muruyama (2016) and Murata (1999) have all suggested that, TiO_2 plays an active role in cement hydration due to its pozzolanic activity; while other scientist have suggested that, TiO_2 is inert and as such has not pozzolanic activity in the hydration of TiO_2-ordinary Portland cement (Folli et al., 2010; Chen et al., 2012).

Zhang et al., (2015) and Chen et al., (2012) arguing in favour of the pozzolanic activities of TiO_2 in ordinary Portland cement hydration have suggested that, TiO_2 role is felt during acceleration phase of cement hydration process which increase the formation of portlandite ,i.e., calcium hydroxide (CH) as well as the CSH gel (Lawrence et al., 2000).

To Kurihara and Maruyama (2016), the pozzolanic role of TiO_2 in cement hydration depends on the cement matrix used, water/cement ratio, percentage of TiO_2 added to the cement as well as size of the TiO_2 added to the cement matrix.

3. Setting Time and workability of TiO_2-Ordinary Portland Cement

Several scientists have suggested that adding TiO_2 to ordinary Portland cement can improve both the setting time and workability of mortar paste. They argue that, adding TiO_2 to Portland cement decreases the initial setting time because of its specific surface area in the cement matrix as well as increase in the viscosity of the cement paste (Chen et al., 2012; Soleymani (2012); Zhang et al., 2015).

However, increasing dose of TiO_2 in ordinary Portland cement paste has been shown decrease the workability of the paste. This is due to the effect the size of the TiO_2, added to the cement paste which also affect the high specific area of the TiO_2 crystals added to Portland cement matrix (Jalal et al., 2013).

4. Compressive strength of TiO_2-Portland Cement

Compressive strength of cementitious materials determines the durability and toughness of civil structures such as buildings constructed from such materials (Hamidi and Aslani, 2019). Several researchers have suggested that adding nano-sized TiO_2 to ordinary Portland cement increases the compressive strength of cement structure through a reduction of its porosity (Rahim and Nair, 2016; Yang et al., 2015; Baoguo et al., 2015; Shekari and Razzaghi, 2011; Li et al., 2017; Salemi et al., 2014). For example, Salemi et al., (2014) argues that adding 2% by weight of nano-sized TiO_2 to ordinary Portland cement increases the compressive strength by 27% as compared to the control, i.e., cement composites without TiO_2.

It has also been observed by Hamid and Aslani (2019), that there is positive association between rate of hydration and compressive strength of cement composites. That is, as the rate of hydration for Portland cement containing TiO_2 increases, it lowers the pores within the TiO_2-cement based composites, thus making the TiO_2-cement based composite more compact, which eventually increases the compressive strength far more than the control.

On the other hand, Han et al., (2017) has suggested that, coating of nano-sized TiO_2 with SiO_2 before adding to the ordinary Portland cement tend to increase both the early and late compressive strength of cement composite. That is, the coated SiO_2 nano-TiO_2 in the cement is well dispersed in water than using only the nano-TiO_2. This is due to presence of negative charges on SiO_2-coated TiO_2 surfaces than ordinary nano-sized TiO_2 particles. Also, SiO_2 hinders crack formation, due to its nanocore effect; as such, adding SiO_2-coated TiO_2 will considerably increase the mechanical properties of the cement composites. SiO_2 coated TiO_2 role in ordinary Portland cement has been shown in Fig. 2.8 below.

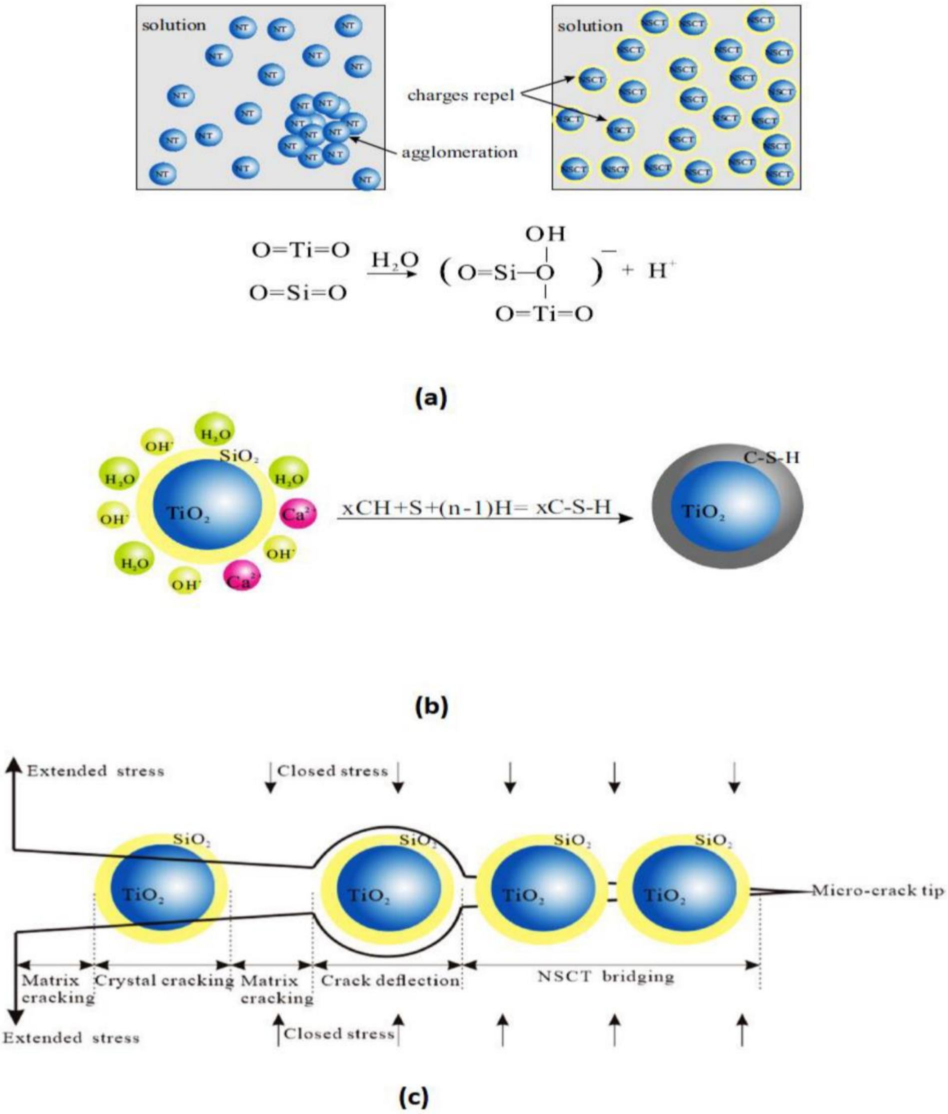

Fig. 2.8: The role SiO_2 Coated TiO_2 Portland Cement in Preventing Micro-cracks in Concrete or Mortar.

As a result of nano-core effect of SiO_2 shown in Fig. 2.8 (c), it has been established that, SiO_2 coated TiO_2 is able to prevent formation and propagation of cracks in concrete or mortar pastes that contain SiO_2 coated nano-TiO_2 ordinary Portland cement composites. That is, mechanical properties of cement composites containing SiO_2 coated nano-TiO_2 particles is improved greatly.

On the contrarily. Noorvand et al., (2013) have suggested that, addition of TiO_2 to cement composites does not improve upon the compressive strength but rather reduce the compressive after day 28, as TiO_2 restrict hydration of C_3S components in ordinary Portland cement. Li (2019) has also collaborated the findings of Noorvand et al., (2013), which suggest adding 10% TiO_2 to ordinary Portland cement composite result in 12% reduction in compressive strength of the cement composite after day 28 but rather improve the flexural strength of engineered cementitious composites such as addition of TiO_2 to ordinary Portland cement. Due to agglomeration of the TiO_2 particles within the cement paste.

5. Flexural strength of TiO_2-Ordinary Portland Cement

Flexural strength is a mechanical property that is used like the compressive strength to determine the toughness of a cementitious material. Several researchers have found that adding TiO_2 to Portland cement improves flexural strength of the cement composites just like the compressive strength (Li, 2019; Nazzari and Rahi, 2011; Rahim and Nair, 2016; Baoguo et al., 2015; Yang et al., 2015; Li et al., 2017; Han et al., 2017; Feng et al., 2013).

According to aforementioned scientists, adding TiO_2 to ordinary Portland cement improves flexural strength base on its nucleation effect and nano-core effect. The nucleation effect is as a result of high surface activity of the nano-TiO_2 particles during the hydration of TiO_2-ordinary Portland cement precipitate on TiO_2 nano-particles surfaces. The TiO_2 particles continue to grow forming conglomerate which contain TiO_2 nano-particles as nucleus. That is, as more and more of the TiO_2 nano-particles continue to disperse and grow in the cement matrix, it promotes compactness of the cement paste or concrete, thereby improving upon the microstructure of the cement composite (Han et al., 2017; Han et al., 2015; Jiang et al., 2018). While the nano-core effect is as a result of ability of the TiO_2 – nano particles to deflect micro-cracks in the cement compsites, thereby producing toughening effect in the cement matrix as shown in Fig. 2.8 above.

2.7 Geochemical composition of kaolin as an important source for TiO_2

Kaolin is a phyllosilicate mineral with chemical formula $Al_2Si_2O_5OH_4$ (Jamo and Abu, 2014). According to Bloodworth et al., (1993), kaolin deposits are classified as primary or secondary source respectively. Primary source kaolin deposits originate from either hydrothermal or residual deposits; while secondary source deposits are from erosion and transportation of clay minerals deposited in deltaic environment or it depends on the genesis of the source rock (Ekosse, 2005). The hydrothermal type of kaolin is formed from changes in the hydrothermal arrangement of alumino-silicate rocks (Bloodworth et a., 1993), while the residual is from weathering of igneous rocks due to heavy rains (Sayin, 2007; Harvey and Murray, 1997).

Geochemical properties of kaolin are used to define its industrial use (Cases et al., 1986; Cravero et al., 1997; Ekosse, 2000; Pinheiro et al., 2005; Siddiqui et al., 2005; López-Galindo et al., 2007). Based on geochemical characteristics of kaolin, it has found to be very useful industries such as; paper, pharmaceutical, cosmetic, etc. Similarly, because most kaolin deposits are interspersed with alumina group of minerals with high sulphate content, they are more suitable in the paper industry and production of white cement (Tagbor et al., (2015), attribute the pozzolanic properties of kaolin in the Anfoega deposits from Volta Region, Ghana to the presence of gibbsites. Thus establishing a strong correlation between geochemistry of kaolin and their pozzolanic properties. Similarly, in Table 2.4, Prasad et al., (1991) have categorised the various uses of kaolin according to their chemical composition.

According to Tagbor et al., (2015), pozzolanic activities of kaolin occurs when it is calcine between 500°C and 850°C which result in dehydroxylation of the kaolin to produce metakaolin; which react with $Ca(OH)_2$ to give pozzolan. The reaction between silica (SiO_2) and lime ($Ca(OH)_2$) gives calcium silicate hydrate (C-S-H), gehlinte hydrate (C_2ASH_8) and tetracalcium aliminate hydrate (C_4AlH_{13}). Also, the reaction between the silica and lime, lead to the formation of secondary calcium silicate C-S-H (Siddique and Khan, 2011; Singh and Garg, 2006). The secondary C-S-H reduces the total porosity and pore structures which improves the strength and impermeability of the hydrated product thus demonstrating the pozzolanic properties of kaolin as a good cementitious material. Similar observations have been made by Yanguatin et al., (2017), where in their scientific review of pozzolanic properties of kaolin, affirmed the strong correlation between mineralogical (i.e., geochemical composition) of kaolin and its pozzolanic activities. The authors argue that, pozzolanic properties of kaolin does not only depend on its percentage purity but its geochemical or chemical composition.

Table 2.4: Standard Chemical Composition Required for Industries that Uses Kaolin

Chemical composition	Standards for Industries that uses kaolin			
	Paper Coating*	Paper Filler*	Ceramics*	Pharmaceuticals & Cosmetics*
SiO_2	45 – 49	46 – 48	48 – 50	44.6 – 46.4
Al_2O_3	36 – 38	37 – 38	36 – 38	38.1 – 39.5
TiO_2	0.5 – 1.3	0.5 – 1.5	0.02 – 0.1	0.0 – 1.5
SO_4	-	-	-	-
K_2O	0.5 – 1.5	0.5 – 1.5	1.2 – 2.7	0.0 – 0.2
Fe_2O_3	0.5 – 1.0	0.5 – 1.0	0.6 – 1.0	0.1 – 0.2
MnO	-	-	-	-
K_2O_5	-	-	-	-
CaO	-	-	-	0.1 – 0.2
MgO	-	-	-	0.1 – 0.2
Na_2O	-	-	-	0.0 – 0.1
LOI	-	-	11.2 – 12.5	13.8 – 13.9

*The standards were derived from Prasad et al., 1991. Source: Prasad et al., (1991)

From Table 2.4, if geochemical properties of kaolin deposits show elevated levels of titanium dioxide and other chemical constituents like Fe_2O_3, they are not fit for use in industries such as; paper, ceramics, pharmaceuticals or cosmetic. Hence, for such kaolin to be used in the above-named industries, their TiO_2 and Fe_2O_3 content needs to be removed.

Studies have shown that TiO_2 removed during treatment of kaolin to make it useful in paper, pharmaceutical or cosmectic industries can be added to Portland cement to make climate – smart cement (Chen and Poon, 2009; Att-ur-Rehman et al., 2018). This is due to photocatalytic properties of TiO_2, makes it useful in the formulation of climate-smart cement as it is able to remove greenhouse gases and other urban pollutants deposited on buildings and other structures. It is also able to protect such building’s ability to resist environmental factors that affect structural integrity of buildings constructed with only ordinary Portland cement (Akyinyemi et al., 2014).

According to Monte et al., (2001) and Luz (1998), there are several ways of removing TiO_2 and Fe_2O_3 contents from kaolin. These include; dispersion, agitation, degritting, fractionation by centrifuge, flocculation, filtering and selective flocculation. However, according to Luz et al., (2000), removal rutile or anatase form of TiO_2 in kaolin using chemical leaching techniques is not economically feasible.

Other scientists such as Ciesla (2012), Asmatulu (2002), and Larroyd et al., (2002) have all suggested that, it is possible to remove TiO_2 and Fe_2O_3 from kaolin deposits using selective flocculation techniques. According to them, this technique is able to extract about 90% of TiO_2 and Fe_2O_3 content in kaolin, while obtaining more that 90% brightness of the treated kaolin. Scientist such as Franklin (1994), Ravishanker and Pradip (1995) and Pradip et al., (1991) have all confirmed that, selective flocculation techniques is able to remove 90% 0f TiO_2 and Fe_2O_3 contents in kaolin.

2.8 Formulation of TiO2-climate smart ordinary Portland cement

Foli (2010), has suggested that TiO_2 ordinary Portland cement, can be made by mixing fixed amounts of powdered TiO_2 and ordinary Portland cement together, stirring continuously to obtain a uniform mixture. TiO_2 added to the Portland cement is stable and inert in the mixture. That is, it does not react with any of the components in the Portland cement. Also, during hydration of the Portland cement, it does not take part in the hydration reaction, but as a material structural support.

2.9 Chapter Summary

This section of the reviewed relevant literature pertinent to this study. From the review, it became clear that much work has been done in the area of modifying inherent properties of Portland cement. The modification has been possible through the use either commercially synthesised nano-sized or micro-sized $TiO_{,2}$ and other materials. However, it emerged that, kaolin contains TiO_2 in quantities that can be extracted and used to produce climate smart Portland cement.

Hence, this study sought to formulate climate smart TiO_2 – Portland cement using TiO_2 extracted from kaolin in selected communities in the Central Region. Mechanical and physical properties of the formulated cement would be tested and compared with commercial synthesised TiO_2.

CHAPTER THREE

METHODOLOGY

3.0 Introduction

This study seeks to extract TiO_2 from locally available kaolin and use it to formulate TiO_2 ordinary Portland cement which can prevent flaking or spalling of mortar paste rendered in buildings and civil structures. Since ordinary Portland cement used in construction can absorbed gases and moisture from the atmosphere resulting in decalcification and increases its permeability and porosity.

The organisation of this chapter is as follows; description of the study areas, sampling techniques, collection, preparations and storage; materials, chemicals and equipment; determination of composition of oxides in kaolin, extraction of TiO_2 from kaolin; formulation of TiO_2-ordinary Portland cement, assessing its physical and mechanical properties of the formulated cement.

3.1 Description of the study areas, sampling techniques, collection, preparations and storage

Kesse (1985), asserts that kaolin can be found in several places in Ghana. However, large deposits of kaolin can be found in Teleku Bokazo – Aluku (Western

Region), Kibi (Eastern Region), Saltpond; Ekon; Waagkron and Assin Foso (Central Region) and Anfoega (Volta Region). Geology of kaolin deposits (Fig. 3.0) in the Central Region shows that, they were formed as a result of weathering of granite, phylite and schist (Kesse, 1985). Kaolinite, quartz and mica are the major minerals found in kaolin deposits in the Central Region, Ghana. For example, it has a kaolinite content of between 60 – 100 percent

(Kesse, 1985). There are about 610,000 metric tonnes of kaolin deposited in the region, which largely remains untapped for commercial purposes (Kesse, 1985).

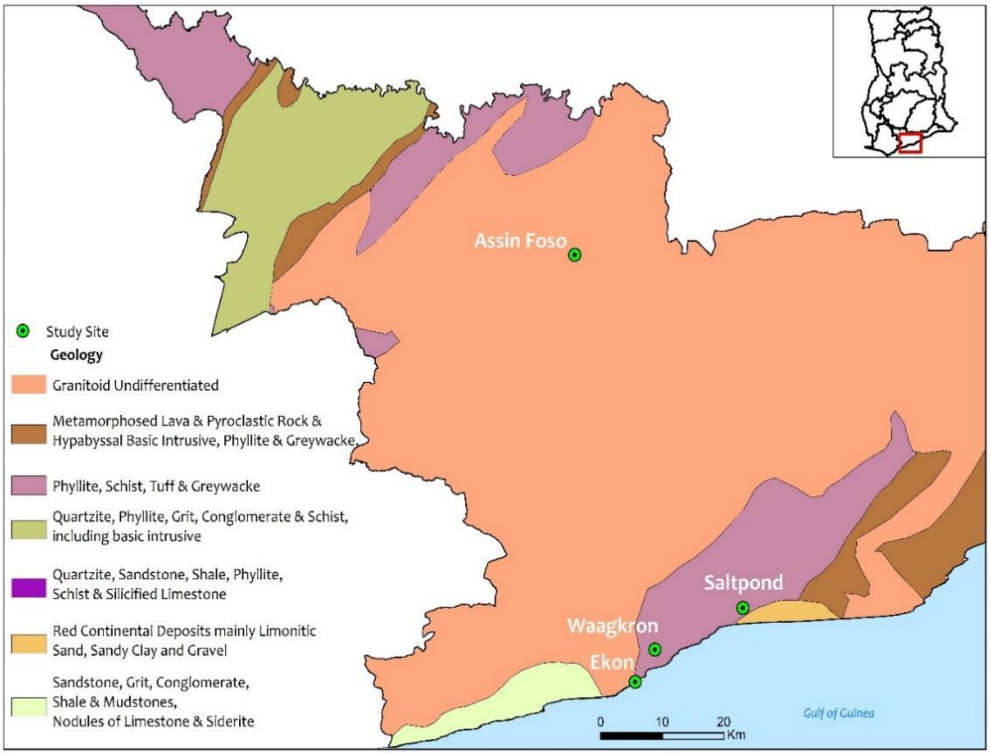

Fig. 3.0: Map of Kaolin Deposits and their Geology in the Central Region, Ghana.

This study adopted purposive sampling techniques in selecting the study areas (Fig. 3.0). Six hundred grams (600 g) of kaolin samples from each of the study areas were collected into a well-labeled containers and conveyed to Research Laboratory at Chemistry Department, University of Cape Coast for analysis.

The samples were air dried and materials such as stones and roots of trees were removed in the lab, milled, sieved through 90 µm mesh and stored in well-labelled plastics containers for analysis.

3.2 Materials, chemicals and equipment

3.2.1 Chemicals and reagents used in this work

1. 10% w/w Ammonium Hydroxide solution, Analytical Grade manufactured by BDH Chemicals, UK. This solution was prepared by dissolving 10 g of previously dried AR NH_4OH in 100 mL volumetric flask containing double distilled water.

2. Double distilled water from the Department of Chemistry

3. 1000 kg of Sodium polyacrylate. Analytical Grade manufactured by BDH Chemicals, UK

4. 1000 kg of Sodium Silicate. Analytical Grade manufactured by BDH Chemicals, UK

5. 250 g of CEREOX-BM-0002-1 powder containing boric acid. Analytical Grade manufactured by Fluxana Chemicals, Germany.

6. Alkyl hydroxamate. Analytical Grade manufactured by BDH Chemicals, UK.

7. 1000 kg of Polyacrylamide N – 9878 Anionic Powder. Analytical Grade manufactured by Yixing Bluwat Chemicals Co. Ltd, China.

8. 1000 kg N – 9806 Anionic Powder containing equal amount of Acrylamide and Acrylic acid. Analytical Grade manufactured by Yixing Bluwat Chemicals Co. Ltd, China.

9. 250 g of Magnessium Carbonate. Analytical Grade manufactured by BDH Chemicals, UK

10. 1 L Acetone, Analytical Grade solution prepared by BDH Chemicals, UK

11. 250 g of micro-sized Titanium Dioxide. Analytical Grade manufactured under the trade name Tioxide A-HR by Huntsman Tioxide Corporation, China.

12. 250 g of Iron (III) Oxide. Analytical Grade manufactured by BDH Chemicals

13. 50 Kg 32.5 R GHACEM Ordinary Portland cement. Manufactured by GHACEM Ltd.

14. 250 g of Sodium Sulphate. Analytical Grade manufactured by BDH Chemicals, UK. 10% w/w solution of Na_2SO_4 was prepared by dissolving 10 g of Na_2SO_4 in 100 mL volumetric flask.

15. 250 g of Rhodamine B dye. Analytical Grade manufactured by BDH Chemicals, UK. 0.001 M Rhodamine B dye was prepared by dissolving 4.79g Rhodamine B dye in 1 dm^3 volumetric flask using double distilled water obtained from Department of Chemistry, UCC

3.2.2 List of equipment

1. Vanta M XRF Machine, Model No. VMR, Waltham, MA, USA 02453 Manufactured by Olympus. Manufactured in August, 2018. Made in USA.

2. Empyrean XRD diffractometer. Model No. 7602 EA Almelo. Manufactured by PAnalytical B. V. Manufactured in February, 2013. Made in the Netherlands

3. Retsch Milling Machine. Model No. SK 100/C Gusseisen. Manufactured by Retsch GmbH. Manufactured in February, 2013. Made in Germany

4. Hunter Lab Ultra Scan Pro. Model No. UltraScan Pro. Manufactured by Hunter Lab. Manufactured in March, 2014. Made in Denmark

5. A flat die made from tungsten carbide of diameter 32 mm to 45 mm. The tungsten carbide die was made as accessories of Vanta M XRF Machine, Model No. VMR, Waltham, MA, USA 02453 Manufactured by Olympus. Manufactured in August, 2018. Made in USA. The die can hold 3 – 5 g of the mixed sample.

6. Fisons Magnetic Stirrer. Model No. SH – 11 – 4C. Manufactured by Hunter Lab in UK in March 2014.

3.3 Determination of composition of oxides in the samples using XRF

In the determination of composition of major oxides in the samples, 4 g of the sample as well as 0.9 g of the binder (CEREOX-BM-0002-1 powder containing boric acid) were respectively weighed together into 1000 mL beaker. The mixture (i.e., the kaolin sample and the boric acid binder) was poured into Retsch Milling Machine operating at a speed of 200 rpm and milled to give a homogeneous mixture.

Three grams of the milled homogeneous mixture (kaolin sample + binder) was poured into 32 mm die and pressed with 15 tons hydraulic press to give 32 mm pellet. This process has been summarised in Fig. 3.1 below. In order to avoid cross contamination, both the 1000 mL beaker used as mixing bowl and die were cleaned with 20 mL acetone after each measurement.

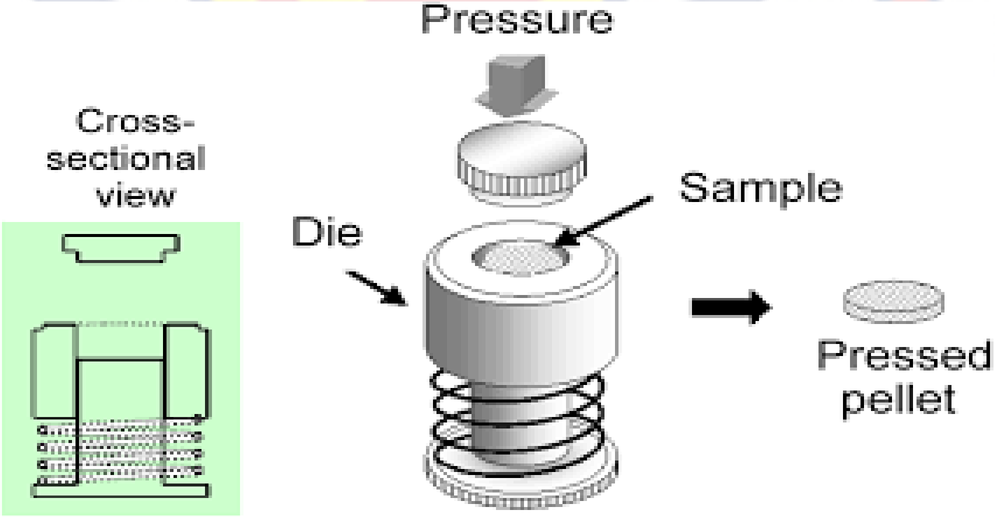

Fig. 3.1: Summarised Flow Chart for Preparing Kaolin Pellets for XRF Analysis Using a Flat Die.

The samples were loaded into Vanta M XRF Machine, Model No. VMR at the Ghana Geological Survey Authority for elemental analysis. Operating at 60 KV and 1 mA respectively to produce X-rays, which is incident on the samples for 10 mins, the emitted traditions from rhodium anode x-ray tube connected to scintillation detector operating at a current of 40 mA and voltage 40 mV is used in the detection of x-ray fluorescence from the kaolin samples.

3.4 Determination of mineralogical composition of the kaolin deposits

The determination of the mineralogical composition of the kaolin samples were carried out using X-ray diffraction (XRD) technique. In this technique, 3 g of the kaolin samples were analysed out using Empyrean XRD Diffractometer, model

No.: Empyrean series 2, CuKα1 (=1.54060 Å) radiation operating at 0.3/min scanning rate of 2 and between 5 – 40° signal mode, with 0.03 phase size at room temperature on XPERT-3 powder diffractometer fortified with a curved position-sensitive detector at the Department of Physics, University of Ghana, Legon. The configurations were verified at 40 mA, 40 kV, and tests were positioned on flat bottom holder.

3.5 Extraction of TiO_2 and purification of kaolin deposits in the study areas

3.5.1 Extraction of TiO_2

Selective flocculation techniques were used to extract TiO_2 from kaolin samples. In this method, 500 g of kaolin samples from each sampling point was added to 607 mL double distilled water in 1000 mL beaker and stirred continuously using a magnetic stirrer at a speed of 200 rpm. This was followed by addition of 2g of sodium polyacrylate and 2 g sodium silicate respectively to kaolin suspension, after which ammonium hydroxide (2 g) was added to the kaolin suspension to adjust the pH and centrifuged at 3100 rpm for 15 mins.

It was filtered through 53 µm sieve into 1000 mL beaker. The filtrate contain kaolin particles of size ≤ 53 µm. To the tailings, i.e., kaolin particles of size ≥ 53 µm, they were centrifuged at 1,800 rpm for 15 min after the addition of 1 g

of alkyl hydroxamate (6,493) as a surfactant. It was followed by the addition of 1.5 g medium anionic flocculant N-9878 (polyacrylamide) and high anionic flocculant N-9806 (50:50 mixture of Acrylamide and Acrylic acid) to both the filtrate and the tailings, stirred for 2 min and allowed to sediment for 30 min, after which both the overflow and the underflow were separated.

3.5.2 Determination of brightness of raw and extracted kaolin samples

One grams (1 g) of raw or extracted kaolin samples was put in a cuvette. The brightness of the sample were measured by measuring the intensity of light reflected back through 453 nm filter using Hunterlab UltraScan PRO instrument with $MgCO_3$ as reference material.

3.5.3 Determination of the concentration of TiO_2 before and after the extraction process

The concentrations of TiO_2 and Fe_2O_3 in the kaolin samples before and after the extraction process using selective flocculation techniques were determined using XRF and XRD techniques as described in sections 3.2 and 3.3 respectively of this thesis.

3.6 Quality Assurance/Quality Control

In this study, the batch technique of extracting titanium dioxide and iron (III) oxide from kaolin samples from the study areas were adopted. Under this technique, the kaolin in the tailings (i.e., $\geq 53\mu m$) was poured into 1,000 mL, to which 607 mL double distilled water from Chemistry Department, University of Cape Coast, 2 g sodium polyacrylate, 2 g sodium silicate and 2 g NH_4OH to adjust pH were respectively added; and stirred for 3 mins, centrifuged for 15 mins at 3100 rpm, and filtered. As discussed in section 3.4.1 above, 1 g alkyl hydroxamate surfactant, of 1.5 g medium anionic flocculant N-9878 (polyacrylamide) and high anionic flocculant N-9806 (50:50 mixtures of Acrylamide and Acrylic acid) were respectively added to the filtrate, stir for 2 mins and allow to settle for 30 mins. Decanted and both were kept (the overflow and underflow). The weight of titanium dioxide and iron (III) oxide recovered from each batch were respectively weighed. The percentage recovery for the titanium dioxide and iron (III) oxide were calculated together with their respective standard deviation.

In order to check efficiency of the method used in extracting titanium dioxide from the kaolin samples, recovery and reproducibility studies were also carried out. That is, 20 g of micro-sized analytical grade titanium dioxide (m-TiO_2 and Fe_2O_3) with trade name Tioxide A-HR manufactured by Huntsman Tioxide Corporation was used to spike 500 g of kaolin samples. The TiO_2 and Fe_2O_3 contents in the spiked kaolin samples were extracted using selective flocculation techniques as discussed in section 3.4.1 above.

The results obtained from the recovery studies have been presented in Table 3.0 below.

Table 3.0: Results of the Recovery Studies

Metal of Interest	Amount of 20 g TiO_2 recovered from spiked samples					Standard Deviation	Percentage Recovered
	1	2	3	4	Mean		
Assin Foso	19.76	19.34	19.59	19.81	19.63	0.21	96.3
Saltpond	19.92	19.96	19.94	19.51	19.83	0.22	98.3
Ekon	20.2	19.94	19.91	19.83	19.97	0.26	99.7
Waagkron	19.60	19.81	19.63	20.2	19.81	0.27	98.1

Source: Field Data (2022)

In the reproducibility studies, the percentage of TiO_2 recovered by spiking 500 g kaolin sample from the study areas with 20 g of micro-sized analytical grade titanium dioxide (m-TiO_2) with trade name Tioxide A-HR manufactured by Huntsman Tioxide Corporation using selective flocculation technique ranged from 96.3% to 99.7% with a standard error ± 0.11 to 0.14. The standard error was less than 1, suggesting that the selective flocculation technique for extracting TiO_2 in kaolin is reproducible (see Table 3.0 above). Similar results were obtained for the removal of iron (III) oxide from the kaolin samples in the study areas using the selective flocculation technique.

3.7 Formulation of TiO_2-Ordinary Portland cement

In this work, Ghacem Super Cool 32.5R Portland cement which conform to ASTM C 150 was used. Varying amount of TiO_2 extracted from kaolin and commercial analytical grade TiO_2 with trade name Tioxide A-HR manufactured by Huntsman Tioxide Corporation were respectively added to different amounts of

Ghacem Super Cool cement. Physical and chemical properties of the ordinary Portland cement as well as the TiO_2 used have been summarised in Tables 3.1 and 3.2 respectively.

Table 3.1: Chemical composition and Physical Characteristics of the Cement

Parameter	Value (% by weight)
SiO_2	21.56
Al_2O_3	6.67
Fe_2O_3	6.17
CaO	49.88
MgO	4.51
SO_3	2.75
K_2O	0.76
Na_2O	0.43
Loss on Ignition (LOI)	2.79
Specific gravity (g/cm^3)	3.18
Specific surface area (cm^2/g)	4,168

Source: GHACEM Specification Sheet (2020)

Table 3.2 Chemical and Physical Properties of TiO_2

Parameter	Extracted TiO_2 powder	Commercial Grade TiO_2 powder
Colour	White	White
Size (μm)	0.68	0.65
Purity (%)	96	99
LOI	0.15	0.13
Form	Anatase	Anatase

Source: Tioxide Data Specification Sheet (2020)

Four different formulations of TiO_2-Ordinary Portland cement were prepared based on the following percentages of TiO_2 added to ordinary Portland cement; i.e., 0% (control – it contains no TiO_2), 1% TiO_2, 3% TiO_2 and 5% TiO_2 respectively. To prepare 1% TiO_2-Ordinary Portland cement, 4.5 g of extracted TiO_2 kaolin as well as the commercial grade TiO_2 were respectively weighed into dry 2,000 mL beaker; and 445.5 g of ordinary Portland cement were respectively weighed and added to the beaker containing 4.5 g TiO_2 and placed on a magnetic stirrer and stir continuously for 2 hours at a speed of 200 rpm to ensure a homogeneous mixture, finally stored for further analysis. This process was repeated for the other percentages of TiO_2-ordinary Portland cement as shown in Table 3.3.

Table 3.3: Mix Proportions of Test Specimens

Sample Code	Water to cement ratio	Weight of Cement/g	Weight of TiO_2/g	Weight of Sand/g
C	0.50	450	0.0	1350
MET 1 (1% TiO_2)	0.50	445.5	4.5	1350
MET 2 (3% TiO_2)	0.50	436.5	13.5	1350
MET 3 (5% TiO_2)	0.50	427.5	22.5	1350
MCT 1 (1% TiO_2)	0.50	445.5	4.5	1350
MCT 2 (3% TiO_2)	0.50	436.5	13.5	1350
MCT 3 (5% TiO_2	0.50	427.5	22.5	1350

Key: MET = Mortar made from Titanium dioxide (TiO_2) extracted from kaolin;
MCT = Mortar made from commercially available Titanium dioxide (TiO_2)
C = Control, i.e., mortar made with only ordinary Portland cement
Source: Field Data (2022)

3.7.1 Determination of mechanical properties of formulated TiO_2-ordinary Portland cement mortar

3.7.2 Preparation of Mortar Samples

The mortar samples were prepared using the formulated TiO_2-ordinary Portland cement described in 3.6 above. From Table 3.3, a total of eight (8) mortar samples were prepared in the laboratory. For example, in the preparation of the control mortar sample, 1,350 g sand and 450 g of GHACEM 32.5R ordinary Portland cement were respectively weighed into 2000 mL capacity stainless steel mixing bowl and 900 mL double distilled water added to it. The mixture was thoroughly mixed together using a flat wooden blade to obtain a homogeneous mixture. Similarly, 1% TiO_2-ordinary Portland cement mortar paste was prepared by weighing 445.5g sand 4.5 g (as shown in Table 3.2) of either extracted TiO_2 or commercial grade TiO_2 was weighed and added to the sand in the 2000 mL capacity stainless steel mixing bowl, followed by addition of 900 mL double distilled water, and stirred continuously to obtain a homogeneous mixture. This procedure was repeated to make mortar samples containing 3% TiO_2, and 5% TiO_2 according weight of cement and sand described in Table 3.3 above as suggested by Shaaban et al., (2020).

The size of mould for samples to be used for both the compressive strength and flexural strength was 160 mm x 40 mm x 40 mm respectively; while the size

of the mould for samples to be used for shrinkage test, water of absorption, water vapour permeability and sulphate attack was 25mm x 25mm x 285 mm respectively. Each test was done in triplicate. After the mortar paste in the mould have set, they were removed, cured at room temperature for 24 hours.

3.7.3 Determination of mechanical properties of mortar samples made with the formulated cement

(i) Workability or Flow Test:

In this study, the slump flow test or the workability test was conducted in accordance with guidelines given by ASTM C1437-7 (ASTM C1437-7, 2007) in Appendix A. The slump flow test was carried out to evaluate the capabilities of TiO_2 extracted from kaolin and commercially available TiO_2 used to formulate the TiO_2-ordinary Portland cement in the slump retention. The density of the mixtures was obtained by weighing the fresh mortar into a standard flow cone with a specific volume.

(ii) Compressive Strength Test:

In this work, testing of compressive strength for the formulated TiO_2-ordinary Portland cement mortar containing different percentages of TiO_2 (i.e., 1%, 3% and 5%) extracted from kaolin as well as commercially available TiO_2 were carried out in accordance with the procedure described in BS EN 196-1(BS EN 196-1) in Appendix B using hydraulic testing machine operating at a controlled rate of 1350 N/s. The compressive strength for each of the sample was calculated using equation 3.0 below:

$$R_c = \frac{F_c}{1600} \quad \ldots \quad (3.0)$$

Where;

Rc = Compressive strength in mega Pascal, MPa;

Fc = The maximum load at fracture, in newton, N; and

1600 = The area of the platens or auxiliary plates (40mm x 40mm), in square millimetres, mm^2

(iii) Flexural Strength Test:

The flexural strength for the formulated TiO_2-ordinary Portland cement mortar containing different percentages of TiO_2 (i.e., 1%, 3% and 5%) extracted from kaolin as well as commercially available TiO_2 were carried out in accordance to BS EN 196-1:2005 (BS EN 196-1, 2005) in Appendix C using hydraulic testing machine operating at a controlled rate of 1350 N/s. The samples were tested at 1, 3, 7, 14, 21, 28, 56 and 90 days of age.

The flexural strength for each mortar sample made from the formulated TiO_2-odrinary Portland cement was calculated using equation 3.1 below:

$$R_f = \frac{1.5\ x\ F_f\ x\ l}{b^3} \quad \ldots \quad (3.1)$$

Where:

R_f = the flexural strength, mega Pascal (MPa);

b = the side of the square section of the prism, millimetres (mm);

F_f = the load applied to the middle of the prism at fracture, Newton (N); and

l = the distance between the supports, millimetres (mm)

(iv) Water Absorption:

This study adopted the method for testing water of absorption for concrete and mortar as described by Khatit and Mangat (1995). In this, method, the cured

mortar samples were air-dried and in an oven at 60°C for 48 hours. The samples were removed from the oven, cooled to room temperature and weighed.

The samples were soaked in double distilled water for 30 mins, 1 Hr, 3 Hr, 24 Hr, 72 Hr and 168 Hr, and re-weighed, respectively, after saturated surface had been dried. The masses of samples at each dipped time were calculated. Water absorption ratio, namely, water absorption mass per unit area, was obtained by dividing the increasing mass value by the surface area of samples.

(v) Shrinkage:

The dry shrinkage of cement mortar pastes was determined in accordance with ASTM. In this method, the cured samples were air-dried in the laboratory. The length and mass of the samples were measured at 1, 7, 14, 21, 28, 35, 42, 49, 56, 63, 70, 77 and 84 days of age.

(vi) Sulphate Attack:

Tittelboom, et al. (2013) and Ferraris, et al. (2018) made minor modifications to ASTM 1012 (ASTM, 2018) in order to determine sulphate attack on mortars and concrete products (Appendix C). For this study, the modified ASTM 1012 method was used to cut the one-year duration down to 90 days and moulded into 40 mm x 10 mm x 10 mm size using their modified ASTM 1012 method.

3.7.4 Removal of air pollutant in mortar paste containing TiO_2-climate smart Portland cement

The mortar paste for the removal of air pollutants by the formulated TiO2-climate smart Portland cement was cast into a 25mm x 25mm x 285mm mould using the data in Table 3.2 above. The test samples were all moulded in triplicate and removed immediately and covered with a plastic sheet to prevent moisture loss before being air-dried for 24 hours at room temperature (25 2°C).

Following the preparation of the mortar samples, 0.1 ml of (10 mM) Rhodamine B was applied on top to represent an organic air pollutant. The samples were exposed to sunlight to simulate real-world conditions, and the color intensity was measured after 24, 48, 72, and 96 hours. The ImageJ® software was used to analyze color removal efficiency in order to determine the best TiO2 dose and size (Elia et al., 2018).

3.8 Data Analysis

The results of the major oxide determination in kaolin samples from the study areas were subjected to multivariate statistics such as principal component analysis and liner regression.

3.9 Chapter Summary

This section of the thesis began with a brief introduction, description of the study areas where kaolin samples were collected. It discusses methods used in the extraction of TiO_2 from kaolin using flocculation techniques were used based on its cost and simplicity. The chapter highlight methods used in the determination of chemical composition of the slides. Methods for formulations of the various percentages on TiO_2-climate smart Portland cement, its mechanical and physical properties as well as its ability of the formulated TiO_2-climate smart to reduce Rhodamine B dye stains on mortar pastes.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.0 Introduction

This section f the thesis is made up of the results chemical and mineralogical investigation of chemical constituent of kaolin, levels of TiO_2 extracted from the kaolin deposits. The results obtained from the formulation of TiO_{-2}-climate smart Portland cement and its physical and mechanical properties are presented and discussed. Key findings made of this study are summarised at the end of the chapter.

4.1 Results of mineralogical composition of kaolin samples in Central Region, Ghana

The findings of the mineralogical composition of the kaolin deposits from the study areas are displayed in Table 4.0. It can be seen from Table 4.0 that, kaolinite, quartz, and anatasse are major minerals present in the samples, whereas magnetite, muscovite, phylites, and schists present in small amounts based on semi-quantitative methods for determining existence of such minerals in the samples adopted from Bukalo et al., (2017). That is, the sign (+++) or 3 is used to indicate the presence of a major mineral, while (++) or 2 shows a minor mineral, whereas (+) or 1 indicate that the mineral in question can be found in small concentrations in the samples. From Table 4.0 below, it can be seen that minerals present in kaolin from Saltpond and Assin Foso have same order of dominance i.e., kaolinite > quartz > calcite > anatase > magnetite > muscovite > phylites > schists; while a different order of dominance for the minerals were found in kaolin from Waagkron (i.e., kaolinite > quartz > anatase > calcite > magnetite > muscovite > phylites > schists) and Ekon (i.e., kaolinite

> quartz > anatase > magnetite > magnetite > muscovite > phylites > schists > calcite).

Table 4.0: Semi-quantitative Mineralogy of Kaolin Samples from the Central Region, Ghana

Study areas	Minerals in the kaolin samples Kaolinite	Quartz	Anatase	Magnetite	Muscovite	Phylites	Schists	Calcite
Saltpond	+++	+++	++	+	+	+	+	+++
Waagkron	+++	+++	++	+	+	+	+	++
Ekon	+++	+++	++	+	+	+	+	+
Assin Foso	+++	++	++	+	+	+	+	+++

Source: Field Data (2022)

Also, shown in Table 4.1 is the results of mean percentage concentration for each of the major oxides present in kaolin from the study areas. It can be seen from Table 4.1 that, percentage concentration of SiO_2 in kaolin samples varies from 58.94% (Saltpond) to 22.51% (Waagkron); while Al_2O_3 concentration from 28.68% (Saltpond) to 19.74% (Waagkron); confirming the richness of the kaolin samples in SiO_2 and Al_2O_3 respectively, and is consistent with findings by Jamo and Abdu (2014), Aroke and El-Nafaty (2014) as well as Shehu et al. (2017) who have suggested that kaolin from Malaysia and Nigeria are rich in SiO_2 and Al_2O_3 respectively.

Also, shown in Table 4.1, the order of percentage concentration of Fe_2O_3 in raw kaolin samples from the study areas is as follows; 2.253% ((Waagkron) > 2.20% (Assin Foso) > 2.14% (Ekon) > 2.10% (Saltpond). Similarly, the order of variation of concentration of TiO_2 in kaolin samples is as follows; 1.73% (Saltpond) < 2.72 % (Waagkron) < 6.45% (Ekon) < 9.21% (Assin Foso).

Table 4.1: Mineralogical Composition of Kaolin Deposits from the Study Areas

Study Areas	Sample Chemical Composition												Total
	Al_2O_3	SiO_2	SO_4	K_2O	TiO_2	Fe_2O_3	MnO	K_2O_5	CaO	MgO	Na_2O	LOI	
Assin Foso	22.25	47.72	0.24	2.37	9.21	2.20	0.20	2.48	0.21	0.36	0.10	12.24	99.96
Ekon	20.54	58.54	0.25	2.43	6.45	2.14	0.22	1.71	0.09	0.45	0.64	7.205	100.0
Saltpond	28.68	58.94	0.26	0.48	1.73	2.10	0.218	0.16	0.12	0.28	0.12	7.531	100.7
Waagkron	19.74	49.43	3.31	0.55	2.72	2.25	0.19	0.92	0.48	2.51	0.48	13.35	95.46
Capim River[a]	39.46	42.34	0.00	0.06	0.06	0.65	0.00	0.00	0.04	0.08	0.04	13.92	99.84
Pugu River[b]	36.93	46.37	0.00	0.11	1.07	0.00	0.00	0.00	0.15	0.09	0.15	15.22	99.94
Makoro River[c]	32.03	51.06	0.00	0.07	1.43	1.80	0.03	0.00	0.08	0.15	0.08	11.95	98.60
Kgwakgwe[d]	28.57	45.34	0.00	3.87	0.68	2.65	5.02	0.00	0.08	1.06	0.08	12.28	99.55
Malaysia[e]	37.76	57.63	-	1.80	0.605	0.86	-	-	0.35	0.60	-	-	99.91
Theoretical kaol	39.50	46.54	-	-	-	-	-	-	-	-	-	13.96	100.0

Note: 0.00 means below detection limit; 1 weight % = 10,000ppp; LOI means Loss on Ignition; [a]Costa et al., (1998); [b]Robertson et al., (1954); [c]Schwaighofer and Muller, (1987); [d]Ekosse, (2000); [e]Shehu et al., (2017); and [f]Deer et al., (1992)

In Table 4.1 and Fig. 4.0, Al_2O_3 concentration in kaolin samples from Central Region, Ghana is lower than kaolin found in Capim River in Bostwana (Costa et al., (1998). When Al_2O_3 concentration measured in kaolin deposits in the study areas were compared with other known kaolin deposits in Africa, Malaysia and theoretical kaolin, it was also found to be lower. This shows that, kaolin found in the Central Region, Ghana are not so much rich in alumina (Deer et al., 1992). Whilst the concentration of SiO_2 in the kaolin samples from this work were found to be comparable to values obtained by the following scientist who measured SiO_2 concentrations in other well-known kaolin deposits in

Africa such as Capim River, Pugu River, Makoro and Kgwakgwe (Ekosse, 2000; Costa and Moraes, 1998; Robertson et al., 1954; Schwiaghofer and Muller, 1987; Ekosse, 2001).

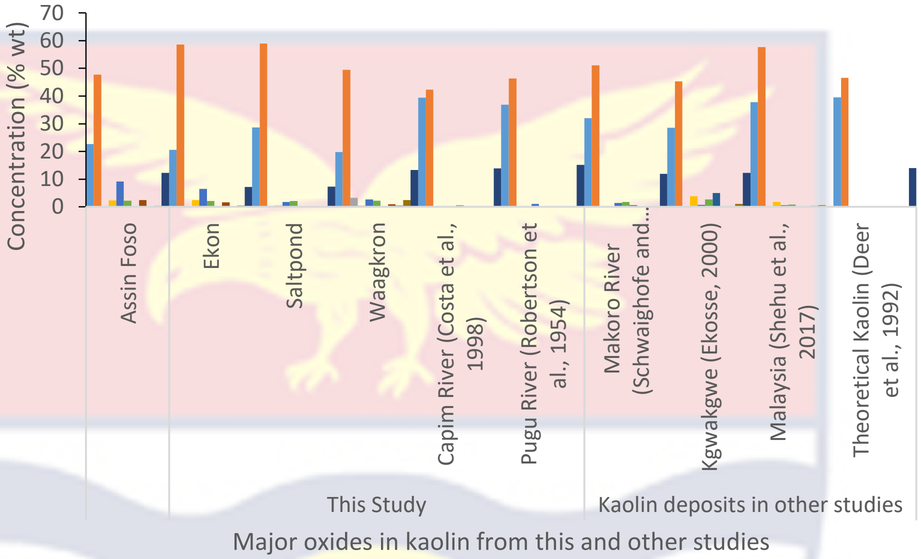

Fig. 4.0: A Graph Comparing Major Oxides found in Kaolin Samples from the Study Areas and other Kaolin Deposits in Published Literature

According to Prasad et al., (1991), the use of kaolin in industry depends to a large extent on its chemical and geochemical characteristics. Hence, in other to understand geochemical composition of kaolin deposits in this study, the data obtained from the determination of composition of major oxides in the kaolin in Table 4.1 were subjected to principal component analysis, whose results has been presented in Table 4.2 below to understand the underlying geology that influenced the concentration of the various oxides.

Table 4.2: Factor Analysis

Elements	Components		
	1	2	3
Al_2O_3	-0.523	- 0.451	0995
SiO_2	-0.648	- 0.405	- 0.522
SO_4	0.922	- 0.235	0.060
K_2O	- 0.273	0.858	0.321
TiO_2	-0.144	0.982	0.047
Fe_2O_3	0.182	0.256	0.917
MnO	0.495	-0.212	0.178
K_2O_5	0.018	0.995	- 0.087
CaO	0.991	- 0.092	- 0.002
MgO	0.947	-0.231	0.009
LOI	0.872	0.204	- 0.155

Source: Field Data (2022)

From Table 4.2, it can be seen that, three components are responsible for 85.2% of the total variance. The first component accounted for 42.2% of the total variance. Oxides in kaolin samples which contributed to component 1 are as follows; MnO, CaO, MgO, etc. That is, component 1 indicate that most of the kaolin may have originated from weathering of kaolinite, quartz, feldspars, calcite and smectite. Component 2, had a total variance of 30.5% with loadings from the following oxides; K_2O, TiO_2 and K_2O_5. The loadings in component 2 shows that kaolin may have been formed from weathering of muscovite, anatase, etc. The third component contains loadings from Al_2O_3, Fe_2O_3 and SiO_2 accounting for 12.5% of the total variance. This indicate weathering of aluminium-silicate minerals.

Kaolin are used in different industries. According to Prasad et al. (1991), the chemical and geochemical properties of kaolin have an impact on how it is used in industry. As a result, Table 4.3 contrasts the chemical makeup of kaolin deposits in the Central Region with a typical kaolin chemical makeup needed for various industries.

A comparison of the composition of major oxides found in kaolin deposits in this study to the respective standards required for industries such as; paper, ceramics, pharmaceuticals, comestics and paints shows that the SiO_2 content of kaolin samples from Assin Foso is suitable for use in paper coating while that of Waagkron kaolin can be used as a paper filler for papers. However, kaolin samples from Saltpond and Ekon can neither be used in paper industry or paper filler industry nor pharmaceuticals or comestics industries respectively. Furthermore, it can be seen in Table 4.3 that, the concentrations of Fe_2O_3, Al_2O_3 and TiO_2 from this study were found to be above the recommended values by the aforementioned industries. Hence, in order for kaolin deposits in Assin Foso, Saltpond, Ekon and Waagkron to be effectively used in paper coating or paper filler industries, TiO_2.

Table 4.3: Comparing chemical Composition of Kaolin in the Study Area with Standard Chemical Composition required for Industries that Uses Kaolin

Chemical composition	Standards for Industries that uses kaolin				This study			
	Paper Coating*	Paper Filler*	Ceramics*	Pharmaceuticals & Comestics*	Assin Foso	Ekon	Saltpond	Waagkron
SiO_2	45 – 49	46 – 48	48 – 50	44.6 – 46.4	47.7	58.5	58.9	49.3
Al_2O_3	36 – 38	37 – 38	36 – 38	38.1 – 39.5	22.3	20.5	28.7	19.7
TiO_2	0.5 – 1.3	0.5 – 1.5	0.02 – 0.1	0.0 – 1.5	9.21	6.45	1.73	2.72
SO_4	-	-	-	-	0.24	0.25	0.26	3.31
K_2O	0.5 – 1.5	0.5 – 1.5	1.2 – 2.7	0.0 – 0.2	2.37	2.43	0.48	0.55
Fe_2O_3	0.5 – 1.0	0.5 – 1.0	0.6 – 1.0	0.1 – 0.2	2.20	2.14	2.10	2.25
MnO	-	-	-	-	0.20	0.22	0.22	0.19
K_2O_5	-	-	-	-	2.48	1.71	0.15	0.92
CaO	-	-	-	0.1 – 0.2	0.21	0.09	0.12	0.48
MgO	-	-	-	0.1 – 0.2	0.36	0.45	0.28	2.51
Na_2O	-	-	-	0.0 – 0.1	0.66	0.10	0.64	0.19
LOI	-	-	11.2 – 12.5	13.8 – 13.9	12.24	7.21	7.53	13.35

Source: Prasad et al., (1991)

and Fe_2O_3 concentrations should be reduced to the standard as set in Table 4.3 above.

The use of kaolin for a specific industry depends on its ratio of Al_2O_3/Fe_2O_3 (Garcia-Valles et al., 2020). For example, kaolin with Al_2O_3/Fe_2O_3 greater than or equal to 5.5 mostly have high alumina (Al_2O_3) concentration and their colour is white, and they are very suitable for making of sanitary wares or use in refractory ceramics industries. On the other hand, kaolin whose Al_2O_3/Fe_2O_3 ratio is less than 5.5, have very high content of iron (III) oxide (Fe_2O_3) and their colour is reddish-brown. This type of kaolin is suitable for manufacturing of building materials such as bricks, tiles, etc. The results of Al_2O_3/Fe_2O_3 for kaolin in this study has been summarised in Table 4.4 below.

Hence, it can be seen in Table 4.4 below that, kaolin in Central region can be used in making refractory ceramics, pharmaceutical and paper industries because its Al_2O_3/Fe_2O_3 ratio is greater than or equal to 5.5.Chen and Poon (2009), have suggested that TiO_2 removed from the benefaction of kaolin in this study could be used to make climate – smart cement. This suggestion has been re-echoed by Atta-ur et al., (2018). They contend that because TiO_2 is photocatalytic, using it to create climate-smart cement and using the formulated cement in buildings would help the buildings self-clean themselves from the deposition of urban pollutants and improve the buildings' resistance to sulphate attack, which typically affects buildings made using only regular Portland cement (Chung, 2000; Akinyemi et al., 2014).

Table 4.4: Quantification of Fe_2O_3 and TiO_2 Levels in Kaolin Samples before and after Extraction

Sampling Point	% Weight/ kg of Fe_2O_3, Al_2O_3 and TiO_2 in the original kaolin samples			Amount of Fe_2O_3 Recovered		Amount of TiO_2 recovered		Al_2O_3/Fe_2O_3 ratio of original kaolin samples	Al_2O_3/Fe_2O_3 ratio after the extraction process
	Fe_2O_3	TiO_2	Al_2O_3	Weight/kg	% recovery	Weight/kg	% recovery		
Assin Foso	2.203	9.21	22.25	1.991	90.4	8.45	91.8	10.09	11.17
Ekon	2.141	6.45	20.54	1.885	88.0	5.82	90.2	9.594	10.90
Saltpond	2.102	1.73	28.68	1.855	87.5	1.49	86.1	13.64	15.21
Waagkron	2.253	2.72	19.74	1.985	88.1	2.47	90.8	8.762	9.945
Capim River[a]	0.650	0.06	39.46	-	-	-	-	60.71	-

Source: Field Data (2022)

4.2 Extraction and quantification of TiO_2 levels in kaolin deposits from the study areas

Table 4.4 compared the percentage of Fe_2O_3 and TiO_2 in the raw kaolin samples to the percentage of Fe_2O_3 and TiO_2 extracted from 53 μm raw kaolin samples from the study areas using selective flocculation techniques. The percentage of TiO_2 extracted using selective flocculation techniques varied as follows; 86.1% (Saltpond) ≤ 90.2% (Ekon) ≤ 90.8% (Waagkron) ≤ 91.8% (Assin Foso) respectively; whereas the percentage of Fe_2O_3 extracted followed the same trend, i.e., 87.5% (Salptond) ≤ 88.0% (Ekon) ≤ 88.1% (Waagkron) ≤ 90.4% (Assin Foso) respectively.

The ratio of Al_2O_3/Fe_2O_3 in Table 4.4, shows that kaolin samples in the study areas before the removal of Fe_2O_3 using the selective flocculation techniques varied from 13.64 (Saltpond) to 8.762 (Waagkron) kaolin samples; while after removal of Fe_2O_3, the ratio of Al_2O_3/Fe_2O_3 varied as follows; Saltpond (15.21) ≥ Assin Foso (11.17) ≥ Ekon (10.90) ≥ Waagkron (9.945) respectively.

Brightness of kaolin plays a crucial role in paper, ceramic or pharmaceutical industries. Impurities such as iron oxides and TiO_2 (i.e., anatase or rutile) affect the brightness of kaolin. As shown in Table 4.4, brightness of kaolin samples from this study improved greatly using selective flocculation techniques to remove Fe_2O_3 and TiO_2 from kaolin samples used in this study. That is, brightness of kaolin samples from Assin Foso and Ekon increased from 82% to 92% at pH 9.5 after using 200 g/ton N-9878 and N-9806 flocculants respectively during the selective flocculation techniques. Similar, observations were made for kaolin samples from Saltpond and Waagkron respectively.

4.3 Results of formulation of TiO_2-ordinary Portland cement

According to Lee (2012), differences in the manufacturing processes and treatments of TiO_2 particles by different manufacturers have resulted in the production of TiO_2-particles that are used as cementitious material with varying properties. TiO_2-cement are usually affected by particle/agglomerate size, dispersability, pH, physical and chemical properties of the TiO_2 used to formulate the cement. The results of such analysis has been presented in Table 4.5 below.

Table 4.5: Chemical and Physical Properties of Extracted TiO_2

Parameter	Extracted TiO_2 powder	Commercial Grade TiO_2 powder
Colour	White	White
Size (μm)	0.68	0.65
Purity (%)	96	99
LOI	0.15	0.13
Form	Anatase	Anatase
Surface Area (m^2/g)	3.8	3.89
pH	4.5 – 5.5 (45g/100 mL or 5% dispersion in water)	4.5 – 5.5 (45g/100 mL or 5% dispersion in water)

Source: Field Data (2022)

From Table 4.5 above, it can be seen that the physical and chemical characteristics of TiO_2 extracted from kaolin compares favourably with the technical data sheet on micro-sized analytical grade TiO_2 Tioxide A-HR manufactured by Huntsman Tioxide Corporation. As shown in Table 4.6 above, properties of TiO_2 extracted from kaolin compared favourably with the most widely used commercial grade TiO_2, four different formulations of climate smart TiO_2-ordinary Portland cement were made with varying percentage of TiO_2 as shown in Table 3.3 of section 3.6 above.

Based on the findings from Lee (2012), that the use of either TiO_2 extracted from kaolin or commercial grade TiO_2 to formulate TiO_2-cement have different effect on the performance of the formulated cement due to the different properties exhibited by either the extracted TiO_2 or the commercial grade because of the different processes or methods used to manufacture the TiO_2 particles. Hence, in this study, the physical, chemical and Bogue Potential composition for TiO_2-ordinary Portland cement made with TiO_2 extracted from kaolin and commercial grade TiO_2 were analysed with accordance in ASTM C 150 (Appendix E) and the results of such analysis have been presented in Table 4.6 below.

It can be concluded that, the results of physical properties of the formulated TiO_2-ordinary Portland cement in Table 4.6 above, is consistent with minimum standards as set in ASTM C 150.

Table 4.6: Physical and Chemical Properties of TiO2-ordinary Portland Cement

Parameter	Value (% by weight)
SiO_2	21.56
Al_2O_3	6.67
Fe_2O_3	6.17
CaO	49.88
MgO	4.51
SO_3	2.75
K_2O	0.76
Na_2O	0.43
Loss on Ignition (LOI)	2.79
TiO_2*	1 – 5%
Specific gravity ($g.cm^3$)	3.18
Insoluble residue	
Tricalcium Silicates (C_3S)**	51.30
Tricalcium Aluminate (C_3A)**	8.01
Dicalcium Silicates (C_2S)**	19.73
Tetracalcium Aluminoferrite (C_4AF)**	9.41

***** Varying amount TiO_2 added ranging from 1% to 5% based on data in Table 3.2 of section 3.7.1. **C=CaO, S=SiO_2, F=Fe_2O_3, and A=Al_2O_3.
Source: Field Data (2022);

4.4 Flow test for TiO_2-ordinary Portland cement

The results of workability or slump flow test of the TiO_2-ordinary Portland cement has been presented in Table 4.7. The flow of fresh mortar is defined as the ability of the mortar to be rendered smoothly on a given surface. This ability of the mortar to be rendered smoothly on any given surface is defined in terms of workability, which is also expressed in terms of its water to cement ratio.

Table 4.7: Mean Results of Slump Flow Test of Mortar

Mortar ID	Mean flow values			Water to cement ratio	Minimum Requirement ASTM C 109 Specification
	OPC with TiO_2 extracted from Kaolin	OPC with Commercial TiO_2	OPC		
Control	0	0	109	0.67	
MET 1 (1% TiO_2)	108	0	0	0.62	110 ± 5 mm
MET 2 (3% TiO_2)	107	0	0	0.64	
MET 3 (5% TiO_2)	106	0	0	0.66	
MCT 1 (1% TiO_2)	0	107	0	0.63	
MCT 2 (3% TiO_2)	0	106	0	0.65	
MCT 3 (5% TiO_2	0	105	0	0.66	

Note: OPC means ordinary Portland cement. Source: Field Data (2022)

As shown in Table 4.8 above, the mean values obtained from the flow table test for all the samples were found to be within the minimum requirement for ASTM C 109 (Appendix E) specification for mortars, i.e., 110 ± 5mm. It was also observed that, the flow test results for mortar specimens made with TiO_2 extracted from kaolin and analytical grade TiO_2 manufactured by Huntsman Tioxide Corporation were all within ASTM C 109 minimum specifications for mortars. That is, no statistically significant difference between the results of the two samples at $p \leq 0.05$ (two tail, 95% confidence interval). This trend is consistent with findings made by Joshaghani (2018), that addition of TiO_2 mortars tend to lubricate cementitious materials and sand in the mortar which increases the flow of the mortar.

Similarly, it was further observed that, mortar consistency; i.e., its flow were found decreased as the percentage of TiO_2 added increases. This observation is as a results of the hydrophilic nature of TiO_2 in the hydrated cement. As noted by Khalafalla et al., (2015), the reduction in mortar flow of cement containing higher percentages of TiO_2 is due to reduction in its flow diameter.

4.5 Strength test for TiO_2-ordinary Portland cement

4.5.1 Compressive strength test

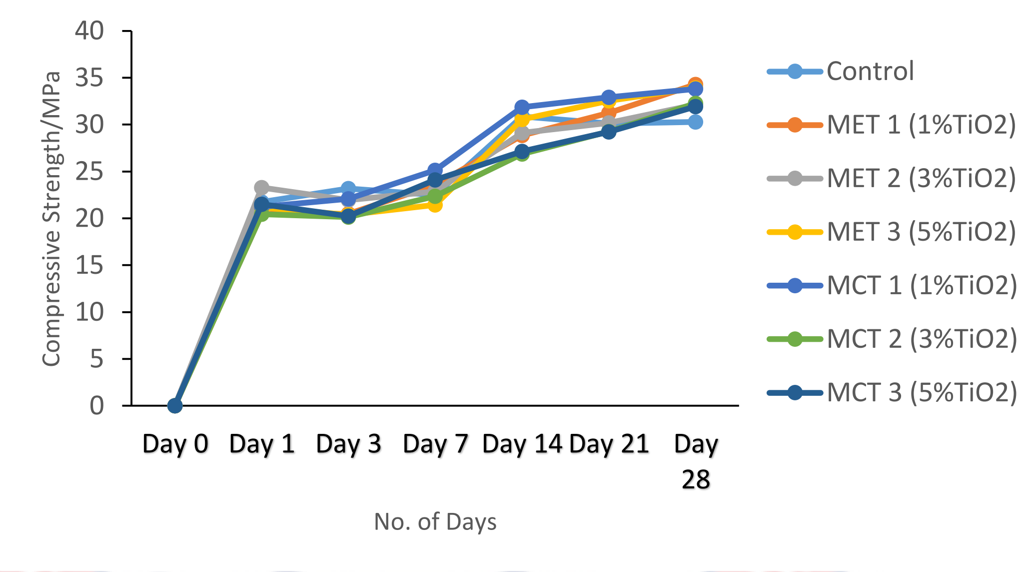

Fig. 4.1: Variation in Compressive Strength Results of TiO_2-Portland Cement Versus Days.

The compressive strength of the cured TiO_2-ordinary Portland cement mortar pastes were measured at 1, 3, 7, 14, 21 and 28 days and the results presented in Fig 4.1. It can be seen from Fig. 4.1 that, mortar specimen containing TiO_2 compressive strength was higher than the control mortar samples. Statistically no significant difference was found between compressive of mortar specimen prepared with TiO_2 extracted from kaolin and the mortar paste prepared with commercial TiO_2.

The compressive strength test results for the control (i.e., without the addition of TiO_2) as well as samples containing TiO_2 extracted from kaolin and commercially procured TiO_2 were found to satisfy BS EN 196 - 1 standard value in Appendix C.

A comparison of compressive strength test results between control samples and samples containing TiO_2 extracted from kaolin as partial replacement of the ordinary Portland cement was carried out with single factor analysis of variance test (ANOVA test) on data from day 1, day 3, day 7, day 14, day 21 and day 28. The significance level for the one way ANOVA test was set at 95% confidence level ($\alpha=0.05$) for samples containing 0% TiO_2, 1% TiO_2, 3% TiO_2 and 5% TiO_2 were compared.

The results of the one way ANOVA for mortar samples containing 0% TiO_2, 1% TiO_2, 3% TiO_2 and 5% TiO_2 respectively were all found to be higher than the significance level at 0.05. These results show that the compressive strength of each mortar sample at the curing days, i.e., from day 1 to day 28 are the same. That is, an increase in the percentage of TiO_2 added to the ordinary Portland cement did not affect strength of the mortar.

Compressive strength of mortar samples containing TiO_2 particles as partial replacement of the ordinary Portland cement was compared to control (Fig. 4.2) and found to be higher than control samples which contain only Portland cement. The noticed increased in compressive strength is as a result of pozzolanic properties of TiO_2, which lead to early and rapid development of the C-S-H gel as compared to the control samples. This observation is similar to findings made by Joshaghani (2018).

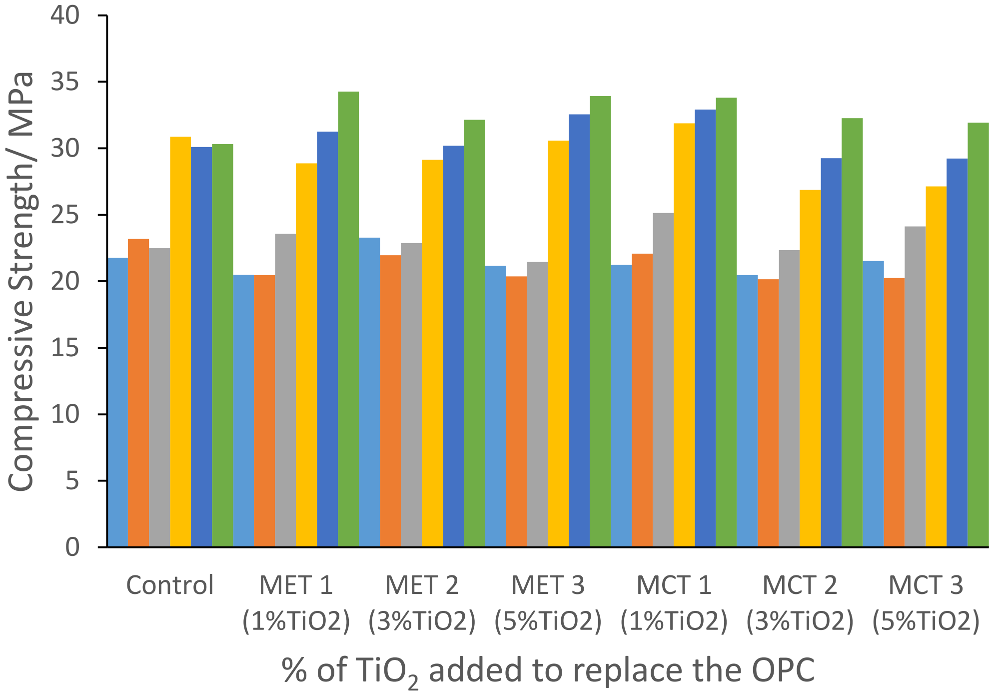

Fig. 4.2: A Graph Comparing the Compressive Strength of Control Samples with Samples Containing TiO_2.

4.5.2 Flexural strength

Results obtained from the flexural strength test for ordinary Portland cement without TiO_2 (control) and ordinary Portland cement containing TiO_2 as partial replacement has been summarised in Fig. 4.3 below.

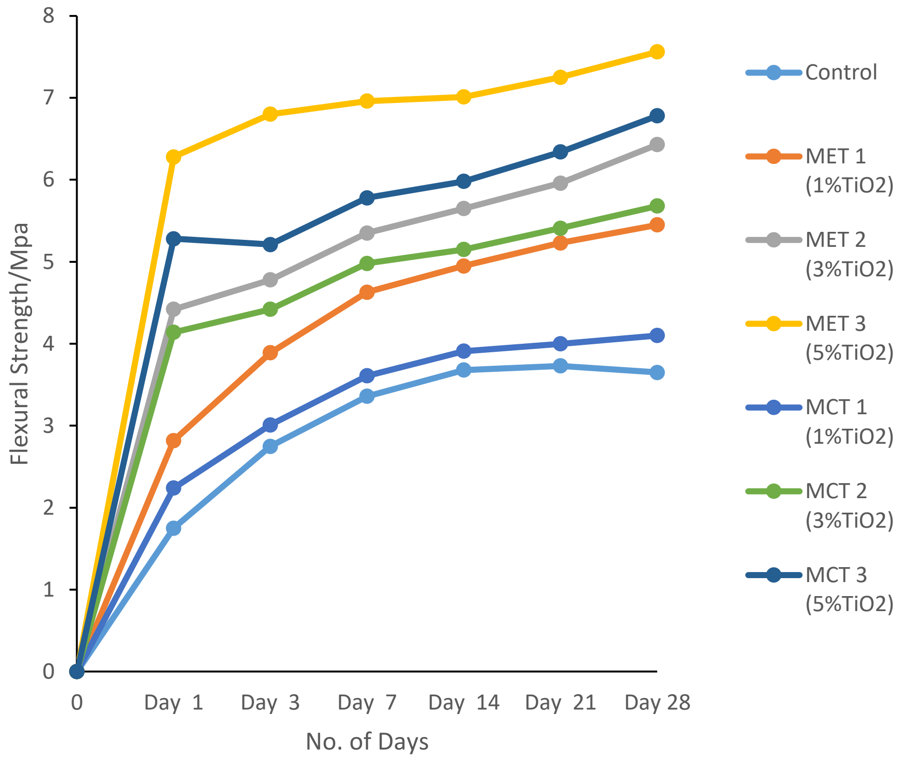

Fig. 4.3: A Graph Comparing Flexural Strength of Ordinary Portland Cement without TiO_2 to Ordinary Portland Cement Containing Different Percentages of TiO_2.

From Fig. 4.3 above, flexural strength for mortar specimens containing TiO_2 were found to be higher than the control which contain only ordinary Portland cement. The results presented in Fig. 4.3 is similar to findings made by Joshaghani (2018) who attributed such increase in the flexural strength to pozzolanic nature of TiO_2.

It can also be seen in Fig.4.3, flexural strength increases with increasing percentage of TiO_2 in ordinary Portland cement mortar paste from day 1 to day 28. However, there was slight decrease in the flexural strength when 1% TiO_2 and 3% TiO_2 respectively were added to the ordinary Portland cement at day 56 and day 90; while there was no increase or decrease in the flexural strength for the control, i.e., the ordinary Portland cement without TiO_2.

Furthermore, adding 5%TiO_2 extracted from kaolin or commercially grade to the ordinary Portland cement improves the flexural strength from day 1 to day 90. This results suggest that there is significant improvement in the flexural strength, which means that the toughness and crack extension resistance of the mortar have apparently been strengthened. This is consistent with the observation made by Ma et al., (2015), who argue that compressive strength and flexural strength of mortar or concrete products made from cementitious materials are useful indicators for determining toughness and crack extension resistance ability of cementitious materials.

A comparison of flexural strength test results between control samples and samples containing TiO_2 extracted from kaolin as partial replacement of the ordinary Portland cement was carried out with one-way ANOVA test for day 1 to day 90. The significance level for the one way ANOVA test was set at 95% confidence level (α=0.05) for samples containing 0% TiO_2, 1% TiO_2, 3% TiO_2 and 5% TiO_2 were compared. The results of the one way ANOVA for mortar samples containing 0% TiO_2, 1% TiO_2, 3% TiO_2 and 5% TiO_2 respectively were all found to be higher than the significance level at 0.05. These results show that the flexural strength of each mortar sample at the curing days, i.e., from day 1 to day 28 are the same.

However, flexural strength mortar pastes with 1% TiO_2 and 3% TiO_2 for day 56 and day 90 respectively decreased as compared to the control as well as when 5% of TiO_2 was added and cured for 56 and 90 days respectively for both mortar samples.

4.5.3 Water Absorption

The water absorption of mortar specimens determines its porosity. The water absorption is higher for mortar samples with larger pore size. The results of water absorption test is presented in Table 4.8 below.

Table 4.8: Results of Water Absorption versus Time

Sample ID	Water to cement ratio	Water absorption (%)					
		30 mins	1Hr	3 Hr	24 Hr	72 Hr	168 Hr
Control	0.5	2.45	3.30	4.17	4.61	4.95	5.29
MET 1 (1% TiO_2)	0.5	4.89	4.40	4.22	3.78	2.85	1.98
MET 2 (3% TiO_2)	0.5	4.98	4.84	3.86	3.35	2.53	1.62
MET 3 (5% TiO_2)	0.5	3.43	3.20	2.98	2.41	1.87	1.45
MCT 1 (1% TiO_2)	0.5	1.86	2.69	3.61	3.98	4.39	4.74
MCT 2 (3% TiO_2)	0.5	1.73	2.56	3.33	3.89	4.13	4.44
MCT 3 (5%TiO_2)	0.5	1.66	2.57	3.28	3.79	3.98	4.35

Source: Field Data, (2022)

As shown in Table 4.8 above, percentage water absorption values for TiO_2-portland cement mixtures were found to be much lower than the control. It can further be seen in Table 4.8, that the performance of TiO_2 extracted from kaolin in reducing the percentage of water absorption was slightly better than commercially available TiO_2 used in formulating TiO_2-portland cement. The improved performance of water absorption for mortar samples containing TiO_2 than the control samples may be due to its high reactivity as well as a filler effect of the TiO_2 particles. Hence, mortar pastes with TiO_2 - ordinary Portland cement has smaller total specific pore volumes than control mortar samples.

As noted by Ma et al., (2015), water absorption is an important technical index used to measure the durability of cementitious materials. This is due to the fact that; durability of cementitious materials is dependent on the ability of water or other fluid to penetrate the micro-structure of either the concrete or mortar product of the cementitious material (Zhang and Zong, 2014). That is, water absorption of cement-based materials is related to its pore structure. The larger the number of pores in the cement-based material the higher the water absorption value (Baoguo et al., 2015). Hence, as shown in Table 4.8, mortar samples containing different percentages of TiO_2 had much lower water absorption ratio than the control sample.

4.5.4 Sulphate Attack

The microstructure of the mortar or concrete product made from ordinary Portland cement is altered by the absorption of sulphate ions. Chen et al. (2012), are of the view that adding TiO_2 to ordinary Portland cement mortar or concrete changes the pore structures and mechanical properties of the cementitious material, enhancing its ability to resist absorption of sulphate ions.

As such, this section of the thesis investigated the ability of TiO_2-cement to resist movement of sulphate ions across its pores. The results obtained from such investigation has been presented in Fig. 4.4.

The absorption of sulphate ions from 10% Na_2SO_4 solution by mortar specimens made from ordinary Portland cement containing varying amount of TiO_2 showed a slight increase in length of the mortar specimen as well as the control specimens from day 1 through day 7 to day 42 (Fig. 4.4). However, after day 56 to day 84, MET 3 (i.e., 5% TiO_2 extracted from kaolin) no change; whereas the other mortar specimen (MET 1, MET 2, MCT 1, MCT 2 and MCT 3) as well as the control mortar specimen observed slight changes in length from day 56 to day 84 respectively.

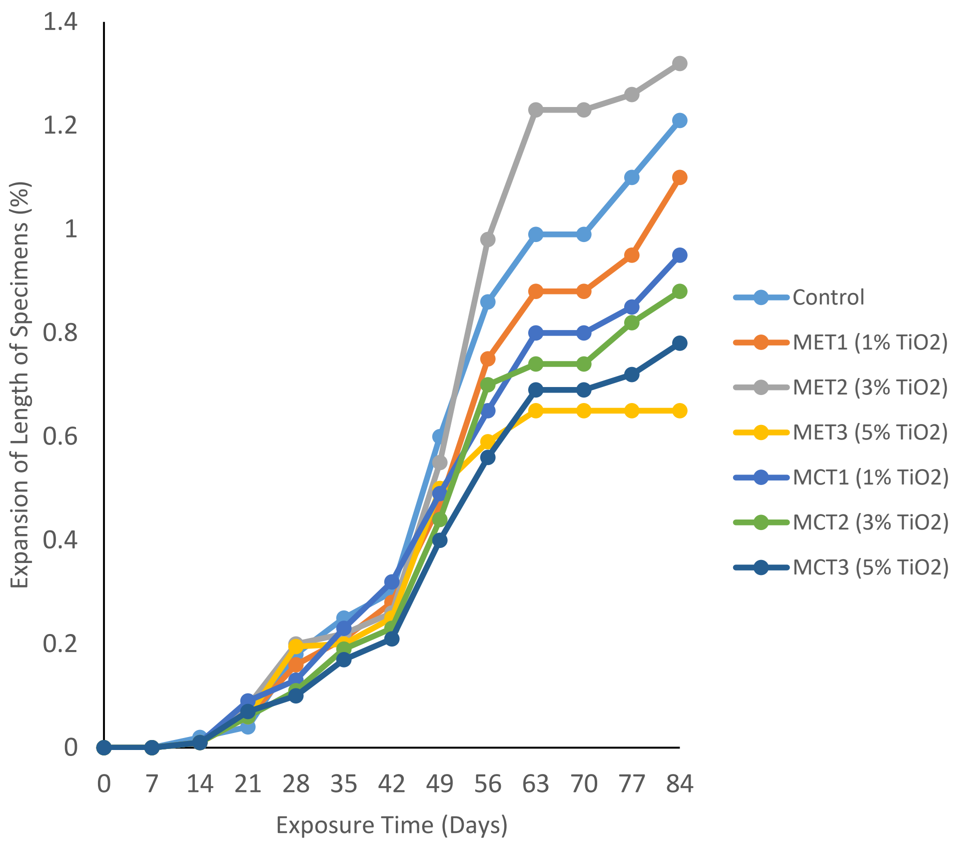

Fig. 4.4: A Graph showing effect of Absorption of Sulphate ions on Length of TiO_2 Containing Ordinary Portland Cement Mortar Specimens.

Also, no statistically significant difference between rate of absorption of sulphate ions to cause changes in length of mortar specimens containing 1% and 3% of TiO_2 extracted and mortar specimen containing 1% and 3% commercial grade TiO_2; while significant statistical difference was observed between the performance of mortar specimen containing 5% TiO_2 extracted from kaolin and that of 5% commercial grade TiO_2 resist absorption of sulphate ions to cause changes in its length. Mehta (1986), has explained this observation as the presence of limited number of pores within mortar specimens containing varying amount of TiO_2. According to Mehta (1986), the TiO_2 in the mortar paste fills most of the available pores in the mortar paste leaving a small number of pores to absorb the sulphate ions, i.e., TiO_2 containing ordinary Portland cement mortars are more resistant to expansion.

Similarly, Atta-ur-Rehman et al., (2018) have postulated that, absorption of sulphate ions from 10% Na_2SO_4 solution by mortar pastes or concrete made with ordinary Portland cement leads to an increase in its mass. The results of determination of changes in mass of mortar specimens containing various percentages of TiO_2 extracted from kaolin as well as commercially procured TiO_2 ordinary Portland cement as well as the control specimens immersed in 10% $NaSO_4$ solution is presented in Fig. 4.5 below.

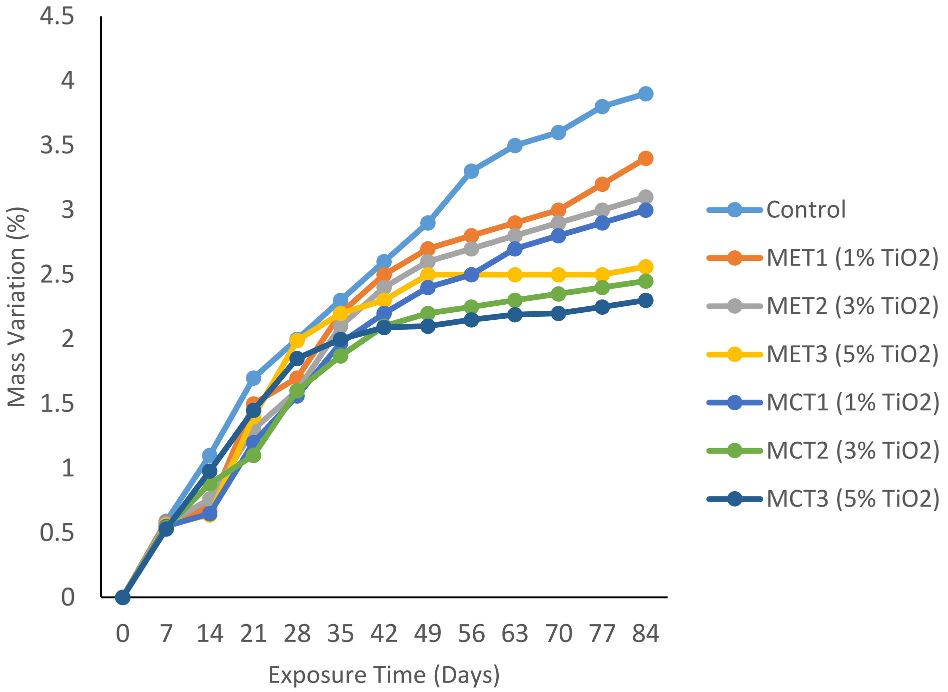

Fig. 4.5: A Graph showing Percentage Variation in Mass of TiO_2 containing Ordinary Portland Cement Mortar Specimen Immersed in 10% Na_2SO_4 Solution

From Fig. 4.5 above, it can be seen that, there is a slight increase in the mass of both the control mortar specimen and those containing different percentages of TiO_2 from day 1 to day 84. This observation has been noted by the following scientists, such as Siddique and Khan (2011), Bouikni et al., (2009) and Menéndez et al., (2013), who have suggested that addition of TiO_2 to ordinary Portland cement mortars or concrete refine the pores as well as reduce the capillary pores and their connectivity, thereby reducing their ability to absorb sodium sulphate solution.

4.5.5 Shrinkage

Shrinkage of mortar pastes or concrete made from cementitious materials is a key parameter that determines the durability of civil structures made of ordinary Portland cement. The results of linear shrinkage of the ordinary Portland cement mortar paste containing varying amounts of TiO_2 extracted from kaolin as well as procured commercially together with control specimen have been summarised in Fig. 4.6 below.

It can be seen in Fig. 4.6 above that, significant change in length of both the mortar specimens containing different proportions of TiO_2 added and the control with number of days of exposure. The results in Fig. 4.6 is similar to findings by Shaaban et al., (2020) that shrinkage of mortar and concrete specimens increases with the exposure duration. However, in the case of mortar specimen MET 3 which contained 5% TiO_2, the variation in length due to linear shrinkage was observed to have increase from day 7 to day 42 after which no further change in length was observed.

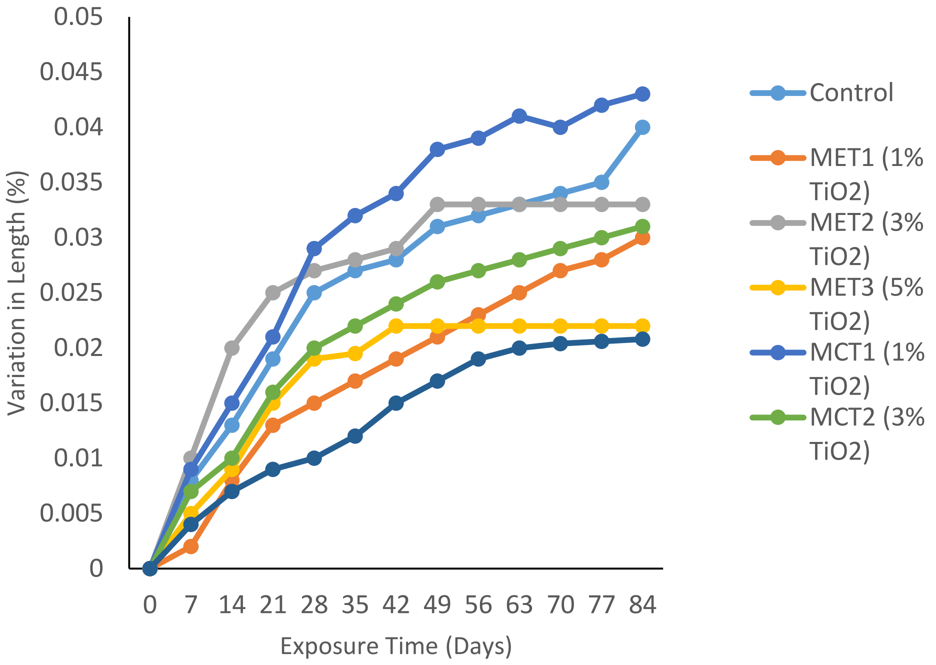

Fig. 4.6: A Graph showing the Variation in Length of Mortar Specimens due to Shrinkage.

Similarly, as noted by Shaaban et al., (2020), increasing the percentage of TiO_2 added to the ordinary Portland cement slightly increased changes in length of the mortar specimen for days of exposure, except that of MET 3 which contains 5% of TiO_2 extracted from kaolin. This observation is in sharp contrast with addition of 5% TiO_2 procured commercially to the ordinary Portland cement mortar specimen. This observation may be attributed to the presence of some impurities in the extracted TiO_2 from kaolin which may have some pozzolanic effects. Also, Fig. 4.6 confirms findings made from other studies which suggest that adding of nano-TiO_2 or micro-sized TiO_2 to ordinary Portland cement mortar paste decreases micro-strain properties of cement matrix. That is, nano-TiO_2 or micro-sized TiO_2 is able to improve the anti-shrinkage property of the cement matrix (Collins and Sanjayan, 2000; Palacios and Puertas, 2007).

However, Shaaban et al., (2020) have demonstrated that anti-shrinkage properties from addition of micro-TiO_2 to cement matrix is similar to that of nano-TiO_2. This assertion by Shaaban et al., (2020) has been confirmed by the results in Fig. 4.6 of this thesis. Which showed the anti-shrinkage properties of micro-TiO_2 extracted from kaolin is the same as that procured commercially.

4.6 Applications of the TiO_2-ordinary Portland climate smart cement

From the discussion of results in section 4.5 above, it was demonstrated that, adding TiO_2 to ordinary Portland cement to form TiO_2-climate smart cement does not affect physical properties but it also improves its mechanical properties, hence this section of the thesis discusses the results from the applications of using TiO_2-ordinary Portland cement to solve the issue of flaking or spalling of buildings and self-cleaning of buildings contaminated with air pollutants such as Rhodammine B dye.

4.6.1 Removal of Rhodamine B dye pollutants by TiO_2-climate smart ordinary Portland cement

To Chen and Poon (2009), TiO_2-cement mortar or concrete has the ability to degrade pollutants on its surface due to its inherent photocatalytic property. It is within this context that the rate of removal of Rhodamine B dye using TiO_2-ordinary Portland cement extracted from kaolin and comparing the results obtained with TiO_2-ordinary Portland cement formulated with commercial grade TiO_2 in this thesis. The results of such comparison is shown in Fig. 4.7 below.

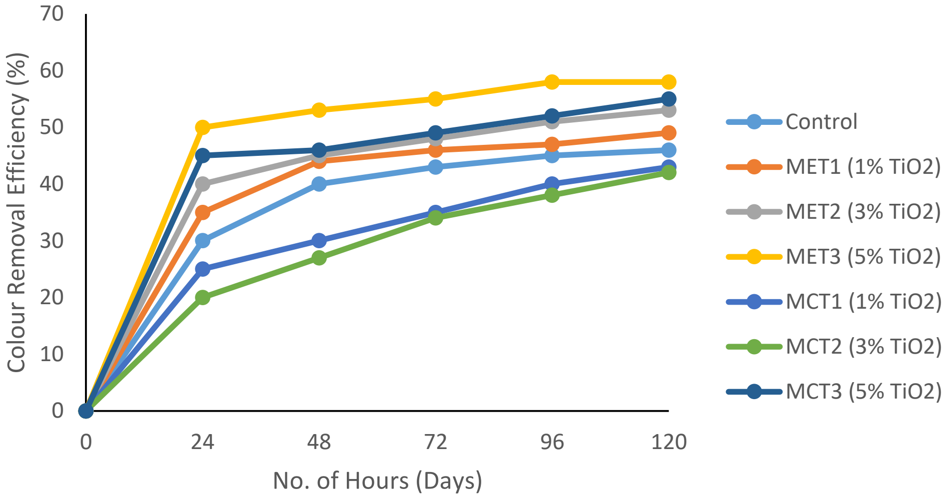

Fig. 4.7: Percentage Efficiency of Colour Removal versus Time

It can be seen in Fig. 4.7 that, both mortar pastes made with 5% micro-sized TiO_2 extracted from kaolin and commercially available TiO_2 were able to eliminate approximately 60% of the Rhodamine B dye respectively within 120 hours (5 days) of application as against the control, i.e., ordinary Portland cement within the same period. However, the self-cleaning property of mortar specimens containing 5% micro-sized TiO_2 extracted from kaolin performed better than commercially available micro-sized analytical grade TiO_2 Tioxide A-HR manufactured by Huntsman Tioxide Corporation. This observation is same as the results obtained by Elia et al., (2018), who found out that the rate of self-cleaning property of TiO_2-cement increases with increasing the percentage of TiO_2 added to formulate the TiO_2-photocatalytic cement. Hence, it can be inferred from Fig. 4.7 that, micro-sized TiO_2 extracted from kaolin can be added to ordinary Portland cement to help self-clean air pollutants especially greenhouse gases deposited on concrete and mortar specimens. Thus, making TiO_2-ordinary Portland cement extracted from kaolin a climate smart cementitious material.

4.6.2 Prevention of flaking or spalling of buildings by the formulated TiO_2-ordinary Portland cement

According to Zhang and Zong (2014), durability of civil structures, rendered mortars or concrete is dependent on the ability of water molecules or other fluid to pass through the pores within its micro-structure. That is, the durability of concrete or rendered mortar is dependent on its permeability. In other words, civil structures, concrete or rendered mortar with very high permeability easily allows movement of water molecules or other fluids through its pores. These water or fluid molecules react and destroy the chemical stability of the hydrated and unhydrated components. De Schutter and Audenaert (2004), has establish a strong relationship between permeability of rendered mortar paste or concrete and its pore structure, intensity of micro-cracks as well as its strength such as compressive and flexural strengths respectively.

The parameter used to examine this relationship between permeability of water molecules through rendered mortar pastes and its durability is water absorption. Hence, this section of the thesis evaluated the effect of water absorption on durability of mortar paste using the formulated TiO_2-ordinary Portland cement such as flexural strength, sulphate attack and compressive strength which lead to flaking or spalling of the rendered mortar.

According to Ekwulo and Eme (2017), there exist a relationship between flexural strength and water absorption which is very useful parameter in determining the durability of cementitious structures, i.e., whether the structures would undergo cracking, flaking or spalling; which have been summarised in Fig. 4.8(a) to 4.8(g) below.

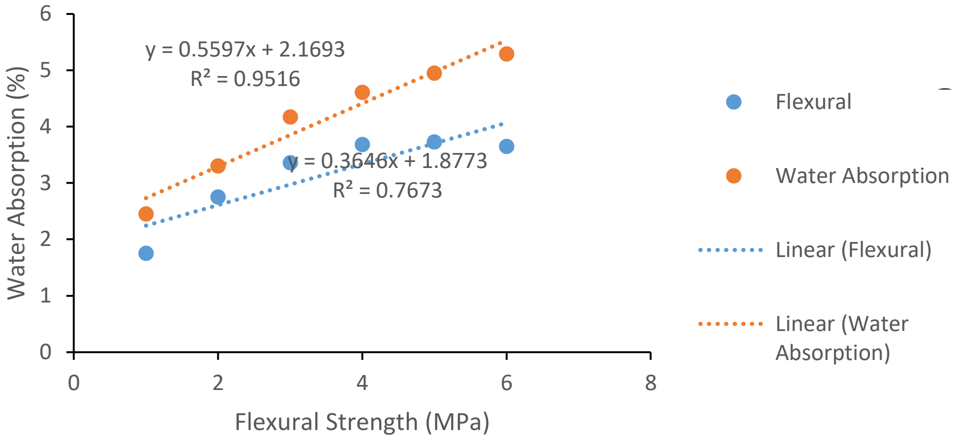

Fig. 4.8 (a): A Graph Comparing Relationship Flexural Strength and Water Absorption for Control Samples.

In Fig. 4.8 (a) above, a positive linear correlation ($R^2 = 0.95$) existed between percentage water absorption and flexural strength for the control mortar specimens. This shows that, as flexural strength of mortar pastes made with only ordinary Portland cement increases, the rate of water absorption also increases. This observation is consistent with findings made by Ekwulo and Eme (2017) and Zhang and Zong (2014), who argues that the ability of water molecules to penetrate through the micro-structure of mortar paste is dependent on the number of pores within the micro-structure of the mortar paste.

However, negative correlation existed between flexural strength and water absorption for mortar pastes containing various percentages of micro-sized TiO_2 either extracted from kaolin or analytical commercial grade. These results have been summarised in Figs. 4.8(b) to 4.8(g).

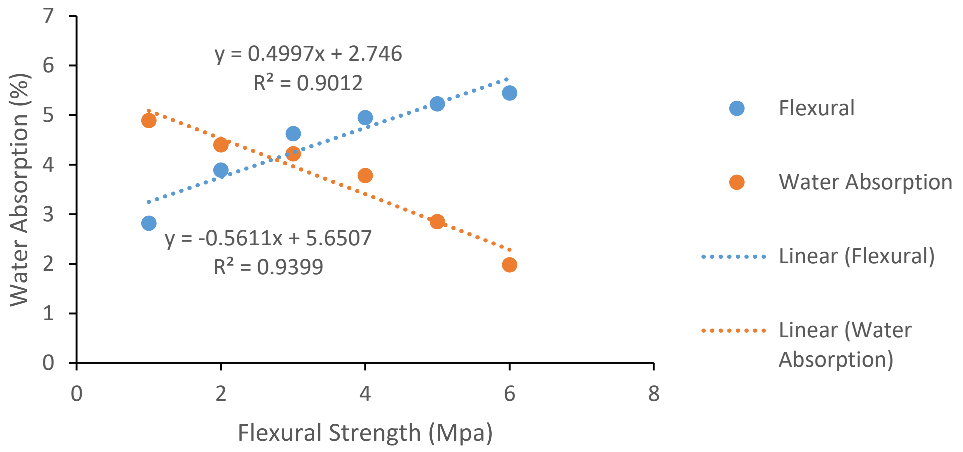

Fig. 4.8 (b): A Graph Comparing the Relationship between Flexural Strength and Water Absorption for Mortar Pastes containing 1% TiO_2 Extracted from Kaolin.

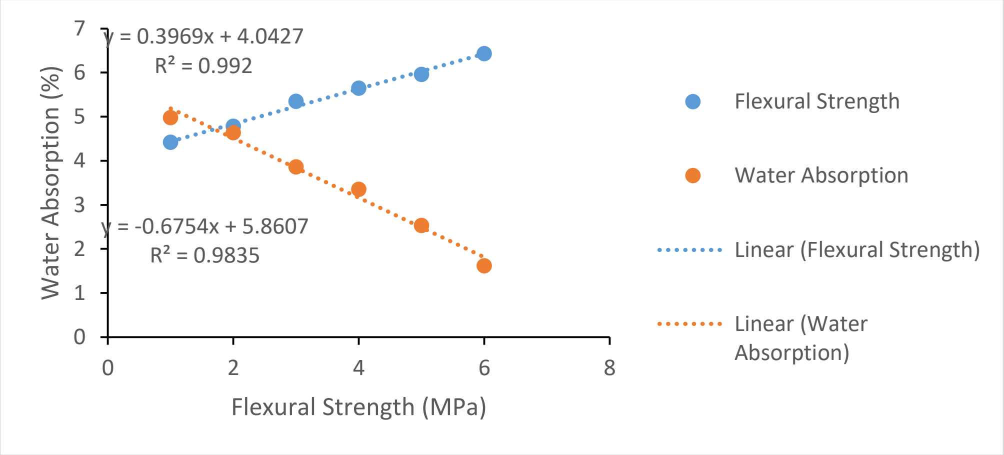

Fig. 4.8 (c): A Graph Comparing the Relationship between Flexural Strength and Water Absorption for Mortar Pastes containing 3% TiO_2 extracted from Kaolin

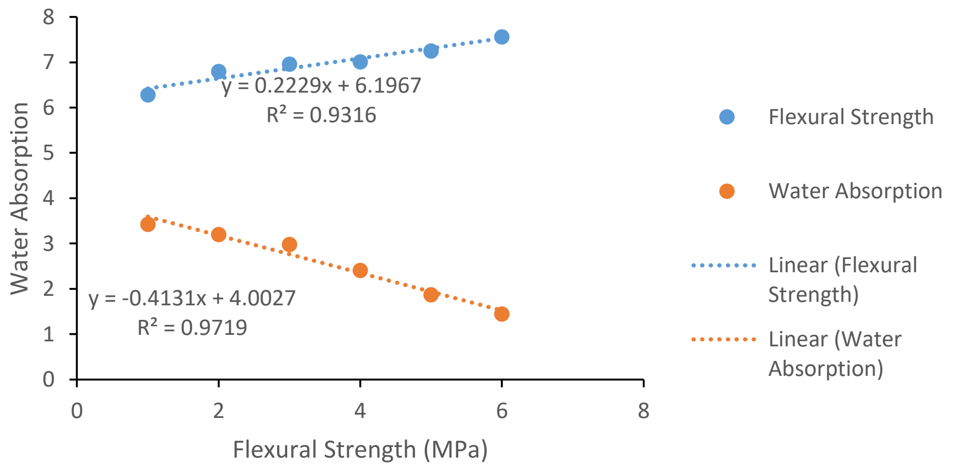

Fig. 4.8 (d): A Graph Comparing the Relationship between Flexural Strength and Water Absorption for Mortar Pastes containing 5% TiO_2 Extracted from Kaolin.

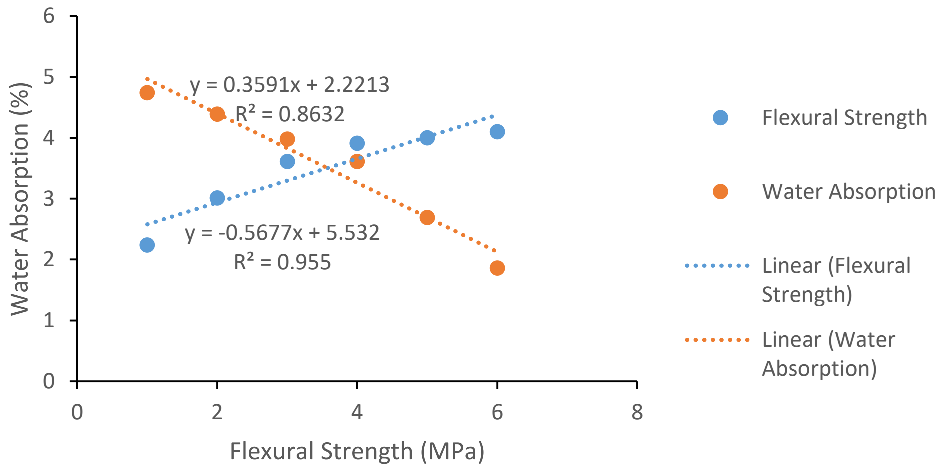

Fig. 4.8 (e): A Graph Comparing the Relationship between Flexural Strength and Water Absorption for Mortar Pastes containing 1% TiO_2 Commercial Grade.

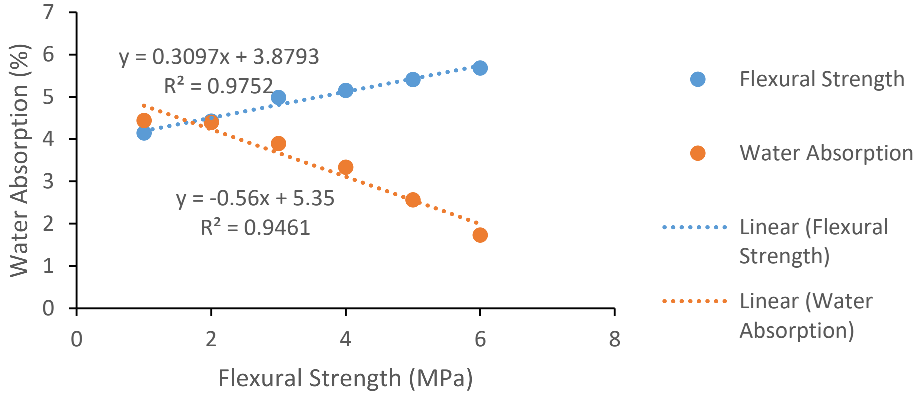

Fig. 4.8 (f): A Graph Comparing the Relationship between Flexural Strength and Water Absorption for Mortar Pastes containing 3% TiO_2 Commercial Grade.

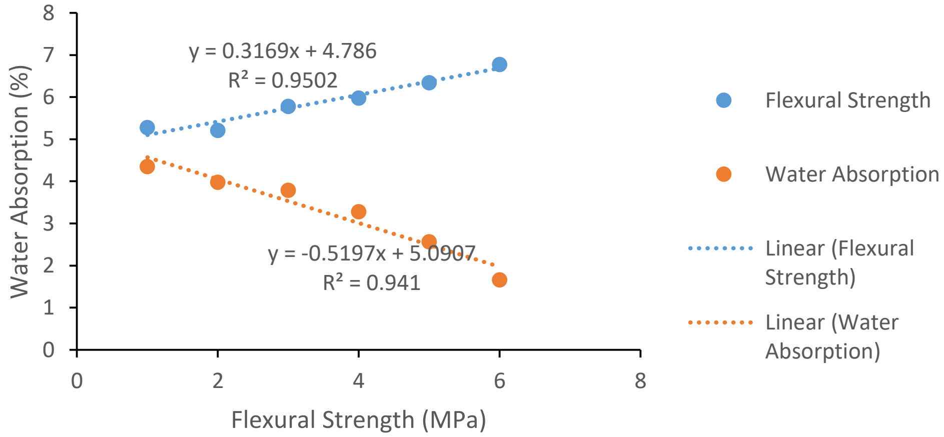

Fig. 4.8 (g): A Graph Comparing the Relationship between Flexural Strength and Water Absorption for Mortar Pastes containing 5% TiO_2 Commercial Grade.

Comparing the results in Fig. 4.8 (a) with that shown in Figs 4.8(b) to 4.8(g) above, it can be said that, the mortar pastes containing formulated TiO_2-ordinary Portland climate smart cement (with either TiO_2 extracted from kaolin or commercial grade TiO_2) had very low pores within them. Hence, their low permeability for water molecules or other fluids to pass through its pores. As a negative relationship existed between their flexural strength and water absorption. That is, the low permeability that exist within the formulated TiO_2-ordinary Portland cement has improve its ability of resisting water molecules or other fluids which may contain sulphate ions, chloride ions, etc to penetrate its pores, thereby reducing the incident of developing of micro-cracks which eventually results in flaking or spalling of the rendered mortar paste (Zhang and Zong, 2014; Mehita and Monteiro, 2006; Alhozaimy and Mirza, 1996; De Schutter and Audenaert, 2004). Thus, improving upon the durability of the building or the civil structure.

Similarly, a negative linear relationship was found to exist between compressive strength and water absorption for the TiO_2-ordinary Portland climate smart cement formulated with TiO_2 extracted from kaolin as well as commercial analytical grade. The coefficient of correlation, R when different percentages of TiO_2 extracted from kaolin and was used to replace the ordinary Portland cement varied from $R^2 = 0.939$ (1%TiO_2) to $R^2 = 0.998$ (5% TiO_2); whilst in the case of the commercial analytical grade TiO_2, the R^2 varied from $R^2 = 0.785$ (1% TiO_2) to $R^2 = 0.892$ (5% TiO_2). These results suggest that, as the percentage of TiO_2 (i.e., extracted from kaolin or commercial grade) added to ordinary Portland cement increases, it leads to reduction in the permeability of the mortar rendered mortar paste. Thus, the low permeability of water molecules or fluids improves the durability of the rendered mortar paste, i.e., improvement in its compressive strength.

The compressive strengths of different percentages of the formulated TiO_2-ordinary Portland cement (i.e., containing micro-sized TiO_2 extracted from kaolin and the commercial) as well as the control mortar specimens (i.e., without the addition of TiO_2) mortar pastes specimens were all immersed in 10% Na_2SO_4 solution were measured from day 1 to day 28. The results obtained from this determination were compared with the compressive strength of the mortar pastes before they were immersed in 10% Na_2SO_4 solution (as discussed in section 4.4.1 above). The result of such comparison has been summarised in Figs. 4.9 (a) to Fig. 4.9 (g) below.

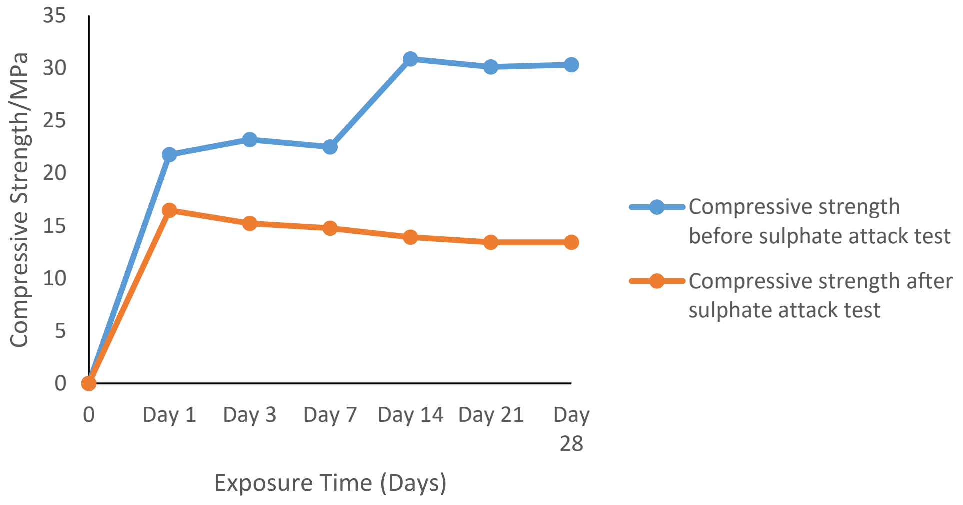

Fig. 4.9 (a): A Graph Comparing Compressive Strengths of Control (containing 0% TiO_2) Cement mortar pastes before and after immersion in 10% Sodium Sulphate solution.

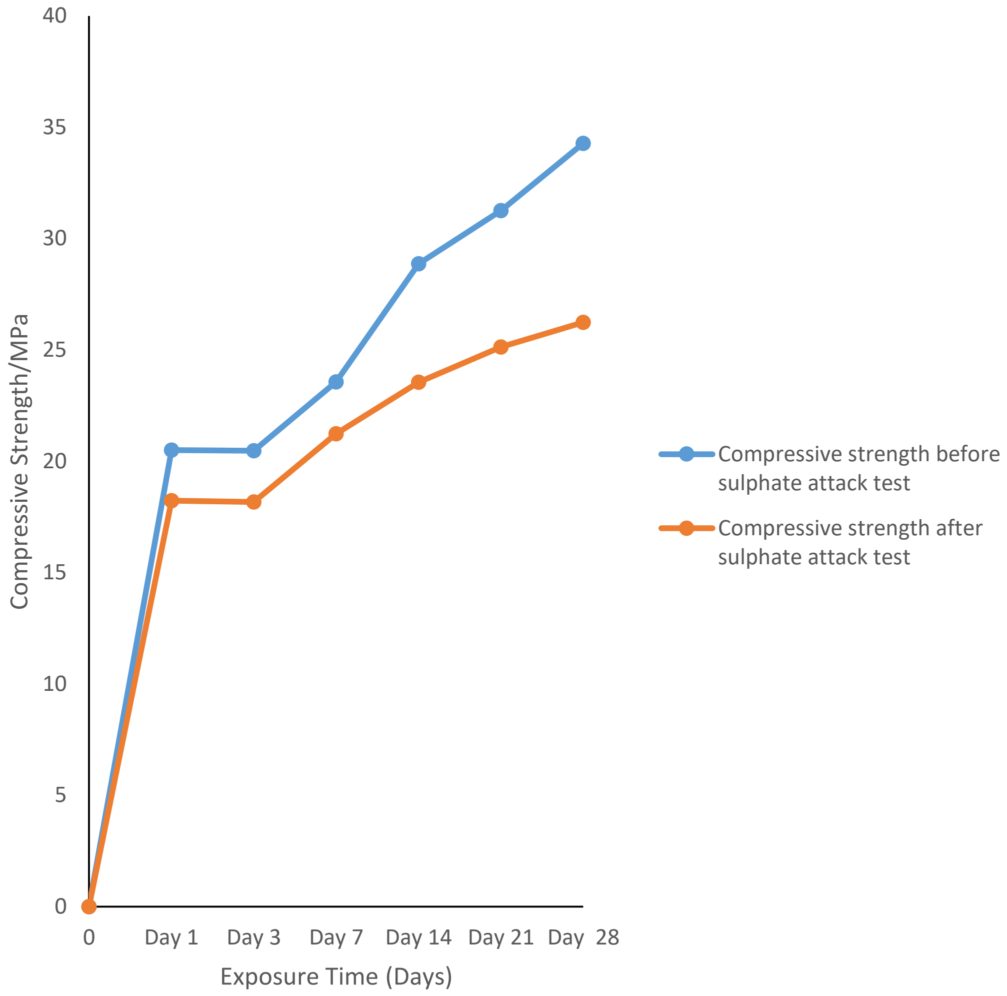

Fig. 4.9 (b): A Graph Comparing Compressive Strengths of 1% TiO_2 Extracted from Kaolin Cement Mortar Pastes before and after immersion in 10% Sodium Sulphate solution.

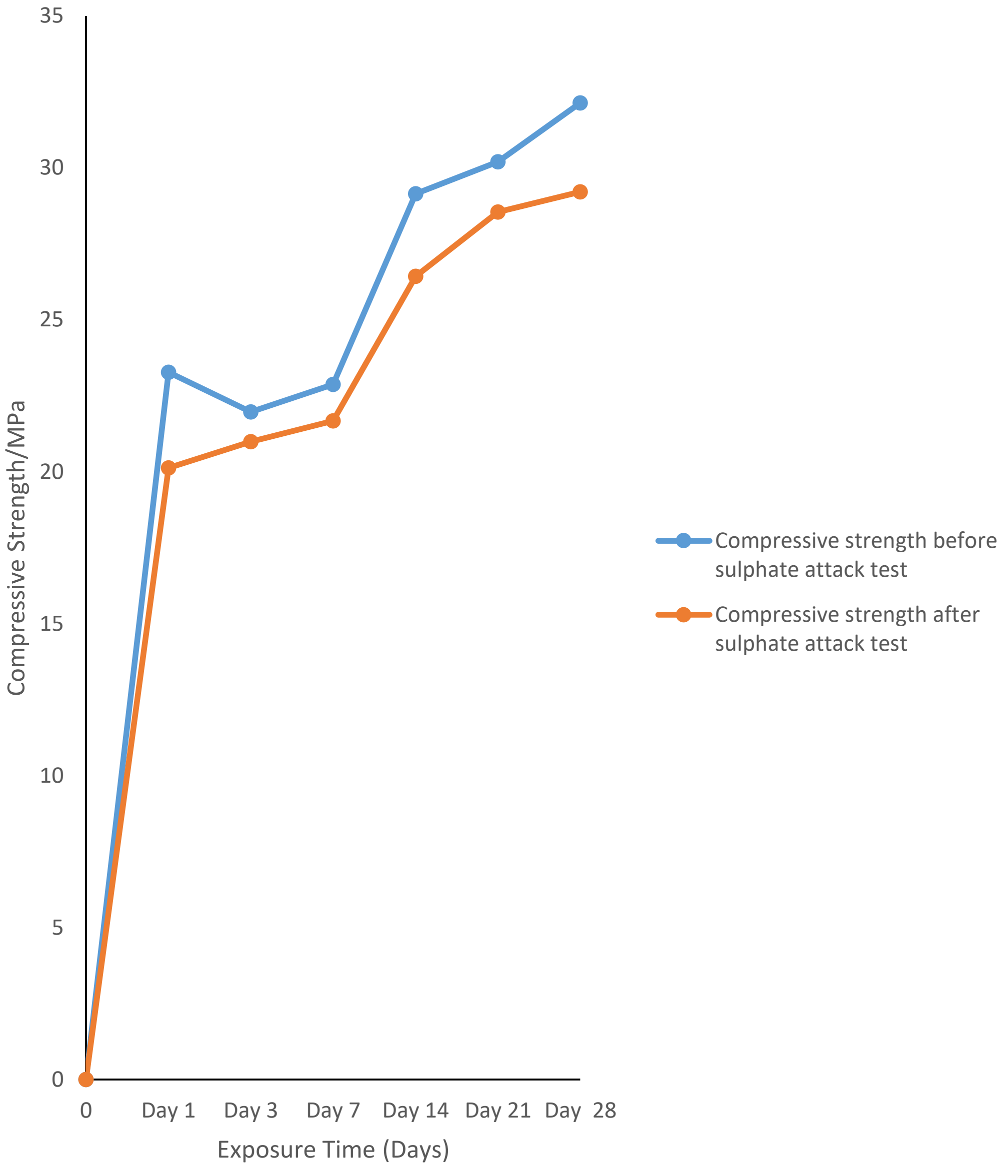

Fig. 4.9 (c): A Graph Comparing Compressive Strengths of 3% TiO_2 Extracted from Kaolin Cement Mortar Pastes before and after immersion in 10% Sodium Sulphate solution.

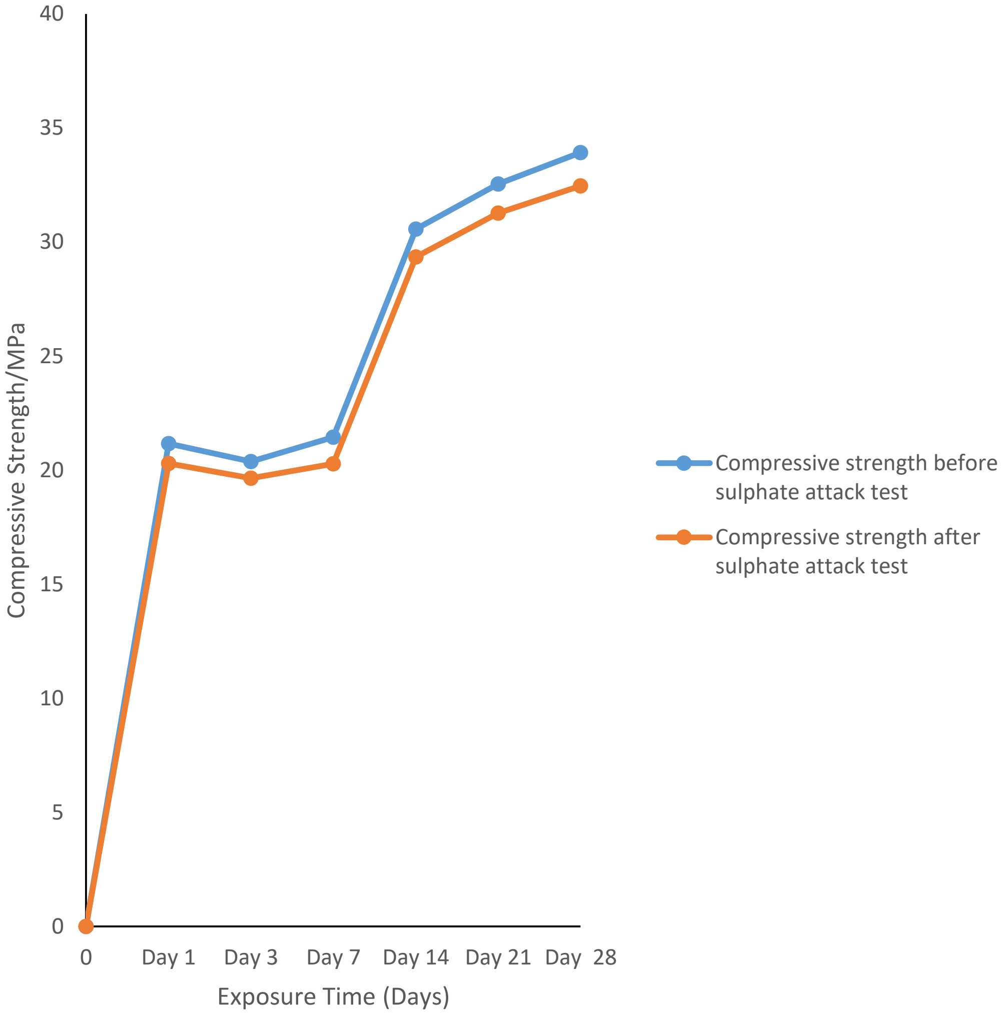

Fig. 4.9 (d): A Graph Comparing Compressive Strengths of 5% TiO_2 Extracted from Kaolin Cement Mortar Pastes before and after immersion in 10% Sodium Sulphate solution.

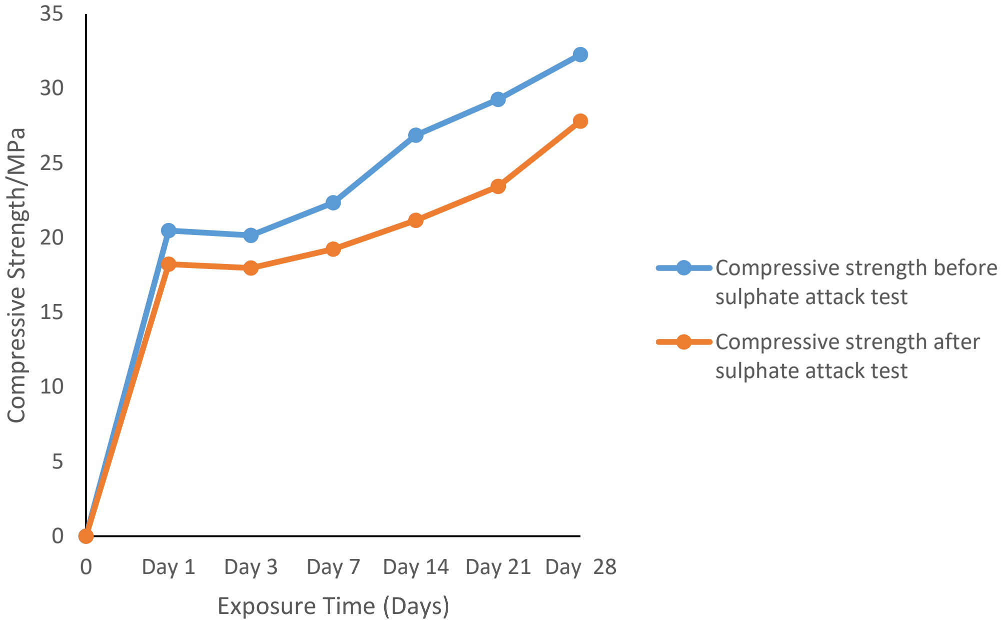

Fig. 4.9 (e): A Graph Comparing Compressive Strengths of 1% TiO_2 Commercial Grade Cement Mortar Pastes before and after immersion in 10% Sodium Sulphate Solution

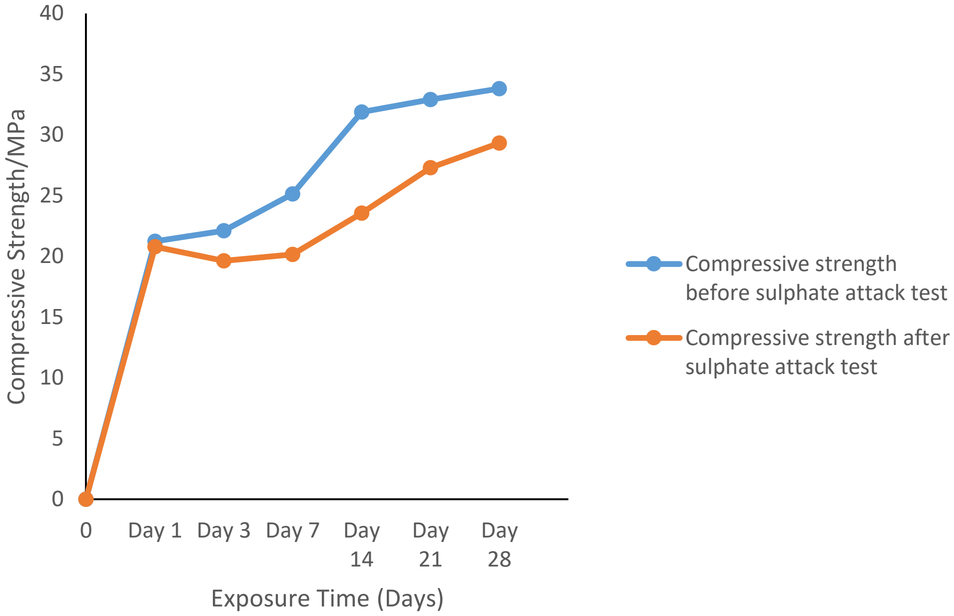

Fig. 4.9 (f): A Graph Comparing Compressive Strengths of 3% TiO_2 Commercial Grade Cement Mortar Pastes before and after immersion in 10% Sodium Sulphate Solution

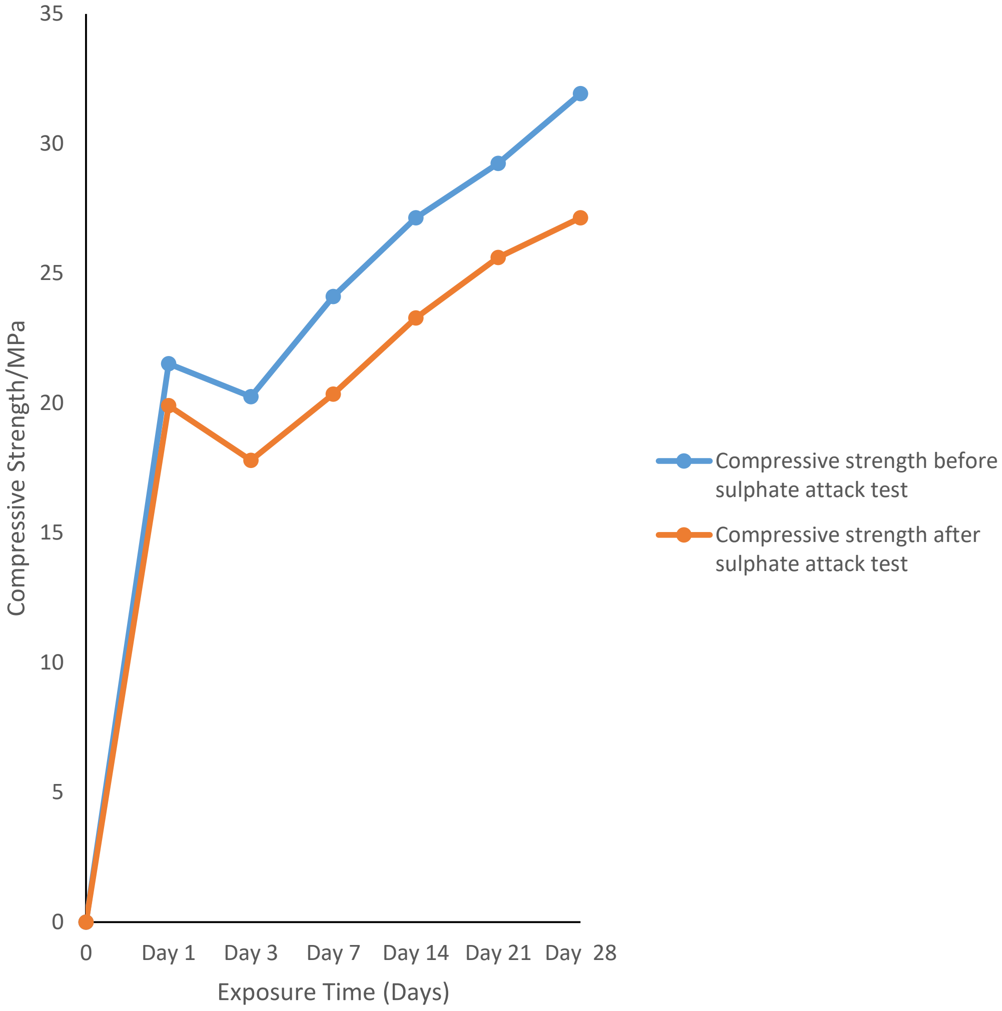

Fig. 4.9 (g): A Graph Comparing Compressive Strengths of 5% TiO_2 Commercial Grade Cement Mortar Pastes before and after immersion in 10% Sodium Sulphate Solution

As shown in Figs. 4.9 (a) to 4.9 (g) above, there was a significant reduction in the compressive strengths of the mortar paste that does contain micro-sized TiO_2 (control samples); for mortar pastes containing TiO_2 extracted from kaolin as well as that of the commercial, a slight reduction in the compressive strengths were observed for mortar specimen containing 1% and 3% TiO_2 respectively, while mortar specimens containing 5% TiO_2 extracted from kaolin showed significantly very low reduction in compressive strength as compared to mortar specimens containing 5% commercial grade TiO_2.

This observation is due to the permeability of the mortar specimens. That is, the continuous movement of fluids containing sulphate ions which attacked both the hydrated and unhydrated components of the cement. This ingress of water molecules containing sulphate ions leads to reduction in the durability of the rendered mortar and hence its compressive strength.

Since, TiO_2 is an inert material, it does not react with water molecules during the hydration of the formulated TiO_2-ordinary Portland cement (Chen et al., 2012; Jayapalan et al., 2010). It therefore acts as sites for nucleation during cement hydration, which allows the hydrated products such as CSH and CH phases to grow around them; thereby filling the empty spaces (i.e., reduction in its porosity) which prevent movement of water molecules or sulphate ions through the mortar paste for it to finally react with either the hydrated or unhydrated phases based on equations (2.0) to (2.4) in section 2.1.1 above (Yang et al., 2015; Zhang et al., 2015; Jimenez-Relinque et al., 2015). Once, equations (2.0) to (2.4) are stopped or their rate reduced drastically, formation of ettringite which causes expansion and development of micro-cracks, flaking or spalling is therefore reduced (Santhanam et al., 2003; Nazari and Raihi, 2011). That is, as shown in Fig. 4.9 (b) to 4.9 (g), as the percentage of TiO_2 added to the cement paste increases, the ability of the sulphate ions in the 10% sodium sulphate solution to passes through the pores within the mortar specimens for reactions described in equations (2.0) to (2.4) in section 2.1.1 above to take places reduces; hence, a very low reduction in the compressive strengths of the mortar and a significant improvement in the durability of the mortar pastes to resist flaking or spalling.

4.7 Chapter Summary

The following findings emerged from the results of the study:

1. Industrial uses of kaolin from the study areas depends on the composition of major oxides as well as properties of the rocks they originated from. For example, Al_2O_3/Fe_2O_3 ratio as well as the concentration of oxides like Fe_2O_3 and that of TiO_2 are used to define the various types of industries that the kaolin samples can be of good use. For instance, the SiO_2 content of Assin Foso kaolin deposit was found to be within the acceptable range for SiO_2 in kaolin required for the paper coating and paper filing industries respectively; while the SiO_2 content for kaolin from Saltpond, Waagkron and Ekon were found not to be suitable for the aforementioned industries;
2. Kaolin in the study areas contains elevated levels of TiO_2, Fe_2O_3, and other impurities;
3. High concentrations of Fe_2O_3 and TiO_2 in kaolin deposits in the study areas may affect its industrial use;
4. Selective flocculation techniques were used to remove high concentrations of TiO_2 and Fe_2O_3 from the kaolin samples in the study areas using medium and high anionic polymers;
5. The result indicated that, through the use of medium and high anionic polymers such as N-9878 and N-9806 in selective flocculation techniques, high percentage by weight of TiO_2 and Fe_2O_3 were recovered in overflow at pH 9.5. That is, 78.6% of Fe_2O_3 were removed from kaolin samples in Waagkron as against the 90.4% of Fe_2O_3 removed from kaolin samples in Assin Foso respectively. Similarly, the

percentage of TiO_2 removed from kaolin deposits in the study areas varies from 86.1% for kaolin samples from Saltpond to 91.8% for kaolin samples from Assin Foso respectively;

6. TiO_2 and Fe_2O_3 removed from the kaolin samples improved its brightness. The brightness of kaolin samples from Assin, Saltpond and Ekon kaolin increased from 82% to 92% at pH 9.5 for the addition of the N-9878 and N-9806 flocculants, while that from Waagkron, the percentage of brightness increased from 82% with addition of 0 g/ton of N-9878 flocculant to 87% with the addition of 100 g/ton of the same flocculant at the same pH;
7. The flow test results for mortar specimens made with either ordinary Portland cement containing TiO_2 removed from kaolin and the commercially available TiO_2 ordinary Portland cement were all within the ASTM C 109 minimum specifications for mortars;
8. Generally, it was found out that adding either TiO_2 extracted from kaolin or procured commercially did not affect the compressive strength of the mortar prepared. However, mortar paste containing 5% TiO_2 extracted from kaolin had a higher compressive strength than all the other percentages of TiO_2 used as partial replacement of the ordinary Portland cement;
9. Similarly, flexural and compressive strength of mortar with the formulated TiO_2-ordinary Portland cement were found to be higher than the control;
10. Percentage water of absorption for all mixtures of the formulated cement were found to be much lower than the control;

11. Also, the performance of TiO_2 extracted from kaolin in reducing the percentage of water of absorption was slightly better than commercially available TiO_2 used in formulating TiO_2-portland cement. The improved performance of water absorption for mortar samples containing TiO_2 than the control samples may be due to its high reactivity as well as a filler effect of the TiO_2 particles;
12. That the mortar's resistance to sulphate attack was enhanced by adding 5% TiO2 extracted from kaolin. Consequently, it became more durable; and
13. The anti-shrinkage properties of micro-TiO_2 extracted from kaolin is the same as that procured commercially micro-TiO_2.
14. The removal of TiO_2 and Fe_2O_3 improved the industrial use of the kaolin in the study areas

CHAPTER FIVE

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.0 Overview

Portland cement is a common binding material that is used to bind fine or coarse aggregates together, to construct bridges, buildings and other civil structures in the built environment. However, in recent times, the use of Portland cement in the construction industry has resulted in several structural defects due to micro-strain, shrinkage, sulphate or acid attack which affect their durability.

To resolve this problem, several studies have been conducted to develop technologies that seeks to improve upon the durability of mortar and concrete made from Portland cement. In this context, several studies have suggested that addition of nano-sized cementitious materials such as, nano-clay, nano-SiO_2, nano-Fe_2O_3, nano-TiO_2 among others are used to improve mechanical characteristics (e.g., compressive strength, ductility, flexural strength, etc), which eventually improve the concrete or mortar service life (Feng et al., 2013; Sanchez and Soboley, 2010; Birgisson et al., 2010; Balaguru and Chong, 2006).

As noted by Feng et al., (20213), titanium dioxide nano-particle has received wide usage in both the construction industry as well as other sector such as environmental preservation, production of solar cells or panels, photocatalysis and photovoltaic cells just to name a few. Similarly, other scientists have demonstrated that mechanical performance of concrete or mortar paste is better when nano-TiO_2 particles are added to Portland cement. That is, mechanical properties such as compressive strength, flexural strength and shrinkage among others as well as its ability to withstand sulphate attack of buildings improves considerably (Baoguo et al., 2015; Pimenta et al., 2016;

Zhang and Li, 2012; Nazari, 2011). On the contrary, scientists such as Shaaban et al., (2020) and Hamidi and Aslani (2019) have suggested that, it is possible to achieve the same results by adding micro-TiO_2 to ordinary Portland cement just like using nano-TiO_2. Shaaban et al., (2020) further suggested that developing countries with nano-technology weak infrastructure can make use of micro-TiO_2 to improve upon the durability as well as the aesthetic values of edifices constructed with ordinary Portland cement.

TiO_2 is widely found in rocks, water bodies, and soils. In Ghana, titanium dioxide is associated with kaolin which are abundant in Ghana. Kaolin in Ghana is mostly used in the ceramic, bricks and tiles, paper filling and pharmaceutical industries where contaminants such as TiO_2 and Fe_2O_3 needs to be removed. Thus, creating an environmental problem for the disposal of titanium dioxide and iron (III) oxide removed from the kaolin.

It was to address this challenge of finding an alternative use for TiO_2 removed from kaolin found in Central Region, Ghana that this study was undertaken to extract TiO_2 for the formulation of titanium dioxide – ordinary Portland cement. The study sought to geological assess the characteristics of kaolin deposits in the study. It was further to assess both physical and mechanical properties of the formulate cement and compare its performance with commercially synthesised TiO_2 on the market.

5.1 Summary of Results

The first objective that this study sought to undertake was to investigate chemical composition and possible uses of kaolin found in the Central Region, Ghana. From th+e results of such determination, it can be concluded that the percentage by weight of major oxides found in kaolin deposits from Saltpond is as follows; SiO_2 (58.94) > Al_2O_3 (28.68) > Fe_2O_3 (2.102) >TiO_2 (1.73) > MgO (0.28) > K_2O (0.478) > CaO (0.120) > Na_2O (0.17) > K_2O_5 (0.159) > MnO (0.218). Similar results were obtained for other study sites. Also, most of the kaolin samples are used in the ceramic, cosmetic, pharmaceutical, paper and other industries, it can be concluded that, there is the need to remove the high levels of Fe_2O_3 and TiO_2 so that the ratio of Al_2O_3/Fe_2O_3 for the raw kaolin samples would be within the recommended value for refractory ceramics, paper, pharmaceutical or paint industry of ≥ 5.5.

The second objective of this study was to investigate whether selective flocculation techniques can be used to remove TiO_2 and Fe_2O_3 levels in kaolin deposits from the study areas, as well as explore whether after the removal of TiO_2 and Fe_2O_3 from the kaolin samples, properties of the kaolin samples have improved its performance in the paper, paint or pharmaceuticals. From the results of the study, it can be concluded that selective flocculation techniques is able to remove high levels of aTiO_2 and Fe_2O_3 thereby improving upon the brightness of the kaolin. The percentage of TiO_2 removed from the kaolin samples using the selective flocculation techniques varied from 86.1% (Saltpond) to 91.8% (Assin Foso), while that of Fe_2O_3 varied from 87.5% (Saltpond) to 90.4% (Assin Foso).

The third thrust of this study was to investigate whether the TiO_2 removed can be used to formulate climate-smart TiO_2-ordinary Portland cement and assess its mechanical properties. From the results of the test, it can be concluded that the formulated Portland cement made with TiO_2 extracted from kaolin and the commercial analytical grade TiO_2 were found to be within the guideline values set in ASTM C 150 for cement. In the case of workability or slump flow test of the mortar pastes, it can be concluded that, both formulated cement were found to be within the requirements set in ASTM C 109 for the flow or workability of mortar also known as the slump test. It can therefore be concluded that, no statistical significant difference were found between mortar specimen containing titanium dioxide extracted from kaolin and the one containing the commercial grade. Similar conclusions can be made from the test of flexural strength, shrinkage and water absorption for mortar specimens containing TiO_2 extracted from kaolin and the commercial grade TiO_2. In almost all the cases, the aforementioned mechanical properties showed an improved performance for mortar pastes containing varying percentages of TiO_2 than the control, i.e., mortar made with only ordinary Portland cement. However, it can be concluded that, mortar pastes containing 5% TiO_2 extracted from kaolin showed improved performance for mechanical properties such as compressive +/strength, flexural strength, workability as well as water absorption.

The ability of the extracted TiO_2 as well as the commercial grade TiO_2 used to formulate climate-smart Portland cement to resist sulphate attack on buildings and other civil structure were investigated in line with ASTM C 1012 guidelines. From the results of the study, it can be concluded that, since titanium dioxide is inert, as such, is not involved in the hydration reaction it rather act as filler of pores within the hydrated cement, which refine the pore structure or micro-structure and thus prevent movement of sulphate ions which later attack both the hydrated and unhydrated phases of the cement in the mortar that leads to the formation of etrringite. It can also be concluded that, no statistical significant difference was observed between mortar pastes containing 5% micro-sized TiO_2 extracted from kaolin and the commercial grade.

Finally, it can be concluded that, adding micro-sized TiO_2 either removed from kaolin or commercial grade added to Portland cement was able to increase the ability of the mortar pastes to prevent flaking or spalling of rendered mortar on the walls. It was also found that, the optimum percentage for TiO_2 added to the Portland cement was 5%. That is, addition of 5% TiO_2 improves upon the durability of the rendered mortar pastes because of its refined pore structure which lead to crack-free mortar pastes.

5.2 Conclusions

Durability of buildings and other civil structures constructed using ordinary Portland cement in recent times are deteriorating at an alarming rate due to the effect of exposure to greenhouse gases which causes climate change have on them. This problem manifest itself in flaking or spalling of rendered mortar pastes or concrete. Hence, the main thrust of this thesis was to formulate a climate-smart ordinary Portland cement using TiO_2 extracted from locally available material such as kaolin that would be able to address the aforementioned problem.

The kaolin samples were randomly sampled from four different locations in the Central Region and TiO_2 content in them were extracted using selective flocculation techniques. The extracted TiO_2 was used to formulate the TiO_2-climate smart Portland cement. The formulated cement was subjected to physical and mechanical analysis such as flow test, sulphate attack, compressive and flexural strength test.

From the results, it can be concluded that, adding 5% of the formulated TiO_2-climate smart ordinary Portland cement to ordinary Portland cement was able to prevent flaking of building and hence improves its overall durability.

5.3 Recommendations

From the results of this study:

1. It is recommended that cement producers in the country consider adding 5% of TiO_2 either extracted from kaolin or commercial grade so as to improve upon the micro-structure of rendered mortar pastes to prevent it from flaking or spalling;
2. A factory should be set up under the One District One Factory initiative by Ministry of Trade and Industries (MOTI), and Central Regional Development Commission (CEDECOM) to remove Fe_2O_3 and TiO_2 from the kaolin to serve as raw material for cement producing industries and others who need them.

5.3.1 Suggestion for further work

From the findings of this study, the following recommendation in terms of future research is made;

1. The photocatalytic properties of the formulated TiO_2-ordinary Portland cement extracted from kaolin for degradation of oxides of nitrogen needs to be investigated;
2. Hydration mechanism for both TiO_2-ordinary Portland cement extracted from kaolin as well as commercial grade TiO_2-portland cement should to be investigated; and

3. The effect of titanium dioxide extracted from kaolin on other materials such as geopolymer in preventing sulphate attack of rendered mortar or concrete should be investigated.

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APPENDICES

APPENDIX A

STANDARD TEST METHOD FOR FLOW OF HYDRAULIC CEMENT MORTAR

APPENDIX B

METHOD OF TESTING CEMENT – PART 1: DETERMINATION OF STRENGTH

APPENDIX C

STANDARD TEST FOR COMPRESSIVE STRENGTH OF HYDRAULIC CEMENT MORTARS (USING 2 – IN OR [50-mm] CUBE SPECIMENS)

APPENDIX D

STANDARD TEST METHOD FOR LENGTH CHANGE OF HYDRAULIC – CEMENT MORTARS EXPOSED TO A SULPHATE SOLUTION

APPENDIX E

STANDARD TEST METHOD FOR FLOW OF HYDRAULIC CEMENT MORTAR

PUBLICATION

PAPER 1

EXTRACTION OF TiO_2 FROM KAOLIN IN THE CENTRAL REGION, GHANA: AN ALTERNATIVE MATERIAL FOR THE FORMULATION OF CLIMATE – SMART PORTLAND

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