DEVELOPMENT OF A PROTOTYPE FOR A RESTORATIVE DENTAL CEMENT IN KENYA

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DECLARATION

I, Olivia M. A. Osiro, hereby declare that this thesis is my original work and that it has not been presented by any other person for research purpose, degree or otherwise in any other University or institution.

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This research thesis has been submitted for the fulfillment of the requirement for the award of PhD in Dental Materials with our approval as University supervisors.

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DEDICATION

For little girls with dreams who become women with vision

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

LIST OF ABBREVIATIONS

ADA	American Dental Association
ANOVA	Analysis of Variance
ARM	Athi River Mining
ART	Atraumatic Restorative Treatment
AS	Aluminosilicates
ASTM	American Society for Testing and Materials
ATR	Attenuated Total Reflectance
BDS	Bachelor of Dental Surgery
BF Slag	Blast Furnace Slag
CAD/CAM	Computer Aided Design and Machining
EAPC	East African Portland Cement
EDXRF	Energy Dispersive X-ray fluorescence
FA	Fly Ash
FDI	International Dental Federation
FISE	Fluoride Ion Selective Electrode
FTIR	Fourier Transform Infra-red Spectroscopy
GFAAS	Graphite Furnace Atomic Absorption Spectroscopy
GIC	Glass Ionomer Cement
ISO	International Organization for Standardization
LMI	Low- and middle-income
MAS-NMR	Magical Angle Spinning - Nuclear Magnetic Resonance
MID	Minimally intervention dentistry
MSc	Master of Science

MTA	Mineral Trioxide Aggregate
MT	Mixing time
PAA	Poly (acrylic acid)
PC	Portland cement
PhD	Doctor of Philosophy
PI	Primary Investigator
ST	Setting time
WT	Working time
XRD	X-ray diffraction
XRF	X-ray fluorescence

DEFINITION OF TERMS

Dental cement: A dental restorative material used as an intermediary to adhere two surfaces and usually constituted from a chemical reaction between a powder and liquid, commonly an acid and base reaction.

Glass ionomer cements (GICs): Dental restorative materials derived from an acid-base reaction between polyacrylic acid, with or without co-polymers, and calcium or strontium fluoroaluminosilicate glass. Conventional GICs are the original materials which set only through the acid-base reaction while resin-modified GICs have resin inclusions such as hydroxyethyl methacrylate (HEMA) and set through combined acid-base and polymerization reactions.

Calcium silicate cements: A group of hydraulic restorative dental materials that are composed primarily of dicalcium silicate and tricalcium silicate.

Portland cement (PC): A generic term referring to a hydraulic product of grinding cement clinker to fine powder and used in the construction industry as an adhesive as well as in concrete. Additives such as gypsum are usually added to the ground clinker to control desirable cement properties.

Clinker: The precursor of Portland cement produced by calcining raw materials such as lime or calcium carbonate, silica or silicon dioxide, alumina or aluminium oxide and ferric oxide in a rotary kiln at temperatures of 1400°C.

Portland Cement Company: Any industrial company whose core business involves the manufacture and sale of Portland cement and related materials. In Kenya, some examples include Bamburi Cement Company, East African Portland Cement (EAPC) Company and Athi River Mining (ARM) Company.

Geo-polymer/ alkaline-activated aluminosilicate: Inorganic polymers comprised of silica aluminate units – (Si-O-Al-O-Si) – derived from mineral ceramic starting materials such as kaolin, pumice and clays activated in an alkaline solution commonly sodium silicate.

Working time: The period of time from the start of mixing to the time when there is a change in viscosity of the material such that it can no longer be manipulated.

Net setting time: The period of time from the end of mixing to the time when the material attains some degree of rigidity.

ABSTRACT

Objective/ Motivation: The aim of this study was to develop a prototype for a restorative dental cement from Portland cement (PC) clinker and related aluminosilicate (AS) materials in Kenya. This was motivated by the need for affordable alternatives in middle-income countries such as Kenya, when dental amalgam, the preferred material, is scheduled for a global phase down by 2020 following the Minamata Convention on Mercury.

Study design: This was a quantitative, laboratory-based exploratory study.

Study setting: The study was conducted at the Schools of Dental Sciences and Physical Sciences, University of Nairobi, Kenya; World Agroforestry Centre (ICRAF), Nairobi, Kenya; Ministry of Mining, Nairobi, Kenya; and, Otto Schott Institute for Materials Research, Friedrich Schiller University, Jena, Germany.

Study materials: The materials evaluated were grey PC clinker, Kaolin, Fly ash (FA) and blast furnace (BF) slag. These were obtained from three cement and one ceramic manufacturing companies in Kenya.

Methods: The project was conducted in three phases. In the first phase, PC, Kaolin, FA and BF slag, together with alkaline-activated AS or geopolymers derived from them, were characterized by X-ray Diffraction, Graphite Furnace Atomic Absorption Spectroscopy, Energy Dispersive X-ray Fluorescence and Fluoride Ion Selective Electrode for compositional analysis and laser diffraction for particle size distribution analysis, in comparison to mineral trioxide aggregate (MTA). In the second phase, ionomer-type dental cements derived from clinker or geopolymers were formulated by mixing them with freeze-dried poly (acrylic acid), CaF_2 and aqueous tartaric acid. The setting reaction of these cements was followed in real time using Fourier Transform Infra-red Spectroscopy 30s to 24m after mixing. In the final phase, promising cement formulations were evaluated for the following properties of a restorative dental cement: 1. Setting time was determined using Gillmore needle apparatus; 2. Compressive strength was tested using Instron Hydraulic Universal Tester; and, 3. Fluoride ion releasing profile was evaluated by FISE. A costing assessment of the cost of production of the cements was also conducted.

Data analysis: R-Studio version 3.4.2 (2017) and Microsoft Excel (2013) were used for descriptive data analysis as well as for hypothesis testing. Continuous data was subjected to analysis of variance (ANOVA) followed by Tukey's post hoc test at α level of 0.05. Results were presented in form of tables and figures.

Results: While MTA and PC comprised mainly of dicalcium and tricalcium silicate phases, geopolymers contained AS phases such as quartz and mullite. The major compounds in the three groups of materials, as determined by EDXRF, were CaO (PC=59.50%wt±7.41, MTA=46.07%wt±10.24, AS=18.35%wt±17.85), SiO_2 (PC=25.65%wt±5.68,

MTA=19.02%wt±0.91, AS=58.10%wt±13.65) and Al_2O_3 (PC=5.49%wt±0.491, MTA=2.65%wt±1.07, AS=15.31%wt±6.25). Bi was present only in MTA (24.72%wt±11.92). The major element in the three groups of materials, as determined by GFAAS, was Ca (PC=51623.00µg/g±5182.00, MTA=77083.00µg/g±4612.00, AS= 16328.00µg/g±18110.00). Only FA contained fluoride (43.33µg/g±5.77). There was no statistically significant difference in the mean composition of MTA and Kenyan PC except in the Bi (PC=0%wt, MTA=24.72%wt±11.92, F statistic=164.4, 2df, p≤0.0001) and Pb content (PC=0.01%wt±0.01, MTA=1.75%wt±0.44, F statistic=44.29, 2df, p≤0.0001). There was no statistically significant difference in the mean particle size distribution of MTA, PC and geopolymers (after sieving through 120µm mesh sieve, D50 for PC=12.46µm±3.18, MTA=7.23µm±3.43, AS=12.74µm±3.79, F statistic=1.87, 2df, p>0.05). The setting reaction of the experimental cements resembled that of glass ionomer cements, characterized by formation of polyacrylates and tartrates, identifiable as characteristic bands on FTIR spectra. The mixing and setting time of the cements ranged between 30–90s and 135–480s, respectively. On exposure to moisture, cements based on FA/ BF slag geopolymer disintegrated, those based on clinker softened and became rubbery while those based on Kaolin geopolymer remained stable. At 28d, the mean highest strength after incubation at 100% humidity was recorded for the cement derived from EAPC clinker (9.96MPa±3.21) while the mean lowest strength was recorded for the cement based on Kaolin geopolymer (2.00MPa±0.23). Mean average compressive strength tested for all cements increased over time (1d=0.41MPa±0.08, 3d=1.69MPa±0.49, 7d=4.31MPa±0.66, 28d=5.90MPa±1.06), with a statistically significant difference at the different time points (F statistic=82.39, 3df, p<0.0001). Although cements based on Kaolin recorded lowest mean strength values, their behavior was most consistent between 1d and 28d, with all samples breaking and a statistically significant difference between means at all the time points within the group (F-statistic=76.64, df=3, unadjusted p<0.0001, adjusted p=0.000). Cements derived from FA and those containing CaF_2 demonstrated fluoride ion release capability, dependent on the amount of fluoride content in the formulation. Kaolin/FA cement demonstrated the highest fluoride ion release (1mmol/L at 28d). Excluding initial investment, the cost of local production of restorative dental cements was found to be less than importation.

Conclusion: Kenyan PC and related materials were found to be similar to MTA, a commercial dental product, regarding composition and particle size. These locally available AS materials were capable of forming ionomer-type cements thus may be utilized to design low-cost yet stable glasses for atraumatic restorative treatment (ART) restorations. Specifically, the cements based on Kaolin were identified as a prototype. Further studies should utilize tooth-coloured materials for aesthetically pleasing restorations.

CHAPTER ONE

1. INTRODUCTION

1.1   Dental caries – a global perspective

Dental caries has become a ubiquitous public health problem despite its pathophysiology being well understood [1] and preventive measures being documented [2-5]. Dental caries is a disease of dental hard tissues characterized primarily by demineralization following acidic attack as described in Keyes' triad [6]. Despite being preventable, Petersen [2,3] asserts that it affects 60 – 90% of children and most adults in industrialized countries. The prevalence has also risen in Asia and Africa and has been attributed to lifestyle changes [2,3] characterized by increased consumption of refined sugar [7].

In Kenya, the first National Oral Health Survey in 2015 [8] reported caries prevalence of 34.3% among adults and 23.9% among 5-, 12- and 15-year old children; alarmingly, the prevalence was 46.3% among 5-year olds. This is a worrisome trend that needs to be addressed urgently.

Untreated dental caries advances into a debilitating condition leading to pain, reduced masticatory efficiency and loss of aesthetics [5]. In low- and middle-income (LMI) countries, extraction is often the cheapest and most readily available form of treatment, providing immediate relief from pain but worsening loss of form and function and reducing quality of life [2-4].

Preventive measures such as fluoridation of water, milk and use of fluoridated dentifrices have been shown to be effective. Moreover, preventive oral health programmes such as school oral health programmes targeting children as well as oral health promotion are well-known. Such methods have been employed successfully in industrialized countries with commendable results [2-5]. In a number of European countries such as Denmark, United Kingdom, Germany and Switzerland, Marthaler *et al.* [9] and Splieth *et al.* [10] report reduced caries prevalence among 12-year olds as a result of active promotion of oral health through controlled water fluoridation, use of fluoridated toothpastes and oral health education.

Unfortunately, the reverse is true in LMI countries where there is hardly any preventive measure employed and dental caries is left virtually untreated with extraction as the most readily available option [2-4]. Stretched resources have created a scenario whereby oral health is often largely ignored when tackling other non-communicable diseases due to their increased risk of being fatal [2-4]. There is a lack of clear structures aimed at implementing preventive measures to tackle the problem of dental caries, among other oral diseases. In Kenya, healthcare consumes only 8% of total Government expenditure; oral health is considered under the umbrella of general health, receiving a meager inadequate 0.0016% of the overall budget allocated for healthcare [11].

1.2 Current concepts in the management of dental caries

Conventionally, dental caries is treated through placement of direct or indirect restorations. Restorative dentistry aims to salvage diseased dental hard tissues through the placement of restorations. As reviewed by Petersen *et al.* [12] and Bayne *et al.* [13], four main classes of direct restorative materials are available: silver-mercury amalgam (dental amalgam), resin

composites, glass ionomers and resin ionomers. Composites are the closest competitor to dental amalgam with adequate mechanical properties and unmatchable aesthetics. Although there are concerns around the degradation products of the monomers, there is no documented case of a health hazard arising from composite restorations. Glass ionomer cements are preferred for their ability to adhere chemically to the tooth structure and to release fluoride; however, their mechanical properties limit their longevity especially in high stress regions [13].

Restorative, or conservative, dentistry traditionally involves placement of restorations to prevent tooth loss by extraction; however, despite advances in restorative dentistry, the greatest challenge remains to find the ideal biomimetic material that can match the properties of hard dental tissues [13,14]. Navigating biocompatibility and environmental impact concerns in the quest for equivalence or superiority to established materials renders the process of biomaterial development tedious and costly. This financial burden is eventually transferred to patients, restricting access to advanced restorative treatment options.

Further, prevention and minimal intervention dentistry are widely accepted concepts for the management of dental caries. Preventive dentistry programmes focusing on risk factors have proven effective in industrialized countries [3,4]. However, the majority of developing countries do not have preventive dentistry programmes [4]. This is mostly due to financial constraints in an environment where public health agendas of various stakeholders often conflict. Despite the fact that disease prevention is ultimately more economical than treatment, limited resources have led to a scenario in which oral health is largely ignored

when tackling other chronic non-communicable and communicable diseases perceived to have a higher risk of mortality [3,4]. There is a lack of strategies and goodwill to invest in and implement oral health promotion and disease prevention.

Minimal intervention dentistry (MID) is a more recent, patient-specific treatment. It is a comprehensive longitudinal approach towards prevention through risk assessment while minimizing operative intervention [15]. Proponents of MID suggest that 'extension for prevention' should be replaced by 'prevention of extension', arguing that the conservative goals of the former are questionable because of the surgical approach to remove diseased tissue prior to placement of a restoration. Preventive dentistry, atraumatic restorative treatment (ART) and adhesive dentistry are practical aspects of MID, with the ultimate goal of preventing or halting progression of disease [16].

Minimizing the need for intervention by arresting disease progression is cost-effective; a key advantage of approaches such as ART and silver diamine fluoride is their simplicity as well as affordability, making them practical in resource-strained settings. However, in Kenya, the dental education curriculum focuses on curative rather than preventive training. Often, these techniques are considered intermediary interventions until the patient can access definitive treatment. Dental amalgam is still the preferred posterior restorative material in LMI countries such as Kenya; therefore, it is anticipated that its phase-down will present challenges in oral health care service delivery.

1.3 The Minamata Convention on Mercury and Dental amalgam phase-down

The Minamata Convention on Mercury was convened by the United Nations Environment Programme in 2013 to address the environmental pollution occasioned by mercury-based products and associated waste. The Convention is a global treaty whose agenda seeks to reduce environmental impact from mercury waste through phase-out of mercury-based products and cessation of manufacture of mercury by 2020. Silver-mercury amalgam (dental amalgam) is the only product subject to a phase-down [13,14,17-19].

Silver-mercury amalgam is one of the oldest and most reliable direct restorative material; none of the other restorative materials out-performs amalgam which has withstood the test of time for more than a century [13]. Several developing countries, including Kenya, are signatories to the Convention. The phase down of dental amalgam is likely to negatively impact the practice of restorative dentistry in these countries because they lack the economic ability as well as the infrastructure to optimize the use of alternative materials.

Moreover, procedures requiring full-time availability of electricity or digital techniques such as computer aided design and machining (CAD/ CAM) are limited and expensive [14,19]; therefore, alternative solutions are warranted.

1.4 Challenges in biomaterials development and contributions by low- and middle-income countries

In light of the imminent global phase down of silver-mercury amalgam, it is imperative that research should focus on innovative materials that may serve as alternatives. This is a herculean task because the ideal material aims at mimicking the natural dental tissues, that is, enamel and dentine. Indeed, Rekow *et al.* state that:

> *"the ideal material is no material"* [14],

further emphasizing the need to prevent dental caries due to the difficulty in developing biomimetic materials.

The criteria for an ideal restorative material include fracture toughness, ease of application and longevity [14]. Unfortunately, none of the available materials can be considered ideal as they exhibit various shortcomings. Their brittle nature renders them prone to failure by fracture hence compromising on their longevity; furthermore, not all materials are readily available globally, a situation brought about by infrastructural and economic limitations as well as stringent cross-border approvals [14,20].

Another requirement of an ideal restorative material is that it should be easy to use even in a resource-strained environment such as is common in LMI countries [14]. Apparently, this is more likely to be achieved with simple formulations such as powder and liquid for manual mixing unlike presentations that require mechanical mixing or light-activated

polymerization utilizing electrical equipment [14]. It is highly unlikely that a single material can meet all the needs globally [14].

Developing countries such as Kenya are thus faced with a challenge of finding a cost-effective solution to address the burden presented by a high prevalence of dental caries. Therefore, it is suggested that they should consider locally available options as a solution to their unique problems regarding dental restorative materials for the management of dental caries.

1.5 Summary and thesis structure

From the aforementioned, it is clear that dental caries presents an expensive public health burden. Additionally, the main available categories of direct restorative dental materials are not ideal; in fact, one of the oldest materials, dental amalgam, is subject to a phase-down by 2020 and alternative materials are not globally accessible. Developing countries are disadvantaged because they are faced with rising disease prevalence yet lack the resources to provide comprehensive management to all. Although ART is a cheap alternative to manage caries in poor countries, the restorative material used, glass ionomers, lack adequate strength to ensure longevity and the few that do are expensive; therefore, ideally, countries such as Kenya should channel their efforts towards disease prevention by adopting policies that incorporate oral health promotion and school oral health programmes.

Furthermore, developing countries should consider utilizing available resources to find solutions that are tailored to their specific needs. A good starting point would be the local industries. It is proposed here that locally available materials may be used to develop a

restorative dental material that can be used in simple and cheap restorative procedures in Kenya. These materials would be readily available and inexpensive, with minimal negative environmental impact than those associated with dental amalgam and other mercury based products. It would also be beneficial by reducing or arresting disease progression while also relieving symptoms thus reducing the urgent need for extractions in the wake of no forthcoming definitive alternative.

Therefore, this project aims to investigate some properties of locally produced Portland cement and related materials, targeting the development of a prototype for a restorative dental cement that can be used in procedures such as ART while also serving as a possible alternative following the phase down of dental amalgam. The overall goal is improve quality of life through improved oral health status of the Kenyan population.

The thesis will be reported in sections as outlined below:

1. A critical review of relevant literature to identify a research gap and justification for the current study by:

a) Describing the burden of dental caries in Kenya and the available treatment options for the same;

b) Describing the natural tooth structure and providing a critique of available restorative materials;

c) Discussing the structure and composition of high viscosity glass ionomer cements, Portland cements, geopolymers and calcium silicate cements and comparing their physico-mechanical properties;

d) Assessing some analytical techniques utilized in the development and evaluation of biomaterials, and which will be employed in the current study; and,

e) Presenting a conceptual framework for the study protocol.

2. A statement of the research problem, justification for the study and description of the aims and objectives of the study.

3. A description of the materials and methods.

4. Presentation of the results.

5. Discussion of the results.

6. Conclusion and recommendations.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Introduction

The aim of this study is to develop a prototype for a restorative dental cement using locally available raw materials in Kenya. The ultimate goal is to address the high prevalence of dental caries in Kenya and other low and middle income countries. This problem is compounded by the fact that such countries lack crucial preventive programmes and cannot afford the high cost of treatment of dental caries; yet they are experiencing a lifestyle change characterized by increased consumption of refined sugar and which is contributing to the rising caries prevalence.

It is proposed here that one solution for the unique problems of such countries may be found in locally available raw materials. An example is Portland cements, whose derivatives, calcium silicate cements are already in use as endodontic materials [21,22]. A worthwhile consideration is to expand their applications in the development of an affordable alternative polyalkenoate restorative dental material. This material may be useful in minimally invasive procedures such as atraumatic restorative treatment, originally developed for managing caries in a resource-strained setting as is commonly found in low and middle income countries [23,24].

The literature reviewed here serves to highlight the research gap that the study aims to fill. This is done by first presenting a situation analysis by describing the burden of caries in Kenya and the treatment options available. Secondly, the biomimetic restorative materials

available are compared to the natural tooth structure, while providing an assessment of currently available ones. Thirdly, a comparison of the materials to be investigated in this study are presented: Glass ionomer cements, and Portland cements and synthetic geopolymers as the raw material pecursors. Fourthly, an assessment of some analytical techniques for biomaterial evaluation is presented. Finally, a conceptual framework within which this research will fit is presented.

The articles included in the literature review were accessed through a systematic search conducted on Pubmed, Google Scholar and WHO Global Health Library using relevant key words. A manual search of gray literature was also performed for additional articles.

2.2 Research gap

The conventional method of treating dental caries involves placement of direct restorations using materials such as dental amalgam, resin composites, glass ionomer cements and resin ionomers [12,13]. It is difficult to define the ideal restorative material but Rekow *et al.* [14] recommend that at the very least, an ideal material should be biocompatible, resistant to fracture, demonstrate longevity, be affordable and easy to manipulate even in a resource strained setting. The last three properties are of particular importance in low- and mid-income countries because of cost implications.

Affordability and ease of manipulation may be perceived as requiring minimal investment in accessory equipment or infrastructure as well as minimal importation costs in order for restorative dentistry to be accessible even in poor countries. Holmgren and Frencken [25] identified a need for advancement in the filling materials used for ART to enable the

restorations last longer than three years. GICs are preferred because of their ability to adhere chemically to the tooth structure, hence providing a seal to prevent disease progression; furthermore, they also demonstrate fluoride leaching capability thus regarded to be anti-cariogenic [26]. Admittedly, nearly two decades later, the ART technique has been shown to be an affordable successful option in underprivileged settings [23,24]; the restorative materials have evolved markedly over the years and there are reports of ten-year survival rates [27].

However, GICs are still characterized by low fracture toughness that impacts negatively on their longevity; arguably, most clinicians consider glass ionomer cements to be temporary or intermediary restorations, an observation reinforced by Petersen *et al.* [12] and Bayne *et al.* [13]. This problem is not unique to GICs; indeed, the review of literature finds that all available direct restorative materials are brittle and Rekow *et al.* [14] emphasize that their success relies heavily on the design of the restoration coupled with the clinician's skill. Undeniably, the ideal restorative dental material remains elusive necessitating continuous research to address the shortcomings of the existing ones.

Another challenge that the dental profession has to contend with is the looming phase-down of dental amalgam by 2020, as documented in the Minamata Convention on Mercury [13,14,17-19]. Apart from its remarkable compressive strength, silver-mercury amalgam is one of the simplest hence affordable restorative materials making it readily accessible. Petersen *et al.* [12] caution that it is highly likely that the phase-down of dental amalgam may hinder access to affordable restorative dental treatment. Therefore, there is an urgent need to find an alternative with minimal negative environmental impact yet still offering the excellent material properties that has been established with amalgam for more than a century [14,19,28,29].

The usage of dental amalgam in low- and middle-income countries far surpasses that of resin composites and resin ionomers [12]. This may be because the advantages of dental amalgam are well established and the latter require sophisticated accessories usually powered by electricity, yet rural electrification remains a challenge [12,13]. Additionally, industrialized countries have found alternatives in indirect restorations; however, these too may be expensive for majority in developing countries because of the technical processes involved in their production [12]. This essentially means that developing countries rely greatly on direct restorative materials to treat dental caries. Nonetheless these materials are not ideal, or are impractical in certain circumstances due to the reasons stated above. Therefore, it is necessary for low- and middle-income countries to seek out local practical solutions to their unique needs.

There is paucity of data on attempts by such countries to contribute to research on restorative dental materials. One apparent area of interest is Portland cement whose derivatives have been successfully marketed for use in endodontic restorative procedures [21,22]. These materials are categorized as calcium silicate cements, a group of hydraulic cements introduced into dentistry by Torabinejad in the early 1990s specifically for endodontic applications [30]. Since then, several modifications have been documented and several commercial brands have become available yet their applications have largely remained endodontic [21,22].

It is well established that these materials are mostly comprised of Portland cement, as documented by Estrela *et al.* [31], Camilleri [32] and Steffen and van Waes [33], among others. Because the commercial versions are expensive and out of reach for many in developing

countries, there have been several investigations on the parent compound, Portland cement, to establish its suitability as a cheaper alternative [34-36]. Moreover, reviews by Steffen and van Waes [33] and Darvell and Wu [37] have concluded that further research is necessary on these relatively new biomaterials with the aim of better understanding their properties and consequently, expanding their applications. None of these studies has been conducted in Kenya hence the feasibility of the Kenyan product as a biomaterial is unknown.

Additionally, the effect of polycarboxylate plasticizers such as poly (acrylic acid) on these materials has not received adequate research attention. This presents an opportunity for further assessments using locally produced Kenyan Portland cement and related materials such as geopolymers or alkaline-activated aluminosilicates.

From the aforementioned, the subsequent literature review will clearly reveal that several studies have compared calcium silicate cements such as mineral trioxide aggregate (MTA) with various brands of Portland cement and have established their similarity regarding composition, hydration reaction, antimicrobial properties and biocompatibility. With the cost of the commercial dental products placing them out of reach of many clinicians and their patients, particularly those in developing countries, there is a sound basis to evaluate Portland cements and related materials in Kenya for the development of polyalkenoate alternatives as a cheaper substitute in expanded restorative applications such as ART. This presents an opportunity to utilize locally available resources in seeking solutions for local and regional-specific challenges. Exploring alternatives provided by local industries may not only be more affordable but may also result in overall improvement of oral public health in the long run through relief of symptoms and slowing down disease progression.

Therefore, this project aims to investigate some properties of locally produced Portland cement and related materials, targeting the development of a prototype for a polyalknoate restorative dental cement that can be used in procedures such as ART while also serving as a possible alternative following the phase-down of dental amalgam. The overarching goal is improve quality of life through improved oral health status of the Kenyan population.

2.3   Burden of dental caries in Kenya

Manji's provocative question in 1986 [38], whether dental caries was increasing in Kenya, concluded that the data was equivocal; although the disease was ubiquitous even then, the rate of progression was slow . Since then, several prevalence studies have been conducted in Kenya with worrisome results all of which lead to the conclusion that more should be done to address the burden of caries in the country. Furthermore, Macigo *et al.* [7] suggest a direct association with increased sugar consumption nationally. This, together with little effort aimed at prevention, have compounded the problem.

Studies among children under 5 years of age have reported caries prevalence above 50%. Njoroge *et al.* [39] recorded a prevalence of 59.5% among children in Kiambaa, Kiambu County with the mandibular deciduous molars and maxillary incisors being most frequently affected. In Nairobi County, Ngatia *et al.* [40] found that the prevalence among a similar age group was 63.5% and reported a positive correlation to consumption of a high sugar diet. In another similar study in Nairobi County, Masiga and Holt [41] reported caries prevalence of 62% among 3-year olds and 50% among 5-year olds, with an observation of more filled teeth among those perceived to be of a higher social class as determined by the occupation of the head of the household.

Other studies conducted among older children have reported equally high prevalence of dental caries. They include that by Masiga and M'Imunya [42] who assessed HIV-positive children aged between 3-15 years and found the overall prevalence to be 65%, specifically 50% in deciduous dentition and 30.9% in permanent dentition. The high caries prevalence in this group was also found to affect their quality of life, negatively impacting their appearance, ability to bite and chew and causing them to miss school due to pain and discomfort.

In another study, Owino *et al.* [43] assessed 12-year olds in Kitale, Trans Nzoia County and reported overall caries prevalence of 50.3%, specifically 44.5% for permanent teeth; moreover, they observed that females were more affected. Makhanu *et al.* [44] also evaluated 13-15 year olds in Kenya and found a statistically significant association between caries experience and dental fluorosis despite no correlation to snacking habits. In other studies involving older children, Ng'ang'a *et al.* [45] found that only 48% of pastoralist children they examined were caries-free while among handicapped children aged 3-15 years examined by Ohito *et al.* [46], it was found that 44% of them suffered from caries; however, in this particular study, a cheap intervention was observed to be effective in reducing plaque and gingivitis in the subjects. Earlier in 1992, 6 to 8 and 13 to 15-year olds in Nairobi examined by Ng'anga' and Valderhaug [47] were found to have a caries prevalence of 46% and 50%, respectively.

Among Kenyan adults, Kassim *et al.* [48] examined a rural community and found that 56.7% of the subjects were caries-free but 72.1% of those with caries were women. This population was also ignorant about dental diseases. In a much earlier study, evaluation of a Kenyan

nomadic group found that caries was relatively rare but periodontal disease was more common particularly among the older patients [49]. Results from the first National Oral Health Survey conducted in Kenya in 2015 showed that caries prevalence was 34.3 % among adults and 23.9% among 5, 12 and 15 year old children; when only 5-year olds were considered, the prevalence was 46.3% [8].

All of these studies have established that there is a high caries prevalence in Kenya therefore recommending that more effort should be placed in its reduction; moreover, the effect of fluorosis due to consumption of highly fluoridated food and water has been established. Despite the initial expense involved, preventive measures such as diet counseling, controlled fluoridation of water, milk and salt and school oral health programmes would greatly contribute to caries prevalence reduction. Without a doubt, the cost-effectiveness of prevention versus treatment of caries in Kenya needs to be evaluated. It is illogical that the disease prevalence is escalating in a country that can ill afford to provide adequate curative services. Nevertheless, even as advocacy for prevention piles up, treatment options need to be explored for those already afflicted.

2.4 Management of dental caries in Kenya

Conventional caries management involves placement of direct or indirect restorations with the intention to eliminate diseased tissue while salvaging sound ones [12,13]. As reviewed by Petersen *et al.* [12] and Bayne *et al.* [13], four main classes of direct restorative materials are available: silver-mercury amalgam (dental amalgam), resin composites, glass ionomers and resin ionomers. However, despite advances in restorative dentistry, the greatest challenge

remains to find the ideal biomimetic material that can match the properties of hard dental tissues [13,14].

In addition to restorative dentistry, prevention and minimal intervention dentistry are widely accepted concepts for the management of dental caries, utilized successfully in industrialized countries [3,4]. However, the majority of developing countries do not have preventive dentistry programmes [4]. Minimal intervention dentistry (MID) is a more recent, patient-specific treatment employing a comprehensive longitudinal approach towards prevention through risk assessment while minimizing operative intervention [15]. Preventive dentistry, atraumatic restorative treatment (ART) and adhesive dentistry are practical aspects of MID, with the ultimate goal of preventing or halting progression of disease [16].

In Kenya, the dental education curriculum is primarily curative to address the heavy disease burden. Although aspects of prevention such as fluoride therapy and preventive resin restorations are taught, the focus is on restorative and prosthetic rehabilitation following extractions. Preventive dentistry programmes such as national school oral health programmes and water fluoridation/ defluoridation are non-existent.

A few studies have been conducted in Kenya to assess usage of direct restorative dental materials. Ganatra *et al.* [50] assessed the selection of direct posterior restorative materials by dentists in Nairobi as well as the reasons determining preference for the indicated materials. They found that dental amalgam was the preferred material for direct posterior restorations in permanent teeth, while GIC was mostly applied for deciduous restorations. Dental amalgam was preferred mainly because of good performance history and easy handling

profile, as compared to composites. Unpublished work by Ndong'a *et al.* in 2012 reported similar findings that dental amalgam was the preferred direct restorative material in posterior permanent teeth among dentists in Nairobi; however; compomers and resin composites were being used more for deciduous teeth restorations than the previously preferred glass ionomer cements.

More recently, Osiro *et al.* [51] evaluated the categorization and selection of direct restorative dental materials by dentists in Kenya and found that all categories of direct restorative materials were readily available in the Kenyan market. Their selection was primarily driven by type and location of cavity, cost and patient preference. While amalgam remained the preferred posterior restorative material, there was increasing use of composites. It is remarkable that most respondents were derived from the urban centres in Kenya, implying the distribution of dentists in Kenya, and suggesting that majority of Kenyans still do not have access to advanced restorative dental care.

In fact, the current dentist-patient ratio in Kenya is 1:40, 000, way below the WHO recommendation of 1:1,000. A paradigm shift in the current curative-focused curriculum is therefore necessary to promote preventive aspects of dentistry that include simple, low-cost approaches such as minimal intervention dentistry and atraumatic restorative treatment.

2.5 Minimal intervention dentistry and atraumatic restorative treatment

Minimal intervention dentistry (MID) is a recent philosophy of oral healthcare provision defined by Tyas as:

"the maintenance and monitoring of oral health through continuous care, comprising comprehensive preventive management; a longitudinal approach to risk assessment and diagnosis of chronic disease; and, a minimal intervention approach to any necessary operative intervention." [52]

Wilson [15] emphasizes that MID is therefore not only linked to the modern management of dental caries, but is equally applicable to the management of other oral conditions such as periodontal disease and chronic mucosal conditions, notably xerostomia. Effective minimally invasive dentistry is both patient specific and patient centered.

With regards to cariology and restorative dentistry, Ericson defines minimal intervention dentistry as:

"a systematic respect for the original tissue by acknowledging that caries is a multi-factorial disease that is not cured by restorations and that cavity preparation weakens the original tooth." [16]

Proponents of MID like Burke [53] and Murdoch-Kinch and McLean [54] argue that G.V. Black's principle of 'extension for prevention' [55] should be replaced by 'prevention of extension' [53,54]. The conservative goal of these principles are considered questionable because they employ a surgical approach to remove diseased tissue followed by placement of a restoration [52,54]. MID advocates for an apparent shift from G.V. Black's principles of cavity preparation which were primarily intended for mechanical retention of dental amalgam. Indeed, with improved understanding of the disease process as well as diagnostic tools, conventional surgical intervention can be delayed as long as possible to preserve the natural tissues [52,54]. Instead, it is recommended that in lesions that need restorations,

minimal cavities should be prepared using less destructive methods such as air-abrasion, lasers and polymer cutting instruments. These may then be restored using adhesive materials such as glass ionomer cements and composite resins. Deep pits and fissures may be sealed without cutting [15]. Moreover, extraction should not be regarded as treatment per se, rather, treatment failure [13].

As illustrated by Banerjee [56] and Gujjar and Sumra [57], successful minimal intervention requires a treatment plan encompassing four elements: identify, prevent, restore and recall. The identification phase involves diagnosis using modern caries detection techniques complete with conducting caries risk assessment of the patient. Prevention involves control of disease progression by employing active standards of care both at individual as well as professional team level. Restoration involves tissue repair through minimally invasive techniques and adhesive materials. Recall phase involves review visits whose number are determined by the susceptibility of the patient.

Therefore, in order to prevent disease progression which would increase the likelihood of extraction, restorations should be placed as soon as possible; the smaller the restorations, the better the prognosis. Additionally, smaller restorations may be achieved more realistically by employing adhesive dentistry [16,53,58]. Preventive dentistry and atraumatic restorative treatment are practical aspects of MID, with the ultimate goal of preventing or stopping progression of disease [16,52].

Atraumatic restorative treatment (ART) was developed specifically for low-income areas, common in developing countries, and was piloted by Frencken in rural Tanzania, East

Africa in the late 1980s [52,59,60]. ART is a method of caries management that involves the use of only hand instruments to remove caries, after which the cavity is filled with a material that chemically adheres to the tooth, preferably a glass ionomer cement [61]. This is possible because there is a better understanding of the process of dental caries, permitting employment of minimal cavity preparations, as well as the development of reliable and effective adhesive restorative materials [62]. Currently, glass ionomer cement (GIC) is the preferred restorative material for the ART approach because: glass ionomers possess chemical bonding and fluoride releasing properties; have the potential to enhance remineralisation; and, these restorations may act as a rechargeable fluoride releasing system by first absorbing fluoride then releasing it gradually [26].

A key feature of the ART approach is the use of hand instruments to scoop out soft dentine, raising the question of residual caries. From studies such as that of Fusayama *et al.* [63,64] and Massler [65], it is now widely accepted that dentine caries can be divided into two layers: the outer soft and infected layer which should be removed, and the deeper hard, often stained affected layer with few micro-organisms which may be preserved [59]. This is depicted in Figure 2.5.1.
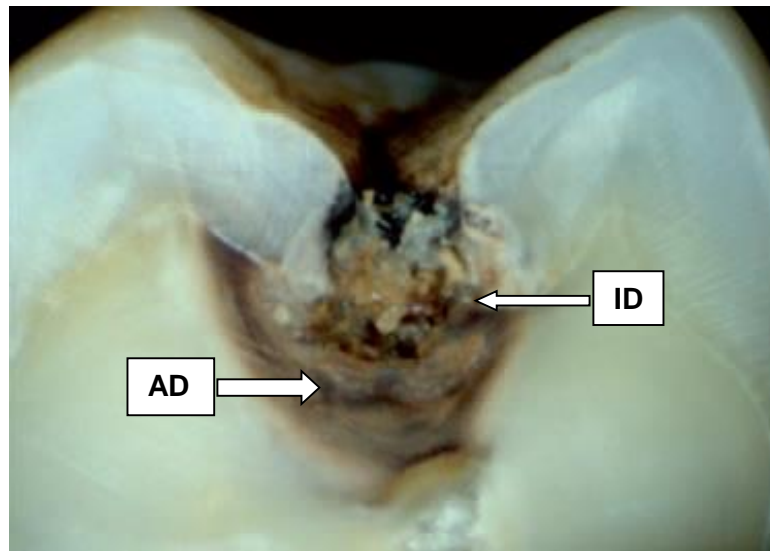
Figure 2.5.1: Illustration of layers of outer infected dentine (ID) and deeper affected dentine (AD) in a caries lesion [59]

As reviewed by Holmgren *et al.* [59], although elimination of micro-organisms is the aim during complete removal of dentine softened by caries, it is not always successful and it has been found that some micro-organisms remained even after soft dentine was completely removed and the cavity disinfected with sodium hypochlorite [66]. Moreover, in young patients, excavation of deep lesions increases chances of pulpal exposure [67]. Indeed, this is one of the criteria when selecting teeth to be restored by the ART technique, that there should be no risk of pulpal exposure which would necessitate advanced treatment. A trained operator should be capable of successfully determining the ideal lesions [68].

To prevent the residual caries from progressing under a restoration, a combination of three measures was prescribed by Weerheijm and Groen [69]. All these measures work to reduce the number of microorganisms responsible for the progression of the lesion. They include

isolation of the caries process from the oral environment using a sealant or restoration, excavating the carious dentin and using a cariostatic filling material.

Firstly, isolation ensures reduction in the number of microorganisms as well as the lesion depth so long as the sealant or restoration is maintained in a secure state for a long time. This was demonstrated by Mertz-Fairhurst *et al.* [70] and Ribeiro *et al.* [71] who found that after 10 years, a completely sealed caries lesion with soft, wet and demineralized dentine left *in situ* neither progressed nor jeopardized the restoration. Secondly, although microorganisms are not always completely removed during excavation, it remains an important step in arresting the caries process by reducing the bacterial load, as shown by Bjornal *et al.* [72] and Mertz-Fairhurst *et al.* [70]. Thirdly, cariostatic properties are attributed to some filling materials such as glass ionomer cements (GIC) which are hypothesized to reduce the number of micro-organisms in residual caries. The cariostatic effect of GIC is thought to be primarily from fluoride release [73-75]. However, glass ionomer cements are, at best, intermediate restorations. More research needs to be dedicated to a restorative material that can last longer and enhance remineralisation of the affected dentine as these are the major shortcomings of the glass ionomers for ART.

Although originally meant for low economic countries with poor access to specialized dental treatment, the ART technique has gained popularity in modern dental practice particularly among paediatric and geriatric patients, as well as other anxious patients [59]. In 1999, Holmgren and Frencken [25] outlined areas of the ART approach that required further investigations as: ART restorations lasting longer than three years duration and evaluated using recognized criteria; multi surface ART restorations; ART restorations in primary

teeth; and, ART sealants . Almost two and a half decades after its inception and with improved materials and a better understanding of the caries process, ART plays a significant role in the management of dental caries, with promising results [24].

Nevertheless, the uptake of ART in Kenya is limited with scarce data available. Osiro *et al.* [76] reported that ART has not been actively promoted as an alternative procedure to improve oral healthcare in Kenya. They found that most dentists were aware of the approach but did not regard it as definitive treatment, expressing the reality that the current dental education curriculum focuses on curative rather than preventive measures. Glass ionomer restorations are also associated with short to mid-term clinical success that limits their application, as reported by Kemoli and van Amerongen [77] who recorded survival rate of glass ionomer ART paediatric restorations of 44.8% after one year, reducing to 30.8% after two years [78].

Other concerns included multi-surface restorations [68,77] and cervical marginal gaps [78]. However, it was concluded that operator's level of experience was insignificant [79] while rubber dam isolation was thought to lead to better results [80]. In a systematic review to assess its practicality, Kemoli [81] concludes that the ART technique would be beneficial in Kenya by aiding in teeth preservation in areas with very few or no dentists or public hospitals that are equipped to provide definitive dental services.

2.6 Natural tooth structure

The natural tooth is an organized composite of three main tissues: enamel, dentine and pulp (Figure 2.6.1). The tooth is divided into the crown which is the part visible in the oral cavity, the roots which are nested within the alveolar bone, and the neck which connects the two.

The tooth is retained in place by the periodontium, comprising the gingiva, the cementum and the periodontal ligament. The pulp is the vital tissue comprising cellular matter and neurovascular tissue.
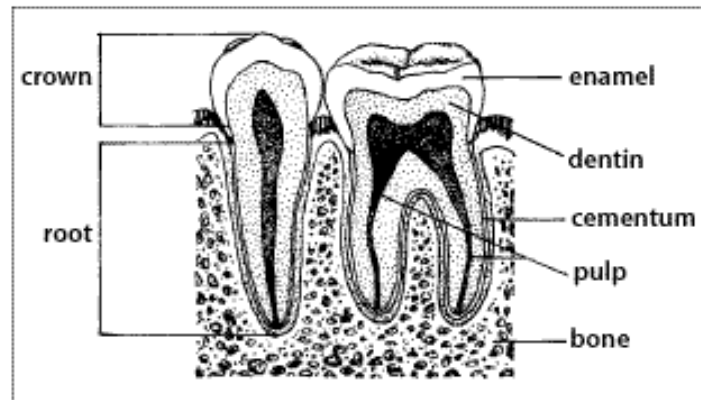
Figure 2.6.1: Cross-section showing natural tooth structure (nih.gov)

Restorative dentistry deals with placement of restorations to prevent tooth mortality by extraction. Dental caries is among the commonest dental diseases, affecting the dental hard tissues through acidic demineralization. Several restorative materials have been developed and marketed including silver-mercury amalgam, gallium alloys, zinc phosphate cements, composite resins, dental silicate cements, zinc polycarboxylate cements and glass ionomer cements [12]. However, Bayne *et al.* [13] and Rekow *et al.* [14] identify the greatest challenge associated with restorative dental materials as to find the ideal one that can match the properties of the natural dental tissues .

Texts by Berkovitz *et al.* [82] and Mann [83] describe enamel as the hardest substance in the human body and a highly ordered structure resulting from biologically controlled

biomineralisation. Enamel is secreted once in a lifetime by ameloblasts which undergo apoptosis thereafter; therefore, enamel is irreplaceable. Mature enamel comprises 96% (by weight) inorganic component made up of hydroxyapatite crystals, 1% organic matter, mostly proteins, and 3% water. This makes enamel majorly ceramic in composition hence its brittle nature.

The principle units in enamel are the prisms or rods which are approximately 5µm wide and are formed by the clustering of the hydroxyapatite crystals, at least 1000 per prism. The prisms run a decussating course from the enamel-dentinal junction to the incisal or occlusal surface, resulting in the pattern described as Hunter-Schreger bands when examined in a longitudinal section. Inter-rod enamel is interspersed between the prisms and consists of hydroxyapatite crystals oriented at 40-60° to the longitudinal axis. This structure results in a brittle, plastic composite with a high mineral density and very low organic and water phases [82,83].

Dentine on the other hand is less mineralized, comprising 67% (by weight) inorganic component, also hydroxyapatite crystals, 13% organic component, mostly collagen and dentine proteins, and 20% water. Dentine is arranged in a tubular manner and the tubules are surrounded by intertubular and peritubular dentine. Dentine is secreted by odontoblasts whose cell bodies reside in the pulp chamber, secreting secondary and tertiary dentine in response to various stimuli throughout an individual's lifetime. Because of the reduced mineral density and increased organic component, dentine is more elastic than enamel and behaves as a shock absorber to cushion and prevent fracture of enamel [82,83].

Evaluation of the mechanical properties of the two tissues have shown that enamel is hard and rigid, with elastic modulus ranging from 50 – 100GPa and hardness values of 2.5 – 6GPa; moreover, it exhibits a high compressive strength (384MPa) but low tensile strength (10MPa), while fracture toughness of surface enamel ranges from 0.7-1.3 MPa.m$^{0.5}$. In contrast, dentine is softer and elastic (elastic modulus 12GPa and hardness 0.5GPa) with lower compressive strength but higher tensile strength (flexural strength 80MPa) as well as higher fracture toughness than enamel (2.4 MPa.m$^{0.5}$) [84-87].

2.7   Ideal properties of a restorative dental material

In order to mimic enamel and dentine, an ideal restorative material should display the following characteristics, outlined by Petersen *et al.* [12]:

Mechanical

The material should have adequate strength that compares to that of enamel and dentine to enable it withstand masticatory forces and wear. Important parameters include compressive, tensile and flexural strength as well as hardness and rigidity.

Physical

Important physical properties include thermal properties such as thermal expansion coefficient, thermal conductivity and thermal diffusivity. Radiopacity is a necessity to enable visualization on radiographs.

Chemical

The material should survive in the harsh oral environment with its fluctuating pH and chemical variations without disintegrating, dissolving or undergoing acidic attack.

Biological compatibility

The material should not elicit an undesirable host response presenting as allergy, toxicity, mutagenicity or carcinogenicity. Desirable responses include bioactivity and chemical adhesion to the tooth structure.

Aesthetic

The ideal material should mimic the natural tissues to avoid being readily distinguished by an on-looker.

Additional properties

The ideal restorative material should also be cheap and readily available even in remote areas. Moreover, it should be easy to manipulate without requiring sophisticated and expensive equipment.

2.8 An assessment of direct restorative dental materials

Although several direct restorative materials are available, they are not ideal. Continuous research is necessary to improve their shortcomings, presented next, in reference to reviews by Petersen *et al.* [12], Bayne *et al.* [13] and Rekow *et al.* [14].

2.8.1 Silver-mercury amalgam (Dental amalgam)

After direct filling gold, silver-mercury amalgam is the oldest direct dental restorative material, its use spanning more than a century. It is an alloy of silver, tin, copper and triple distilled mercury. The alloy powder is triturated with the liquid mercury into a soft pliable mass that is condensed into a cavity and carved prior to setting to a rigid solid. The first dental amalgam alloys comprised less than 6% of copper and were associated with several disadvantages due to the formation of the gamma 2 phase (tin-mercury phase) during the setting reaction. These included higher creep, increased propensity to corrosion and marginal failure.

These disadvantages were reduced with the development of higher copper amalgams which contain between 13 to 30% of copper. The increased copper content results in elimination of the gamma 2 phase. In the admixed alloys, high copper content is achieved through a silver-copper eutectic alloy which reacts with gamma 2 in a secondary reactive step to form gamma 1 and eta phases. For uni-composition alloys, high copper is realized through addition of copper-tin epsilon phase which reacts with gamma to form the eta phase but no gamma 2 phase at all. Dental amalgam has several advantages. It has adequate compressive strength of more than 400MPa, it is cheap and easy to manipulate. It is also radiopaque and exhibits a self-sealing ability due to corrosion products.

However, its disadvantages include its metallic appearance as well as its tendency to corrode in the oral cavity that renders it unaesthetic. Although it has adequate compressive strength, dental amalgam is brittle in tension thus requires extensive tooth preparation to ensure adequate bulk to prevent fracture. It is not adhesive and relies on mechanical features

for retention necessitating further destruction of tooth tissues. Moreover, silver-mercury amalgam is a mercury based product and is now scheduled to be phased down following the Minamata Convention on Mercury to reduce environmental impact from mercury waste. Although there is no documentation of an unwanted biological reaction in humans from dental amalgam, mercury is a well-known toxic substance and due precaution is mandatory when handling it in the dental surgery.

2.8.2 Gallium alloys

Because of the disadvantages of silver-mercury amalgam, gallium was proposed as a substitute for mercury in gallium alloys. Gallium is a liquid metal at 29.78°C and addition of tin and indium makes it liquid at room temperature. However, gallium alloys have largely been unsuccessful in the market because their setting reaction is difficult to control due to chemical instability. Moreover, they are expensive and have been associated with poor clinical outcome.

2.8.3 Zinc phosphate cements

Zinc phosphate cement is the oldest cements developed for luting applications. It is formed by reacting zinc oxide powder and phosphoric acid hence the cement is very acidic when initially mixed. Zinc phosphate demonstrates adequate properties for a luting, including film thickness less than 25μm, compressive strength of 75MPa, solubility of less than 0.2% (by weight) and radiopacity. However, it can only be used as a base or temporary restoration and is unsuitable for other restorative procedures.

2.8.4 Composite resins

Dental composite resins are restorative materials comprising an organic resin matrix, inorganic fillers and an organosilane coupling agent. The resins include monomers of Bisphenol glycidyl dimethacrylate (Bis-GMA), Urethane dimethacrylate (UDMA) and Ethylene glycidyl dimethacrylate (EGDMA) which undergo a polymerisaton reaction. Introduced in the mid-1960s, dental composites have transitioned from the chemically activated versions to the highly successful visible blue light activated types available currently.

Dental composites are highly aesthetic due to their availability in various tooth-coloured shades and are capable of being polished to a smooth and glossy finish. Additionally, the filler component imparts adequate strength, in some instances, as high as dental amalgam thus they can be successfully utilized even in high stress bearing regions. The fillers also impart radiopacity to the materials. Composites are retained micromechanically with the aid of adhesive bonding agents therefore do not require extensive tooth preparation as seen with dental amalgam. They are therefore conservative even in small lesions. Modern composites are associated with minimal shrinkage, solubility and wear.

Nevertheless, all these advantages render them expensive. Moreover, dental composites are technique sensitive and demand skilled manipulation for best results. They also need expensive equipment such as light curing units and assorted finishing accessories. These requirements limit optimal use of composites in remote areas, some of which do not have electricity.

2.8.5 Dental silicate cements

Silicate cements were the first dental cements to be developed in the 1870s. They were tooth coloured hence aesthetic, and had the ability to leach fluoride. Silicate cements were produced by reacting aluminosilicate glass with phosphoric acid. However, they were soluble and disintegrated in the moist oral environment; moreover, they were also acidic, causing severe pulpal irritation. They were considered to lack biological compatibility and were therefore withdrawn from clinical use. They were replaced by zinc polycarboxylate cement.

2.8.6 Zinc polycarboxylate cements

Zinc polycarboxylate or zinc polyacrylate cement was the first chemically adhesive dental cement to be developed for luting. It is produced from an acid-base reaction of zinc oxide powder and poly (acrylic acid). Although preferred for its chemically adhesive property, the cement has been largely replaced by glass ionomer cements. Its disadvantages include lower mechanical strength than zinc phosphate and glass ionomers (compressive strength 55-67MPa and low elastic modulus 2.4-4.4GPa) and increased solubility in organic acids.

2.9 Glass ionomer (polyalkenoate) cements

Glass ionomer or polyalkenoate cements (GICs) are currently the preferred restorative dental cements. Developed in 1971 by Wilson and Kent [26,88] following a commission to improve dental silicate cements, they are the result of merging dental silicate and zinc polycarboxylate cements. Their powder component is calcium fluoroaluminosilicate glass (derived from the powder of silicate cements) whereas the liquid is poly (acrylic acid) similar to that of zinc polycarboxylate cements.

GICs are an improvement of the two cements and have overcome their disadvantages by reduced solubility and acidity, reduced pulpal irritation, improved aesthetics and mechanical properties (compressive strength up to 270MPa has been reported). Salient properties of GIC are chemical adhesion to tooth structure and fluoride release following acidic attack of the glass particles. Therefore, glass ionomer cements have a myriad of restorative applications that include bases, intermediate restorations, permanent restorations in deciduous dentition, cementation of indirect restorations and sandwich restorations with composites [88-90].

Indeed, glass ionomer cements are the restorative material utilized in the ART approach of managing dental caries (described in section 2.5).

2.9.1 Formulation of GICs

Glass ionomer cements are presented as powder and liquid components with the following formulation outlined by Wilson *et al.* [26,88-91]:

a) Powder

The powder used in GICs comprises fluoro-aluminosilicate glasses. They are different from everyday glasses such as those used in windows and bottles, which are mainly soda-lime-silica based. The difference arises from the fact that everyday glasses comprise a chemically stable unreactive structure as a result of a highly cross-linked O-Si-O network formed from individual $[SiO_4]$ tetrahedra as described in the Random Network model of Zacheriasen, while ionomer glasses are highly reactive and susceptible to acid decomposition as a result of disruption of the oxygen bonds through the introduction of glass modifiers such as CaO

and CaF_2 within the composition. The glass modifiers are necessary for charge balancing the net negative charge following addition of aluminium as a glass intermediate to replace some of the $[SiO_4]$ tetrahedra [92].

As clarified by McLean *et al.*:

> *"The term glass-ionomer cement is reserved exclusively for a material consisting of acid-decomposable glass and a water-soluble acid that sets by neutralization reaction which takes place within a clinically acceptable time."* [90]

The basic composition of fluoro-aluminosilicate glasses and the effect of the constituents is summarized in Table 2.9.1. The formulations of the original glasses are listed below in increasing order of complexity and have remained largely similar to those used in silicate cements although with somewhat higher basicity [92]:

1. SiO_2-Al_2O_3-CaF_2

2. SiO_2-Al_2O_3-CaF_2-Al_3PO_4

3. SiO_2-Al_2O_3-CaF_2- Al_3PO_4-Na_3AlF_6

Table 2.9.1: Components of fluoroaluminosilicate glasses and their effects [89]

Component	Percentage	Effects
SiO_2	29.0	These are the three essential glass components which fuse to form the
Al_2O_3	16.6	calcium fluoro-aluminosilicate glass. Glasses higher in SiO_2 (>40%) are
CaF_2	34.2	more transluscent whereas those high in CaF_2 and Al_2O_3 are more opaque.
Na_3AlF_6	5.0	Complements the fluxing action of CaF_2 i.e reduces the fusion temperature.
Al_3PO_4	9.9	Improves translucency and adds body to the cement paste.
Sr, Ba, La salts	-----	Replace Ca fully or partially to impart radiopacity to the glass.

The glasses are prepared by melting alumina, silica, metal oxides, metal fluorides and metal phosphates at temperatures ranging from 1100°C to 1500°C following which the melt is quenched in cold water. Components such as sodium, potassium, aluminium, barium and silver may be incorporated to provide specific properties [93]. The glass is then ground to fine powder, with the particle size dependent on the intended clinical application [91].

b) Liquid

The original liquid was aqueous poly (acrylic acid), which is very viscous and tends to gel on storage; therefore, it was co-polymerised with itaconic or maleic acids, which apart from preventing gelation, also slowed the setting reaction [91]. Tartaric acid is yet another important additive; it prolongs and sharpens the setting time, and also increases the compressive strength of the cement [94].

To maintain the molecular weight of poly (acrylic acid) it may, together with tartaric acid, be incorporated into the powder in a freeze-dried form. This presentation is then mixed with distilled water or, if tartaric acid is not in the freeze-dried form, with an aqueous solution of tartaric acid [95].

2.9.2 Mechanism of setting reaction of GICs

On the basis of the definition of McLean *et al.* [90], GICs are classified as acid-base cements because of their setting reaction [96]. The reaction results in the release of metal cations such as Al^{3+} and Ca^{2+} through surface dissolution of the glass particles; thereafter, the ions crosslink the poly-acid network to form a rigid poly-salt matrix. As reviewed by Nicholson [92] and illustrated by Griffin and Hill [97], the setting reaction of GICs comprises three distinct stages (Figure 2.9.1):
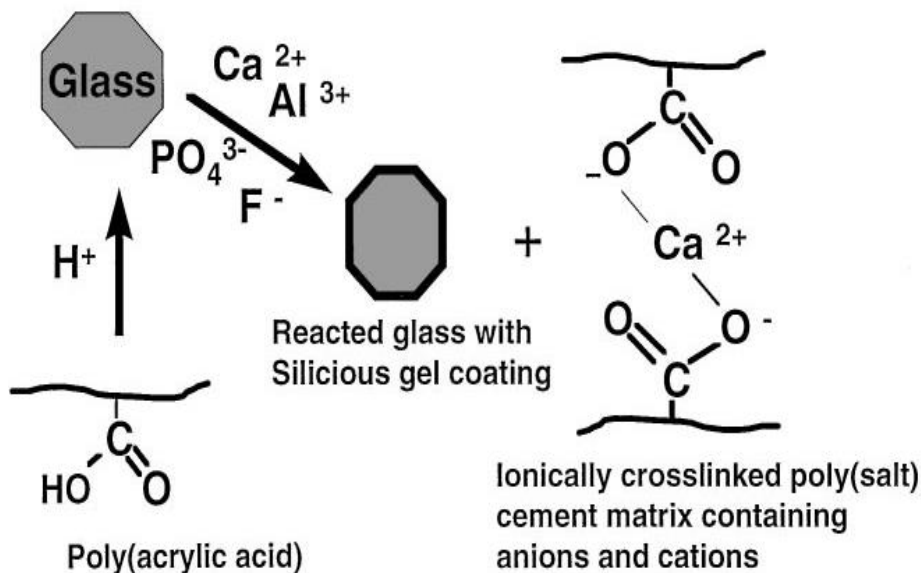
Figure 2.9.1: Schematic summary of the setting reaction of glass ionomer cements [97]

a)   *Dissolution/ Decomposition of the glass powder*

On mixing the glass powder and liquid, H^+ ions from the aqueous poly (acrylic acid) attack the peripheries of the glass particles leading to release of various constituent ions of Ca^{2+}, Al^{3+}, PO_4^{3-} and F^-. Barry *et al.* [98] observed that dissolution occurred preferentially at calcium rich sites, a finding that was supported by Cook [99] and Wasson and Nicholson [96]. They concluded that this is essentially a consequence of the contribution of these ions to the charge balancing of Al^{3+} in a silicate glass, while also making these zones more basic. In aluminosilicate glasses, the negative charge acquired where Si_4^+ is replaced by Al_3^+ is balanced by a positive charge of a network dwelling cation such as Ca^+. The linking oxygen between the two tetrahedral is vulnerable to acidic hydrolysis [97].

b)   *Gelation*

Studies by Nicholson *et al.* [100], Young *et al.* [101] and Talal *et al.* [102] using Fourier Transform Infrared (FT-IR) spectroscopy identified spectra consistent with the formation of Ca^{2+} and Al^{3+} poly-carboxylate salts (Table 2.9.2); these were seen 45 seconds and 9 minutes after the start of mixing, respectively. They suggested that although these ions are dissolved at the same time, as stated above, Ca^{2+} ions are believed to be more reactive than the Al^{3+} ions hence are thought to neutralize the acid faster.

Table 2.9.2: Infrared spectroscopic bands of reference carboxylate salts formed during the setting reaction of GICs [100]

Salt	C-O asymmetric stretch (cm⁻¹)	C-O symmetric stretch (cm⁻¹)
Ca-PAA	1550	1410
Al-PAA	1559	1460
Ca-tartrate	1595	1385
Al-tartrate	1670	1410

c) Hardening/ Maturation

This starts about 3 hours after gelation and may continue up to a year following placement of the restoration; during this stage, the Al^{3+} ions further crosslink with the carboxylic end groups leading to the final unique set or maturation of these cements [96,103]. Furthermore, an inorganic component comprising silicon and phosphorus is also thought to contribute to the increasing strength of these cements with age, as concluded by Zainuddin *et al.* [104] from a long-term study of the setting reaction of GICs using MAS-NMR spectroscopy. Nicholson had earlier reviewed this aspect and reiterated the inorganic component existed because of the glass component and contributed to the insolubility of GICs as well as the gradual increase in compressive strength with time [92]. Therefore, the fully set cement is a composite of residual glass particles embedded in a siliceous hydrogel and bonded in a metal-polyacrylate matrix.

Because of the important role of water in the initial stage of setting, glass ionomer cements are sensitive to both excess moisture as well as dehydration. Moisture contamination will affect the gelation and maturation, while desiccation will retard the reaction, resulting in shrinkage and crazing [89]. The cements become increasingly rigid as they age while their

moisture sensitivity decreases as they mature; moreover, their strength is directly related to the ratio of bound (non-evaporated) to unbound (evaporated) water, or the degree of hydration. This ratio increases with time, with the amount of unbound or loose water reducing in comparison to bound water [100].

2.9.3 Polyalkenoate cements derived from other silicate materials and glasses

Research endeavours have led to exploration of a myriad of alternatives in the search for ideal restorative dental materials. In some documented cases, instead of a typical fluoroaluminosilicate glass, other silicate minerals have been used to form cements.

One of the earliest efforts include that by Wilson [105] who, while experimenting with precursors of the aluminosilicate poly (acrylic acid) (ASPA) cements, described formation of polyalkenoate-like cements derived from mixtures of naturally occurring aluminosilicates and poly (acrylic acid). These naturally occurring silicates, whose reactions with organic acids were first investigated by Murata in 1943, are categorized as: orthosilicates, pyrosilicates, cyclic or chain metasilicates and aluminosilicates. Further reports on their reaction with polycarboxylic acids were made by Crisp *et al.* [106].

They concluded that cements from these materials arose from an acid-base reaction characterized by acidic attack of the mineral phases to form ionic polymer (ionomer) complexes. Just like is observed in glass ionomer cements, the reactivity was dependent on the ratio of aluminium to silicon which determines the network charge and susceptibility to disruption on penetration by protons following acidic attack. Among the promising silicate materials, they further observed that cement stability, particularly in aqueous media, was

dependent on the nature of the cations in the matrix. For example, zinc based cements were found to be more stable and to demonstrate compressive strength as high as 34MPa, faring better than calcium based aluminosilicates [105,106].

Using FTIR, they also followed the setting reaction of the ASPA cement and described the formation of calcium and aluminium poly (acrylates), as presented in Table 2.9.3.

Table 2.9.3: Infrared spectroscopic bands of components in setting ASPA cements [105]

Species	Band (cm^{-1})	Mode	Components	Fresh paste (5m)	Set cement (1h)	Hardened cement (24h)
COOH	1700	C=O Stretch	L – strong	Strong	Attenuated	Weak
COOH-Al	1600	COO$^-$ Asym. stretch			Appears	Strong
COOH-Ca	1540	COO$^-$ Asym. stretch		Appears	Enhanced	Strong
Silica gel	1050	Si-O Stretch		Appears	Appears	Strong
ASPA glass	940		P – strong			

A patent registered by Akahane *et al.* in 1990 [107] also describes use of kaolin and silica sand together with other additives to form variable sintered glasses capable of forming glass ionomer cements for luting applications.

While investigating some properties of glass ionomer cements, Griffin and Hill [97] highlighted the importance of the ratio of glass constituents in the formation of the cements. Specifically, a Si: Al ratio close to or greater than one and a Ca: Al ratio of 1:2 or more are necessary for formation of glass polyalkenoate cements which are hydrolytically stable and having adequate mechanical properties. Otherwise, glass dissolution or reactivity is impeded due to the stability of the crystalline phase relative to the glass phase. The

importance of the Si: Al ratio was demonstrated further by Sullivan *et al.* [108] who also investigated glass polyalkenoate cements based on waste gasifier slags, which are simple $CaO-Al_2O_3-SiO_2$ systems. They found that a higher ratio was associated with a lower ratio and vice versa.

Obviously, other factors also contributed to these properties, such as the glass transition temperature and cross-link density of the glass network. In these cements, Sullivan and Hill [109] also found that compressive and flexural strength increased with increasing molar mass of poly (acrylic acid) and time. On the other hand, Young's modulus increased with time but independent of the poly (acrylic acid) molar mass while fracture toughness increased initially but decreased after one week, dependent on molar mass, with higher decrease for higher molar mass. The influence of poly (acrylic acrylic) molar mass on mechanical properties of glass ionomer cements has been extensively investigated by Fennel and Hill [110-112]. Similarly, they found an increase in compressive strength with increasing molar mass and at higher concentrations [110], increase in Young's modulus with increasing poly (acrylic acid) concentration up to 50% m/m but independent of molar mass [111] and increase in fracture toughness with increasing molar mass at higher concentrations [112].

To improve understanding on the role of various elements in the glass design, subsequently affecting the glass behavior in various cement applications, investigations have also employed glasses in which some elements were included or excluded. Examples include Fluoride-free and phosphate-containing glasses for ionomer and bioactive glass applications.

Typically, CaF_2 or SrF_2 is added as a glass modifier and a flux to lower the fusion temperature while melting glasses. In glass ionomer cements, it was also serendipitously found that its inclusion later plays a role in their beneficial fluoride leaching ability [88]. Brauer *et al.* [113] and Shah [114] reported similar findings about fluoride-containing bioactive glasses. Moreover, they observed that the presence of fluoride resulted in reduced pH rise in aqueous solutions as well as formation of fluoroapatite to a certain extent, beyond which fluorite replaced fluoroapatite formation. However, Mneinme *et al.* [115] found that addition of phosphate to fluoride-containing bioglasses resulted in fluoroapatite formation at lower pH. Additionally, higher phosphate content was associated with faster fluoroapatite formation which was not replaced by fluorite. In ionomer glasses, Al_3PO_4 was added to improve translucency and add body to the cement paste [89].

2.9.4 Physico-mechanical and biological properties of GICs

The properties of glass ionomer cements have been extensively studied and have been determined to be largely influenced by the glass composition, reviewed by Nicholson [92] and evaluated by Griffin and Hill [97,116-118]; particle size, evaluated by Arita *et al.* [119], De Caluwe *et al.* [120], Gu *et al.* [121]; and, the poly (acrylic acid) molar mass, evaluated by Guggenberger *et al.* [122] and Fennel and Hill [110-112]. Williams *et al.* [123] have reported compressive strength as high as 220MPa in mature high viscosity glass ionomer cements attributed to the hardening phase during the extended setting reaction.

A salient property of these materials is their ability to release fluoride, attributed to dissolution of the glass following acidic attack during the setting reaction [92]. However, the mechanism of fluoride release is described by Luo *et al.* [124] as diffusion controlled and not

dissolution controlled; moreover, Hill *et al.* showed that an 'initial fluoride' burst is associated with an monovalent sodium ion (Na^+) [125].

The anti-cariogenic effect of topical fluoride is explained by three mechanisms documented by Featherstone in 1999 [126]: inhibiting bacterial metabolism through formation of hydrogen fluoride which inhibits bacterial enolase; inhibiting demineralization by substituting the hydroxyl atom in the hydroxyapatite crystal to form a more acid-resistant fluoroapatite; and, enhancing remineralization through precipitation of fluoroapatite crystals in an oral solution supersaturated with calcium, phosphate and fluoride ions.

Furthermore, reviews on delivery and mechanism of action of topical fluoride in preventing dental caries have recommended that to be effective, the process should be extended and continuous. Some of the earliest reports include those by Rolla and Saxegaard [127] and ten Cate [128] who focused on CaF_2 and concluded that a low oral pH is ideal for dissolution of CaF_2 to release fluoride ions which are crucial for formation of fluoroapatite in an early carious lesion. They documented that salivary flow caused the fluoride ions deposited from dentifrices and oral rinses to get depleted exponentially during which the oral pH also returned to neutral. However, molecules with low reactivity such as CaF_2 provided a medium for slow but constant delivery of fluoride critical for remineralization at low pH. The release, recharge and rerelease of fluoride by GICs and associated materials is well documented [129-132].

Apart from fluoride, it is also thought that elements such as strontium may play a synergistic anti-cariogenic role with fluoride, as reviewed by Lippert and Hara [133]. Although strontium

is primarily substituted for calcium in the glass to confer radiopacity to GICs, a study by Dabsie *et al.* [134] showed anti-bacterial property while a remineralizing effect was shown by Ngo *et al.* [135] and Knight *et al.* [136], suggesting that these findings in strontium-containing GICs could be due to this synergistic effect.

From the preceding assessment, it is clear that several restorative materials are available; however, none is considered ideal because of various shortcomings. Further research is required to explore alternatives that seek to address the issues raised. Glass ionomer cements are very promising with regards to ease of manipulation, adhesive and anti-cariogenic properties. However, the cost of the best ART restorations in the market remains prohibitive. Importantly, developing countries are limited by inadequate facilities as well as expenses associated with some of these materials. Therefore, innovative approaches utilizing locally available aluminosilicate materials as aimed for in this study is not only timely but also justified.

2.10 Portland cements and Portland cement industry in Kenya

Portland cement is the product of grinding cement clinker to a fine powder. It is considered hydraulic because it relies on a hydration reaction with water in order to set. As reviewed by Steffen and van Waes [33], the primary constituents of Portland cement are lime or calcium carbonate (65%), silica or silicon dioxide (20%), alumina or aluminium oxide and ferric oxide (10%). Other compounds or elements such as heavy metals like lead and arsenic constitute the remaining 5%. Portland cements are classified as Type I to V according to the ASTM standards; calcium silicate cements are comparable to Type I Portland cements.

The raw materials are mixed and ground in the correct proportions then heated to 1400°C by a process known as calcination which is usually done in a rotary kiln hence the name clinker. Calcination produces physical and chemical changes, resulting in the clinker that is finally ground to the desired particle size. For optimum setting reaction and strength, it is desirable that at least 90% of the particles are 50µm and below; particles larger than this tend to remain unreacted and may compromise the cement properties. Small amounts of gypsum are added during the grinding process to retard the setting reaction and enable adequate working time during construction techniques [33].

The two principal phases in Portland cement are tricalcium silicate or alite and dicalcium silicate or belite. The setting reaction is a hydration reaction characterized by dissolution and precipitation. The sequence involves dispersion of the ground clinker in water, crystal growth of hydration products, coalescing of the various crystals and finally hardening to a set mass in which the hydrated gel and the crystalline particles are dispersed. The simplified alite and belite phase reactions may be expressed as shown below by equations 1 and 2, respectively [33]:

$$2Ca_3OSiO_4 + 6H_2O \rightarrow 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2 \quad (1)$$
$$2Ca_2SiO_4 + 4H_2O \rightarrow 3CaO.2SiO_2.3H_2O + Ca(OH)_2 \quad (2)$$
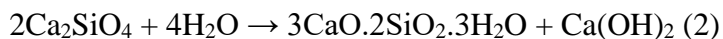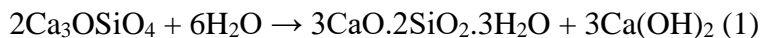
The alite phase reaction (1) occurs faster and is responsible for initial set and strength in the first few weeks. The belite phase reaction (2) is slower and contributes to later strength development.

Apart from the calcium-silicate-hydrates, calcium hydroxide is the other major product of the hydration reaction of Portland cements, comprising about one third of the volume of the final products. It is responsible for the high alkalinity of Portland cements. Several studies have established that the setting reaction of Portland cements is the same as that of calcium silicate cements and is attributed to the major similarity in composition [33].

Although the setting reaction of Portland cements results from hydration and subsequent dissolution and precipitation of crystalline phases as described above, the presence of an amorphous phase in the clinker has been the subject of several investigations. X-ray Diffraction with Rietveld refinement has been employed successfully to quantify the amorphous phase in clinker although there is hardly any information on its contribution to the cement setting reaction and properties. Such reports have been documented by Bijen [137], Suherman *et al.* [138], Jansen *et al.* [139] and Whitfield and Mitchel [140].

Records available at the Ministry of Mining [141] show that Kenya is rich in mineral deposits which contribute to approximately 1% of the national GDP. There are about ten major mining companies established in Kenya while several more are prospectors whether as companies or individuals [141,142]. Major minerals mined in Kenya include soda ash (trona), fluorspar, diatomite, kaolin, carbon dioxide and limestone. Some of the minerals are exported as raw while others are used in local industries, one being the vibrant Portland cement industry [141,142].

Most of the limestone mined in Kenya is utilized in the cement and construction industry. Limestone is a sedimentary rock comprising various forms of calcium carbonate ($CaCO_3$)

such as calcite and aragonite. Limestone is often mined in a grainy form and is mainly used as a building material in a crushed or block form. In addition, it has several applications such as a filler, abrasive, generation of cement, calcium oxide and calcium hydroxide and to neutralize acidic soils.

Apart from limestone and ordinary clay, another raw material used in the production of Portland cement is kaolin. Kaolin, also known as China clay, is hydrous aluminosilicate ($Al_2O_3.2SiO_2.2H_2O$). Kaolin is soft, white clay that forms an essential ingredient in the manufacture of china and porcelain. It is also widely used in the making of paper, rubber, paint and several other products. In its natural state, kaolin is a white, soft powder which consists primarily of the mineral kaolinite ($Al_4Si_4O_{10}.8OH$). Natural kaolin also contains varying amounts of other minerals such as muscovite, feldspar and quartz.

In addition, crude kaolin is usually stained yellow by iron hydroxide pigments, necessitating chemical bleaching of the clay to remove the pigment as well as washing with warm water to remove the other minerals in order to prepare the kaolin for commercial use. Although there are some deposits of kaolin in Kenya such as in Nyeri and Kitui counties, Kenya relies mostly on imports for commercial use. To make white Portland cement, ordinary clay is substituted by kaolin which is whiter with less iron content and other impurities. The clinker may also be bleached to whiten it further.

Fluorspar (also known as fluorite) is the mineral form of calcium fluoride (CaF_2); it belongs to the halide group of minerals. Fluorspar is a colourful mineral from which the term 'fluorescence' originates. This is because of its ability to colour and appear different in both

ultra-violet and visible light hence its applications in ornamental products and lapidary. Industrially, fluorspar is used as a flux when smelting metals and alloys such as steel, and also to manufacture certain glasses and other ceramic products. It is also liberates hydrogen fluoride and hydrofluoric acid on reaction with concentrated sulfuric acid. In Kenya, fluorspar is mined by Kenya Fluorspar Company from Kerio Valley in Elgeyo Marakwet County; Kerio Valley is known for its significant fluorspar deposits which were first discovered in 1967.

It is noteworthy that these readily available raw materials have never been exploited in the local manufacture of some dental materials which borrow heavily from ceramics due to their unique aesthetic properties; therefore, the basis of this study is to harness these raw materials employed in the cement and construction industries to develop a prototype for a polyalkenoate-type dental cement.

There are several Portland cement producing companies in Kenya with the three major companies being: Bamburi (LaFarge), East African Portland and Athi River Mining [141]. From approximately 2.3 million tonnes of cement annually for both local consumption as well as export in 2007 [141,142], records available at the Kenya National Bureau of Statistics indicate that the annual production of these companies in 2017 increased to 6.3 million tonnes. Bamburi Cement Company obtains its supply of limestone from dead coral largely available in the coastal region of Kenya while the other companies are supplied from Machakos and Kajiado Counties.

While one of the major problems associated with mining is the environmental impact directly from quarrying and indirectly from carbon dioxide emissions, the mining companies have the moral obligation to find solutions to rehabilitate the affected sites. This has been successfully accomplished in some areas such as the world renowned Haller Park that was a former limestone quarry wasteland of Bamburi Cement Company, Mombasa County, Kenya [143]. Moreover, geo-polymers present an alternative to Portland cement due to a lower carbon dioxide footprint [144-147].

2.11 Alkaline-activated aluminosilicates/ Geopolymers

Alkaline-activated aluminosilicates or geopolymers are cementitious materials synthesized through a low temperature reaction (typically below 100°C) between aluminosilicate precursors and alkaline sodium silicate solution. Notable reviews of these materials include those by Palomo *et al.* [148], Provis [149], Provis and Bernal [144], Davidovits [145], Liew *et al.* [146] and Criado *et al.* [147], among others. The aluminosilicate precursors are usually clay-based materials such as calcined clays, metakaolin and volcanic rocks as well as industrial by-products, commonly fly ash (FA) and blast furnace (BF) slag [144-149].

These materials are used extensively in the construction industry as a substitute for Portland cement clinker due to the high energy costs and carbon footprint associated with production of the latter. Additionally, they set within a shorter time while gaining considerable strength within the first 24 hours [144-149].

2.11.1 Chemistry and setting reaction of geopolymers

All geopolymers are reacted with a friendly sodium silicate solution defined as a potentially irritant alkaline solution different from the corrosive ones and having a $SiO_2:Na_2O$ ratio > 1.45. Geopolymers are classified on the basis of the aluminosilicate precursors as follows [145]:

1. Slag-based comprised of blast furnace slag and metakaolin
2. Rock-based comprised of blast furnace slag, metakaolin and volcanic tuffs
3. Fly ash-based comprised of fly ash and blast furnace slag
4. Ferro-sialate-based comprised of geological elements high in iron oxide content.

Although the chemistry of geopolymers is similar to that of Portland cements due to the same originating materials, Davidovits [145,150] proposed that they should be categorized as Si/Al based inorganic polymers rather than classical ceramics. He described these materials as mineral polymers, christened polysialates (Figure 2.11.1), derived from heating mixtures of aqueous alkali silico-aluminates with a general formula:

M_n [--(Si--O_2 --)$_z$ --Al--O_2 --]$_n$,wH_2O (3)

where z is 1, 2 or 3, M is sodium, or sodium plus potassium, n is the degree of polycondensation, and w has a value up to about 7 [150].
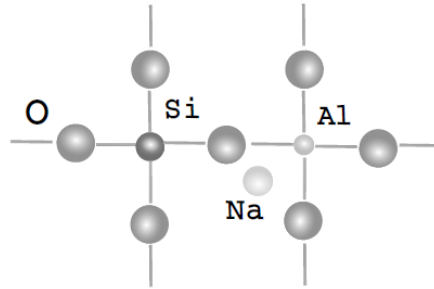
Figure 2.11.1: Illustration of polysialates which form the basic structure of geopolymers [145]

He argues that while the setting reaction of Portland cements is a hydration reaction producing calcium silicate hydrates and calcium hydroxide, geopolymers undergo a condensation polymerization reaction of an oligomer giving rise to a polymer. This comparison is illustrated in figure 2.11.2.
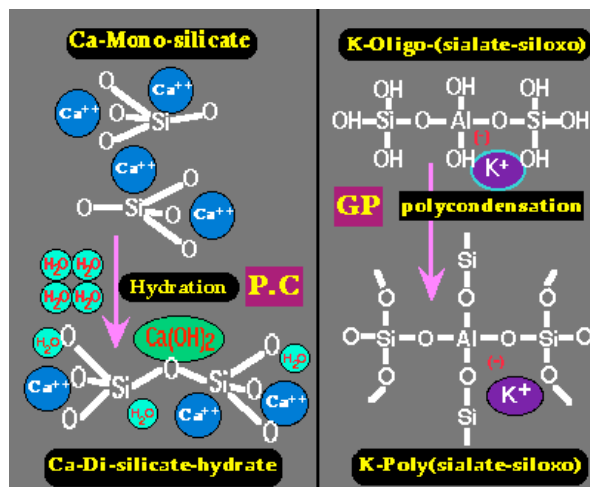
Figure 2.11.2: Comparison of hydration reaction of Portland cements and polycondensation reaction of geopolymers [145]

As presented in Figure 2.11.3, the geopolymer formation reaction has been described simply in 3 steps by Davidovits [145] as follows:

1. Alkalination of orthosilicates released from solid aluminosilicates such as metakaolin using sodium hydroxide silicate solution. This results in charge balancing of the orthosilicates by Na^+ to form Al tetrahedra ends.

2. Condensation of orthosilicates or oligo-siloxonates into oligomers.

3. Polycondensation of oligomers into nano-metre sized micelles which agglomerate into a 3-dimensional solid material with mesopores.
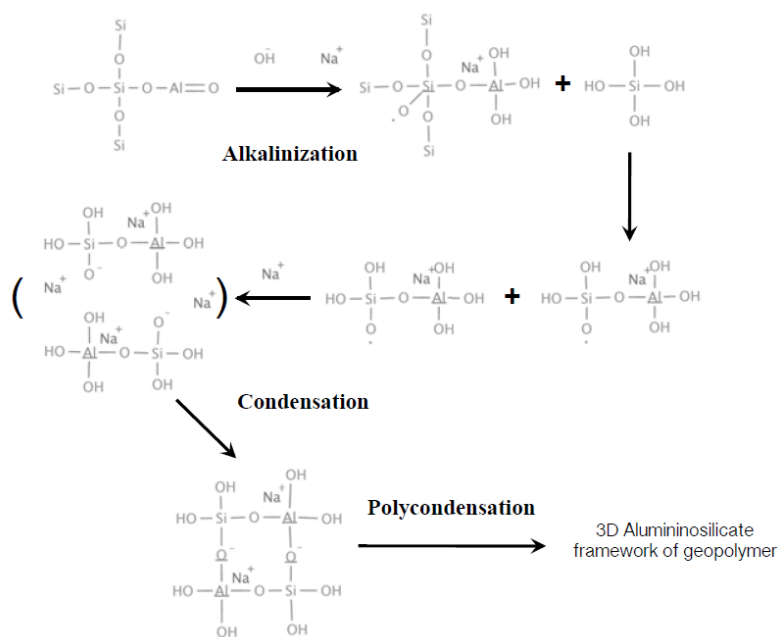
Figure 2.11.3: Geopolymer formation process [145]

2.11.2 Physico-mechanical and biological properties of geopolymers for biomaterial applications

Until recently, research on geopolymers has focused on their primary application in the construction industry where they have been found to be comparable to Portland cement. However, there is paucity of data on their biological properties and potential as biomaterials.

Jamstorp *et al.* [151-154] and Forsgren *et al.* [155] have described optimized geopolymers for controlled drug delivery. These materials have potential for controlled release of toxic opioid pharmacological compounds for pain control in terminal illness. Their advantages included adequate mechanical properties [151], tunable sustained drug release through structured porosity [152,154,155] and gastric acid resistance through incorporation of polymer excipients [153] while resisting tampering for non-medical use, as evaluated by Cai *et al.* [156].

Bioactivity of geopolymers with potential as bone substitutes have also been described. Pangdaeng *et al.* [157,158] demonstrated apatite formation on the surface of geopolymers containing white Portland cement following immersion in simulated body fluid for 28 days. The same materials, with geopolymer/Portland cement ration of 1:1 also exhibited rapid setting and compressive strength of 59MPa. In a similar study, Sutthi *et al.* [159] investigated bioactivity of hydroxyapatite derived from golden apple snail shell mixed with calcined kaolin. They found that a mixture of 25% hydroxyapatite and 75% kaolin exhibited compressive strength of 33MPa and surface apatite formation after 28 days in simulated body fluid.

During the initial stages of the development of glass ionomer cements, referred to as aluminosilicate poly (acrylic acid) or ASPA cements, Wilson [105] documented that certain naturally occurring silicate materials could react with PAA to form cements; however, these cements were weak mechanically with low compressive strength of 30MPa or less, as compared to the ASPA cements that could attain 200MPa within 24 hours.

Towler *et al.* [160], Stanton *et al.* [161], Henry *et al.* [162] and Bijen [137] have shown that blast furnace slag and fly ash contain a mixture of an amorphous and crystalline phase and this may provide an explanation as to the ability of such naturally occurring aluminosilicates to react with PAA to form cements. Furthermore, Palomo *et al.* [148], Palomo *et al.* [163] and Alonso and Palomo [164] have described the mechanism of activation of these materials as well as the reaction products and shown that the aluminosilicate precursors are largely amorphous in nature and remain so following alkaline activation.

It is obvious that the applications of geopolymers as biomaterials is a little researched area thus more studies could improve the knowledge base in the search for alternative dental materials, as proposed in the current project.

2.12 Calcium silicate cements

As reviewed by Dawood *et al.* [21] and Jefferies [22], and evaluated by Camilleri [32] and Chang [165], among others, calcium silicate cements are a group of hydraulic or water-setting cements presented as powders comprising mainly calcium disilicate and calcium trisilicate. In addition, other reviews by Steffen and van Waes [33], Camilleri and Pitt Ford [166] and Prati and Gandolfi [167] show that it is well established that these cements are derived from Portland

cement which is the main provider of the calcium silicate elements, with the addition of a radiopacifier such as bismuth oxide. However, Roberts et al. [168] caution that the commercial versions are highly purified and manufactured through strict regulatory standards by ethical medical material manufacturers.

Several categories of calcium-based cements have been utilized in medical and dental restorative techniques for decades. They include those based on calcium phosphate such as bioglasses, calcium aluminate such as glass ionomer cements and calcium silicate [22]. The first calcium silicate cement for dental applications, mineral trioxide aggregate (MTA), was introduced by Torabinejad in the early 1990s and marketed as an endodontic material in collaboration with Tulsa Dental Products, a branch of Denstply in Tulsa, Oklahoma in 1995 [30,32]. Several other brands of these cements have been developed and marketed ever since as rivals to the original MTA. They include Biodentine®, Bioaggregate®, Endosequence®, Calcium-enriched mixture cement® and TheraCal® [21].

Presently, there is a heated debate on whether ordinary Portland cement can be a substitute for commercial calcium silicate cements. Earlier reviews by Camilleri and Pitt Ford [166] and Roberts et al. [168] discouraged substitution of a Portland cement intended for the construction industry for a medical or dental application on ethical grounds as well as the fact that these specific cements were relatively new biomaterials; however, this presents a dilemma for developing countries because these materials are very expensive. On the other hand, more recent reviews have concluded that there are no compelling reasons not to use Portland cements as a cheaper alternative. Steffen and van Waes [33] further state that more clinical trials should be conducted using pure Portland cement while Darvell and Wu [37] and Islam

et al. [169] emphasize that more studies are required to evaluate the parent compound in order to increase understanding of the same as a precursor for expanded medical and dental applications .

In a country like Kenya with a vibrant Portland cement industry, this presents an opportunity for further evaluations on this product and potential applications in polyalkenoate-type cements. This study will also provide information on the constituents of Kenyan Portland cement and whether it can be a cheap but safe substitute for expensive commercial calcium silicate cements such as mineral trioxide aggregate (MTA).

2.12.1 Formulation of calcium silicate cements

Commercial silicate cements are often presented as powder and liquid with the following formulation, as reviewed by Dawood *et al.* [21], Camilleri [32] and Chang [165]:

Powder:

Main constituents - Dicalcium silicate, tricalcium silicate, tetracalcium aluminate and tricalcium aluminferrite

Additional constituents – Bismuth oxide to confer radiopacity

Liquid:

Distilled water

This was the formulation of the original MTA. The formulation of some of the currently available brands is summarized in Table 2.12.1.

Table 2.12.1: Formulation of commercial calcium silicate cements [21]

Cement	Presentation	Composition
MTA	Powder	Purified Portland cement (dicalcium silicate, tricalcium silicate, tricalcium aluminate, calcium sulphate, tetracalcium aluminoferrite, bismuth oxide, small quantities of silica, lime, magnesium oxide, potassium and sodium sulphate
	Liquid	Distilled water
Biodentine®	Powder	Tricalcium silicate, dicalcium silicate, calcium carbonate, calcium oxide, zirconium dioxide
	Liquid	Water, calcium chloride, hydrosoluble polymer
Bioaggregate®	Powder	Tricalcium silicate, dicalcium silicate, hydroxyapatite, calcium silicate oxide, tantalum oxide, calcium phosphate silicate
	Liquid	Distilled water
Endosequence®	Paste or putty	Calcium silicates, monobasic calcium phosphate, zirconium oxide, tantalum oxide, proprietary fillers, thickening agents
Calcium-enriched mixture cement®	Powder	Calcium oxide, sulphur trioxide, phosphorus pentoxide, silicon dioxide, trace amounts of alumina, soda, magnesium oxide, chloride
	Liquid	Distilled water
Theracal®	Light-cured paste	Type III Portland cement, strontium glass, fumed silica, barium suphate, barium zirconate, Bis-GMA and PEGDMA resins

2.12.2 Setting reaction of calcium silicate cements

Calcium silicate cements are hydraulic or water setting. They set through a hydration reaction that proceeds through two separate reactions as described by Camilleri [32,170] and Chang [165] as follows:

- An initial reaction between tricalcium aluminate and water in the presence of gypsum to form ettringite, and later monosulphate on depletion of gypsum.

- A second, and main, reaction between the calcium silicates and water to yield calcium silicate hydrate gel and calcium hydroxide.

It is noteworthy that because of low levels of tricalcium aluminate in MTA, the first reaction is limited. Lovschall *et al.* [171] have suggested this to be the likely reason for the long setting time and poor handling profile of MTA. Moreover, the bismuth is incorporated in the calcium silicate hydrate as calcium-silicate-bismuth-hydrate [32,165,170].

2.12.3 Physical and biological properties of calcium silicate cements

The particle size of MTA is a little researched area. A few studies have compared the particle size of MTA and PC and how this influences the properties of these materials.

Khan *et al.* [172] investigated the chemical composition and particle morphology of white MTA and white PC. They found that the materials were similar in composition and that they had irregular particles, although the particles in the MTA were of finer morphology than those of PC.

Ha *et al.* [173] used laser diffraction and scanning electron microscopy to assess the influence of atmospheric moisture on unsealed MTA packages. They found that after two years, there was a 6-fold increase in the particle size of ProRoot MTA left in a folded over open package as compared to a 2-fold increase in MTA Angelus left in a jar with a twistable lid. The increase in particle size was attributed to clumping together following absorption of atmospheric moisture and was thought to affect the material properties negatively hence the manufacturers' recommendation for single use. In a different study, they also used laser diffraction in an attempt to deconvolute the distribution of the particles contributed by PC and bismuth oxide in MTA. They found that, generally, PC component contributed larger particle sizes while bismuth oxide contributed smaller particle sizes in MTA [174].

In yet another study, Ha *et al.* [175] used laser diffraction to assess the influence of particle size on the setting time of MTA and PC. They concluded that despite variations in particle size between MTA and PC, smaller particle size was associated with faster setting times. However, among the three percentiles of particle sizes (D10, D50 and D90), D90 showed the highest positive linear correlation to setting time in both MTA and PC.

However, a recent *in vivo* animal study by Torabinejad *et al.* [176] failed to show the influence of reduction in particle size of MTA on dento-alveolar and osseous healing following root-end fillings. Two earlier studies by Komabayashi and Spangberg [177,178] attempted to describe the particle shape and aspect ratio of the two materials, speculating that smaller particles may penetrate open dentinal tubules and may be clinically useful in bioactive materials. It is impossible to make accurate inferences on the influence of particle size and shape on the behavior and properties of these materials from such few studies. This presents an opportunity for further investigations on this aspect of MTA and PC in Kenya.

Hydration of calcium silicate cements leads to formation of calcium silicate hydrate and calcium hydroxide; the latter is responsible for their high alkalinity. Moreover, these cements further react in the presence of specialized body fluids to form calcium depleted apatite, a property known as bioactivity, which is characterized by ability to bond to bone [22,165,166].

Several studies have been conducted to evaluate other properties of calcium silicate cements. Their key selling points are: their bioactive properties that contribute to their ability to cause regeneration of hard tissues; their hydrophilic properties that make them

ideal in the moist oral environment; and, their biocompatibility evidenced by preservation of pulp vitality and absence of signs of inflammation [166,167].

However, MTA exhibits a poor handling profile and its long setting time which are its major disadvantages [167]. Other calcium silicate cements fair better in these areas due to various modifications, reviewed next.

2.12.4 Mechanical properties of calcium silicate cements

Calcium silicate cements have low mechanical properties which is not a major concern for their endodontic applications; however, this restricts their dental applications to endodontics only [21,167,171]. Such applications include apexification, apexogenesis, pulp capping, repair of root perforations and root end filling, all of which do not involve high stresses. Only Biodentine® is being marketed as a dentine substitute thus can be used as a base beneath the definitive restoration [21,179].

Jefferies [22] reviewed several aspects of these cements and concluded that further research should focus on expanding their restorative applications. There is definitely room to modify calcium silicate cements with the aim of using them as definitive restorations, as is the basis of the current study.

Data is scarce on attempts to improve mechanical properties of these cements. The original compressive strength values of 40-67MPa reported by Torabinejad *et al.* [30] have not changed significantly because they are generally regarded to be adequate for their endodontic applications, which are usually in low stress zones [21,165,167]. This limits the

benefits of these bioactive cements in other restorative procedures. One area under investigation in the present study is whether mechanical properties of calcium silicate cements can be improved by adding polycarboxylic acids.

There is little documentation of attempts at addition of fluoride releasing elements and polycarboxylate plasticizers in calcium silicate cements. This may be because most modifications have targeted endodontic applications, leaving room for improvement to enable utilization in other restorative procedures. Polycarboxylate plasticizers are well known in the construction industry where they are utilized to ensure initial early strength of Portland cements as well as overall durability among other desirable qualities.

This study will incorporate poly (acrylic acid) (PAA), a polycarboxylic acid used in dental cements such as glass ionomer cements and zinc polycarboxylate cements. In such cements, PAA has been shown to be responsible for strength development through an acid base reaction and entanglement of the polymer chains, as reviewed in section 2.9.2 and 2.9.3.

A patent registered in America by Lovschall *et al.* [171] describes the addition of PAA to Portland cement clinker with resultant improvement in mechanical properties of the restorative dental cements; moreover, addition of fluoride releasing elements also resulted in fluoride release from the cements. Wongkornchaowalit and Lertchirakarn [180] have also reported that incorporation of polycarboxylate superlasticizers resulted in reduction of setting time of accelerated Portland cement to clinically practical values. In both of these studies, elimination of gypsum additives from the cement clinker was recommended. A

similar methodology involving addition of poly (acrylic acid) and fluoride releasing elements to Portland cement and related materials in Kenya is intended in the present study.

Studies on calcium silicate cements have focused on endodontic applications, creating a gap to expand their applications to other dental restorative procedures.

2.12.5 Other modifications of calcium silicate cements

As detailed in Table 2.12.1, calcium silicate cements have been modified extensively from the original MTA to improve their properties in endodontic procedures. Some of the modifications address the powder/ liquid formulation and proportions, the setting time, the handling profile and radiopacity.

During the debut of MTA in 1995, Torabinejad *et al.* [30] identified two key disadvantages associated with the material to be its poor handling profile and long setting time of up to four hours. These issues have persisted for almost two decades, as reiterated by Atmeh *et al.* [179], and have been the focus of concerted effort aimed at improvement. There are reports of accelerated cements which set in a shorter time of 25 minutes and below, developed by the addition of 10% calcium chloride, as documented by Dawood *et al.* [21], Bortoluzzi *et al.* [181] and Wynn-Jones *et al.* [182]. One of the newer calcium silicate cements with the shortest setting time, Biodentine®, contains calcium chloride in the liquid component [21]. Moreover, it also contains some plasticizers that improve its texture and handling.

Additionally, calcium silicate cements are inherently radiolucent hence radiopaque elements must be added to enable their visualization in radiographs, a mandatory clinical

requirement. Several radiopaque elements have been utilized, more commonly being bismuth oxide in MTA, as documented by Torabinejad et al. [30] and Parirokh and Torabinejad [183]. Others include zirconium oxide, evaluated by Cutajar et al. [184] and Guerreiro et al. [185], also found in Biodentine®, and tantalum oxide found in Bioaggregate® and Endosequence® [21].

2.12.6 A comparison of Portland cement and calcium silicate cements

Estrela et al. [31] were the first to report the similarity between MTA and Portland cement stating that the only difference was the presence of bismuth oxide in MTA and its absence in Portland cement. Several other studies have been conducted to compare the two materials and most of them have established that they are quite similar. Several aspects have been investigated, including: composition by Camilleri et al. [32,170,186-188], Islam et al. [169], Asgary et al. [189], Hwang et al. [190]; setting reactions by Camilleri et al. [170,191-193], Bortoluzzi et al. [181], Wynn-Jones et al. [182]; and, biocompatibility by Estrela et al. [31], Camilleri et al. [193,194].

On this basis, Steffen and van Waes [33] and Darvell and Wu [37] have concluded that more studies utilizing Portland cement are required to evaluate the possibility of substituting it for the expensive commercial versions. This is especially important in developing countries such as Kenya with strained meagre resources yet bearing an overwhelming burden of dental caries that requires intervention.

Admittedly, the greatest concern raised by Camilleri and Pitt Ford [166] and Roberts et al. [168], who discourage direct substitution of an ethically manufactured biomaterial with a cheap version intended for the construction industry, is the potential danger of toxicity from

impurities, justly attributed to the fact that Portland cements have not been proven to be clinically safe. However, a few studies to evaluate the level of such impurities report variable results.

Duarte *et al.* [195] studied two gray Portland cements, a white Portland cement and two gray MTA cements and found that all of them released similar low amounts of arsenic. Because the values were below those considered to be harmful, they concluded that all the cements tested would be safe for clinical applications. Further, De-Deus *et al.* [196] compared the levels of arsenic in some brands of MTA and Portland cement and found that negligible amounts of type III arsenic could be detected; interestingly, the highest and lowest values of arsenic were detected in two different brands of MTA while the Portland cements and two other MTA cements were shown to have either intermediate values or no arsenic. In yet another study to determine whether the levels of arsenic in MTA and Portland cements complied with the ISO recommended limit for water-based cements of 2mg per kilogram of cement (2mg/kg), Monteiro Bramante [197] found that all the materials tested contained arsenic; moreover, one of the MTA cements had levels as high as 5.91mg/kg while one of the white Portland cements had a low value of 0.52mg/kg.

Such lack of consensus only justifies further the need to study Portland cements for a better understanding of their composition and biocompatibility; moreover, it presents room to evaluate Kenyan Portland cement for the possibility of dental applications. The introduction of white MTA into the market has further compounded the problem because its superior quality of being aesthetic and being associated with less tooth discoloration has rendered it more expensive than the grey version hence not readily accessible.

There is little documentation of the actual formulation as well as the processes involved in the production of the calcium silicate cements available in the market. This is rather unfortunate because it makes it difficult to justify their high costs yet there is sufficient evidence to conclude that they originate from Portland cement which is a cheap and readily available product [33].

2.13 A review of some analytical techniques utilized in biomaterial evaluation

2.13.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) is a non-destructive technique commonly used for structural and chemical analysis of crystalline substances. Developed from Bragg's law, which explains the interference of X-ray patterns by crystals, diffraction is used to study all states of matter using any beam that bears a wavelength similar to the inter-atomic spaces of the substance being studied. As illustrated in Figure 2.13.1, derivation of Bragg's law explains how constructive interference by the crystal is used to identify a substance by its diffraction pattern [198,199].

$n\lambda = AB + BC$, and $AB = BC$, therefore $n\lambda = 2AB$ (4)

$Sin \Theta = AB/d \implies AB = dSin\Theta$, therefore $n\lambda = 2dSin\Theta$ (Bragg's law) (5)
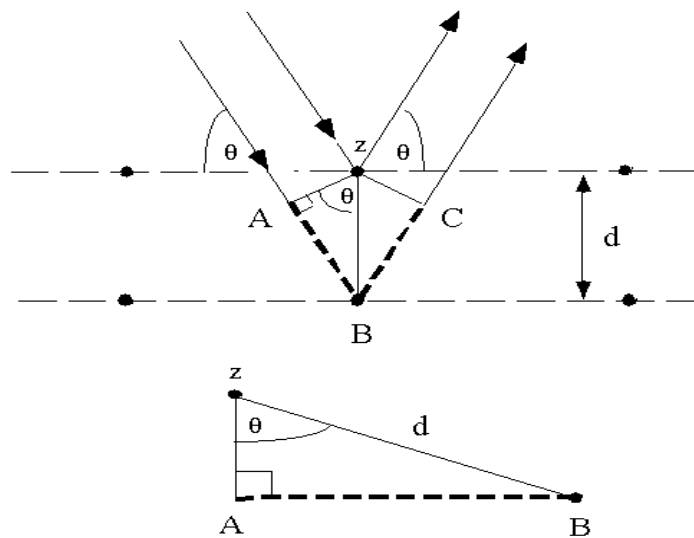
Figure 2.13.1: Illustrating the derivation of Bragg's law of diffraction [199]

XRD is based on a phenomenon in which the atomic planes of a crystal cause interference within an incident beam of X-rays as they exit the crystal. Diffraction occurs only if Bragg's law is satisfied, resulting in constructive interference (Figure 2.13.2). In crystalline matter, the atoms are arranged regularly within the crystal lattice; however, in non-crystalline matter, the atoms are randomly positioned. Therefore, they fail to satisfy Bragg's law and accordingly record an amorphous diffraction pattern.
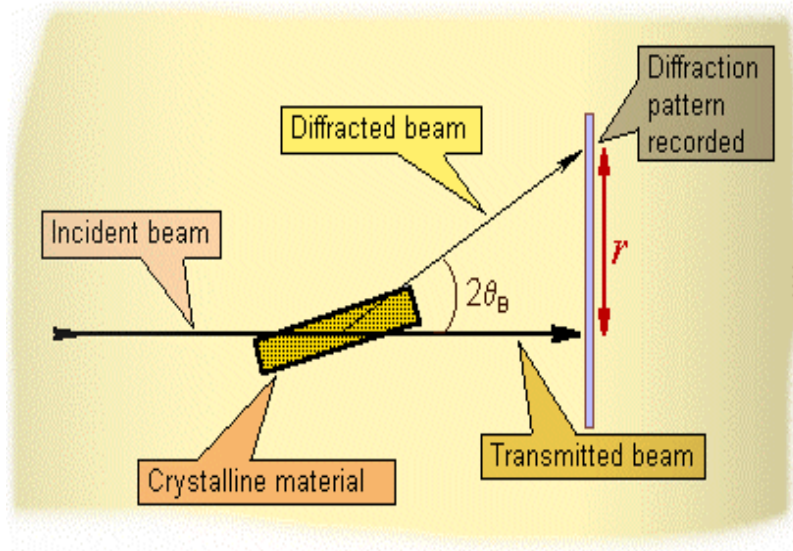
Figure 2.13.2: Illustration of constructive interference resulting in a diffraction pattern [199]

2.13.2 X-ray fluorescence (XRF)

X-Ray Fluorescence (XRF) is a non-destructive analytic technique for determination of major and minor atomic elements in a sample [200]. XRF analyzers determine the chemistry of a sample by measuring the fluorescent (or secondary) x-ray emitted from a sample when it is excited by a primary short wavelength x-ray or gamma-ray source. Each of the elements present in a sample produces a set of characteristic fluorescent x-rays, unique for that specific element, making XRF spectroscopy an excellent technology for both qualitative and quantitative analysis of material composition.

On exposure to radiation with a greater ionization energy, an atom is forced to eject one or more electrons from its inner orbitals, becoming unstable. When this happens, electrons in outer orbitals fall into the inner vacant orbitals to stabilize the atom. This is characterized

by release of energy in the form of a photon. Moreover, this energy irradiates at a lower wavelength than the primary x-ray in a phenomenon known as fluorescence (absorption of a higher wavelength energy and its re-emission at a lower wavelength).

XRF may be energy dispersive or wavelength dispersive. In energy dispersive XRF (EDXRF), the energy dispersed by the photons are directed into a solid-state detector which collects it in form of a continuous distribution of pulses. These are then processed by a multichannel analyzer to produce a digital spectrum (Figure 2.13.3). In wavelength dispersive XRF (WDXRF), the energy dispersed by the photons are directed into a diffraction grating monochromator, which is usually a single crystal, before detection (Figure 2.13.4).

Based on the principle of Bragg's law described in section 2.13.1, by varying the angle of incidence and take-off on the crystal, a unique wavelength pattern in the form of a spectrum is created by specific elements of interest. On this basis, WDXRF is more accurate and has higher resolution than EDXRF. However, EDXRF is cheaper and has sufficient accuracy and resolution for quick detection of multiple elements in a sample.
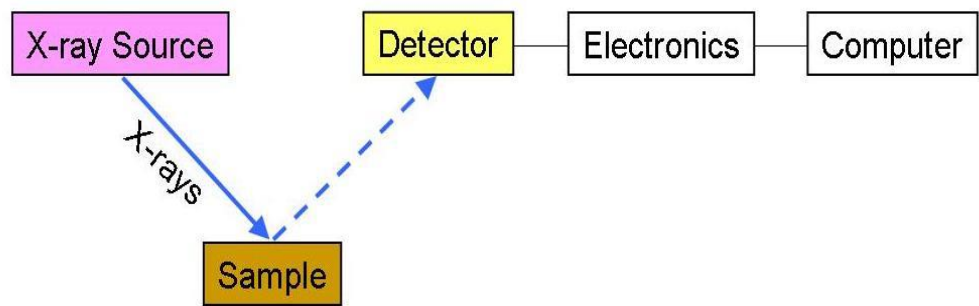
Figure 2.13.3: Simplified version of a EDXRF system (Wikipedia.org)
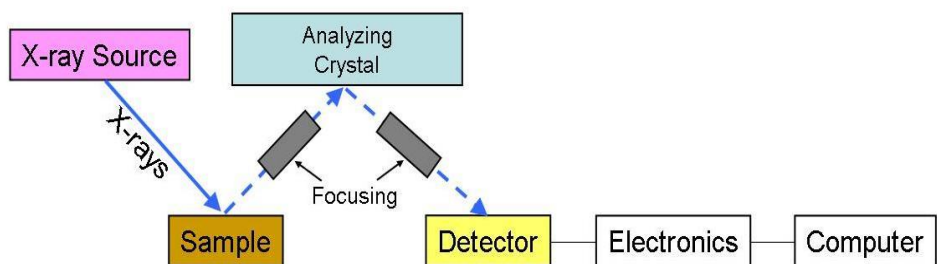
Figure 2.13.4: Simplified version of a WDXRF system (Wikipedia.org)

2.13.3 Graphite furnace atomic absorption spectroscopy (GFAAS)

Atomic spectroscopy is a technique of determining the elemental composition of an analyte by its electromagnetic or mass spectrum. Trace elements in a variety of samples, from agricultural to biological and environmental in origin, may be assessed using this technique. Several atomic spectroscopy techniques are available based on the analytical methods of atomic absorption, atomic emission or mass spectrometry, and they include: flame atomic absorption, graphite furnace atomic absorption, inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectroscopy

(ICP-MS). It is important to select the right technique in order to achieve more accurate and reliable results [201].

In atomic absorption spectrometry, light of a specific wavelength is passed through the atomic vapour of an element of interest, and measurement is made of the attenuation of the intensity of the light as a result of absorption. Qualitative analysis is dependent on the accuracy of the measurement of the light intensity and the assumption that the absorbed radiation is proportional to the atomic concentration. Samples to be analysed by atomic absorption are vaporized or atomized, either using a flame or a graphite furnace. The graphite furnace is an electrothermal atomizer that can produce temperatures as high as 3000°C. The heated graphite furnace produces the thermal energy required to break chemical bonds within the sample, producing free ground-state atoms. These ground state atoms can then absorb energy in the form of light and are subsequently converted to an excited state; the amount of light energy absorbed is dependent on the elemental concentration of the sample.

Graphite furnace atomic absorption spectroscopy (GFAAS) is an improved technique as compared to flame atomic absorption. In this technique, the sample is introduced directly into a graphite tube, which is then heated in a programmed series of steps to remove the solvent and other major matrix components and then atomize the remaining sample. All of the analyte is atomized, and the atoms are retained within the graphite tube (and within the light path which passes through the tube) for an extended period of time (Figure 2.13.5). The longer retention time enables improved sensitivity and detection limits as compared to flame atomic absorption [201].
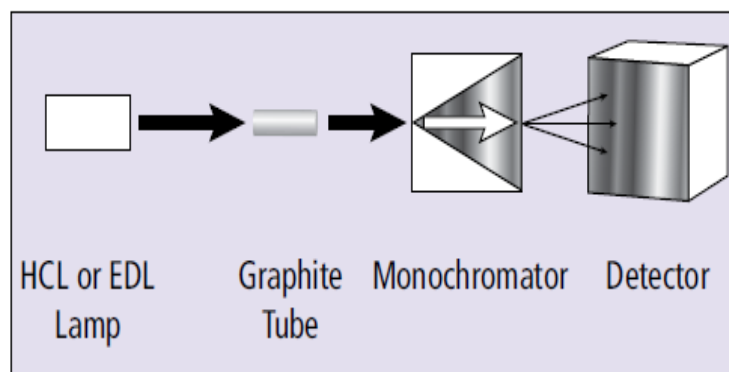
Figure 2.13.5: Simplified version of a Graphite furnace atomic absorption system [201]

Although atomic absorption is inferior to both atomic emission and atomic spectrometry in terms of detection limits, GFAAS significantly expands the limits of atomic absorption due to its enhanced sensitivity and ability to analyze very small samples as compared to flame absorption. Over 40 elements can be determined in microlitre samples which translates to detection limits 100 to 1000 times better than flame absorption; however, graphite furnace analysis times are longer than those for flame sampling.

2.13.4 Fluoride ion selective electrode (FISE)

Fluoride ion selective electrode (F^- ISE) is a quick and accurate method of measuring fluoride ions in solution [202]. The electrode consists of a single crystal of lanthanum fluoride as the membrane, bonded into a glass or an epoxy body. An electrode potential, dependent on the level of free fluoride ions in a solution, develops across the membrane when it comes into contact with a solution containing fluoride ions; the potential is then measured using an amplifier and a computer software interface against a constant reference potential.

2.13.5 Laser diffraction particle size analysis

The use of laser diffraction is a fast and simple technique for particle size analysis, based on the fact that spatial distribution of a monochromatic beam of scattered light is a function of the particle size within a sample (Figure 2.13.6).
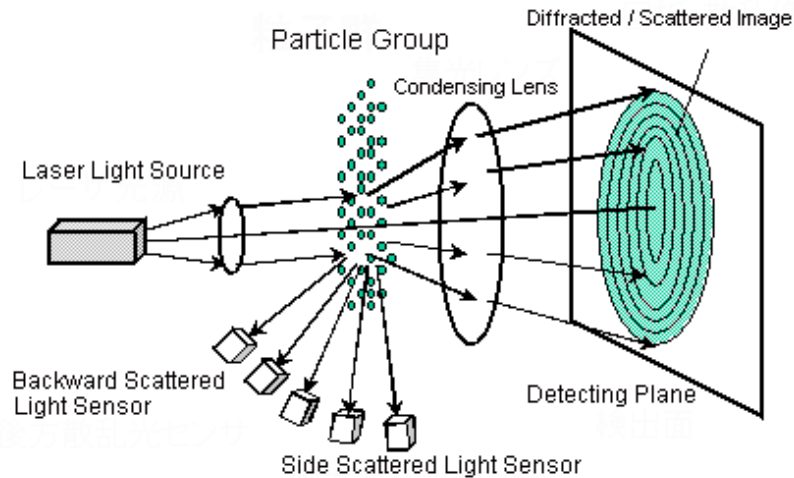
Figure 2.13.6: Schematic representation of laser diffraction (www.shimadzu.com)

On illuminating the particle, usually in a suspension, the laser forms a diffraction image; the intensity of the diffraction rings as well as the distance between them is then measured [203]. The angle formed by the diffracted light, which is inversely proportional to the particle size, is then converted to a particle size distribution; therefore, small particles produce larger angles of scattered light and vice versa.

2.13.6 Gillmore needle apparatus

Gillmore needle apparatus (Figure 2.13.7) is a stainless steel equipment that comprises two needles with a specified weight and diameter and is used to determine the initial and final

setting time of Portland cement and other hydraulic cements. It is recommended by ASTM standards C91, C141, C150 among others.

Both of the cylindrical flat-end needles are 0.0375" (4.8mm) in diameter with a specific tip. The initial set needle tip is 1/12" (2.12mm) in diameter and weighs 1/4lb. (113.4g). The final set needle tip is 1/24" (1.06mm) in diameter and weighs 1lb (453.6g).
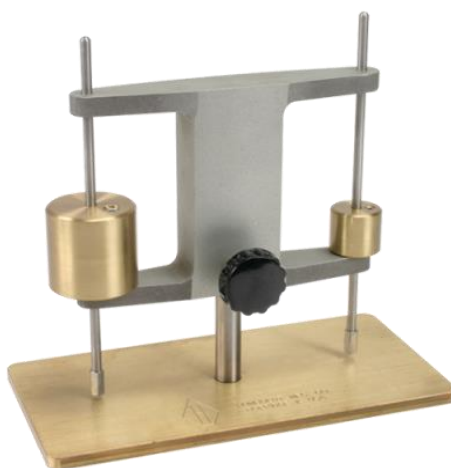
Figure 2.13.7: Gillmore needle apparatus (www.humboldtmfg.com)

2.13.7 Fourier transform infra-red spectroscopy (FTIR)

Infra-red spectroscopy is the

> *"absorption measurement of different infrared (IR) frequencies by a sample positioned in the path of an IR beam."* [204]

IR spectroscopy identifies compounds by their unique absorption frequency which is dependent on the chemical functional groups present in the sample; it is based on the

principle that all atoms in a molecule are in continuous vibration with respect to each other, producing a net change in the dipole moments. When the frequency of a specific vibration is equal to the frequency of the IR radiation directed on the molecule, the molecule absorbs the radiation. The major types of molecular vibrations are stretching and bending. On absorption of the IR radiation, the associated energy is converted into these types of motions which lead to the characteristic absorption bands observed on the spectrum.

Previously, IR spectroscopy was dispersive, relying on a prism to separate the frequencies one at a time; obviously, this scanning process was lengthy. This has been overcome by a simple optical device known as an interferometer, which produces an interferogram signal or a scan of all the IR frequencies simultaneously thus significantly shortening the scanning time. Moreover, the technique is non-destructive, precise and sensitive.

The IR radiation originates from a glowing black-body source, through an aperture that controls its energy, to the interferometer which employs a beam-splitter to split the IR beam into two optical beams. Thereafter, one beam reflects off a fixed flat mirror, while the other beam reflects off a second mirror that moves a few millimeters away from the beam-splitter; eventually, the two beams are reflected off the respective mirrors, and back to the beam-splitter. The first beam travels a fixed length while the other changes depending on the movement of the second mirror; therefore, the signal results from the two beams 'interfering' with one another, and is accordingly referred to as an interferogram.

From the interferometer, the beam enters the sample, where it is reflected or transmitted, and the energy frequencies unique to the sample are absorbed; thereafter, final

measurements are performed by specially designed detectors. The measured interferogram signal, resulting from data points compiled from the IR source, is then decoded by the connected computer, using the mathematical technique known as Fourier transformation to give the IR spectrum.

Attenuated Total Reflectance (ATR) accessories are useful for samples that are difficult to examine by normal transmission such as thick, highly absorbing solid and liquids including films, pastes and powders. ATR occurs when a beam of radiation with a higher refractive index enters a sample with a lower refractive index: the incident angle increases with a reciprocal increase in the fraction of the reflected beam. Therefore, ATR add-ons trap the incident waves from the sample, causing them to be reflected several times before transmission to the detectors (Figure 2.13.8); these multiple interactions between the sample and the IR beam amplify the signal and improve the resolution of the spectrum, which would otherwise be weakened by the physical nature of such samples.
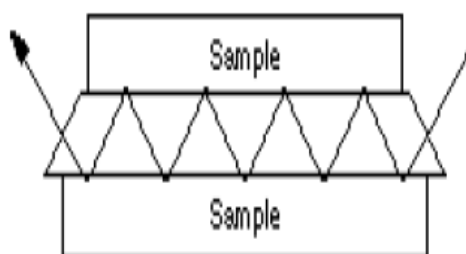
Figure 2.13.8: Schematic representation of the ATR mechanism [204]

2.13.8 Universal testing machine

A universal testing machine or universal tester is an equipment used to test the tensile and compressive strength of materials. The term universal implies that it can perform several standard tensile and compression tests. Tests are conducted according to specified material standards.

Most universal testers comprise of: a load frame consisting of two support frames for the machine; a load cell which measures the force applied on the sample; a cross-head which applies the load on the sample; means of measuring extension or deformation of the sample on loading; test fixtures; output device; and, environmental conditioning as required by the specific test.

2.14 Conceptual framework

Figure 2.14.1 is a summary of the challenges faced by developing countries such as Kenya, in addressing the burden of dental caries.
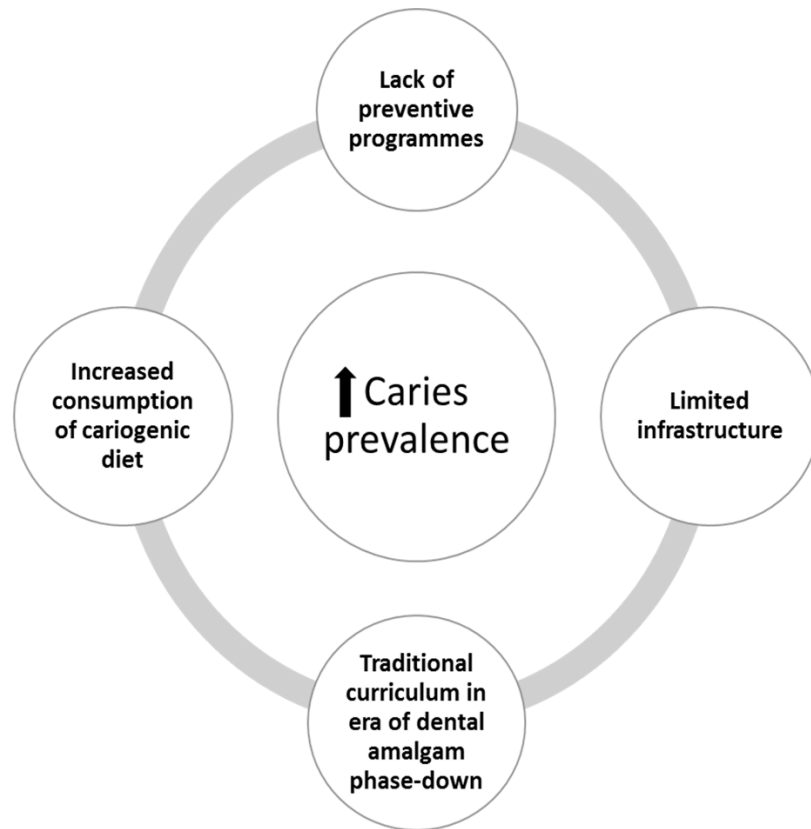
Figure 2.14.1: Challenges faced by LMI countries in addressing the burden of dental caries

The FDI Vision 2020 aims to shape the future of oral healthcare through a responsive and fair model defined by the following priority areas:

"1) Meeting the increasing need and demand for oral healthcare; 2) Expanding the role of existing oral healthcare professionals; 3) Shaping a responsive education model; 4) Mitigating the impacts of socio-economic dynamics; and, 5) Fostering fundamental and translational research and technology". [205]

Banerjee described the golden triangle of minimally invasive operative caries management by interlinking three factors with the aim of realizing optimal adhesive minimally invasive restorations. The three factors are:

> *"1) The histopathology of the disease and the tissues; 2) Adhesive and bonding aspects of materials science; and, 3) Clinical and patient management skills."*
> [56]

Pitts *et al.* [18] considered aspects of incorporation of new materials and techniques into dental clinical practice in the era of dental amalgam phase down. Their focus was on timely adoption of materials and techniques to improve patient care and health systems with minimal environmental impact.

In this project, a model incorporating these three concepts is proposed with the aim of contributing to development of alternative materials through translational research (Figure 2.14.2). These affordable alternative materials may be employed in minimally invasive techniques such as atraumatic restorative treatment thus addressing increased demand for oral healthcare in resource-strained settings while mitigating impacts of socio-economic dynamics. The timing coincides with the dental amalgam phase down by 2020.
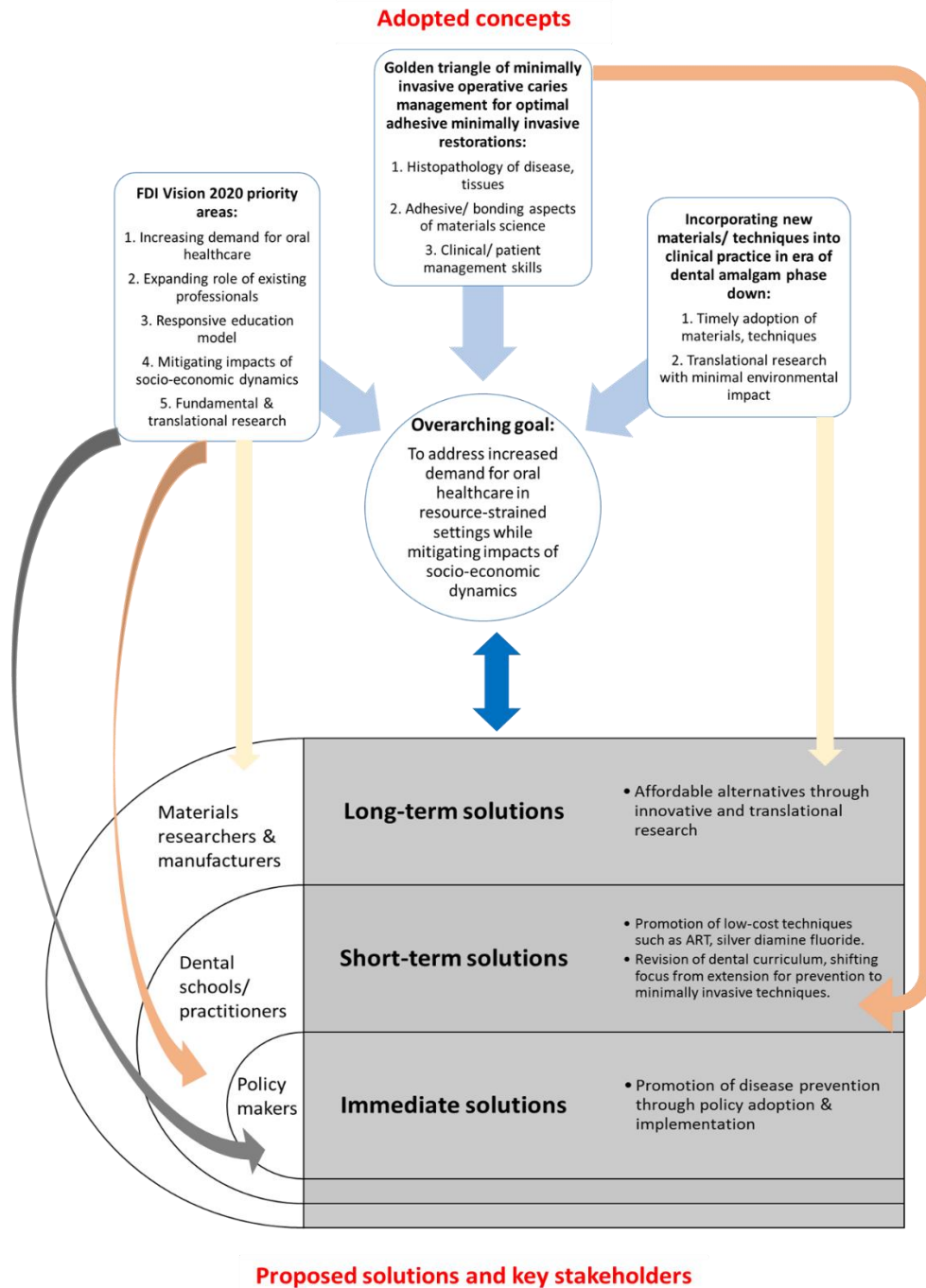
Figure 2.14.2: Project conceptual framework (adapted from Glick *et al.* [205], Banerjee [56] and Pitts *et al.* [18])

2.15 Conclusion

The review of literature has revealed the astounding disease burden presented by dental caries in Kenya, as evidenced by the high prevalence. Moreover, the limited promotion of preventive measures has created a great need for restorative materials. Yet currently available ones have limitations. Additionally, low- and middle-income countries such as Kenya may not afford the expensive and sophisticated accessories often required for the more advanced materials. Further, dental amalgam is scheduled for a global phase down.

Portland cements have been investigated extensively and have been found to be useful biomaterials in restorative dentistry. It is a vibrant manufacturing industry in Kenya yet no study has ever been conducted locally to assess this alternative application. It is therefore proposed that these locally available materials may be investigated for the development of an affordable alternative polyalkenoate-type cement for use in minimally invasive caries management procedures such as ART.

Therefore, this study is not only justified but also timely: firstly, because it presents an opportunity for a middle-income country to contribute to research in a restorative dental biomaterial with the specific aim of addressing the unique problems stated above; and, secondly, because the dental profession and dental materials industry are also tasked with dealing with the global challenge of phasing down dental amalgam in line with the Minamata Convention on Mercury, by seeking alternative materials. Thus the aim of this study is to develop a prototype for a restorative dental cement using raw materials for Portland cement clinker production in Kenya.

CHAPTER THREE

3. STATEMENT OF THE RESEARCH PROBLEM, JUSTIFICATION AND STUDY OBJECTIVES

3.1 Research problem statement

The global prevalence of dental caries remains high despite the availability of well documented preventive measures such as controlled water fluoridation and oral health promotion. [2,4]. Although Petersen [2,3] asserts that 60 – 90% of children and most adults in industrialized countries are affected, there are reports of reduced caries prevalence among 12-year olds as a result of prevention strategies in European countries such as Denmark, United Kingdom, Germany and Switzerland [9,10].

However, in Kenya, several prevalence studies have been conducted and the burden of caries has been shown to be overwhelming across most age groups [39,43,44,48]. The most recent is the first National Oral Health Survey in 2015 [8] which reported caries prevalence of 34.3 % among adults and 23.9% among 5-, 12- and 15-year old children. It is rather disturbing that when only 5-year olds were considered, the prevalence was found to be 46.3%. In developing countries, the rising prevalence has been linked with increased consumption of refined sugar [7] yet within these same countries is the cost of treatment as well as prevention most prohibitive [3]. In Kenya, oral disease prevention policy is poor or totally lacking.

Secondly, the looming phase-down of silver-mercury amalgam by 2020, as documented in the Minamata Convention on Mercury [13,14,17-19] has necessitated an urgent need to find an alternative with minimal negative environmental impact yet still offering the excellent

material properties that have been established with the use of amalgam for more than a century [14,19,28,29]. Apart from its remarkable compressive strength, dental amalgam is one of the simplest yet affordable restorative materials making it readily accessible. Additionally, limited rural electrification has contributed in making its use in developing countries to far surpass that of resin composites and resin ionomers which require sophisticated accessories [13]. The phase down of dental amalgam will greatly disadvantage the poor by hindering access to affordable restorative dental treatment in developing countries such as Kenya.

Thirdly, the FDI has advocated for a dental curriculum review incorporating more aspects of prevention as well as minimally invasive dentistry. Atraumatic restorative treatment (ART) is a minimally invasive technique of caries management that involves the use of only hand instruments and an adhesive material, usually a glass ionomer cement [52]. The ART technique was developed specifically for low socio-economic settings, common in developing countries, with no running water nor electricity that would be necessary to operate sophisticated dental equipment [61]. Several reviews of the ART approach have concluded that this modality of treatment offers a successful short to mid-term solution to dental care in poor countries [24,27]. However, as recommended by Holmgren and Frencken [25], there is need for advancement in the filling materials used for ART to enable the restorations last longer than three years. Arguably, most clinicians consider glass ionomer cements to be temporary or intermediary restorations [13].

High caries prevalence in the face of poor disease prevention policy, dental amalgam phase-down, expensive and technique-sensitive alternatives and low uptake of minimally invasive approaches such as ART have contributed to the oral disease burden in Kenya. The

consequence of this is that the available alternatives for restorative treatment are unaffordable to the majority of the population. With limited options, most resort to extraction as an easy solution and ultimately this results in reduced quality of life due to premature tooth mortality.

3.2 Study justification

The conceptual framework (section 2.14) proposed immediate, short-term and long-term solutions aimed at addressing the burden of caries in low-and middle-income countries, Kenya included. Although industrialized countries have found alternatives in indirect restorations in the era of dental amalgam phase down, these are too expensive for the majority in developing countries. Industrialized countries also have robust prevention policies and have embraced minimally invasive techniques which are lacking in developing countries.

This project sought to address the long-term solutions through contribution to fundamental and translational research. Kenya has a vibrant Portland cement industry, presenting a starting point by providing a source of raw materials for the development of an affordable restorative material that is also easy to manipulate. Calcium silicate cements are a group of bioactive cements that were developed for use in various medical and dental applications [22]. These derivatives of Portland cement have been successfully marketed for use in endodontic restorative procedures [21,22]. It was hypothesized that, similarly, locally available materials utilized in the production of Portland cement may be investigated further to explore their role in the development of alternative ionomer-type dental cements in Kenya.

This study aimed to provide a solution for the inadequate dental care in Kenya using locally available raw materials. Furthermore, it also offered suggestions to expand the applications of a beneficial biomaterial. The ultimate goal was to reduce cost of dental treatment and improve oral health status while also providing a platform for a long-term research agenda with the aim of promoting local development and testing of other biomaterials and medical devices in Kenya.

3.3   Research questions

This study sought to answer the following research questions:

1. What is the composition and particle size of locally produced Portland cement clinker and geopolymers?

2. What is the effect of addition of freeze-dried poly (acrylic acid) (PAA), CaF_2 and tartaric acid on the setting reaction of clinker-based ionomer cements and synthetic geopolymer-based ionomer cements?

3. What is the effect of addition of freeze-dried PAA, CaF_2 and tartaric acid on the rheology, mechanical properties and fluoride ion releasing properties of clinker-based and geopolymer-based ionomer cements?

4. What is the economic viability of local production of an ionomer restorative dental cement?

3.4   Study objectives

3.4.1   Main objective:

To develop a prototype for a dental cement using locally available raw materials in Kenya.

3.4.2 Specific objectives:

1. To describe the chemical composition of Portland cement clinker and geopolymers locally produced in Kenya, in comparison to mineral trioxide aggregate (MTA).

2. To describe the particle size of Portland cement clinker and geopolymers locally produced in Kenya, in comparison to MTA.

3. To formulate a restorative dental cement from locally produced clinker or synthetic geopolymers and poly (acrylic acid).

4. To describe the setting characteristics of restorative dental cements derived from locally produced clinker or synthetic geopolymers and poly (acrylic acid).

5. To evaluate the setting time, mechanical and fluoride ion releasing properties of restorative dental cements derived from locally produced clinker or synthetic geopolymers and poly (acrylic acid).

6. To conduct an assessment of the cost of production of the cements.

3.5 Hypotheses

1. Ho: $\mu_{MTA\ COMPOSITION} = \mu_{PC\ COMPOSITION}$, where μ is mean elemental composition. (There is no major difference in the mean elemental composition of Kenyan Portland cement clinker/synthetic geopolymer and MTA).

   Ha: $\mu_{MTA\ COMPOSITION} \neq \mu_{PC\ COMPOSITION}$ (There is a major difference in the mean elemental composition of Kenyan Portland cement clinker/synthetic geopolymer and MTA).

2. Ho: $\mu_{MTA\ PARTICLE\ SIZE} = \mu_{PC\ PARTICLE\ SIZE}$, where μ is mean particle size. (There is no major difference in the mean elemental composition of Kenyan Portland cement clinker/synthetic geopolymer and MTA).

Ha: $\mu_{\text{MTA PARTICLE SIZE}} \neq \mu_{\text{PC PARTICLE SIZE}}$ (There is a major difference in the mean elemental composition of Kenyan Portland cement clinker/synthetic geopolymer and MTA).

3. Ho: $\mu_{\text{GIC SET}} = \mu_{\text{PC SET}}$, where μ is cement setting products (There is no difference in the setting products of experimental cements formulated from Portland cement clinker, geo-polymers and glass ionomer cements).

Ha: $\mu_{\text{GIC SET}} \neq \mu_{\text{PC SET}}$ (There is a difference in the setting products of experimental cements formulated from Portland cement clinker, geo-polymers and glass ionomer cements).

4. Ho: $\mu_{\text{GIC PROPERTIES}} = \mu_{\text{PC PROPERTIES}}$, where μ is mean cement properties (There is no difference in the setting rheology, mechanical and fluoride ion releasing properties and cost of production of the experimental cements and glass ionomer cements).

Ha: $\mu_{\text{GIC PROPERTIES}} \neq \mu_{\text{PC PROPERTIES}}$ (There is a difference in the setting time, mechanical and fluoride ion releasing properties and cost of production of the experimental cements and glass ionomer cements).

3.6 Study variables

The study variables are described in Table 3.6.1.

Table 3.6.1: Variables and measurable outcomes

Variable name	Type	Measurable outcome
Elemental composition (specific elements by name)	Independent, continuous (quantitative)	Ca, Si, Al, F, As, Pb, others (µg/g or %wt)
Particle size (specific size by diameter)	Independent, continuous (quantitative)	D10, D50, D90 (µm)
Mixing ratios	Independent, discrete (quantitative)	Mixing ratios of geopolymers, clinker, fluoride containing additives, PAA (gm), aqueous tartaric acid (mL).
Cement setting characteristics	Dependent (qualitative)	Identifiable setting reaction products.
Cement setting rheology	Dependent, continuous (quantitative)	Mixing time and net setting time (min).
Cement mechanical properties	Dependent, continuous (quantitative)	Compressive strength (MPa)
Cement fluoride ion releasing profile	Dependent, continuous (quantitative)	F^- (mmol/L per time point)
Assessment of cost of production	Dependent, discrete (quantitative)	Cost of production (USD)

CHAPTER FOUR

4. MATERIALS AND METHODS

4.1 Study design

The study was exploratory and laboratory-based. The study was multi-stage, comprising three phases as follows:

1. Evaluation of Kenyan Portland cement and raw materials for Portland cement production to determine their suitability for the development of an ionomer-type dental cement prototype.

2. Formulation of an ionomer-type dental cement using Portland cement clinker or a synthetic geo-polymer and poly (acrylic acid).

3. Evaluation of the cements' properties together with an economic assessment to select a prototype for use as a restorative dental cement.

The planned study fits within the conceptual framework as shown in Figure 4.1.1. The methodology is described next.
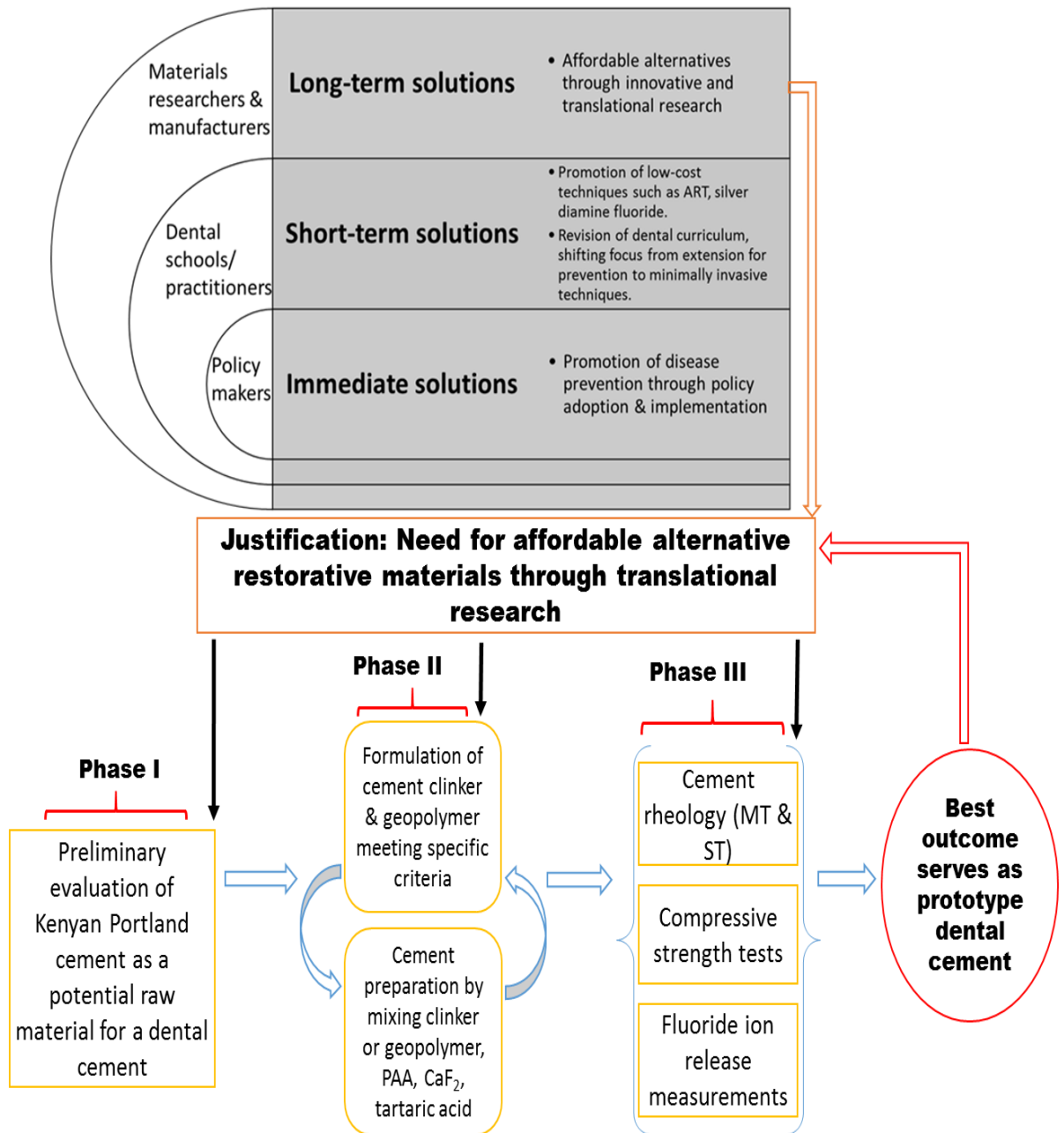
Figure 4.1.1: Relationship between proposed conceptual framework and study design

4.2 Study setting

The study experiments were conducted at research laboratories available at: Ministry of Mining, Nairobi, Kenya; World Agroforestry Centre (ICRAF), Nairobi, Kenya; Schools of Physical and Dental Sciences, University of Nairobi, Kenya; and, Otto Schott Institute for Materials Research, Friedrich Schiller University, Jena, Germany.

4.3 Study population

The initial phase of the study utilized Portland cement clinkers as well as raw aluminosilicate materials for clinker production, that is, blast furnace (BF) Slag and Fly ash (FA) from three major cement manufacturers in Kenya: Bamburi, East African Portland (EAPC) and Athi River Mining (ARM). In addition, a raw aluminosilicate material for geopolymer synthesis, kaolin, was obtained from Saj Ceramics, Athi River, Kenya.

The second and third phases utilized Portland cement clinker from the three major cement companies above as well as a geopolymers or alkaline-activated aluminosilicates synthesized from the said raw aluminosilicate materials in the School of Physical Sciences, University of Nairobi, Kenya. A descriptive summary of the materials is presented in Table 4.3.1.

Table 4.3.1: Summary of study population

No.	Material description	Source	Batch/ lot no. / Expiry date	Collection date
1.	PC clinker	EAPC, Athi River, Kenya	Unavailable	April, 2017
2.	PC clinker	ARM, Athi River, Kenya	Unavailable	July, 2017
3.	PC clinker	Bamburi, Athi River, Kenya	Unavailable	November, 2017
4.	BF Slag	ARM, Athi River, Kenya	Unavailable	July, 2017
5.	FA/ Pozzolana	Bamburi, Athi River, Kenya	Unavailable	November, 2017
6.	Kaolin	Saj Ceramics, Athi River, Kenya	Unavailable	December, 2017
7.	MTA Cem	NexoBio, Chungcheongbuk-do, Korea	1013 MC160516 2019.02 1013 MC150817 2018.05	September, 2017
8.	ProRoot MTA	Dentsply Sirona, York, Pennsylvania, USA	A040500000400/ 0000108513/ 2018.02.02	September, 2017

4.4   Sampling and sourcing of materials

Samples of materials were randomly selected. Specimen samples and dimensions were majorly governed by the ISO standard 9917-1: 2007, for testing of dental cements and ASTM C114 – Standard test methods for chemical analysis of hydraulic cements. Other relevant ISO standards applied where necessary, as specified in the relevant sections in the methodology.

Sourcing of raw materials and clinkers was conducted by the Primary Investigator (PI, the student) and an assistant. Samples were obtained from random batches within the three identified companies, as specified by ASTM C183 – Standard Practice for sampling and the amount of testing of hydraulic cements. Samples were collected from the companies' Nairobi Grinding Plants storage bins prior to packaging.

Each sample weighed at least 1kg and was placed in a sealed moisture-proof, air-tight container. Samples from each site were labelled consecutively according to the order in which they were collected. An element of blinding was introduced by using coded labels; however, the raw materials were distinguished from the clinkers. Coding, labelling and storage was conducted by the assistant who only revealed this information once results of Phase I had been obtained. The PI only accessed the materials from the store and began the testing once all the samples had been collected to ensure that they were truly blinded.

4.5 Inclusion criteria

1. Portland cement manufacturing companies in Kenya which source their raw materials locally.
2. Portland cement manufacturing companies in Kenya which have grinding plants in Athi River and its environs.
3. Portland cement manufacturing companies in Kenya which meet the two criteria above and consented to participate in the study.
4. Any brand of MTA that was available in Kenya.

4.6 Exclusion criteria

1. Portland cement manufacturing companies in Kenya which do not source their raw materials locally.
2. Portland cement manufacturing companies in Kenya which do not have grinding plants in Athi River and its environs.
3. Portland cement manufacturing companies in Kenya which did not consent to participate in the study.
4. Any brand of MTA that is not available in Kenya.

4.7 Phase I: Evaluation of Kenyan Portland cement and raw materials for Portland cement production

4.7.1 Powder X-ray diffraction for phase identification

Powder XRD (XRD; D2 Phaser, Bruker Corporation, Billerica, Massachussets, USA) was used to identify the compositional phases of ground Portland cement clinkers as well as the raw aluminosilicate materials for clinker production, on the basis of their crystallographic patterns. Random samples were obtained from the Nairobi Grinding Plants of Bamburi, EAPC and ARM Cement Companies. Two commercial brands of MTA, MTA Cem and ProRoot MTA, were used as controls.

Samples were prepared and tested as follows:

1. Dry samples were ground to a fine talc-like powder for 10s in a ball mill.

2. The powdered samples were transferred to appropriately labelled glass bottles.

3. Thereafter, enough powder to fill a plastic sample holder (approximately 1g) was removed from the labelled sample bottle, and gently pressed flush into the sample holder using a glass slide to ensure a smooth surface.

4. Excess powder was removed from the edges of the sample holder before it was carefully place in the appropriate XRD slot. Readings were taken at ambient temperature using CuKα radiation at 40kV voltage and 40mA current, within a scan range of 10–80° 2θ and a scan speed of 2° 2θ per minute.

5. Raw data was converted into a Microsoft Excel readable format from which diffraction patterns were charted into spectra, and matched to the International Centre for Diffraction Data database (International Centre for Diffraction Data, Newton Square, PA, USA).

4.7.2 Powder X-ray fluorescence for compositional analysis

Powder EDXRF (XRF; Rigaku NEX CG, Rigaku Corporation, Tokyo, Japan) was used to identify the elemental composition of ground Portland cement clinkers as well as the raw materials for clinker production. Random samples were obtained from the Nairobi Grinding Plants of Bamburi, EAPC and ARM Cement Companies. Two commercial brands of MTA, MTA Cem and ProRoot MTA, were used as controls.

Samples were prepared and tested as follows:

1. Approximately 1g of each sample was removed from a labelled sample bottle, and gently pressed flush into the sample holder using a glass slide to ensure a smooth surface.

2. Excess powder was removed from the edges of the sample holder before it was carefully place in the appropriate XRF slot. Readings were taken at ambient temperature at 30kV voltage and 1.0mA current.

4.7.3 Graphite furnace atomic absorption spectroscopy

Graphite furnace atomic absorption spectroscopy (iCE 3000, Thermo Fisher Scientific, Waltham, Massachussets, USA) was used to identify the elemental composition of ground Portland cement clinkers as well as the raw materials for clinker production. Random samples were obtained from the Nairobi Grinding Plants of Bamburi, EAPC and ARM Cement Companies. Two commercial brands of MTA, MTA Cem and ProRoot MTA, were used as controls.

Samples were prepared and tested as follows:

1. Acid digestion of dry samples was conducted by moistening approximately 1g of each sample in 20ml of distilled water, dissolving it in 20ml 1M HCl, then drying the solution by evaporating over a hot plate.

2. Without heating the residue, further digestion was conducted by adding 20ml of 1M HCl and 20ml of distilled water progressively to the sample until it was completely dissolved, after approximately 2hours. The solution was diluted using 20ml of hot distilled water and filtered.

3. The process was repeated to obtain the residue for determination of silica and 100ml of the filtrate for determination of other elements.

4. At least five standard solutions of elements of interest were prepared by serial dilution of the samples and stored in appropriately labelled bottles.

5. Thereafter, sample readings were taken on the GFAAS at ambient temperature, using argon as a purge gas. Flame photometry was used to quantify the major element (calcium).

6. Raw data was entered on a Microsoft Excel spreadsheet from which standard plots were obtained and sample data presented in tables.

4.7.4   Fluoride ion selective electrode for analysis of fluoride content

F$^-$ISE (Orion 9609BNWP, Thermo Fisher Scientific, Waltham, Massachussets, USA) was used to determine the F$^-$ content of ground Portland cement clinkers as well as the raw materials for clinker production. Random samples were obtained from the Nairobi Grinding Plants of Bamburi, EAPC and ARM Cement Companies. Two commercial brands of MTA, MTA Cem and ProRoot MTA, were used as controls.

Samples were prepared and tested as follows:

1. Samples were prepared by acid digestion as described in section 4.7.3.

2. Prior to measurement, the electrode tip was flushed with deionised water and then calibrated using standard solutions of 0.5, 1 and 10ppm fluoride and TISAB II. Fluoride concentration in the samples was recorded in ppm with a corresponding RmV, then converted to µg/g.

3. There were three specimens for each sample; therefore, the stable reading for each specimen was recorded, and the average value taken as the amount of fluoride ion content in the material.

4.7.5 Laser diffraction particle size analysis

Laser diffraction particle analysis (Partica, LA-950, Horiba Scientific, Kyoto, Japan), which can determine particle size between 0.022–2000µm, was used to determine the particle size of MTA, PC clinkers as well as the raw and alkaline-activated AS (geopolymers). Powder samples were dispersed in 200ml of a solution of deionized water and Calgon (refractive index (n) – 1.478), and sonicated for 10min at ambient temperature to ensure the complete dispersion before running through the LD-PSD analyzer. Tests were performed in triplicate, before and after sieving through a 120µm mesh sieve (Endecotts Ltd, London, UK). Ideally, the powder particle size for restorative dental cements should be less than 45µm as stated in ADA specification number for dental cements. This was compared to two commercial brands of MTA.

4.7.6 Variables and sampling

Table 4.7.1 summarizes the variables under investigation in Phase I and the number of samples for each group of materials. Tests were conducted thrice to ensure validity and reliability.

Table 4.7.1: Sample size and variables for specific objectives in Phase I

Specific objective	Study population	Sample size	Type of test	Number of tests
1. **To describe the composition of Kenyan PC and raw materials for PC production, in comparison to MTA.**	Randomly selected batches of clinker, raw materials for clinker production (BF Slag, FA) from Bamburi, EAPC and ARM companies, Kaolin from Saj Ceramics, two brands of MTA (MTA Cem and ProRoot MTA).	3 sets of samples of each material totaling 24 samples.	XRD, XRF, GFAAS and FISE analysis	3 runs for each sample (from 3 different batches)
2. **To describe the particle size of Kenyan PC and raw materials for PC production, in comparison to MTA.**	Randomly selected batches of clinker, raw materials for clinker production (BF Slag, FA) from Bamburi, EAPC and ARM companies, Kaolin from Saj Ceramics, two brands of MTA (MTA Cem and ProRoot MTA).	3 sets of samples of each material totaling 24 samples.	Laser diffraction analysis	3 runs for each sample (from 3 different batches)

4.8 Phase II: Formulation of experimental ionomer-type dental cements from Portland cement clinker and geopolymers

4.8.1 Formulation of experimental ionomer-type cement powders

Experimental cement powders were designed from Portland cement clinker and synthetic geopolymer powders to meet specific criteria as follows:

1. Firing of raw materials in a rotary kiln to ensure that maximum amounts of calcium aluminates are retained in the clinker [32,171].

2. No gypsum additives during the grinding of the clinker [33,171,180].

3. The synthetic geopolymer was produced through alkaline activation of the raw materials used for clinker production [144-146,151].

4. The ground clinker and synthetic geopolymer was sieved through a 120μm analytical sieve to control the particle size; only the sieved powders were used in the following series of experiments [33,92,175].

4.8.2 Synthesis and characterization of geopolymers

Geopolymers were prepared through alkaline activation of aluminosilicate materials (BF Slag, Fly ash or Kaolin) for production of PC as follows [145,147]:

1. Approximately 100g of various ratios of BF Slag/ FA (0:100, 20:80, 40:60, 60:40, 80:20 and 100:0) and Kaolin/ FA (100:0 and 80:20) were weighed separately.

2. One litre of the alkaline activation solution was prepared by adding 85% 14M NaOH to 15% Na_2SiO_3. Laboratory grade reagents, 98% NaOH pellets and Na_2SiO_3 (both Sigma Aldrich, Gillingham, UK) with a final constitution of 9.1% Na_2O, 27.5% SiO_2 and 63.4% H_2O and SiO_2/Na_2O ratio of 3.02, were used.

3. Approximately 55ml of the alkaline activation solution was placed in eight 250ml capacity glass beakers and the weighed out powders added to each corresponding labelled beaker. The powder/ liquid ratio was approximately 0.55.

4. The solutions were stirred vigorously for a few minutes then transferred to an oven set at 85°C for 24 hours.

5. After 24 hours, the dried product was removed from the oven, bench cooled and left at ambient temperature for 90 days.

6. Thereafter, the products were retrieved from the beakers, sprayed with ethanol to stop further activation, placed and sealed in labelled, airtight sample bags, pulverized and characterized.

7. The composition and particle size of the alkaline-activated aluminosilicates or geopolymers was then evaluated using XRD, XRF, GFAAS and laser diffraction particle size analysis as described in sections 4.7.1, 4.7.2, 4.7.3 and 4.7.5, respectively.

4.8.3 Preparation of ionomer-type experimental dental cements

Experimental dental cement pastes were prepared by mixing various ratios of clinker or geopolymer powder, PAA (mw 35KDa) (S & C Polymer GmbH, Elmshorn, Germany), CaF_2 and aqueous tartaric acid (both Sigma Aldrich, Gillingham, UK). Several ratios were attempted to attain a promising mixture with reasonable mixing and setting time, and which exhibited a workable dough consistency for intended restorative cement application.

Selection of clinker powder for the cements was on the basis of similarity of the composition to MTA; moreover, the percentage ratios of silica, alumina and calcite as the major compounds was similar to that of original ionomer glasses (21:16.6:34.2). FA/ BF slag geopolymers were selected for the same reason, although FA had low CaO content. However, it increased with increasing BF slag content. Kaolin geopolymers also had high ratios of alumina and silica but low CaO content hence likely to react with PAA similarly to aluminosilicate materials.

The various experimental cement preparation ratios and outcomes for clinker and geopolymer derived cements are presented in Table 4.8.1.

Table 4.8.1: Experimental cement preparation ratios and outcomes

Material ID	Powder (gm)	CaF$_2$ (gm)	PAA (gm)	10% tartaric acid (mL)	Outcome – MT(s), ST(min), consistency
1. EAPC clinker	0.5	-	0.1	0.1	Grainy mixture
2. EAPC clinker	0.5	-	0.2	0.25	Grainy mixture
3. EAPC clinker	0.4	0.1	0.2	0.25	30s, 1.32min, paste
4. EAPC clinker	0.3	0.2	0.2	0.25	30s, 4.42min, paste
5. ARM clinker	0.4	0.1	0.2	0.25	30s, 1.35min, paste
6. ARM clinker	0.3	0.2	0.2	0.25	30s, 3.08min, paste
7. Bamburi clinker	0.3	0.2	0.2	0.25	30s, >7min, fluid
8. Bamburi clinker	0.4	0.2	0.2	0.25	30s, 5min, paste
9. FA100 geopolymer	0.5	-	0.2	0.25	Fluid
10. FA100 geopolymer	0.8	0.2	0.2	0.25	60s, >10min, fluid
11. FA100 geopolymer	0.6	0.4	0.2	0.25	60s, >10min, fluid
12. FA100 geopolymer	1.0	-	0.2	0.25	60s, 7.04min, paste
13. FA100 geopolymer	1.5	-	0.3	0.2	90s, 4.19min, paste
14. FA100 geopolymer	1.0	-	0.1	0.15	90s, 5.20min, paste
15. FA80/BF slag20 geopolymer	1.0	-	0.1	0.20	90s, 8.13min, paste
16. All FA/BF slag geopolymers	1.0	-	0.1	0.15	90s, 5.20min, paste
17. Kaolin100 geopolymer	1.0	-	0.2	0.25	30s, 30s, paste
18. Kaolin100 geopolymer	0.7	-	0.2	0.25	60s, 3.41min, paste
19. Kaolin100 geopolymer	0.7	-	0.1	0.20	60s, 2.15min, paste
20. Kaolin80/FA20 geopolymer	0.7	-	0.1	0.20	60s, 2.40min, paste

4.8.4 Evaluation of the setting characteristics of experimental cements

FTIR spectroscopy (Cary 630, Agilent Technologies, Ratingen, Germany) was used to evaluate the setting characteristics of the experimental cements. Kinetic measurements were conducted on cement pastes 30s after mixing and followed up to 25 minutes after mixing.

The clinker and geopolymer powders, freeze-dried poly (acrylic acid) and tartaric acid powders were also scanned as reference materials. Data was collected in the IR region between 3600 cm^{-1} to 500 cm^{-1}.

4.8.5 Variables and sampling

Table 4.8.2 summarizes the variables under investigation in Phase II and the number of samples for each group of materials.

Table 4.8.2: Sample size for specific objectives in Phase II

Specific objective	Study population	Sample size	Type of test	Number of tests
1. **To formulate experimental dental cements from PC clinker and geopolymers.**	PC from Bamburi, EAPC and ARM companies; BF Slag/ FA and Kaolin/ FA geopolymers	8 material groups	-	-
2. **To describe the setting characteristics of experimental dental cements derived from PC clinker and geopolymers.**	PC from Bamburi, EAPC and ARM companies; BF Slag/ FA and Kaolin/ FA geopolymers	8 material groups	FTIR analysis	-

4.9 Phase III: Evaluation of experimental cements' properties and an economic assessment

4.9.1 Preparation of ionomer-type experimental dental cements

Ionomer-type experimental dental cements were prepared by mixing the PC clinker or geopolymer powders with high molecular weight (35KDa) freeze-dried poly (acrylic acid)

(PAA) (S & C Polymer GmbH, Elmshorn, Germany), CaF_2 and aqueous tartaric acid (both Sigma Aldrich, Gillingham, UK) in pre-determined ratios, as detailed in section 4.8.3.

4.9.2 Evaluation of mixing and setting time of experimental cements

The mixing time of the cements was recorded as the amount of time in seconds required to obtain a homogenous dough consistency from all the constituents dispensed on a glass slab and mixed using a stainless steel spatula with continuous long strokes.

Initial setting time of the cements was recorded using a Gillmore needle apparatus (Humboldt Mfg, Elgin, Illinois, USA) at ambient temperature as specified in ISO 9917 – 1: 2007 for hydraulic dental cements, as follows:

1. Once the desired cement consistency was obtained, samples were condensed in preformed cuboids, $8mm^2$ by 10mm, made from modelling wax. Three specimens were prepared for each cement sample.
2. The Initial set needle was held in a vertical position and applied lightly to the surface of the cement. This was repeated until the Gillmore needle did not cause an appreciable indentation on the cement surface. The time was recorded in seconds.

4.9.3 Compressive strength testing of experimental cements

The compressive strength tests were performed on cement cylinders 4.0mm in diameter by 6.0mm in height, according to ISO 9917 – 1:2007. The specimen fabrication and compressive strength tests were conducted as follows:

1. The cylindrical specimens were fabricated by condensing freshly mixed cement pastes into teflon moulds containing three bores of the above dimensions.

2. Thereafter, the moulds were clamped between two steel plates and placed in a preheated oscillating oven at 37°C for 24 hours. After the recommended one hour, the cements had not obtained final set hence the extension of the period to 24 hours.

3. After 24 hours, they were retrieved from the moulds, placed in centrifuge bottles at 100% humidity achieved by damp tissues and incubated at 37°C for 24 hours, 3 days, 7 days and 28 days. Some of the cements were unstable in aqueous media hence the modification to incubate at 100% humidity. The specimen dimensions as well as weight before incubation and prior to testing was recorded.

4. A 30kN load cell was used to load the samples using a compression cage on a Universal Testing machine (ProLine Z050TN, ZwickRoell, Ulm, Germany) at a crosshead displacement speed of 1mm min^{-1}.

5. Six cement cylinders were fabricated and tested for each PC clinker and geopolymer ionomer cement sample.

6. Compressive strength was calculated using the formula:

$$\sigma_c = F \div \pi r^2 \ (6)$$

Where: σ_c is compressive strength (MPa); F is applied load at failure (N); and, r is the sample radius as measured prior to testing (mm).

4.9.4 Fluoride ion release measurements of experimental cements in Tris buffer, deionized water and artificial saliva

Ion release measurements were conducted in deionized water, Tris buffer and artificial saliva. The three elution media were selected on the basis of their neutral pH as well as few elemental content which may form complexes hence interfere with the ion release processes of the cements. For comparison at different pH, ion release was also conducted in an acidic

(pH 5) and basic (pH 9) version of deionized water and Tris buffer, achieved by 1M HCl and NaOH solutions, respectively.

To prepare Tris buffer solution, 15.090gm of tris-(hydroxymethyl) aminomethane (Sigma Aldrich, Gillingham, UK) was dissolved in 800ml of deionized water while stirring, followed by 44.2ml of 1M hydrochloric acid (HCl) (Sigma Aldrich). The mixture was stored in an incubator at 37°C and, 24 hours later, the pH was checked using a pH meter (Orion 9609BNWP, Thermo Fisher Scientific, Waltham, Massachussets, USA) and adjusted to 7.35 using 1M HCl. The solution was then filled up to 2 litres by addition of deionized water, and stored at 37°C.

As previously described (section 4.9.3), cement cylinders were fabricated for ion release measurements, three cylinders for each clinker and geopolymer sample. On retrieval from the incubator after 24 hours, they were stored in a 15ml centrifuge bottle containing 10ml of each elution medium and returned to storage at 37°C. Fluoride ion release in the elution media was measured at specified time points of 1, 3, 7, 28 days for clinker-based cements, and 10, 20, 40 and 60 minutes for geopolymer-based cements, as follows:

1. Prior to measurement, the electrode tip was flushed with deionised water and then calibrated using standard solutions of 0.5, 1 and 10ppm fluoride and TISAB II. Fluoride concentration in the samples was recorded in ppm with a corresponding RmV, then converted to mmol/L.

2. There were three specimens for each sample; therefore, the stable reading for each specimen was recorded, and the average value taken as the amount of fluoride ion content in the material.

4.9.5 Assessment of cost of production of experimental dental cements

Cost of production of experimental dental cements was estimated in USD, in comparison to the purchase price of commercial brands. A simple formula factoring fixed costs and variable costs was used, where fixed costs included utilities while variable costs included raw materials.

4.9.6 Variables and sampling

Table 4.9.1 summarizes the variables under investigation in Phase III and the number of samples for each group of materials. Tests were repeated to ensure validity and reliability.

Table 4.9.1 Sample size for specific objectives in Phase III

Specific objective	Study population	Sample size	Type of test	Number of tests
1. **To evaluate cement mixing and setting time.** 2. **To evaluate cement mechanical properties.** 3. **To evaluate cement ion releasing properties.** 4. **To assess cost of production of cements.**	Promising cement mixtures from PC clinker and geopolymers.	3 to 6 specimens for each promising cement sample.	Mixing time and initial setting time, Compressive strength test, FISE	At least 3 tests for each sample

4.10 Minimizing errors and bias

To enhance validity of results and minimize errors, experiments were conducted in triplicate. Tests were governed by ISO and ASTM standards with reasonable modifications where appropriate. To minimize bias, samples were randomly selected from different

batches of materials and were subject to blinding where possible. Results were compared to established brands of materials where appropriate.

4.11 Ethical considerations

Ethical approval was sought and obtained from the Kenyatta National Hospital and University of Nairobi Ethics and Research Standards Committee prior to commencement of the study.

4.12 Data analysis and results presentation

Microsoft Excel (2013) and R-Studio statistical software version 3.4.2 (2017) were used for data management and analysis.

Data entry and clean-up: Data was entered manually in Microsoft Excel spreadsheets in groups of the relevant variables under study. The data was scrutinized to ensure that it answers the research questions. Invalid or missing data was excluded from analysis.

Data analysis: R-Studio was used for descriptive analysis presented in the form of frequencies, range, sum and mean. Hypothesis testing was conducted by multivariate analysis by way of one-way analysis of variance (ANOVA) of continuous data followed by Tukey's post hoc test at 95% confidence interval and α level set at 0.05.

Data presentation: Results were presented in form of tables and figures.

4.13 Significance of the study/ Study outcome

1. The potential suitability of locally produced Kenyan Portland cement clinker as a cheaper alternative to commercial calcium silicate cements was established.

2. Locally available raw materials in Kenya were identified as potentially suitable for developing a prototype for a restorative dental cement that may serve as:

   i. An alternative to the glass ionomer cements currently used in the ART technique to manage dental caries.

   ii. An alternative to dental amalgam in line with the phase down advocated for in the Minamata Convention on Mercury.

3. Industrial collaboration was initiated to enable future development and testing of biomaterials in Kenya.

CHAPTER FIVE

5. RESULTS

The aim of this study was to develop a prototype for a restorative dental cement in Kenya. PC clinker and aluminosilicate (AS) materials for production of PC clinker were collected from three PC and one ceramic manufacturing companies in Kenya and evaluated in a laboratory-based study in three phases.

In the first phase, the composition of the PC clinker and geopolymers synthesized by alkaline-activation of the aluminosilicates for clinker production, in comparison to MTA, was evaluated by EDXRD, XRF, GFAAS and F⁻ISE, while particle size of the same materials was analyzed by laser diffraction.

In the second phase, an experimental ionomer-type dental cement was formulated by mixing PC clinker or geopolymer powders with CaF_2, freeze-dried PAA and aqueous tartaric acid in various ratios to obtain a suitable consistency with reasonable setting time. The setting characteristics of the cements was evaluated using FTIR.

In the third phase, the experimental cements' initial setting time, mechanical properties and fluoride ion releasing profile was evaluated using Gillmore needle apparatus, Universal testing machine, FISE, respectively. A costing assessment of the experimental cements was also conducted.

The results of the three phases are presented in this chapter. Statistical analysis of relevant data was conducted by one-way ANOVA of continuous variables followed by Tukey's post hoc test at 95% confidence interval ($\alpha=0.05$).

5.1 Phase I: Evaluation of Kenyan PC clinker and raw materials for PC clinker production, in comparison to MTA

5.1.1 Phase identification by Powder X-ray diffraction

Figure 5.1.1 shows the diffraction patterns of Portland cement clinker and MTA. The spectra show similar peaks of di-calcium silicate and tri-calcium silicate in MTA and Portland cement clinkers. They also show peaks of Bi_2O_3 unique to MTA.
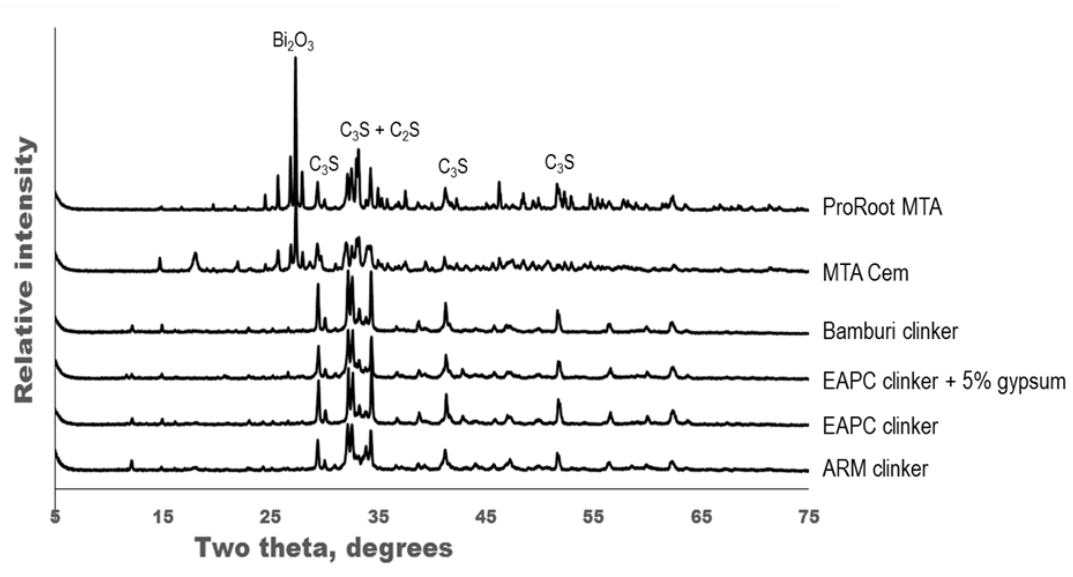
Figure 5.1.1: Powder X-ray diffraction patterns of PC clinker and MTA

Figure 5.1.2 shows the diffraction patterns of raw aluminosilicates and alkaline-activated aluminosilicates (geopolymers). The spectra show similar peaks of quartz, calcite and mullite within the various materials. Following alkaline-activation, the quartz and mullite peaks were markedly enhanced in 100% BF slag, and mixtures of BF slag and FA (80:20 and 60:40).
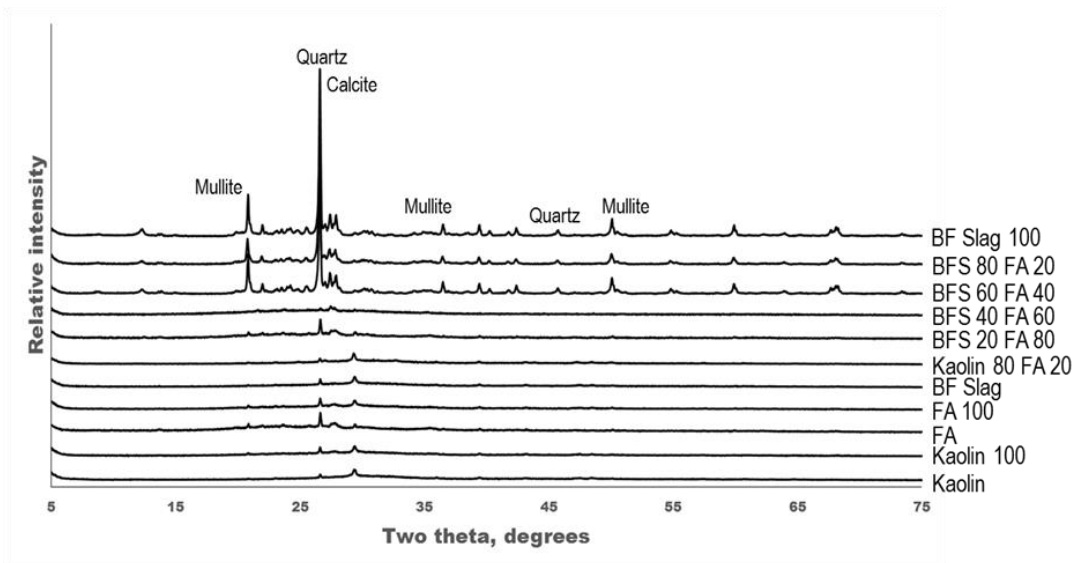
Figure 5.1.2: Powder X-ray diffraction patterns of raw and alkaline-activated aluminosilicates

5.1.2 Composition analysis by Energy dispersive x-ray fluorescence

Table 5.1.1 summarizes the major constituents (%wt) of the materials as analyzed using EDXRF. MTA Cem, ProRoot MTA, ARM, Bamburi and EAPC clinkers, raw and alkaline-activated BF slag and alkaline-activated mixtures of mixtures of BF slag and fly-ash (60:40 and 80:20) were found to have high proportions of CaO, ranging from 24.56%wt to 65.04%wt. All the materials contained SiO_2 ranging from 18.38%wt to 74.65%wt.

All the materials also contained Al_2O_3; however, MTA Cem, ProRoot MTA, ARM, Bamburi and EAPC clinkers contained less amounts (1.89%wt to 5.96%wt) while raw and alkaline-activated BF slag, alkaline-activated mixtures of mixtures of BF slag and fly-ash and, raw and alkaline-activated Kaolin contained higher amounts of Al_2O_3 (10.32%wt to 27.69%wt). MTA Cem and ProRoot MTA were also found to have high proportions of Bi (16.25%wt and 33.19%wt, respectively).

Table 5.1.2 presents a descriptive summary while Table 5.1.3 presents ANOVA of compositional analysis by EDXRF. There was a statistically significant difference for CaO, SiO_2, Al_2O_3, P_2O_5, S, Pb and Bi content among all materials. However, Tukey's post hoc test returned no statistically significant difference between PC and MTA except for Pb (p=0.000) and Bi (p<0.0001). For PC and aluminosilicate materials, Tukey's post hoc test returned statistically significant difference for CaO (p=0.006), SiO_2 (p=0.004), Al_2O_3 (p=0.04) and P_2O_5 (p<0.0001) while for MTA and aluminosilicates, Tukey's post hoc test returned statistically significant difference for SiO_2 (p=0.003), Al_2O_3 (p=0.03), P_2O_5 (p=0.003), S (p=0.003), Pb (p=0.000) and Bi (p<0.0001).

Table 5.1.1: Composition of MTA, PC clinker, raw and alkaline-activated aluminosilicates by EDXRF (%wt)

Sample name	CaO	SiO$_2$	Al$_2$O$_3$	P$_2$O$_5$	S	Cl	K$_2$O	MgO	Fe	As	Sr	Pb	Bi	Others	Total
MTA Cem	53.31	18.38	3.40	0.44	6.17	0.04	0.14	0.00	0.10	0.00	0.02	1.44	16.25	0.32	100.00
ProRoot MTA	38.83	19.66	1.89	0.47	2.37	0.43	0.17	0.00	0.18	0.00	0.15	2.06	33.19	0.58	100.00
ARM	65.04	21.99	5.96	0.75	0.52	0.08	1.47	0.00	3.15	0.00	0.03	0.01	0.00	1.00	100.00
EAPC	62.38	22.77	5.53	0.42	0.99	0.00	1.01	3.67	2.67	0.00	0.06	0.01	0.00	0.49	100.00
Bamburi	51.09	32.19	4.99	0.66	3.08	0.02	2.48	0.00	4.64	0.00	0.10	0.00	0.00	0.76	100.00
BF Slag	42.77	35.54	13.08	0.30	1.82	0.04	0.42	4.73	0.66	0.00	0.01	0.00	0.00	0.64	100.00
BF Slag100	45.57	38.53	12.78	0.07	1.40	0.03	0.28	0.00	0.64	0.00	0.07	0.00	0.00	0.63	100.00
Kaolin	0.65	62.88	27.69	0.03	0.00	0.08	3.95	2.72	1.68	0.00	0.01	0.00	0.00	0.30	100.00
Kaolin100	0.61	68.44	23.45	0.03	0.08	0.09	3.84	1.91	1.29	0.00	0.01	0.01	0.00	0.24	100.00
Kaolin80: FA20	1.02	70.77	20.71	0.00	0.03	0.07	3.89	1.03	2.11	0.00	0.01	0.01	0.00	0.34	100.00
FA100	3.18	74.65	10.32	0.00	0.12	0.14	5.18	0.00	5.58	0.00	0.01	0.01	0.00	0.81	100.00
BF Slag20: FA80	19.59	59.41	10.75	0.11	0.55	0.11	3.05	2.40	3.33	0.00	0.03	0.00	0.00	0.67	100.00
BF Slag40: FA60	10.66	68.31	10.88	0.09	0.34	0.15	4.16	0.00	4.64	0.00	0.02	0.00	0.00	0.76	100.00
BF Slag60: FA40	24.56	54.41	11.77	0.17	0.73	0.15	2.58	2.10	2.79	0.00	0.04	0.01	0.00	0.71	100.00
BF Slag80: FA20	34.86	48.07	11.69	0.19	1.02	0.10	1.49	0.00	1.85	0.00	0.05	0.01	0.00	0.68	100.00

Table 5.1.2: Descriptive summary of composition determined by EDXRF (%wt)

Compound	Material category	Mean (SD)	Min	Max
CaO	PC (n=3)	59.50 (7.41)	51.09	65.04
	MTA (n=2)	46.07 (10.24)	38.83	53.31
	AS (n=10)	18.35 (17.85)	0.61	45.57
SiO_2	PC	25.65 (5.68)	21.99	32.19
	MTA	19.02 (0.91)	18.38	19.66
	AS	58.10 (13.65)	35.54	74.65
Al_2O_3	PC	5.49 (0.49)	4.99	5.96
	MTA	2.65 (1.07)	1.89	3.40
	AS	15.31 (6.25)	10.32	27.69
P_2O_5	PC	0.61 (0.17)	0.42	0.75
	MTA	0.46 (0.02)	0.44	0.47
	AS	0.10 (0.01)	0.00	0.30
S	PC	1.53 (1.36)	0.52	3.08
	MTA	4.27 (2.69)	2.37	6.17
	AS	0.61 (0.63)	0.00	1.82
Cl	PC	0.03 (0.04)	0.00	0.08
	MTA	0.24 (0.28)	0.40	0.43
	AS	0.10 (0.04)	0.30	0.15
K_2O	PC	1.65 (0.75)	1.01	2.48
	MTA	0.16 (0.02)	0.14	0.17
	AS	2.88 (1.66)	0.28	5.18
MgO	PC	1.22 (2.12)	0.00	3.67
	MTA	0.00 (0.00)	0.00	0.00
	AS	1.49 (1.8)	0.00	4.73
Fe	PC	3.49 (1.03)	2.67	4.64
	MTA	0.14 (0.06)	0.10	0.18
	AS	2.46 (1.65)	0.64	5.58
As	PC	0.00 (0.00)	0.00	0.00
	MTA	0.00 (0.00)	0.00	0.00
	AS	0.00 (0.00)	0.00	0.00
Sr	PC	0.06 (0.04)	0.03	0.1
	MTA	0.09 (0.09)	0.02	0.15
	AS	0.03 (0.02)	0.01	0.07
Pb	PC	0.01 (0.01)	0.00	0.01
	MTA	1.75 (0.44)	1.44	2.06
	AS	0.01 (0.01)	0.00	0.01
Bi	PC	0.00 (0.00)	0.00	0.00
	MTA	24.72 (11.92)	16.25	33.19
	AS	0.00 (0.00)	0.00	0.00
Others	PC	0.75 (0.26)	0.49	0.88
	MTA	0.45 (0.18)	0.32	0.52
	AS	0.58 (0.21)	0.24	0.73

Table 5.1.3: ANOVA of composition determined by EDXRF (%wt)

Compound	Material category	F statistic, df, p-value	Tukey's post hoc adjusted p-value	Diff (95% CI)
CaO	PC (n=3) MTA (n=2) AS (n=10)	8.73, 2 df $p \leq 0.01$**	PC:AS = 0.006**	-41.16 (-69.30, -13.01)
SiO$_2$	PC MTA AS	14.33, 2df $p \leq 0.001$***	PC:AS = 0.004** MTA:AS=0.003**	32.45 (11.29, 53.61) 39.08 (14.19, 63.98)
Al$_2$O$_3$	PC MTA AS	6.98, 2df $p \leq 0.01$**	PC:AS = 0.04* MTA:AS = 0.03*	9.82 (0.30, 19.34) 12.67 (1.46, 23.87)
P$_2$O$_5$	PC MTA AS	29.5, 2df $p \leq 0.0001$***	PC:AS<0.0001*** MTA:AS=0.003**	-0.51 (-0.70, -0.32) -0.36 (-0.58, -0.13)
S	PC MTA AS	9.33, 2df $p < 0.004$**	MTA:AS=0.003**	-3.66 (-5.93, -1.39)
Cl	PC MTA AS	3.12, 2df $p=0.08$		
K$_2$O	PC MTA AS	3.2, 2df $p=0.08$		
MgO	PC MTA AS	0.71, 2df $p=0.51$		
Fe	PC MTA AS	3.12, 2df $p=0.08$		
As	PC MTA AS	-		
Sr	PC MTA AS	3.06, 2df $p=0.08$		
Pb	PC MTA AS	164.4, 2df $p<0.0001$***	PC:MTA=0.000*** AS: MTA=0.000***	1.74 (1.43, 2.05) -1.75 (-2.01, -1.48)
Bi	PC MTA AS	44.29, 2df $p<0.0001$***	PC:MTA<0.0001*** AS:MTA<0.0001***	2.47 (16.30, 33.14) -2.47 (-31.87, -17.57)
Others	PC MTA AS	1.30, 2df $p=0.31$		

$*p<0.05$, $**p \leq 0.01$, $***p \leq 0.0001$

5.1.3 Composition analysis by Graphite furnace atomic absorption spectroscopy

Table 5.1.4 summarizes the major constituents (μg/g) of the materials as analyzed using GFAAS. Calcium was found to be a major constituent of all the materials (32656.86μg/g, sd 4484.23 to 79186.67μg/g, sd 2315.18) except Fly-ash. Iron was also a constituent of all the materials (1554.67μg/g, sd 163.22 to 2134.33μg/g, sd 73.32) except BF slag. MTA Cem, ProRoot MTA, ARM and Bamburi clinkers were found to have some levels of Pb (0.59μg/g to 3.57μg/g).

Table 5.1.4: Composition of MTA, Portland cement clinker and raw aluminosilicates (µg/g) (std dev in parenthesis)

Sample name	Zn	Fe	Ni	Pb	Cu	Cd	Cr	Ca	Mn	PO$_4^{3-}$
MTA Cem	3.58 (0.09)	1554.67 (163.22)	0.20 (0.15)	1.89 (0.12)	1.5 (0.00)	0.01 (0.00)	2.15 (0.29)	79186.67 (2315.18)	0.00 (0.00)	56.12 (7.83)
ProRoot MTA	3.06	77.26	0.37	0.59	1.46	0.09	0.00	70772.00	0.00	17.75
ARM	129.87 (13.85)	2030.93 (385.25)	3.13 (0.98)	1.90 (1.61)	4.49 (0.60)	0.07 (0.00)	5.99 (10.38)	45576.16 (20.70)	94.024 (5.19)	16.32 (5.06)
Bamburi	250.53 (4.48)	2134.33 (73.32)	0.001 (0.00)	3.57 (0.00)	163.61 (3.80)	0.05 (0.04)	4.32 (0.31)	55944.00 (4480.82)	16.97 (0.63)	23.55 (1.68)
EAPC	2.89 (2.16)	1768.33 (82.08)	0.45 (0.06)	0.001 (0.00)	3.79 (0.14)	0.001 (0.00)	0.001 (0.00)	53348.01 (15.31)	63.47 (1.67)	21.49 (1.24)
FA	4.56 (0.04)	1921.67 (378.73)	0.001 (0.00)	0.001 (0.00)	0.82 (0.61)	0.011 (0.08)	0.001 (0.00)	0.00 (0.00)	25.33 (0.37)	7.44 (0.24)
BF Slag	0.27 (0.02)	0.001 (0.00)	0.001 (0.00)	0.001 (0.00)	7.30 (0.65)	0.01 (0.20)	4.23 (0.00)	32656.86 (4484.23)	67.66 (3.09)	4.11 (0.64)

5.1.4 Fluoride ion content analysis by fluoride ion selective electrode

Table 5.1.5 shows that F^- was detected in only fly-ash (43.33μg/g, sd 5.77).

Table 5.1.5: F^- composition of MTA, Portland cement clinker and raw aluminosilicates (μg/g) (std dev in parenthesis)

Sample name	F^- content
MTA Cem	0.00
ProRoot MTA	0.00
ARM	0.00
Bamburi	0.00
EAPC	0.00
FA	43.33 (5.77)
BF Slag	0.00

Table 5.1.6 presents a descriptive summary while Table 5.1.7 presents ANOVA of compositional analysis by GFAAS and FISE. There was a statistically significant difference for Ca, Zn, Fe, Pb, Mn, PO_4^{3-} and F^- among all materials. However, Tukey's post hoc test returned no statistically significant difference between PC and MTA except for Ca (p=0.004), Zn (p=0.04), Mn (p=0.01) and PO_4^{3-} (p<0.001) content. For PC and aluminosilicate materials, Tukey's post hoc test returned statistically significant difference for Ca (p<0.0001), Zn (p=0.02), Pb (p=0.04), PO_4^{3-} (p=0.03) and F (p=0.02). For MTA and aluminosilicate materials, Tukey's post hoc test returned statistically significant difference for Ca (p<0.0001) and PO_4^{3-} (p<0.001).

Table 5.1.6: Descriptive summary of composition as analyzed by GFAAS and FISE

(µg/g)

Element	Material category	Mean (SD)	Min	Max
Ca	PC (n=9)	51623.00 (5182.00)	45555.00	61118.00
	MTA (n=4)	77083.00 (4612.00)	70772.00	81860.00
	AS (n=6)	16328.00 (18110.00)	0.00	37835.00
Zn	PC	127.80 (107.50)	0.41	255.50
	MTA	3.45 (0.27)	3.06	3.66
	AS	2.42 (2.35)	0.25	4.60
Fe	PC	1978.00 (258.50)	1709.00	2472.00
	MTA	1185.00 (750.60)	77.26	1726.00
	AS	960.80 (1079.00)	0.001	2245.00
Ni	PC	1.19 (1.54)	0.001	4.25
	MTA	0.24 (0.15)	0.09	0.37
	AS	0.001 (0.00)	0.001	0.001
Pb	PC	1.83 (1.74)	0.001	3.57
	MTA	1.57 (0.66)	0.59	2.02
	AS	0.001 (0.00)	0.001	0.001
Cu	PC	57.30 (79.76)	3.63	166.40
	MTA	1.50 (0.03)	1.46	1.52
	AS	4.06 (3.60)	0.47	7.97
Cd	PC	0.04 (0.04)	0.001	0.10
	MTA	0.03 (0.04)	0.007	0.09
	AS	0.06 (0.08)	0.001	0.20
Cr	PC	3.44 (5.84)	0.001	17.97
	MTA	1.61 (1.10)	0.00	2.43
	AS	2.12 (2.32)	0.001	4.23
Mn	PC	58.15 (33.72)	16.34	99.84
	MTA	0.00 (0.00)	0.00	0.00
	AS	46.50 (23.27)	25.10	69.74
PO_4^{3-}	PC	20.46 (4.23)	13.00	25.08
	MTA	46.53 (20.23)	17.75	64.67
	AS	5.78 (1.87)	3.42	7.58
F	PC	0.00 (0.00)	0.00	0.00
	MTA	0.00 (0.00)	0.00	0.00
	AS	21.67 (24.01)	0.00	50.00

Table 5.1.7: Descriptive summary and ANOVA of composition as analyzed by GFAAS and FISE (µg/g)

Element	Material category	F statistic, df, p-value	Tukey's post hoc adjusted p-value	Diff (95% CI)
Ca	PC (n=9) MTA (n=4) AS (n=6)	39.33, 2df $p<0.0001$***	PC:MTA=0.004** PC:AS<0.0001*** MTA:AS<0.0001***	25460.28 (8480.93, 42439.62) -35294.29 (-50186.16, -20402.42) -60754.57, (-78993.31, -42515.83)
Zn	PC MTA AS	6.40, 2df $p<0.001$**	PC:MTA=0.04* PC:AS=0.02*	-124.31 (242.19, -6.43) -125.35 (-228.74, -21.96)
Fe	PC MTA AS	4.17, 2df $p=0.04$*	PC:AS=0.04*	-1017.03 (-1981.73, -52.33)
Ni	PC MTA AS	2.45, 2df $p=0.12$		
Pb	PC MTA AS	3.96, 2df $p=0.04$*	PC:AS = 0.04*	-1.82 (-3.54, -0.10)
Cu	PC MTA AS	2.19, 2df $p=0.14$		
Cd	PC MTA AS	0.46, 2df $p=0.64$		
Cr	PC MTA AS	0.31, 2df $p=0.74$		
Mn	PC MTA AS	6.46, 2df $p\leq0.01$**	PC:MTA = 0.01**	-58.15(-100.30, -16.04)
PO_4^{3-}	PC MTA AS	23.04, 2df $p\leq0.0001$***	PC:MTA<0.001** PC:AS = 0.03* MTA:AS ≤0.001**	26.07 (11.63, 40.51) -14.68 (-27.35, -2.01) -40.75(-56.26,-25.24)
F	PC MTA AS	5.35, 2df $p=0.02$*	PC:AS = 0.02*	2.17 (3.41, 39.92)

*$p<0.05$, **$p\leq0.01$, ***$p\leq0.0001$

5.1.5 Particle size distribution analysis by Laser diffraction

Table 5.1.8 shows the particle size distribution of MTA, clinker and raw aluminosilicate materials before sieving. For MTA, D10 ranged between 0.67 and 1.68μm, D50 ranged between 4.80 and 9.65μm while D90 ranged between 21.61 and 126μm.

For the clinkers and raw aluminosilicates, D10 ranged between 2.25 and 6.86μm, D50 ranged between 19.70 and 370μm while D90 ranged between 393.80 and 1488.75μm.

Table 5.1.8: Particle size analysis of MTA, Portland cement clinker and raw aluminosilicates (μm) (not sieved)

Sample name	D10 (μm)	D50 (μm)	D90 (μm)
MTA Cem	1.68	9.65	126.92
ProRoot MTA	0.67	4.80	21.61
ARM	2.75	54.18	786.07
BF Slag	3.36	57.80	1423.75
Bamburi	6.86	370.74	1488.75
FA	2.25	19.70	393.80
Kaolin	3.29	20.61	1050.33

Table 5.1.9 shows the particle size distribution of the clinkers, raw and alkaline-activated aluminosilicate materials after sieving through a 120μm sieve. The D10 ranged between 0.59 and 2.60μm, D50 ranged between 8.10 and 16.83μm while D90 ranged between 44.05 and 112.11μm.

Table 5.1.9: Particle size distribution of Portland cement clinker and, raw and alkaline-activated aluminosilicates (µm) (sieved)

Sample name	D10 (µm)	D50 (µm)	D90 (µm)
ARM	1.69	14.71	44.05
EAPC	0.59	10.22	112.11
BF Slag	2.60	16.20	52.90
Kaolin 80: FA 20	1.51	9.07	66.56
Kaolin100	1.36	8.10	60.90
FA100	1.47	8.86	52.45
BF Slag 20: FA 80	1.52	11.55	69.05
BF Slag 40: FA 60	1.86	12.40	60.04
BF Slag 60: FA 40	1.44	12.15	72.12
BF Slag 80: FA 20	1.36	12.51	60.53
BF Slag100	1.31	16.83	110.05

Table 5.1.10 presents a descriptive summary as well as ANOVA of particle size distribution analysis by laser diffraction. There was no statistically significant difference of the particle size of the materials, both sieved and not sieved ($p > 0.05$).

Table 5.1.10: Descriptive summary and ANOVA of particle size distribution of MTA, Portland cement clinker and alkaline-activated aluminosilicates (µm)

Descriptive summary LDPSA (unsieved) (µm)

Percentile	Material category	Mean (SD)	Min	Max	F statistic, df, p-value
D10	PC (n=2)	2.97 (2.74)	0.59	6.86	1.29, 2 df
	MTA (n=2)	1.18 (0.71)	0.67	1.68	p = 0.30
	AS (n=3)	1.94 (0.76)	1.31	3.36	
D50	PC	112.50 (173.30)	10.22	370.70	2.38, 2 df
	MTA	7.23 (3.43)	4.80	9.65	p = 0.13
	AS	17.15 (13.44)	8.10	57.80	
D90	PC	607.70 (676.10)	44.05	1489.00	0.93, 2df
	MTA	74.27 (74.47)	21.61	126.90	p = 0.42
	AS	960.80 (1079.00)	52.45	1424.00	

Descriptive summary LDPSA (sieved) (µm)

Percentile	Material category	Mean (SD)	Min	Max	F statistic, df, p-value
D10	PC (n=2)	1.14 (0.78)	0.59	1.69	1.46, 2 df
	MTA (n=2)	1.18 (0.71)	0.67	1.68	p = 0.28
	AS (n=9)	1.67 (0.44)	1.31	2.60	
D50	PC	12.46 (3.18)	10.22	14.71	1.87, 2 df
	MTA	7.23 (3.43)	4.80	9.65	p = 0.2
	AS	12.74 (3.79)	8.10	19.70	
D90	PC	78.08 (676.10)	44.05	112.10	0.08, 2df
	MTA	74.27 (74.47)	21.61	126.90	p = 0.92
	AS	99.84 (104.60)	52.45	393.80	

5.2 Phase II: Formulation of experimental dental cements from Portland cement clinker or synthetic geopolymer, and poly (acrylic acid)

5.2.1 Formulation sequence of experimental ionomer-type dental cements

Figure 5.2.1 summarizes the formulation sequence of the experimental ionomer-type dental cements. The cement powder was selected on the basis of similarity to MTA (calcium silicate content) and GIC glass (aluminosilicate content). Several mixing ratios were attempted but some were found to be grainy, fluid or set rapidly (Table 4.8.1).

On exposure to distilled water, cements based on Kaolin geopolymer remained stable, those based on clinker softened and became rubbery while those based on BF slag/FA geopolymer disintegrated.

1. Selection basis

Type of material	Label/ID	Reason for selection
• Clinker • FA/Slag geopolymer • Kaolin geopolymer	• Clinker: ARM, EAPC, EAPC+5% gypsum, Bamburi • FA/ BF Slag geopolymer: 0:100, 20:80, 40:60, 60:40, 80:20, 100:0 • FA/ Kaolin geopolymer: 0:100, 20:80	• Composition similar to MTA • Composition similar to MTA and GIC • Composition similar to GIC

2. Initial mixtures of powder, PAA, CaF$_2$, tartaric acid

→

3. Promising mixtures

Grainy
• Clinker
• 0.5:0.1:0.1
• 0.5:0.2:0.25

Fluid
• FA/Slag geopolymer
• 0.5:0.2:0.25
• 1:0.2:0.25

Rapid set
• Kaolin geopolymer
• 1:0.2:0.2

Stable in water

Kaolin geo-polymer cement

Softened in water

Clinker cement

Disintegrated in water

Slag/FA geopolymer cement
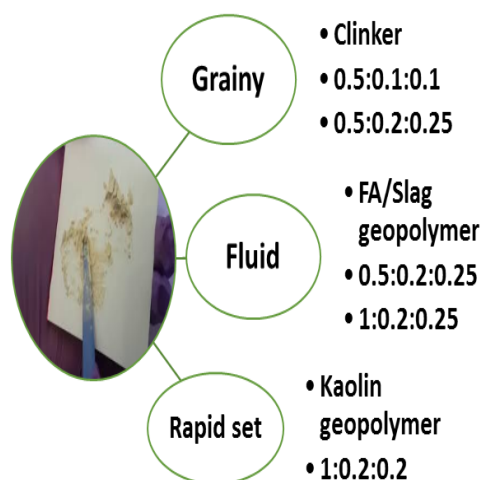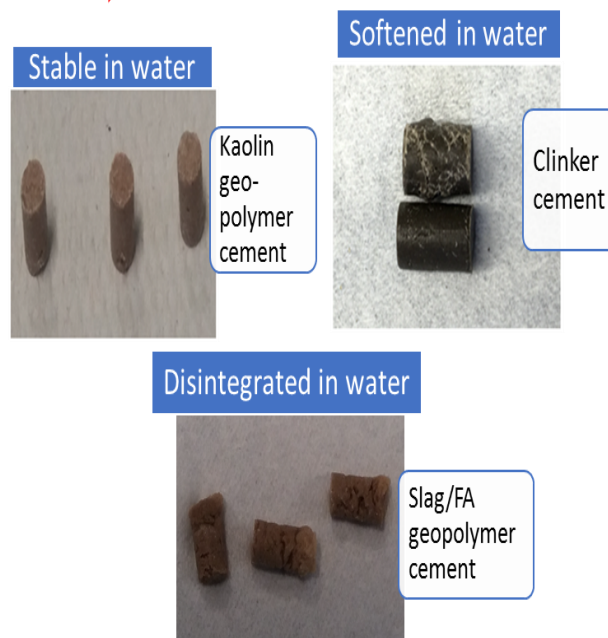
Figure 5.2.1: Formulation sequence of experimental dental cements

5.2.2 Preparation of experimental ionomer-type dental cements

Table 5.2.1 summarizes the acceptable cement mixing ratios. The clinkers (0.3 – 0.4gm) were mixed with 0.2gm of CaF_2, 0.2gm of PAA and 0.25mL of aqueous tartaric acid.

The activated aluminosilicates (0.7 – 1.0gm) were mixed with 0.1gm of PAA and 0.15 – 0.25mL of aqueous tartaric acid.

Table 5.2.1: Experimental cement mixing ratios

Sample name	Si:Al ratio	Ca:Al ratio	Clinker/geopolymer powder (gm)	CaF_2 (gm)	PAA (gm)	10% tartaric acid (mL)
ARM	3.69	10.91	0.3	0.2	0.2	0.25
EAPC	4.12	11.28	0.3	0.2	0.2	0.25
Bamburi	6.45	10.24	0.4	0.2	0.2	0.25
BF Slag100	3.01	3.57	1.0	-	0.1	0.2
Kaolin100	2.92	0.03	0.7	-	0.1	0.2
Kaolin80: FA20	3.42	0.05	1.0	-	0.1	0.25
FA100	7.23	0.31	1.0	-	0.1	0.2
BF Slag20: FA80	5.53	1.80	1.0	-	0.1	0.15
BF Slag40: FA60	6.28	0.98	1.0	-	0.1	0.15
BF Slag60: FA40	4.62	2.09	1.0	-	0.1	0.2
BF Slag80: FA20	4.11	2.98	1.0	-	0.1	0.2

5.2.3 Setting characteristics of experimental ionomer-type dental cements

5.2.3.1 Setting characteristics on mixing with PAA and aqueous tartaric acid

Figure 5.2.2 shows the kinetic setting characteristics of cement derived from ARM clinker, 30s to 25min after mixing with CaF_2, PAA and 10% aqueous tartaric acid. Prominent bands were identified at 1321 cm^{-1}, 1403 cm^{-1} and 1539cm^{-1}. Smaller bands were also visible at 1054 cm^{-1}, 1142 cm^{-1}, 1455 cm^{-1} and 1636 cm^{-1}.
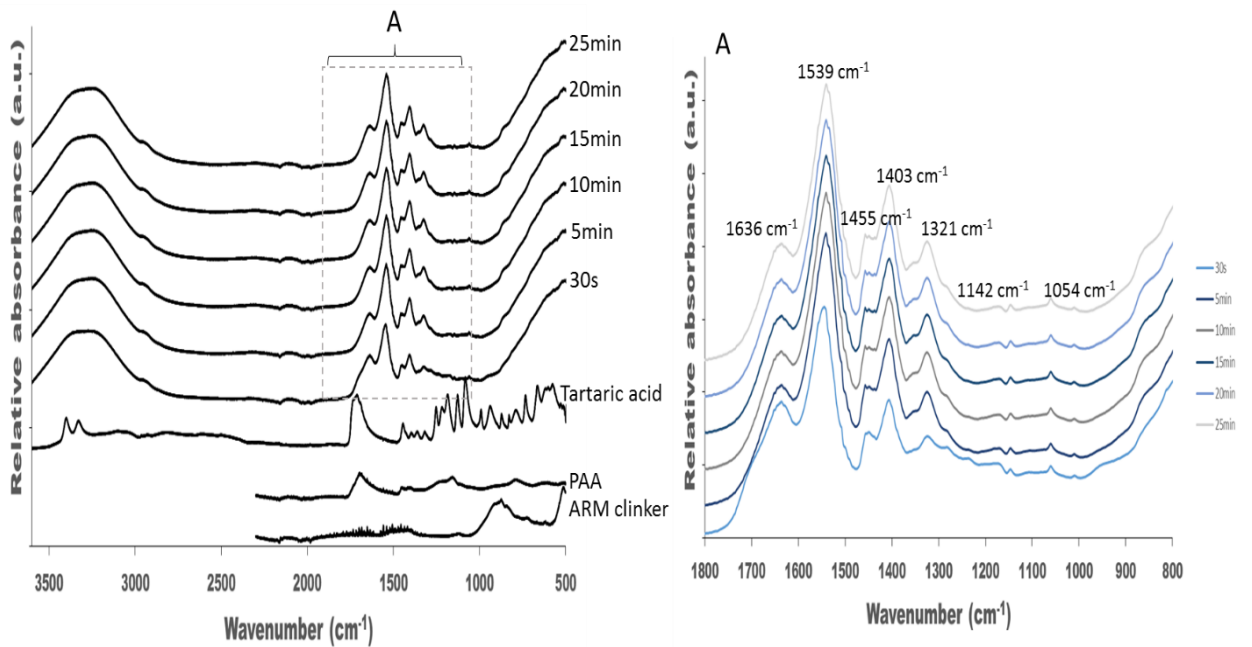
Figure 5.2.2: Setting characteristics of ARM clinker cement

Figure 5.2.3 shows the kinetic setting characteristics of cement derived from Bamburi clinker, 30s to 25min after mixing with CaF_2, PAA and 10% aqueous tartaric acid. Prominent bands were identified at 1321 cm^{-1}, 1403 cm^{-1} and 1539 cm^{-1}. Smaller bands were also visible at 1054 cm^{-1}, 1142 cm^{-1}, 1455 cm^{-1} and 1636 cm^{-1}.
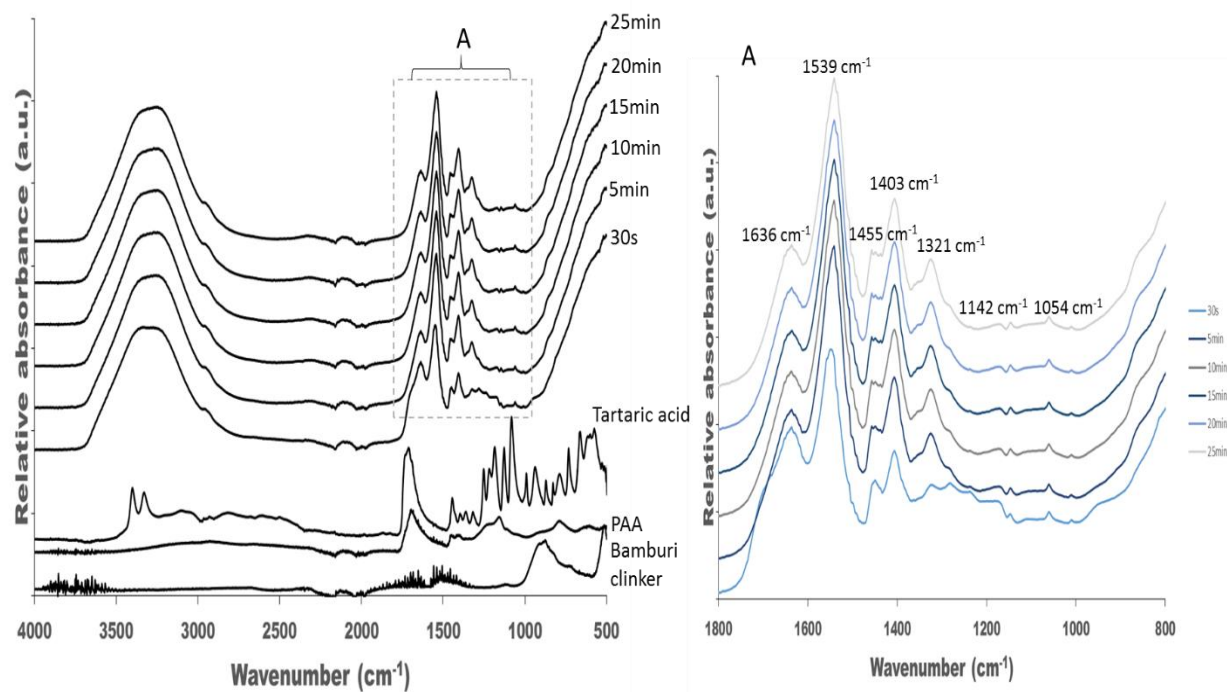
Figure 5.2.3: Setting characteristics of Bamburi clinker cement

Figure 5.2.4 shows the kinetic setting characteristics of cement derived from EAPC clinker, 30s to 25min after mixing with CaF_2, PAA and 10% aqueous tartaric acid. Prominent bands were identified at 1321 cm^{-1}, 1401 cm^{-1} and 1535cm^{-1}. Smaller bands were also visible at 1056 cm^{-1}, 1140 cm^{-1}, 1453 cm^{-1} and 1640 cm^{-1}.
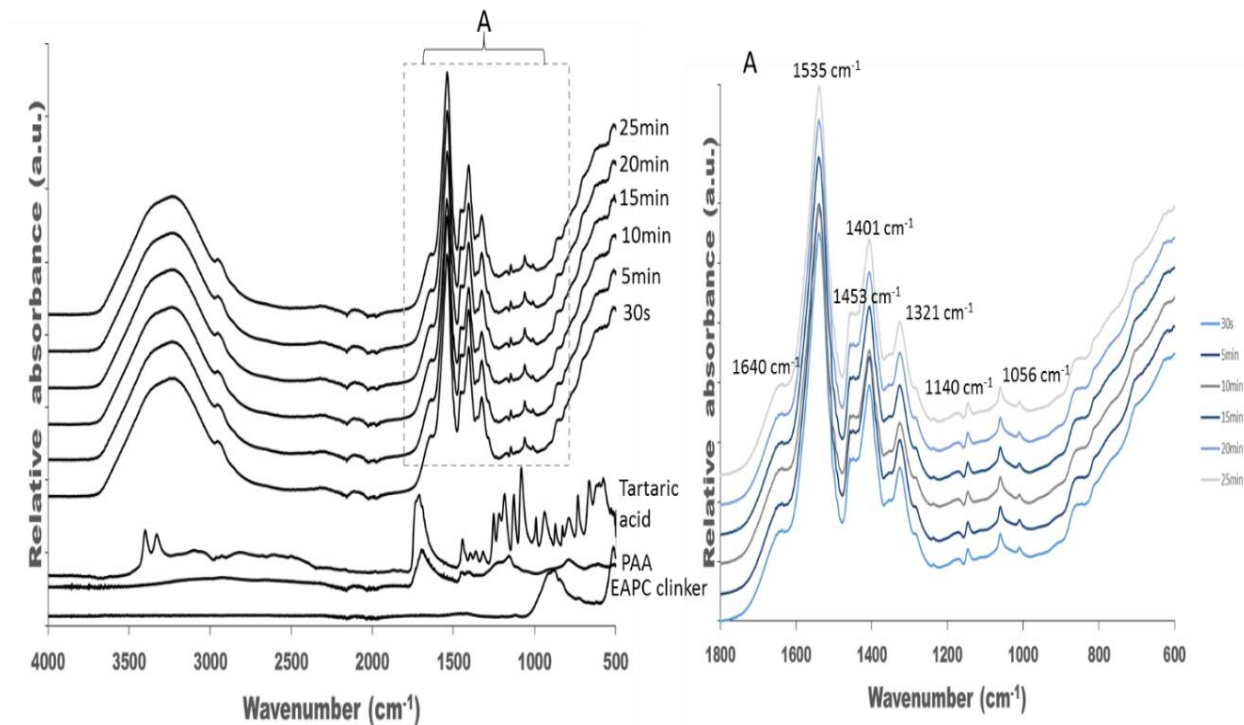
Figure 5.2.4: Setting characteristics of EAPC clinker cement

Figure 5.2.5 shows the kinetic setting characteristics of cement derived from EAPC clinker + 5% Gypsum, 30s to 25min after mixing with CaF_2, PAA and 10% aqueous tartaric acid. Prominent bands were identified at 1321 cm^{-1}, 1403 cm^{-1} and 1537cm^{-1}. Smaller bands were also visible at 1056 cm^{-1}, 1140 cm^{-1}, 1453 cm^{-1} and 1638 cm^{-1}.
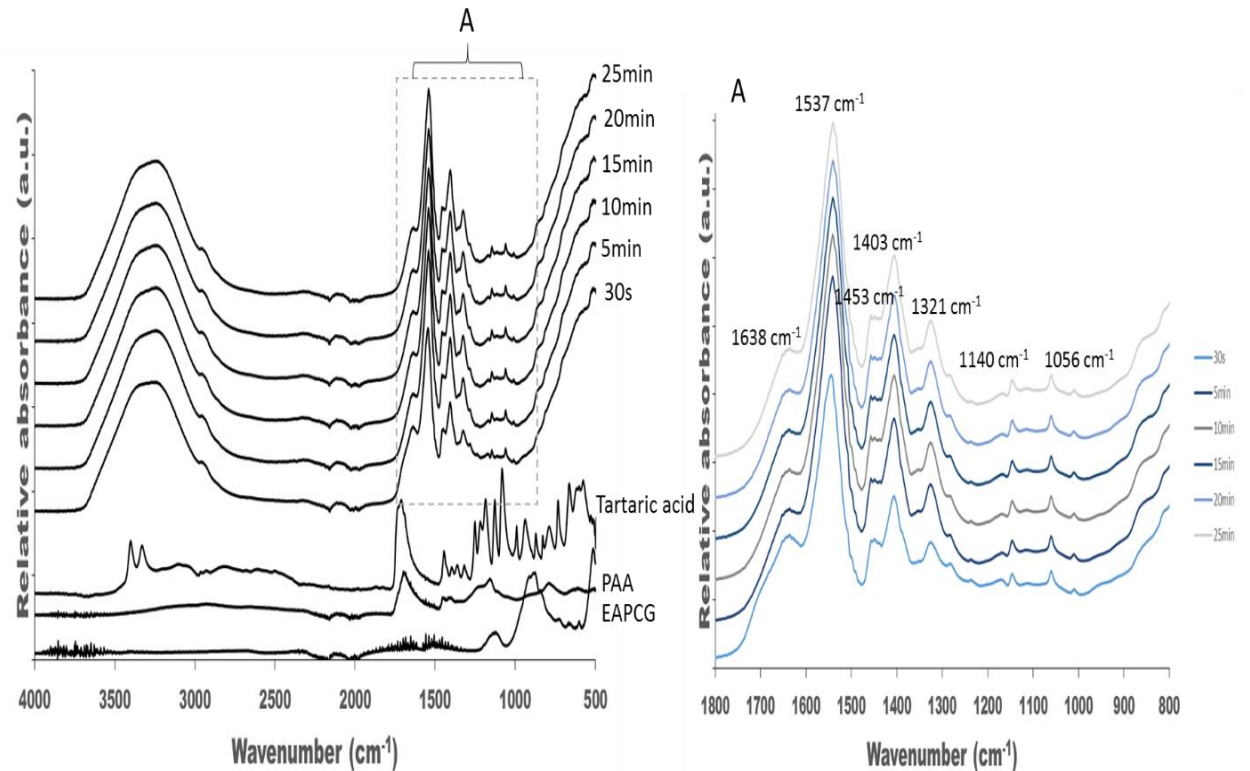
Figure 5.2.5: Setting characteristics of EAPC clinker + 5% Gypsum cement

Figure 5.2.6 shows the kinetic setting characteristics of cement derived from 100% alkaline-activated Kaolin, 30s to 25min after mixing with PAA and 10% aqueous tartaric acid. Prominent bands were identified at 1636 cm^{-1}, 1375 cm^{-1}, 1095 cm^{-1}, 1028 cm^{-1}, 1010 cm^{-1} and 909 cm^{-1}. Smaller bands were also visible at 1558 cm^{-1}, 1455 cm^{-1} and 935 cm^{-1}.

Figure 5.2.6: Setting characteristics of alkaline-activated Kaolin (100%) cement

Figure 5.2.7 shows the kinetic setting characteristics of cement derived from a mixture of alkaline-activated Kaolin and Fly ash (80:20), 30s to 25min after mixing with PAA and 10% aqueous tartaric acid. Prominent bands were identified at 1625 cm^{-1}, 1371 cm^{-1}, 1095 cm^{-1}, 1028 cm^{-1}, 1006 cm^{-1} and 909 cm^{-1}. Smaller bands were also visible at 1556 cm^{-1}, 1453 cm^{-1}, 939 cm^{-1}.
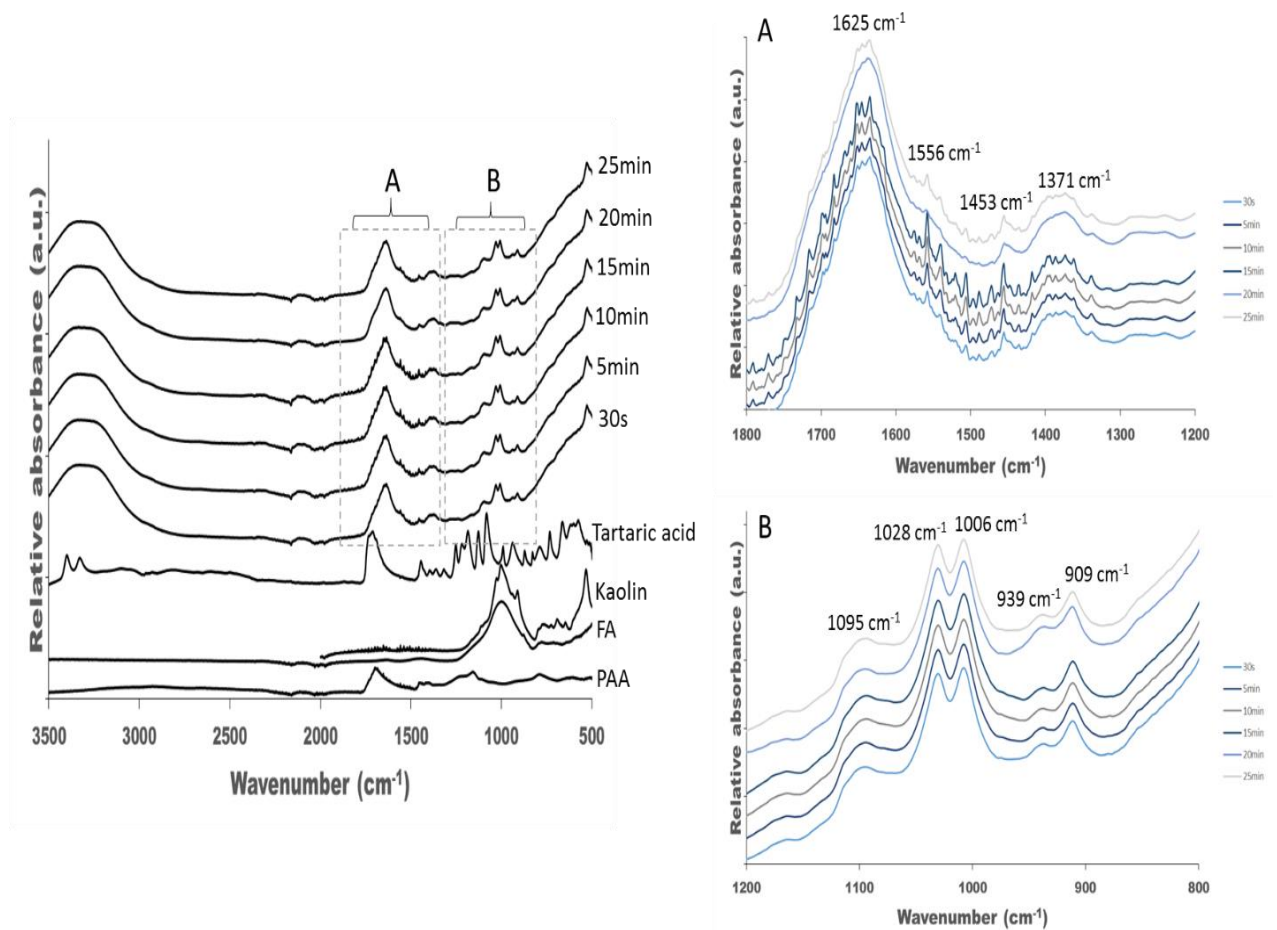
Figure 5.2.7: Setting characteristics of alkaline-activated Kaolin/Fly ash (80:20) cement

Figure 5.2.8 shows the kinetic setting characteristics of cement derived from a mixture of alkaline-activated BF Slag and Fly ash (80:20), 30s to 25min after mixing with PAA and 10% aqueous tartaric acid. Prominent bands were identified at 1537 cm^{-1}, 1403 cm^{-1} and 1321 cm^{-1}. Smaller bands were also visible at 1056 cm^{-1}, 1140 cm^{-1}, 1453 cm^{-1} and 1632 cm^{-1}.
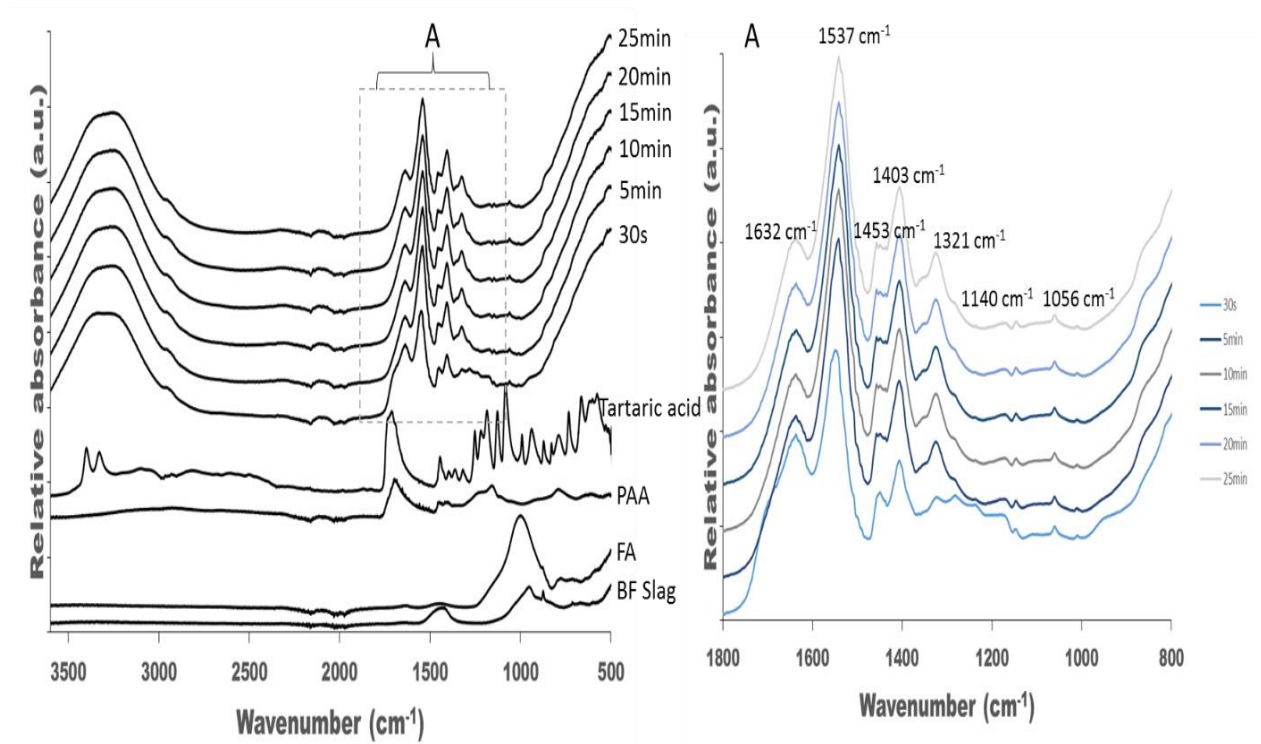
Figure 5.2.8: Setting characteristics of alkaline-activated BF Slag/ Fly ash (80:20) cement

Figure 5.2.9 shows the kinetic setting characteristics of cement derived from a mixture of alkaline-activated BF Slag and Fly ash (60:40), 30s to 25min after mixing with PAA and 10% aqueous tartaric acid. Prominent bands were identified at 1539 cm^{-1}, 1403 cm^{-1}, 1321 cm^{-1} and 1004 cm^{-1}. Smaller bands were also visible at 1647 cm^{-1}, 1453 cm^{-1} and 872 cm^{-1}.
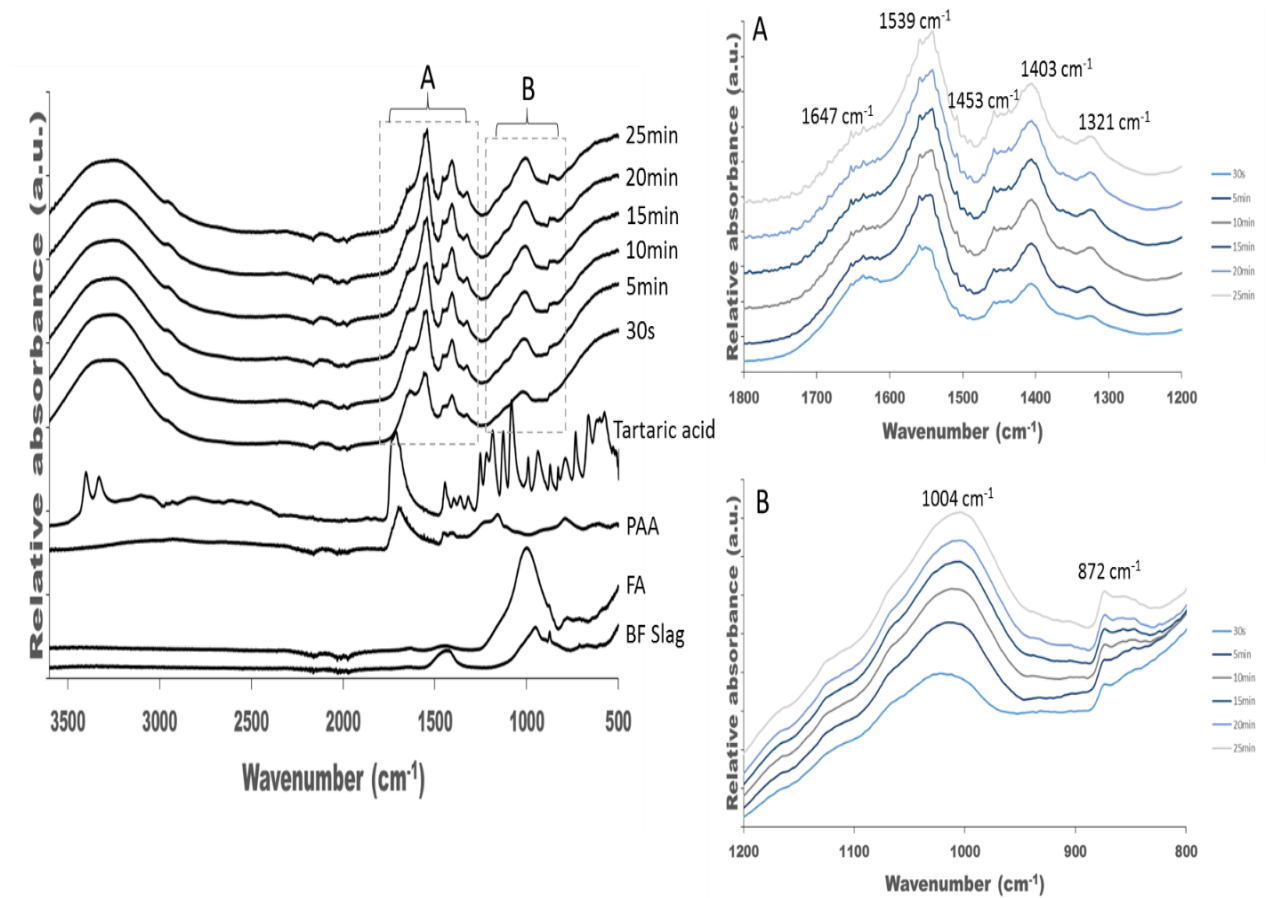
Figure 5.2.9: Setting characteristics of alkaline-activated BF Slag/ Fly ash (60:40) cement

Figure 5.2.10 shows the kinetic setting characteristics of cement derived from a mixture of alkaline-activated BF Slag and Fly ash (20:80), 30s to 25min after mixing with PAA and 10% aqueous tartaric acid. Prominent bands were identified at 1539 cm^{-1}, 1403 cm^{-1}, 1321 cm^{-1} and 1004 cm^{1}. Smaller bands are also visible at 1647 cm^{-1}, 1455 cm^{-1}, and 872 cm^{-1}.
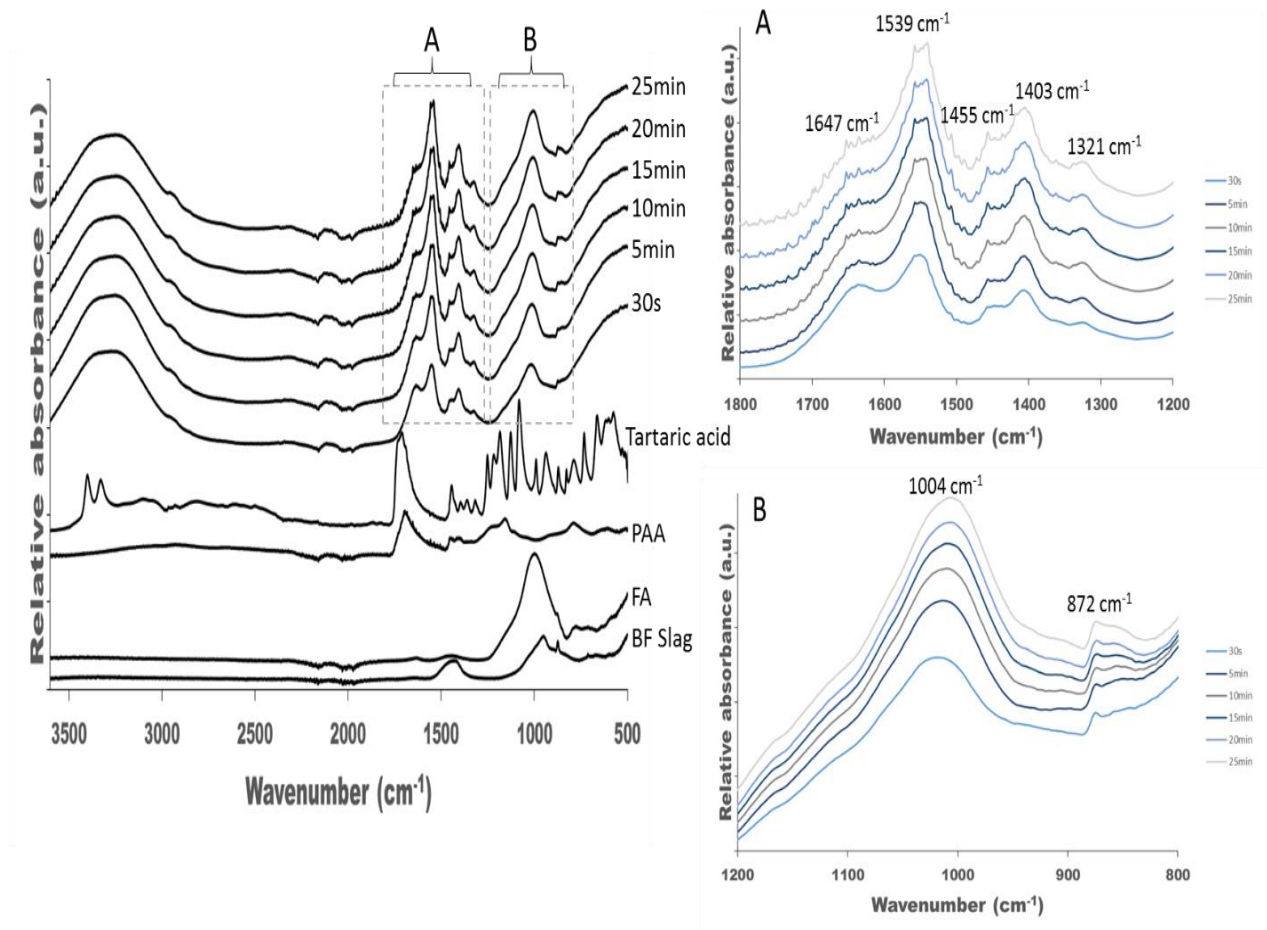
Figure 5.2.10: Setting characteristics of alkaline-activated BF Slag/ Fly ash (20:80) cement

5.2.3.2Setting characteristics on mixing with either aqueous tartaric acid or PAA

Figure 5.2.11 shows the kinetic setting characteristics of EAPC clinker on mixing with CaF_2 and, either 10% aqueous tartaric acid (A) or PAA (B). On mixing with tartaric acid, one prominent band was identified at 1632 cm^{-1}. On mixing with PAA, prominent bands were identified at 1321 cm^{-1}, 1403 cm^{-1} and 1537 cm^{-1} while smaller bands were visible at 1453 cm^{-1} and 1632 cm^{-1}.
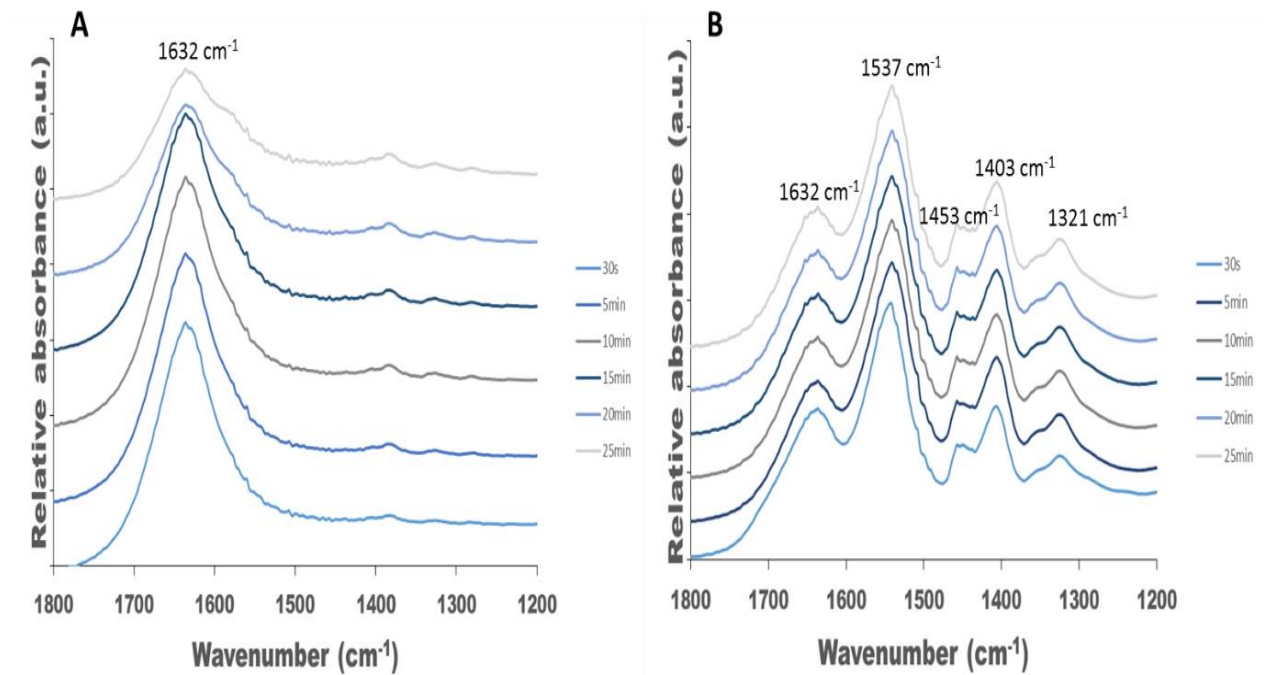
Figure 5.2.11: Setting characteristics of EAPC clinker on mixing with aqueous tartaric acid (A) or PAA (B)

Figure 5.2.12 shows the kinetic setting characteristics of alkaline-activated Kaolin (100%) on mixing with either 10% aqueous tartaric acid (A, C) or PAA (B, D). On mixing with tartaric acid, prominent bands were identified at 1634 cm^{-1}, 1373cm^{-1}, 1025cm^{-1}, 1000 cm^{-1} and 909 cm^{-1} while smaller bands were visible at 1110cm^{-1} and 935cm^{-1} and. On mixing with PAA, prominent bands were identified at 1645 cm^{-1}, 1369 cm^{-1}, 1095 cm^{-1}, 1028 cm^{-1}, 1004 cm^{-1} and 909 cm^{-1} while smaller bands were visible at 1558 cm^{-1}, 1455 cm^{-1} and 937 cm^{-1}.
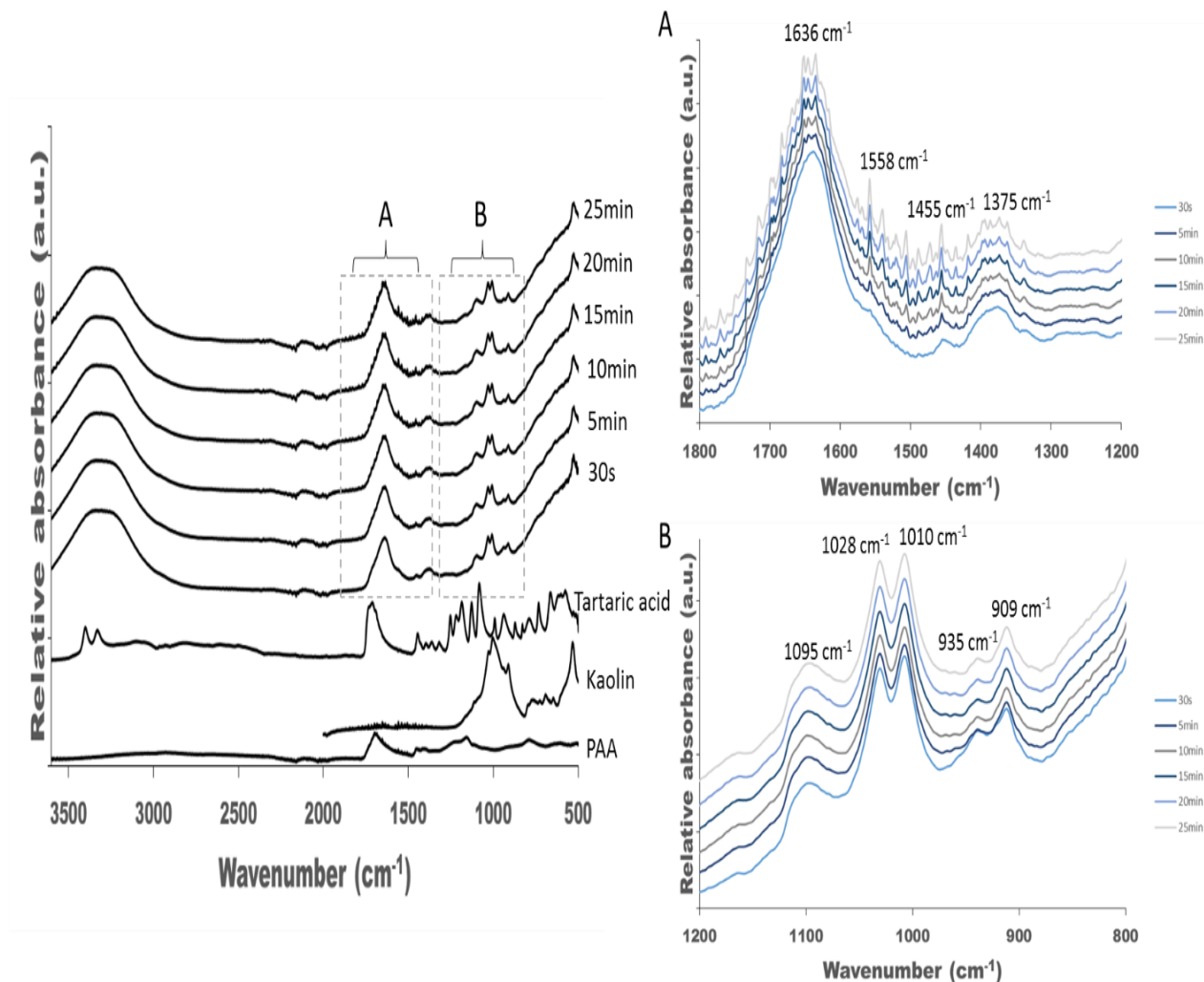
Figure 5.2.13 shows the kinetic setting characteristics of alkaline-activated Kaolin and Fly ash (80:20) on mixing with either 10% aqueous tartaric acid (A, C) or PAA (B, D). On mixing with tartaric acid, prominent bands were identified at 1632 cm^{-1}, 1382cm^{-1}, 1025cm^{-1}, 1000 cm^{-1} and 909 cm^{-1} while smaller bands were visible at 1110cm^{-1} and 935cm^{-1}. On mixing with PAA, prominent bands were identified at 1632 cm^{-1}, 1558 cm^{-1}, 1455 cm^{-1}, 1401 cm^{-1}, 1028 cm^{-1} and 1006 cm^{-1} while smaller bands were visible at 1095 cm^{-1} and 909 cm^{-1}.
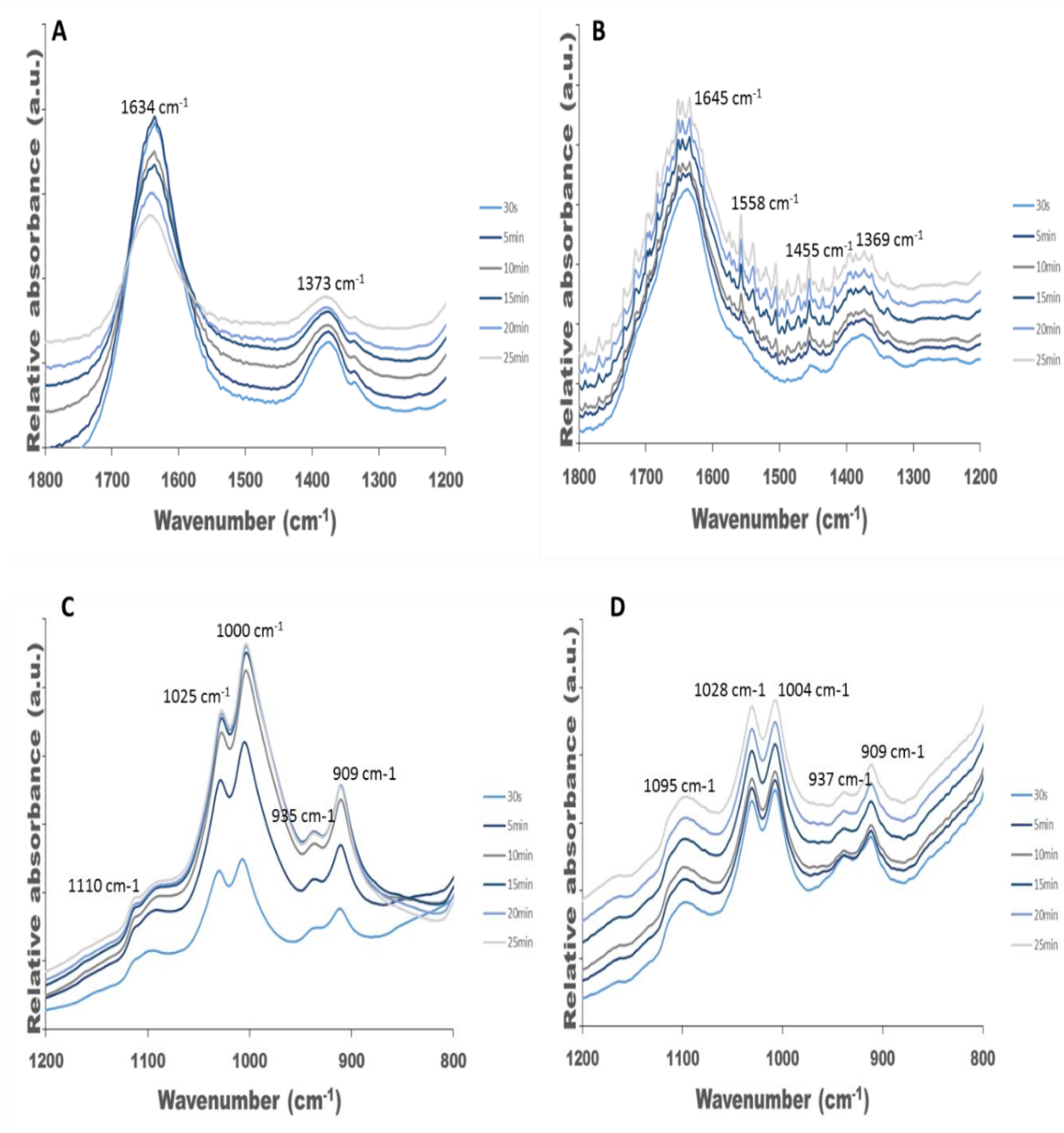
Figure 5.2.12: Setting characteristics of alkaline-activated Kaolin (100%) on mixing with aqueous tartaric acid (A, C) or PAA (B, D)
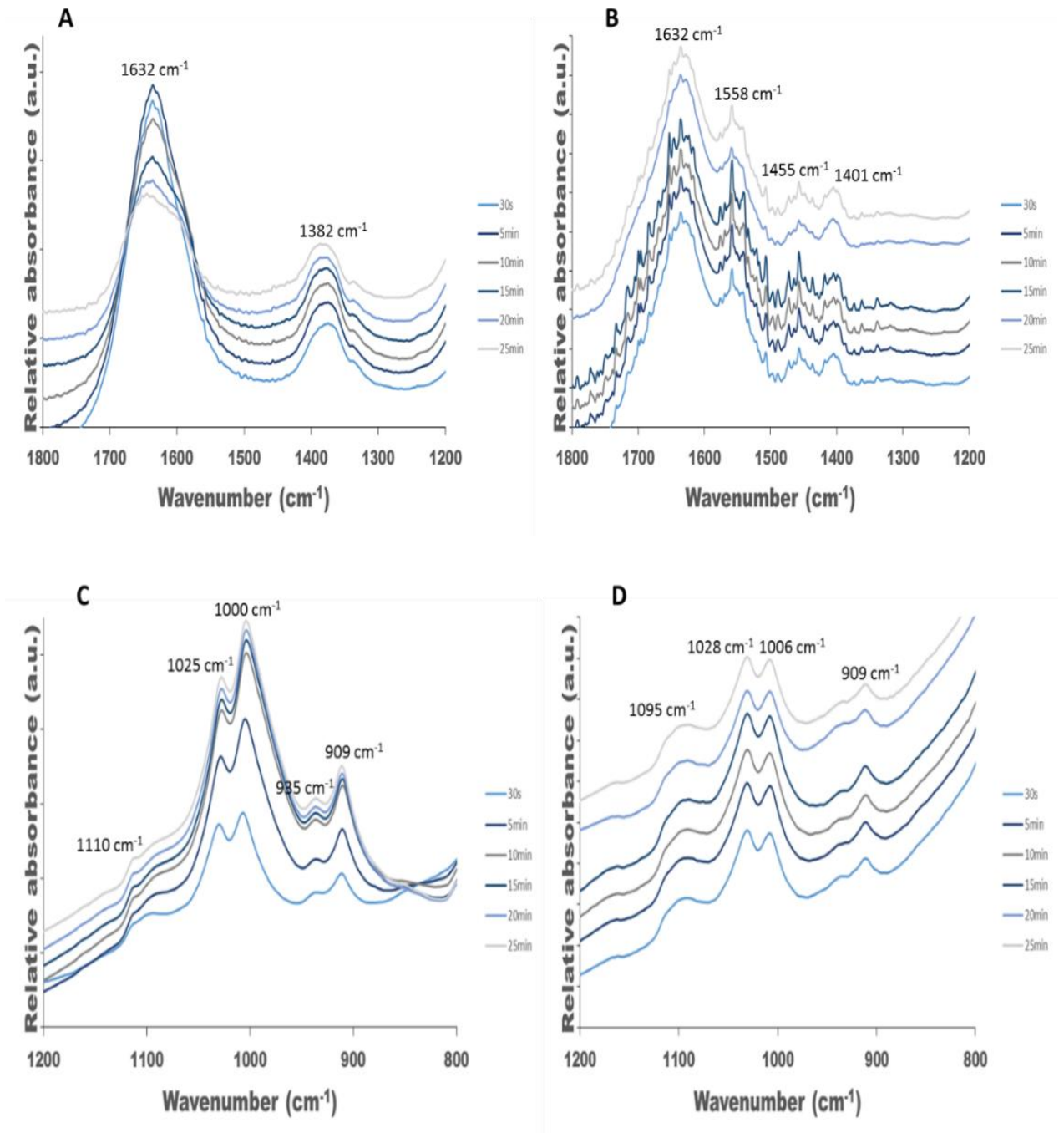
Figure 5.2.13: Setting characteristics of alkaline-activated Kaolin/ Fly ash (80:20) on mixing with aqueous tartaric acid (A, C) or PAA (B, D)

Figure 5.2.14 shows the kinetic setting characteristics of alkaline-activated BF Slag and Fly ash (80:20) on mixing with either 10% aqueous tartaric acid (A, C) or PAA (B, D). On mixing with tartaric acid, prominent bands were identified at 1626 cm^{-1}, 1384 cm^{-1}, 1121 cm^{-1} and 1064cm^{-1} within 30s of mixing. However, these bands diminished afterwards. On mixing with PAA, prominent bands were identified at 1643 cm^{-1}, 1541 cm^{-1}, 1405 cm^{-1}, 1321 cm^{-1} and 995 cm^{-1} while smaller bands were visible at 1455 cm^{-1} and 872 cm^{-1}.

Figure 5.2.15 shows the kinetic setting characteristics of alkaline-activated BF Slag and Fly ash (60:40) on mixing with either 10% aqueous tartaric acid (A, C) or PAA (B, D). On mixing with tartaric acid, prominent bands were identified at 1632 cm^{-1}, 1585 cm^{-1}, 1384 cm^{-1}, 985 cm^{-1} and 870 cm^{-1} while smaller bands were visible at 1328 cm^{-1}, 1146 cm^{-1}, 1125 cm^{-1} and 1058cm^{-1}. On mixing with PAA, prominent bands were identified at 1640 cm^{-1}, 1543 cm^{-1}, 1405 cm^{-1}, 1321 cm^{-1} and 1000 cm^{-1} while smaller bands were visible at 1453 cm^{-1} and 872 cm^{-1}.

Figure 5.2.16 shows the kinetic setting characteristics of alkaline-activated BF Slag and Fly ash (20:80) on mixing with either 10% aqueous tartaric acid (A, C) or PAA (B, D). On mixing with tartaric acid, prominent bands were identified at 1630 cm^{-1}, 1382 cm^{-1}, 985 cm^{-1} and 870 cm^{-1} while smaller bands were visible at 1585 cm^{-1}, 1144 cm^{-1}, 1125 cm^{-1} and 1058cm^{-1}. On mixing with PAA, marked bands were identified at 1643 cm^{-1}, 1539 cm^{-1}, 1403 cm^{-1},1321 cm^{-1} and 1000 cm^{-1} while smaller bands were visible at 1455 cm^{-1}and 870 cm^{-1}.
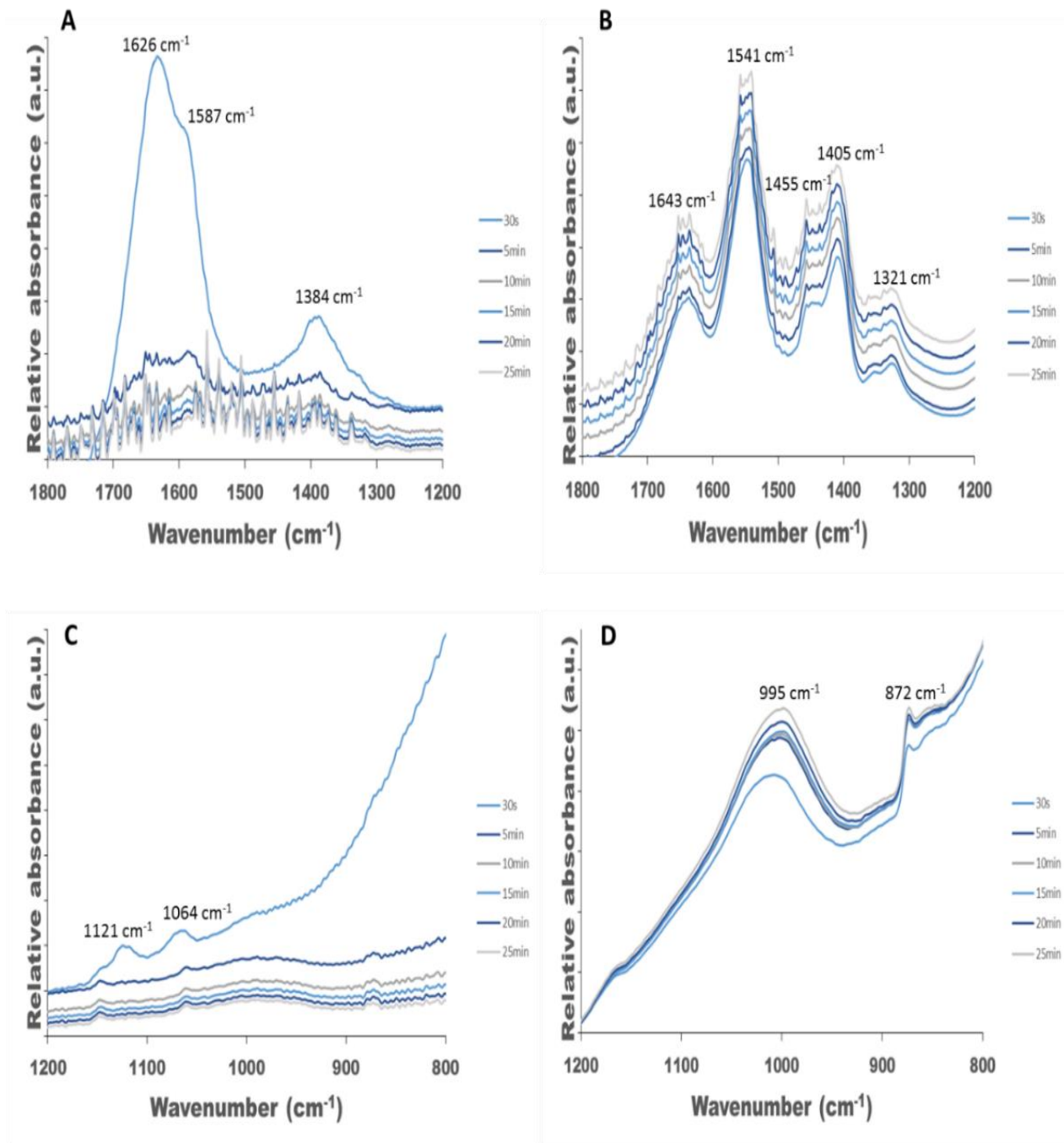
Figure 5.2.14: Setting characteristics of alkaline-activated BF Slag/ Fly ash (80:20) on mixing with aqueous tartaric acid (A, C) or PAA (B, D)
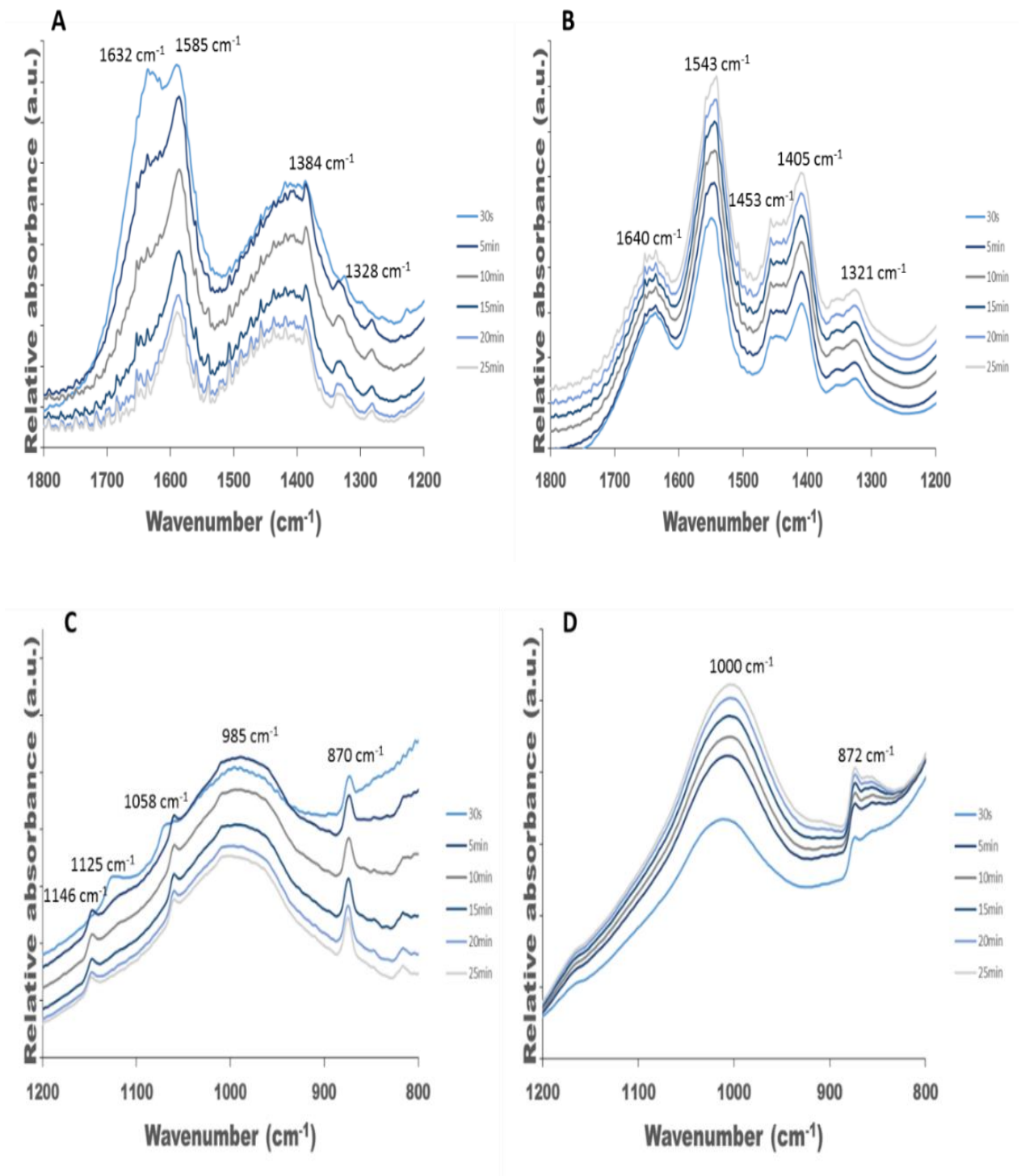
Figure 5.2.15: Setting characteristics of alkaline-activated BF Slag/ Fly ash (60:40) on mixing with aqueous tartaric acid (A, C) or PAA (B, D)
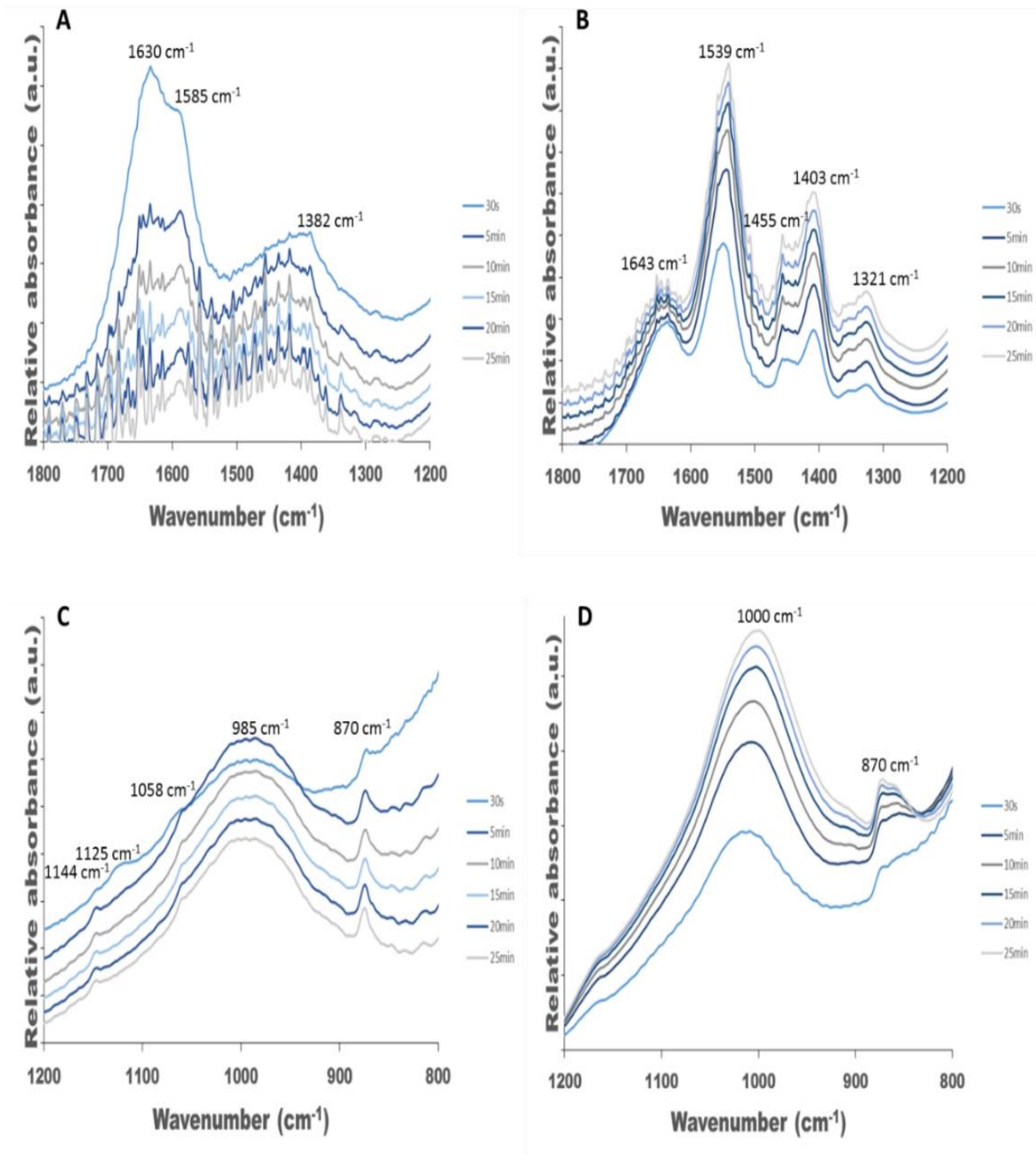
Figure 5.2.16: Setting characteristics of alkaline-activated BF Slag/ Fly ash (20:80) on mixing with aqueous tartaric acid (A, C) or PAA (B, D)

5.3 Phase III: Evaluation of properties and cost assessment of experimental dental cements

5.3.1 Mixing and setting time of experimental dental cements

Table 5.3.1 summarizes the cement mixing and setting times. The mixing time for the clinker cements was 30s while the setting time ranged from 190 – 300s. The mixing time for the alkaline-activated aluminosilicates ranged from 60 – 90s while the setting time ranged from 135 – 480s.

Table 5.3.1: Experimental cement mixing and setting times

Sample name	MT (sec)	ST (sec)
ARM	30	190 – 300
EAPC	30	190 – 300
Bamburi	30	190 – 300
BF Slag100	60	260
Kaolin100	60	135
Kaolin80: FA20	60	135 – 240
FA100	60 – 90	260
BF Slag20: FA80	60 – 90	260 – 480
BF Slag40: FA60	60 – 90	260 – 480
BF Slag60: FA40	60 – 90	260 – 480
BF Slag80: FA20	60 – 90	260 – 480

Figures 5.3.1 and 5.3.2 show the correlation between increasing D10 and cement mixing and setting time, respectively. There was a moderate positive correlation between D10 and cement mixing time but no correlation between D10 and cement setting time.
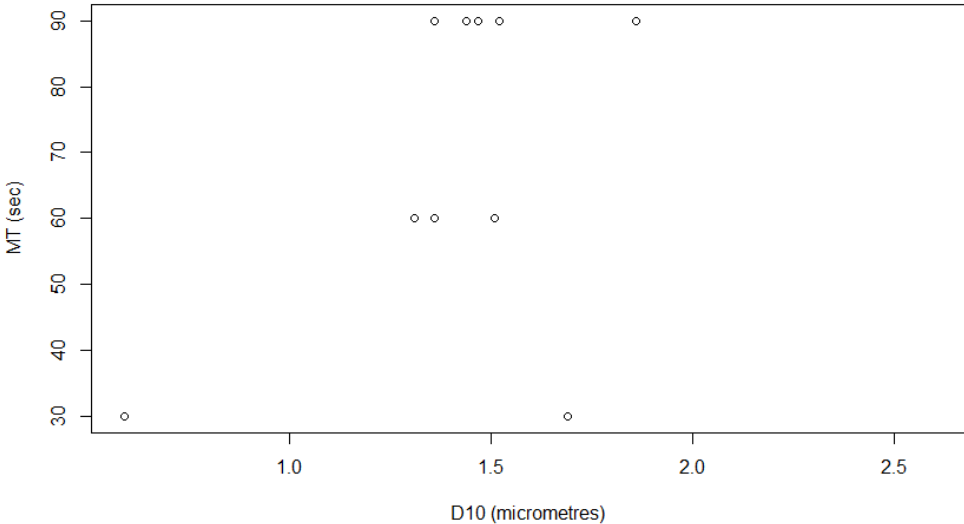
Pearson's *r* correlation = 0.46

Figure 5.3.1: Correlation between D10 and cement mixing time
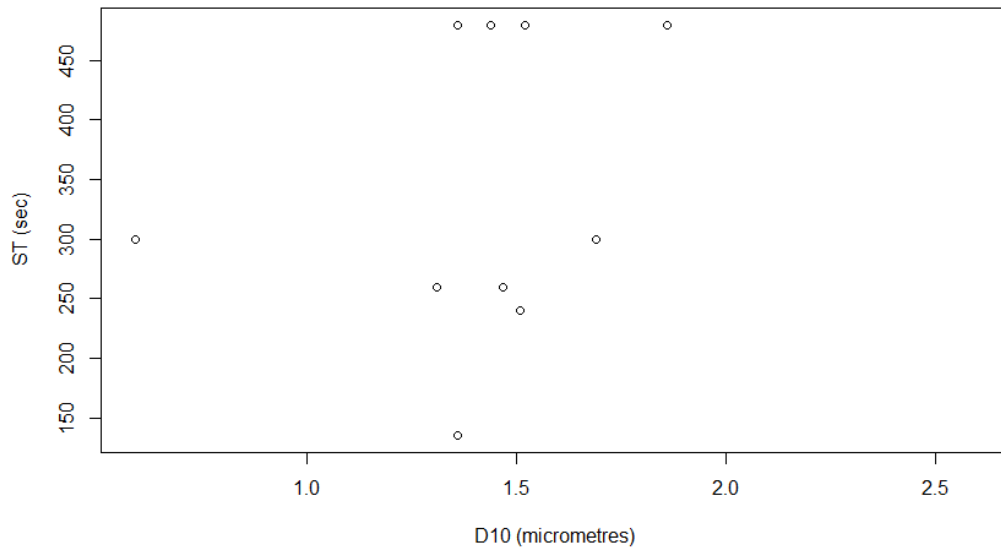
Pearson's *r* correlation = 0.26

Figure 5.3.2: Correlation between D10 and cement setting time

Figures 5.3.3 and 5.3.4 show the correlation between increasing D50 and cement mixing and setting time, respectively. There was a weak negative correlation between D50 and cement mixing time but no correlation between D50 and cement setting time.
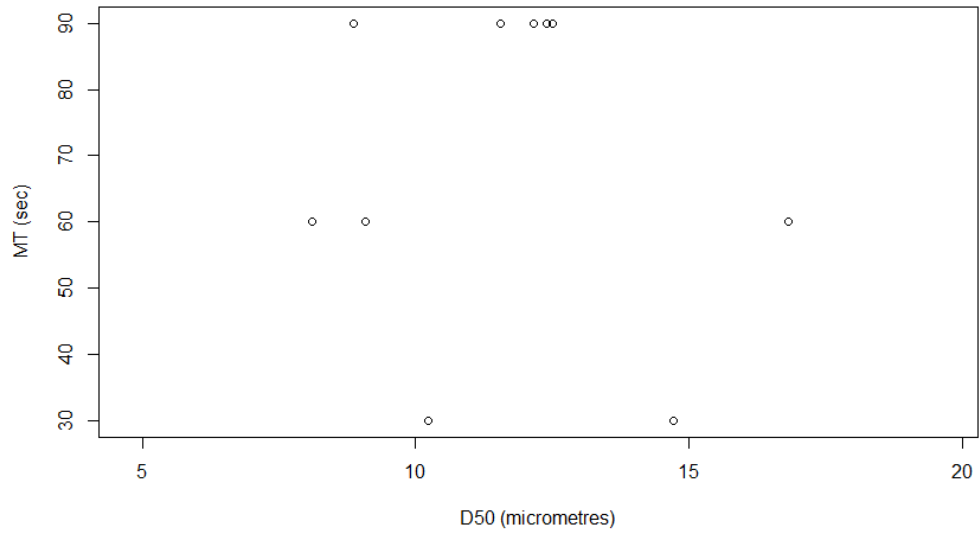
Pearson's *r* correlation = -0.12

Figure 5.3.3: Correlation between D50 and cement mixing time
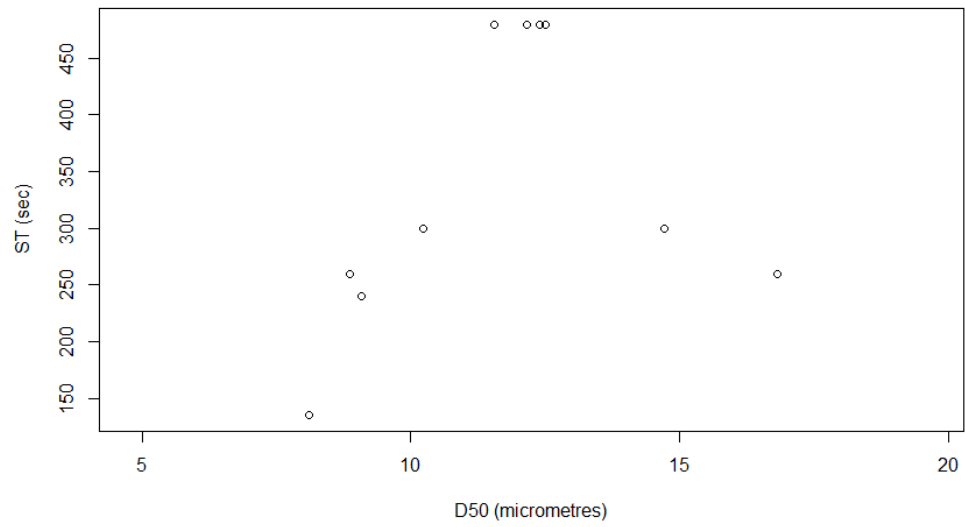
Pearson's *r* correlation = 0.32

Figure 5.3.4: Correlation between D50 and cement setting time

Figures 5.3.5 and 5.3.6 show the correlation between increasing D90 and cement mixing and setting time. There was a weak negative correlation between D90 and both cement mixing and setting times.
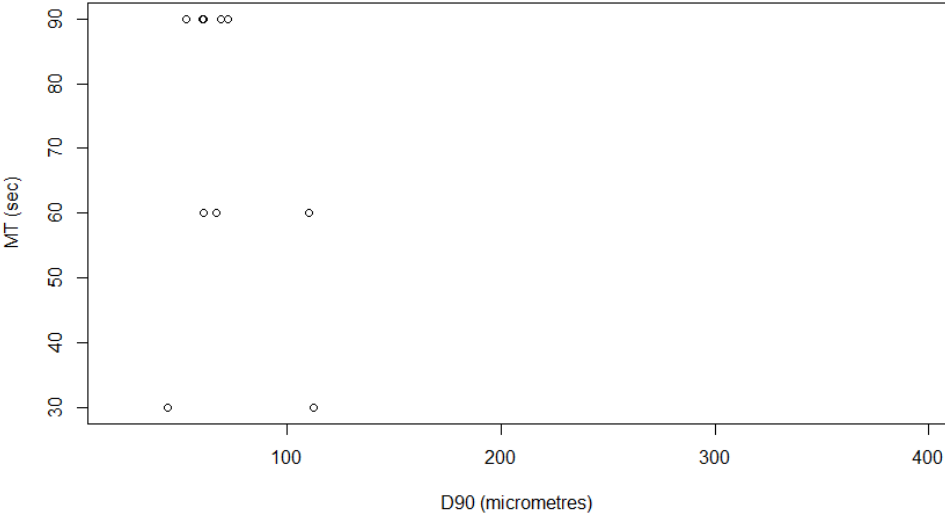
Pearson's *r* correlation = -0.13

Figure 5.3.5: Correlation between D90 and cement mixing time
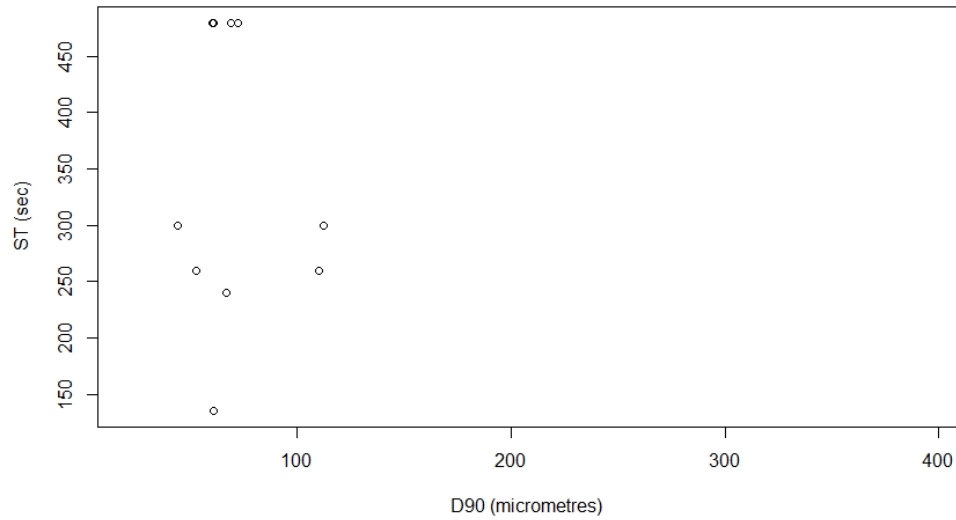
Pearson's *r* correlation = -0.11

Figure 5.3.6: Correlation between D90 and cement setting time

Figures 5.3.7 and 5.3.8 show the correlation between the types of material and cement mixing and setting time, respectively. There was a strong positive correlation between the type of material (PC clinker or aluminosilicate) and cement mixing time but no correlation between the type of material and cement setting time.
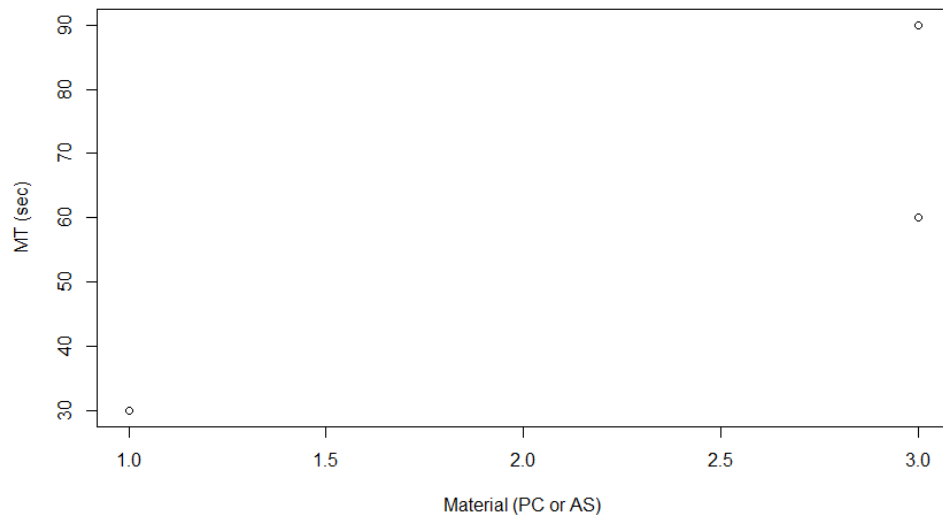
Pearson's *r* correlation = 0.83

Figure 5.3.7: Correlation between type of material and cement mixing time
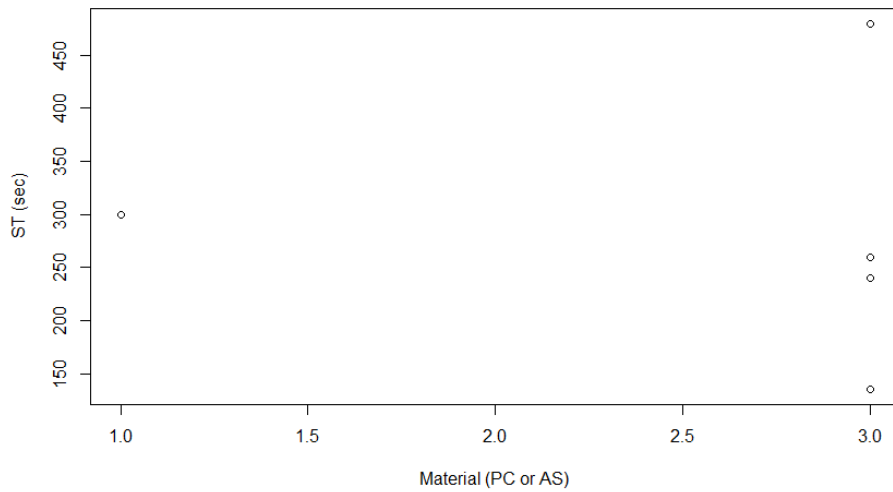
Pearson's *r* correlation = 0.17

Figure 5.3.8: Correlation between type of material and cement setting time

5.3.2 Compressive strength of experimental dental cements

Figure 5.3.9 shows the compressive strength of ARM cements after 3, 7 and 28d. The cements increased in strength between 3d and 28d. The 1d samples failed to break during the test hence no compressive strength reading was obtained.
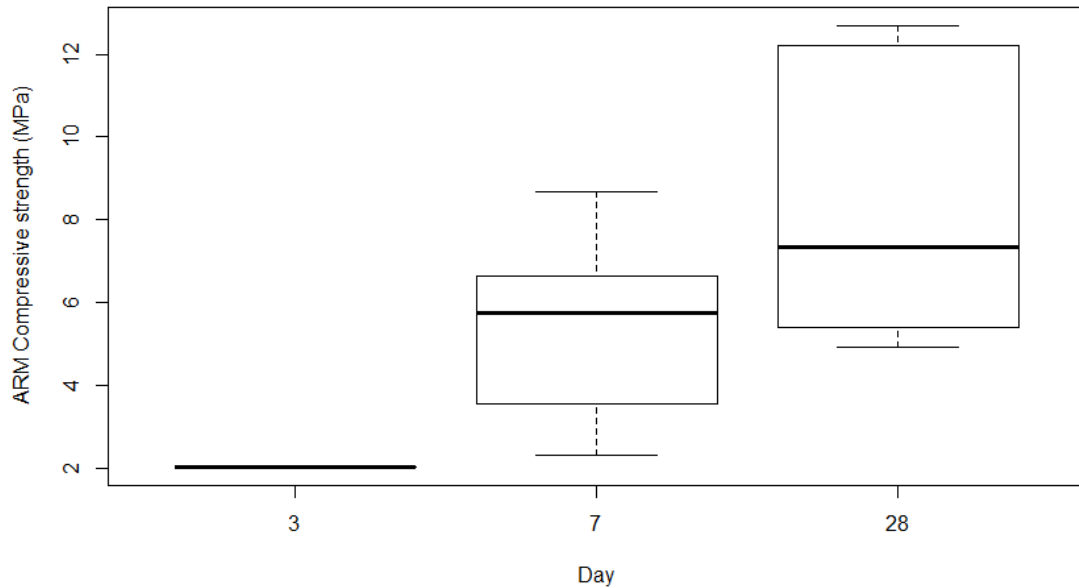
Figure 5.3.9: Compressive strength of ARM cement samples after 3, 7 and 28d

Figure 5.3.10 shows the compressive strength of Bamburi cements after 3, 7 and 28d. The cements increased in strength between 3d and 28d. The 1d samples failed to break during the test hence no compressive strength reading was obtained.
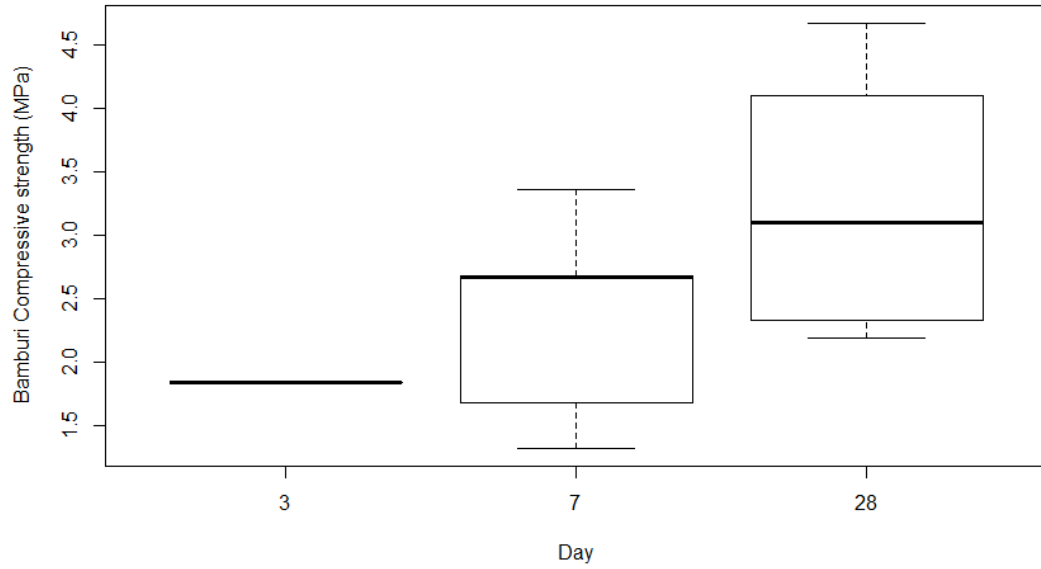
Figure 5.3.10: Compressive strength of Bamburi cement samples after 3, 7 and 28d

Figure 5.3.11 shows the compressive strength of EAPC cements after 1, 3, 7 and 28d. The cements increased in strength between 1d and 7d with a slight reduction on day 28.
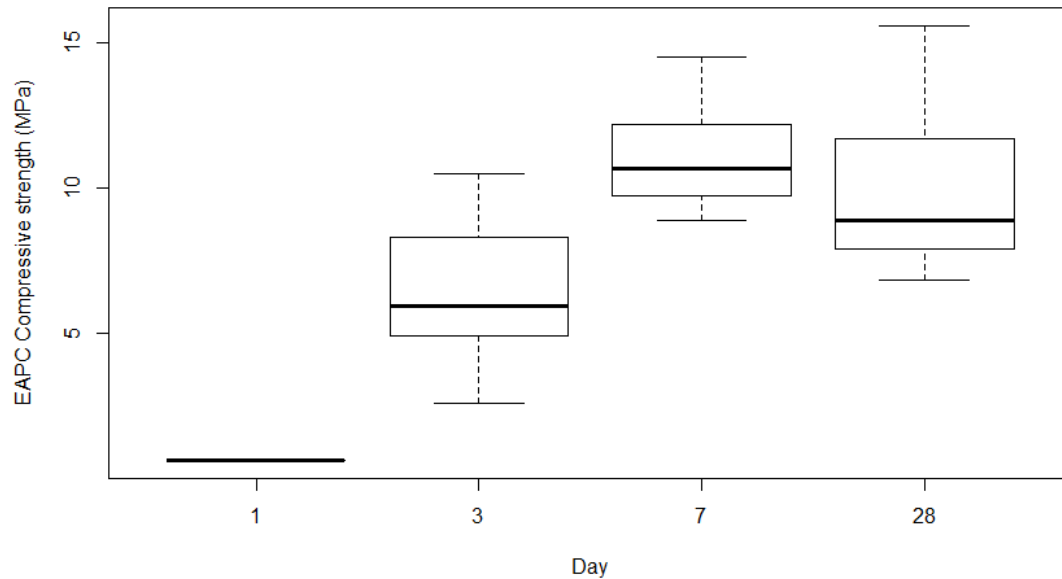
Figure 5.3.11: Compressive strength of EAPC cement samples after 1, 3, 7 and 28d

Figure 5.3.12 shows the compressive strength of EAPC + 5% Gypsum cements after 7 and 28d. The cements increased in strength between 7d and 28d. The 1d and 3d samples failed to break during the test hence no compressive strength reading was obtained.
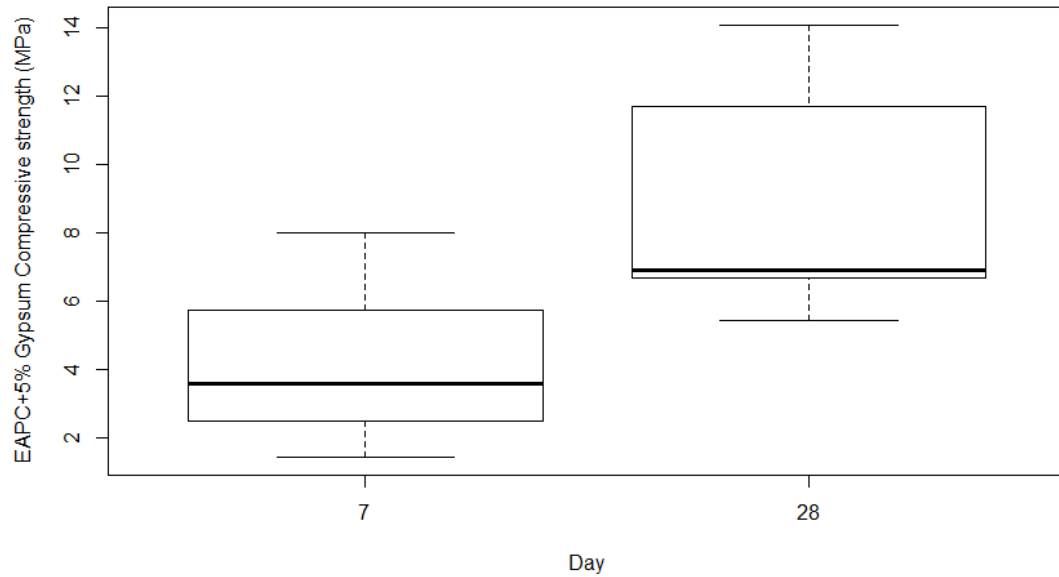
Figure 5.3.12: Compressive strength of EAPC+5% Gypsum cement samples after 7 and 28d

Figure 5.3.13 shows the compressive strength of Kaolin80FA20 cements after 1, 3, 7 and 28d. The cements increased in strength between 1d and 28d.
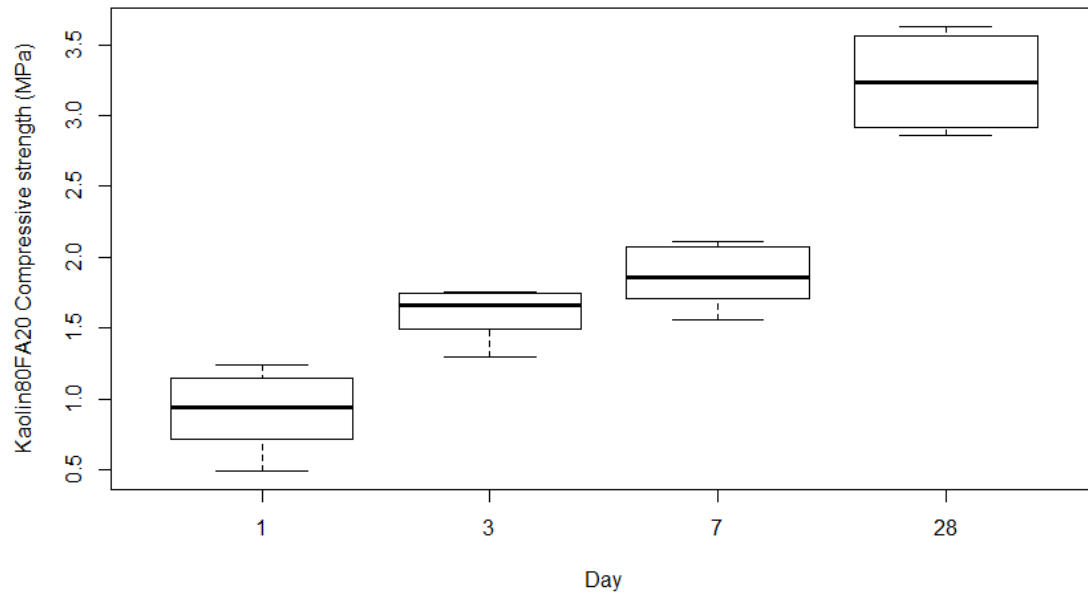
Figure 5.3.13: Compressive strength of Kaolin80FA20 cement samples after 1, 3, 7 and 28d

Figure 5.3.14 shows the compressive strength of Kaolin100 cements after 1, 3, 7 and 28d. The cements increased in strength between 1d and 28d, except for a dip on day 7.
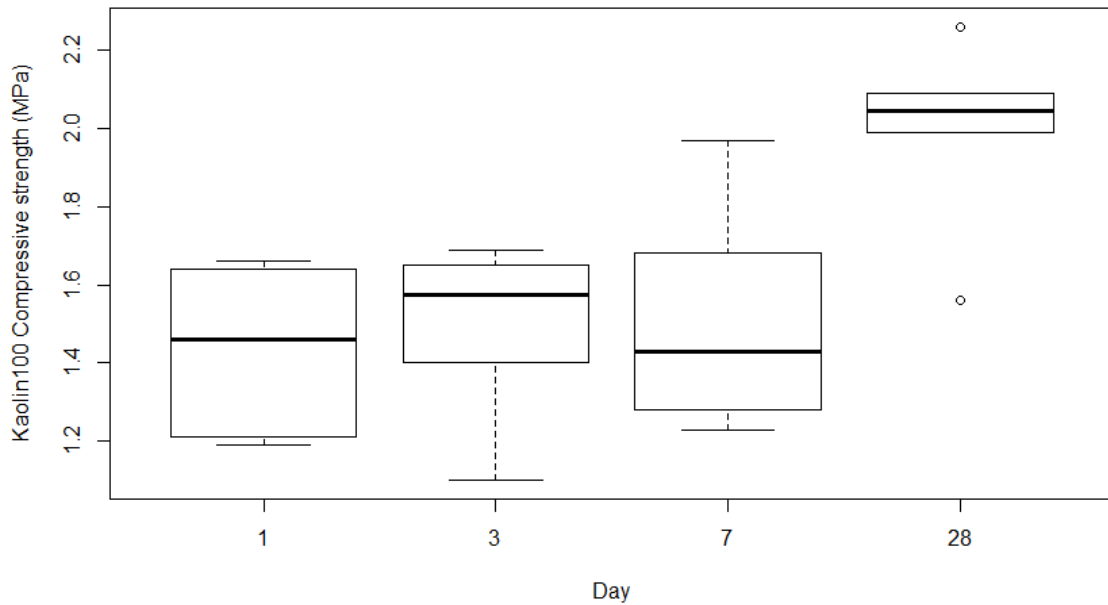
Figure 5.3.14: Compressive strength of Kaolin100 cement samples after 1, 3, 7 and 28d

Table 5.3.2 presents a descriptive summary while Table 5.3.3 presents ANOVA of individual cement compressive strengths. There was a statistically significant difference at the various time points among cements based on EAPC, 100% Kaolin and 80% Kaolin/ 20% FA further confirmed by Tukey's post hoc test ($p < 0.05$).

Table 5.3.2: Descriptive summary of cement compressive strength (MPa)

Sample name	Time	Mean (SD)	Min	Max
ARM	1 (n=0)	-	-	-
	3 (n=1)	2.02 (-)	2.02	2.02
	7 (n=6)	5.45 (2.26)	2.31	8.68
	28 (n=6)	8.32 (3.48)	4.91	12.70
Bamburi	1 (n=0)	-	-	-
	3 (n=1)	1.84 (-)	1.84	1.84
	7 (n=6)	2.40 (0.75)	1.32	3.36
	28 (n=6)	3.25 (0.99)	2.19	4.67
EAPC	1 (n=1)	0.62 (-)	0.62	0.62
	3 (n=6)	6.37 (2.75)	2.57	10.50
	7 (n=6)	11.10 (2.00)	8.89	14.50
	28 (n=6)	9.96 (3.21)	6.82	15.60
EAPC +	1 (n=0)	-	-	-
5%Gypsum	3 (n=0)	-	-	-
	7 (n=6)	4.26 (2.64)	1.44	8.02
	28 (n=6)	8.64 (3.43)	5.46	14.10
Kaolin80/	1 (n=6)	0.92 (0.29)	0.49	1.24
FA20	3 (n=6)	1.61 (0.19)	1.30	1.76
	7 (n=6)	1.86 (0.22)	1.56	2.11
	28 (n=6)	3.24 (0.36)	2.86	3.63
Kaolin100	1 (n=6)	1.44 (0.21)	1.19	1.66
	3 (n=6)	1.50 (0.22)	1.10	1.69
	7 (n=6)	1.50 (0.29)	1.23	1.97
	28 (n=6)	2.00 (0.23)	1.56	2.26

Table 5.3.3: Descriptive summary and ANOVA of cement compressive strength (MPa)

Sample name	Time	F statistic, df, p-value	Tukey's post hoc adjusted p-value	Diff (95% CI)
ARM	1 (n=0)	2.70, 2 df	-	
	3 (n=1)	p = 0.12		
	7 (n=6)			
	28 (n=6)			
Bamburi	1 (n=0)	1.99, 2 df	-	
	3 (n=1)	p = 0.19		
	7 (n=6)			
	28 (n=6)			
EAPC	1 (n=1)	6.50, 3df	7:1 = 0.01**	10.49 (2.09, 18.89)
	3 (n=6)	p = 0.005**	28:1 = 0.03*	9.35 (0.95, 17.75)
	7 (n=6)		7:3 = 0.04*	4.73 (0.24, 9.22)
	28 (n=6)			
EAPC + 5%Gypsum	1 (n=0)	5.43, 1df		
	3 (n=0)	p = 0.05	-	
	7 (n=6)			
	28 (n=6)			
Kaolin80/ FA20	1 (n=6)	76.64, 3df	1:3 = 0.002**	0.69 (0.25, 1.13)
	3 (n=6)	p < 0.0001***	1:7 = 0.000***	0.94 (0.50, 1.38)
	7 (n=6)		1:28 = 0.000***	2.32 (1.88, 2.76)
	28 (n=6)		3:28 = 0.000***	1.63 (1.19, 2.07)
			7:28 = 0.000***	1.38 (0.94, 1.82)
Kaolin100	1 (n=6)	7.09, 3df	1:28 = 0.003**	0.56 (0.17, 0.95)
	3 (n=6)	p = 0.002**	3:28 = 0.01**	0.50 (0.11, 0.89)
	7 (n=6)		7:28 = 0.01**	0.50 (0.11, 0.88)
	28 (n=6)			

*p<0.05, **p<0.01, ***p≤0.0001

Figure 5.3.15 compares the compressive strength of the experimental cements after 1, 3, 7 and 28d. The compressive strength of the cements generally increased from 1d to 28d.

After 1d, the compressive strength of the cements derived from EAPC clinker, alkaline-activated mixture of Kaolin and fly-ash (80:20) and 100% alkaline-activated Kaolin ranged between 1.0 and 1.6MPa. The remaining cement samples did not break during testing hence no record of compressive strength was made. After 3d, the compressive strength of the cements ranged from 1.6 – 6.2MPa. The remaining cement samples did not break during testing hence there was no record of compressive strength. After 7d, the compressive strength of the cements ranged from 1.8 – 11.0MPa while after 28d, the compressive strength of the cements ranged from 2.0 – 10.0MPa.
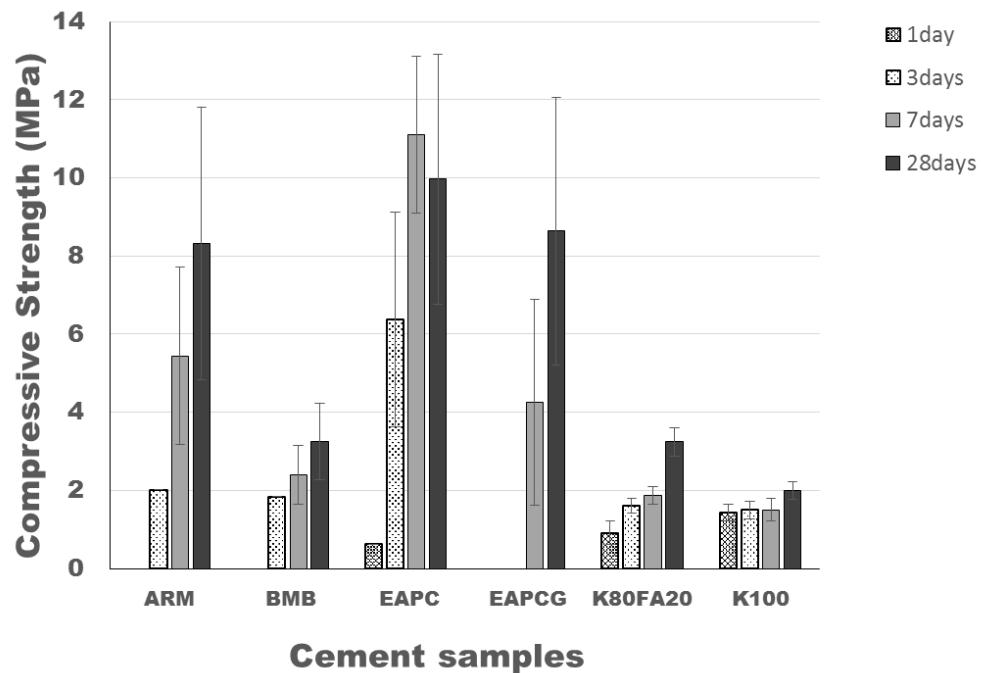
Figure 5.3.15: Comparative cement compressive strength after 1, 3, 7 and 28d

Figure 5.3.16 compares the compressive strength of the experimental cements after 1d. The highest compressive strength was recorded for 100% activated Kaolin while the least strength was recorded for EAPC cements. ARM, Bamburi and EAPC+5% gypsum samples failed to failed to break during testing hence no compressive strength reading was obtained.
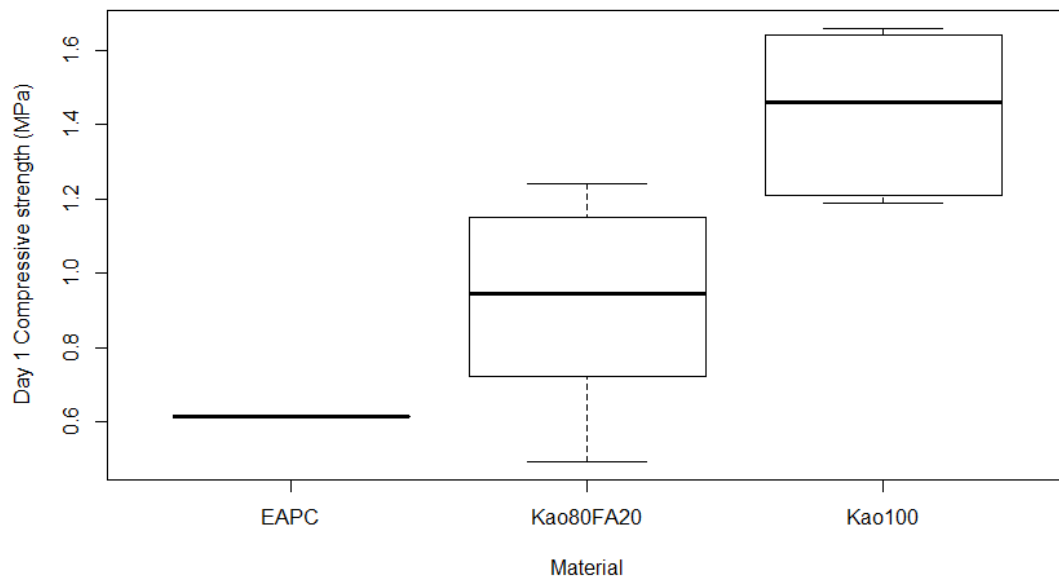
Figure 5.3.16: Comparative individual cement compressive strength after 1d

Figure 5.3.17 compares the compressive strength of the experimental cements after 3d. The highest compressive strength was recorded for EAPC while the lowest strength was recorded for 100% activated Kaolin. EAPC+5% gypsum samples failed to failed to break during testing hence no compressive strength reading was obtained.
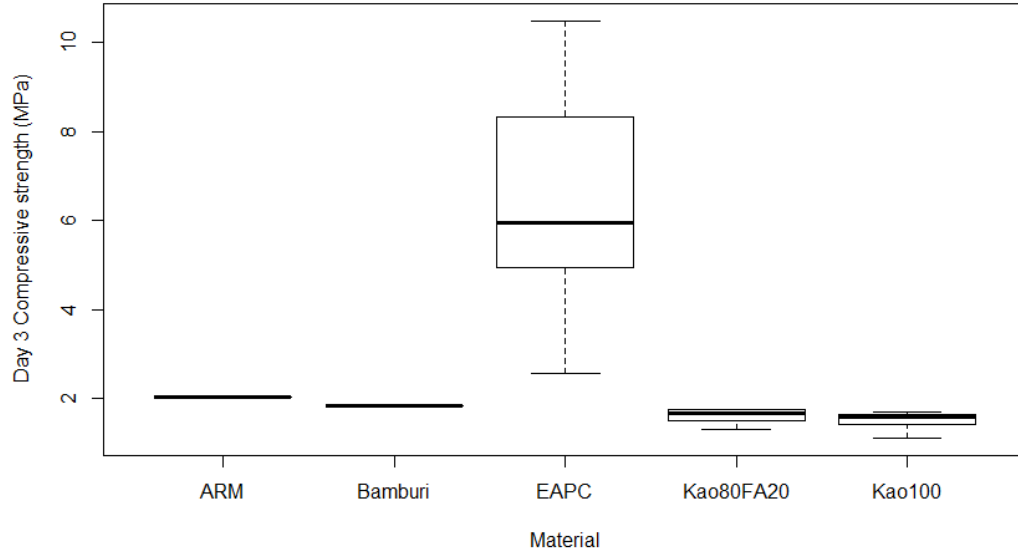
Figure 5.3.17: Comparative individual cement compressive strength after 3d

Figure 5.3.18 compares the compressive strength of the experimental cements after 7d. The highest compressive strength was recorded for EAPC while the lowest strength was recorded for 100% activated Kaolin.
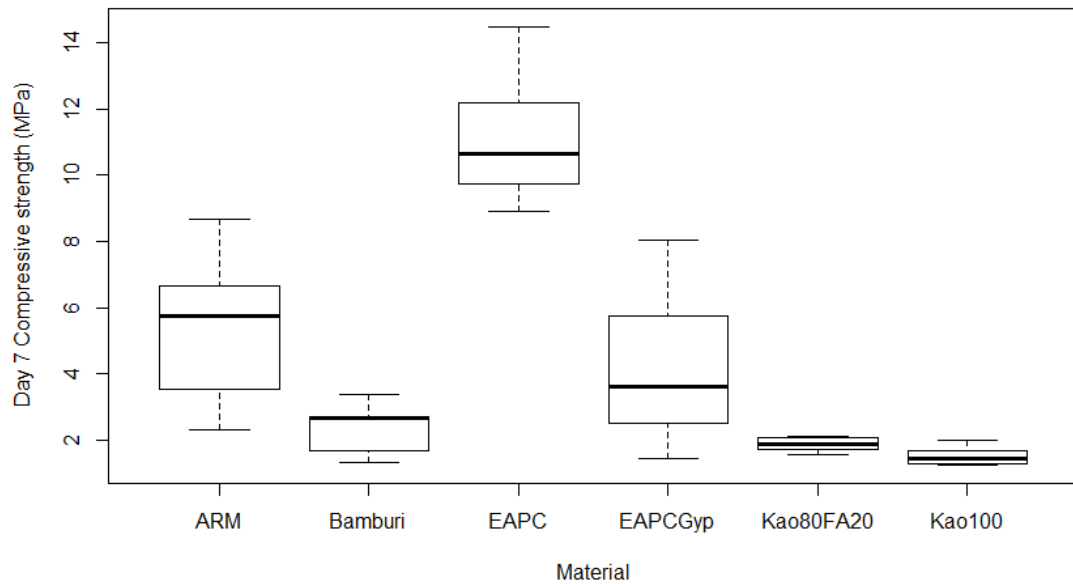
Figure 5.3.18: Comparative individual cement compressive strength after 7d

Figure 5.3.19 compares the compressive strength of the experimental cements after 28d. The highest compressive strength was recorded for EAPC while the lowest strength was recorded for 100% activated Kaolin.
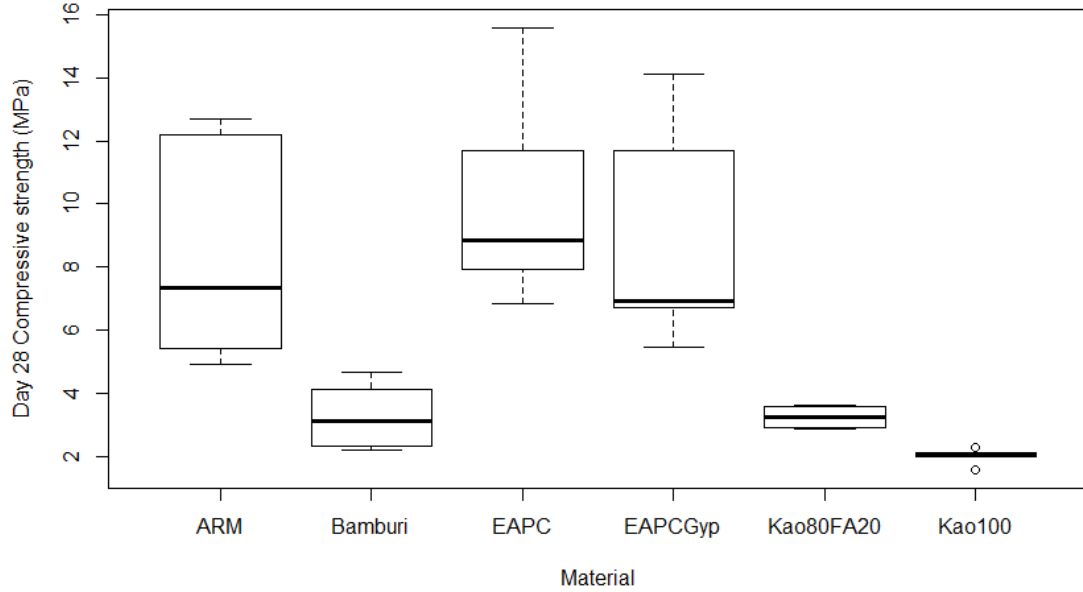
Figure 5.3.19: Comparative individual cement compressive strength after 28d

Figure 5.3.20 compares the average compressive strength of the experimental cements after 1, 3, 7 and 28d. The compressive strength of the cements generally increased from 1d to 28d.
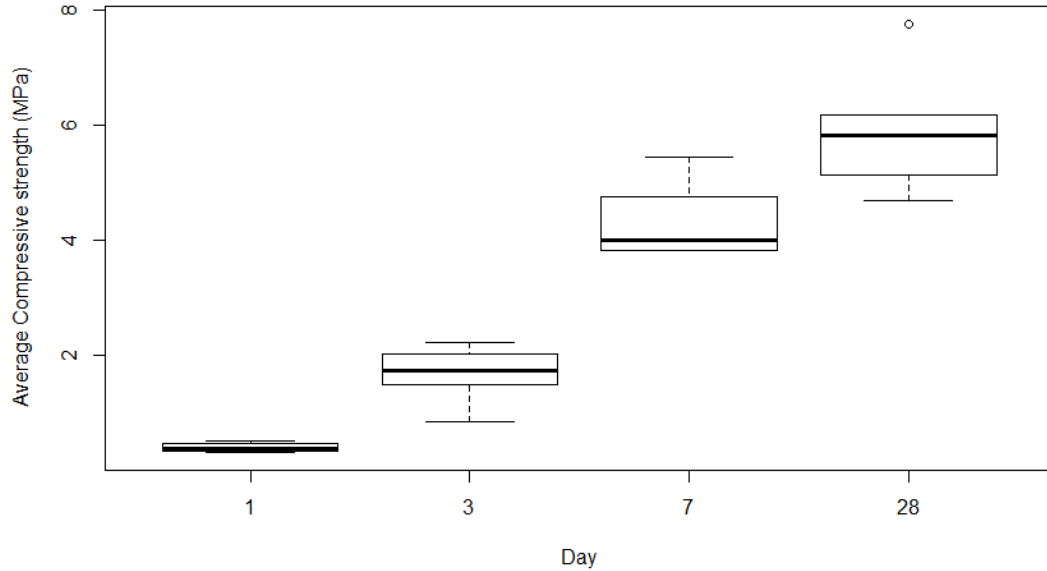
Figure 5.3.20: Comparative average cement compressive strength after 1, 3, 7 and 28d

Table 5.3.4 presents a descriptive summary while Table 5.3.5 presents ANOVA of the cement compressive strength at different time points. There was a statistically significant difference among all the cements and at all the time points further confirmed by Tukey's post hoc test ($p < 0.05$).

Table 5.3.4: Descriptive summary of individual material compressive strength at different times (MPa)

Time	Sample	Mean (SD)	Min	Max
Day 1	ARM (n=0)	-	-	-
	Bamb (n=0)	-	-	-
	EAPC (n=1)	0.62 (-)	0.62	0.62
	EAPCGyp (n=0)	-	-	-
	Kao80FA20 (n=6)	0.92 (0.29)	1.19	1.66
	Kao100 (n=6)	1.44 (0.21)	2.00	1.24
Day 3	ARM (n=1)	2.02 (-)	2.02	2.02
	Bamb (n=1)	1.84 (-)	1.84	1.84
	EAPC (n=6)	6.37 (2.75)	2.57	10.50
	EAPCGyp (n=0)	-	-	-
	Kao80FA20 (n=6)	1.61 (0.19)	1.30	1.76
	Kao100 (n=6)	1.50 (0.22)	1.10	1.69
Day 7	ARM (n=6)	5.45 (2.26)	2.31	8.68
	Bamb (n=6)	2.40 (0.75)	1.32	3.36
	EAPC (n=6)	11.10 (2.00)	8.89	14.50
	EAPCGyp (n=6)	4.26 (2.64)	1.44	8.02
	Kao80FA20 (n=6)	1.86 (0.22)	1.56	2.11
	Kao100 (n=6)	1.50 (0.29)	1.23	1.97
Day 28	ARM (n=6)	8.32 (3.48)	4.91	12.70
	Bamb (n=6)	3.25 (0.99)	2.19	4.67
	EAPC (n=6)	9.96 (3.21)	6.82	15.60
	EAPCGyp (n=6)	8.64 (3.43)	5.46	14.10
	Kao80FA20 (n=6)	3.24 (0.36)	2.86	3.63
	Kao100 (n=6)	2.00 (0.25)	1.56	2.26
Average	1 (n=6)	0.41 (0.08)	0.32	0.51
	3 (n=6)	1.69 (0.49)	0.86	2.22
	7 (n=6)	4.31 (0.66)	3.83	5.45
	28 (n=6)	5.90 (1.06)	5.90	7.76

Table 5.3.5: ANOVA of individual material compressive strength at different times (MPa)

Time	Sample	F statistic, df, p-value	Tukey's post hoc adjusted p-value	Diff (95% CI)
Day 1	ARM (n=0)	8.42, 2df	Kao100:EAPC=0.03*	0.82 (0.06, 1.58)
	Bamb (n=0)	p=0.007**	Kao100:Kao80FA20=0.01**	0.52 (0.12, 0.93)
	EAPC (n=1)			
	EAPCGyp (n=0)			
	Kao80FA20 (n=6)			
	Kao100 (n=6)			
Day 3	ARM (n=1)	9.41, 4df	Kao80FA20:EAPC=0.001**	-4.77 (-7.61, -1.92)
	Bamb (n=1)	p<0.001**	Kao100:EAPC=0.001**	-4.87 (-7.72, -2.03)
	EAPC (n=6)			
	EAPCGyp (n=0)			
	Kao80FA20 (n=6)			
	Kao100 (n=6)			
Day 7	ARM (n=6)	29.38, 5df	ARM:Bamb=0.03*	-3.05 (-5.92, -0.18)
	Bamb (n=6)	p<0.0001***	ARM:EAPC= 0.000***	5.66 (2.79, 8.52)
	EAPC (n=6)		ARM:Kao80FA20=0.01**	-3.59 (-6.45, -0.72)
	EAPCGyp (n=6)		ARM:Kao100=0.003**	-3.94 (-6.81, -1.08)
	Kao80FA20 (n=6)		Bamb:EAPC= 0.000***	8.71 (5.84, 11.57)
	Kao100 (n=6)		EAPC:EAPCGyp= 0.000***	-6.84 (-9.85, -3.84)
			EAPC:Kao80FA20= 0.000***	-9.24 (-12.11, -6.38)
			EAPC:Kao100= 0.000***	-9.60 (-12.47, -6.73)
Day 28	ARM (n=6)	12.06, 5df	ARM:Bamb=0.01**	-5.07 (-9.33, -0.81)
	Bamb (n=6)	p<0.0001***	ARM:Kao80FA20=0.01**	-5.08 (-9.34, -0.82)
	EAPC (n=6)		ARM:Kao100=0.001**	-6.32 (-10.58, -2.06)
	EAPCGyp (n=6)		Bamb:EAPC= 0.001**	6.72 (2.45, 10.98)
	Kao80FA20 (n=6)		Bamb:EAPCGyp= 0.01**	5.39 (1.13, 9.65)
	Kao100 (n=6)		EAPC:Kao80FA20= 0.001**	6.72 (-10.99, -2.46)
			EAPC:Kao100= 0.0001***	-7.96 (-12.23, -3.70)
			EAPCGyp:Kao80FA20=0.01**	-5.40 (-9.66, -1.14)
			EAPCGyp:Kao100= 0.01**	-6.64 (-10.90, -2.38)
Average	1 (n=6)	82.39, 3df	1:3=0.02*	1.28 (0.19, 2.36)
	3 (n=6)	p<0.0001***	1:7=0.000***	3.90 (2.82, 4.98)
	7 (n=6)		1:28=0.000***	5.49 (4.41, 6.57)
	28 (n=6)		3:7=0.000***	2.62 (1.54, 3.71)
			3:28=0.000***	4.21 (3.13, 5.30)
			7:28=0.003**	1.59 (0.51, 2.67)

*p<0.05, **p≤0.01, ***p≤0.0001

5.3.3 Fluoride ion releasing profile of experimental cements

Figure 5.3.21 shows the cumulative fluoride ion release profile of clinker-based cements in deionized water, 37°C and at varying pH. The fluoride release had a linear relationship to square root of time ($t^{1/2}$), with $R^2 > 98.5$ but low intercept values. A lower clinker to CaF_2 ratio was associated with increased fluoride release at pH 5 and 7. EAPC clinker-based cement demonstrated highest fluoride ion release at both ratios and all pH.

Figure 5.3.22 shows the fluoride ion release profile of clinker-based cements in Tris buffer, 37°C and at varying pH. The fluoride release had a linear relationship to square root of time ($t^{1/2}$), with $R^2 > 95$ but low intercept values. A lower clinker to CaF_2 ratio was associated with increased fluoride release at all pH. EAPC clinker-based cement demonstrated highest fluoride ion release at both ratios and all pH.

Figure 5.3.23 shows the fluoride ion release profile of clinker-based cements in artificial saliva, 37°C and at pH 7. The fluoride release had a linear relationship to square root of time ($t^{1/2}$), with $R^2 > 97$ but low intercept values. A lower clinker to CaF_2 ratio was associated with increased fluoride release. ARM clinker-based cement demonstrated highest fluoride ion release at both a lower clinker to CaF_2 ratio (0.65mmol/L) and at a higher clinker to CaF_2 ratio (0.38mmol/L).
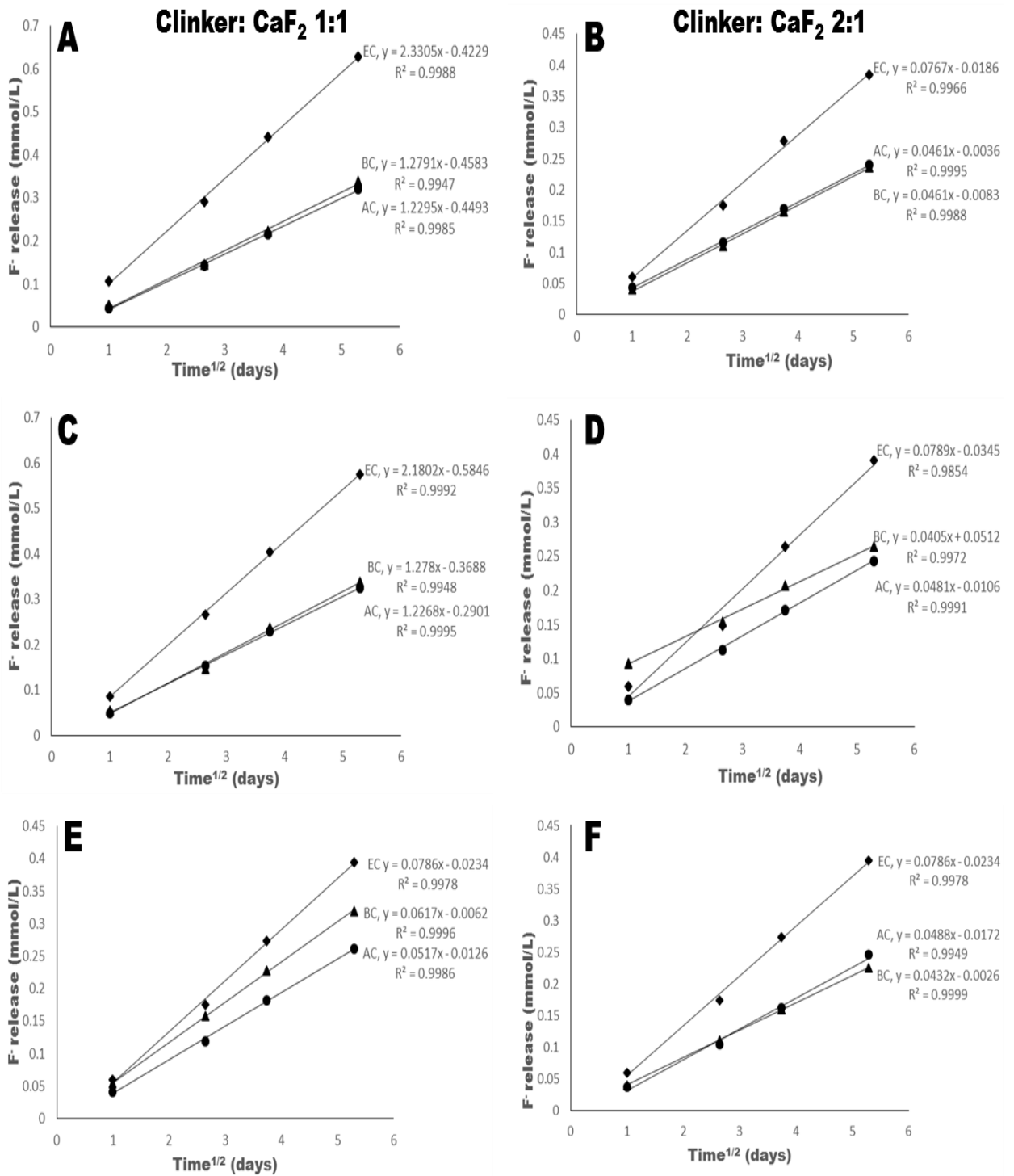
Figure 5.3.21: F⁻ release profile of clinker-based cements in deionized water (A & B – pH 5; C & D – pH 7; E & F – pH 9)
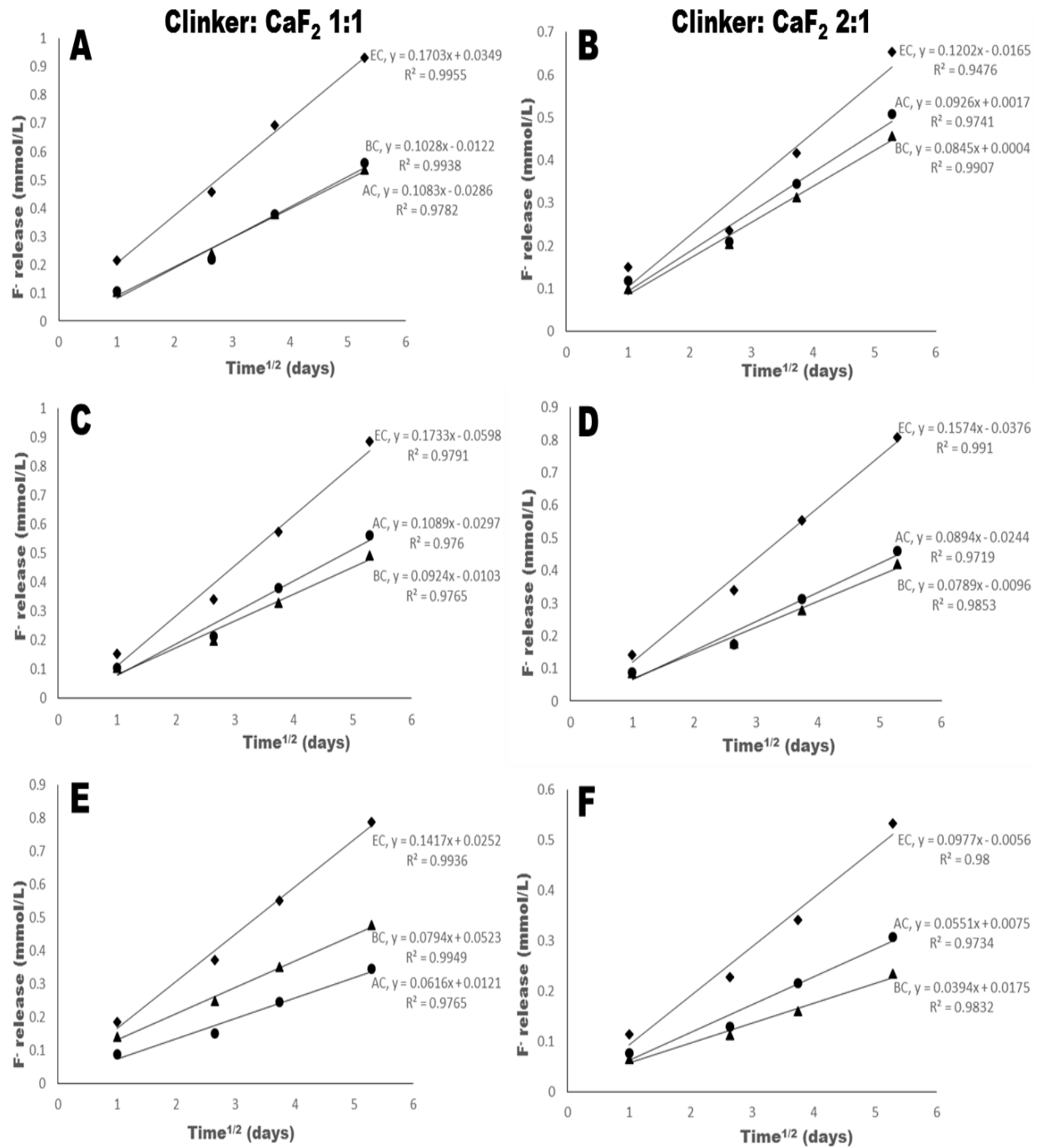
Figure 5.3.22: F⁻ release profile of clinker-based cements in Tris buffer (A & B – pH 5; C & D – pH 7; E & F – pH 9)
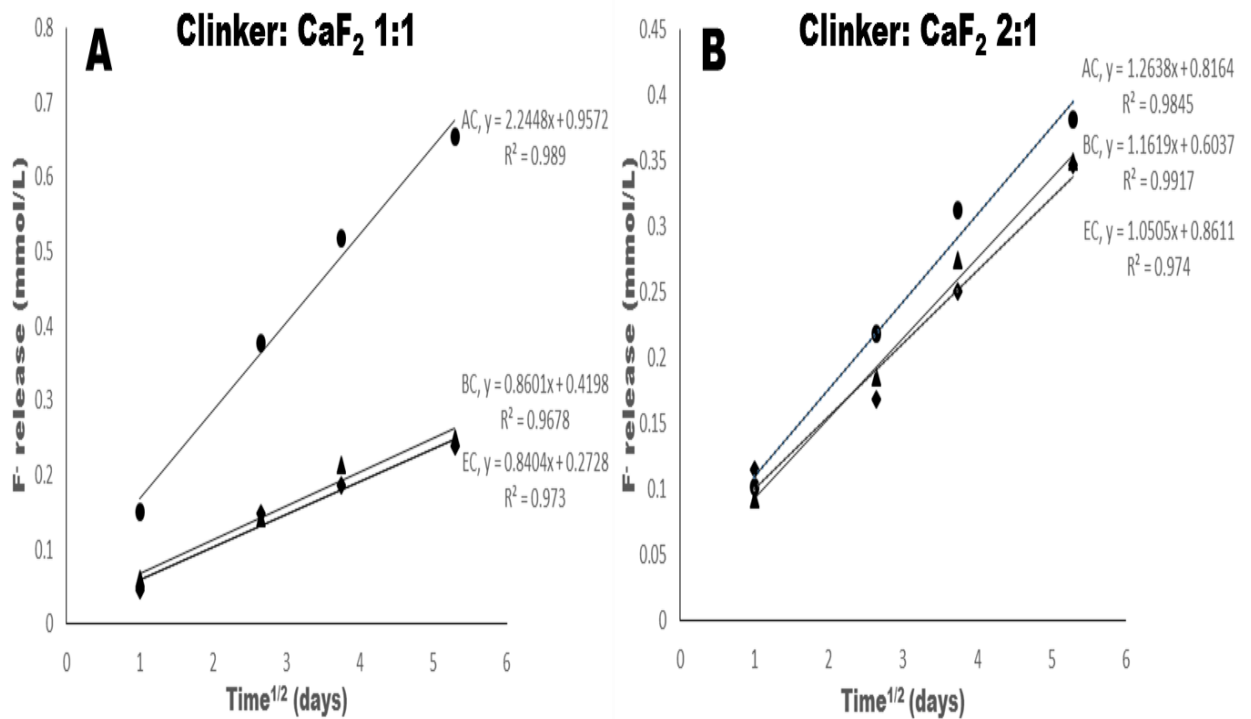
Figure 5.3.23: F⁻ release profile of clinker-based cements in artificial saliva, pH 7

Figure 5.3.24 shows the fluoride ion release profile of geopolymer-based cements in artificial saliva (A) and deionized water (B), both 37°C and at pH 7. The fluoride release had a linear relationship to square root of time ($t^{1/2}$), with $R^2 > 90$ but low intercept values. 100% Kaolin-based cements showed minimal fluoride release (< 0.2mmol/L) in both media. For a 1:1 ratio of Kaolin and CaF_2, there was increased fluoride release which followed a similar trend in both media. For combinations of Kaolin and fly-ash, the cements released more fluoride in deionized water than in artificial saliva. However, overall, the highest fluoride release was observed from the Kaolin/ FA cement (1.0mmol/L).
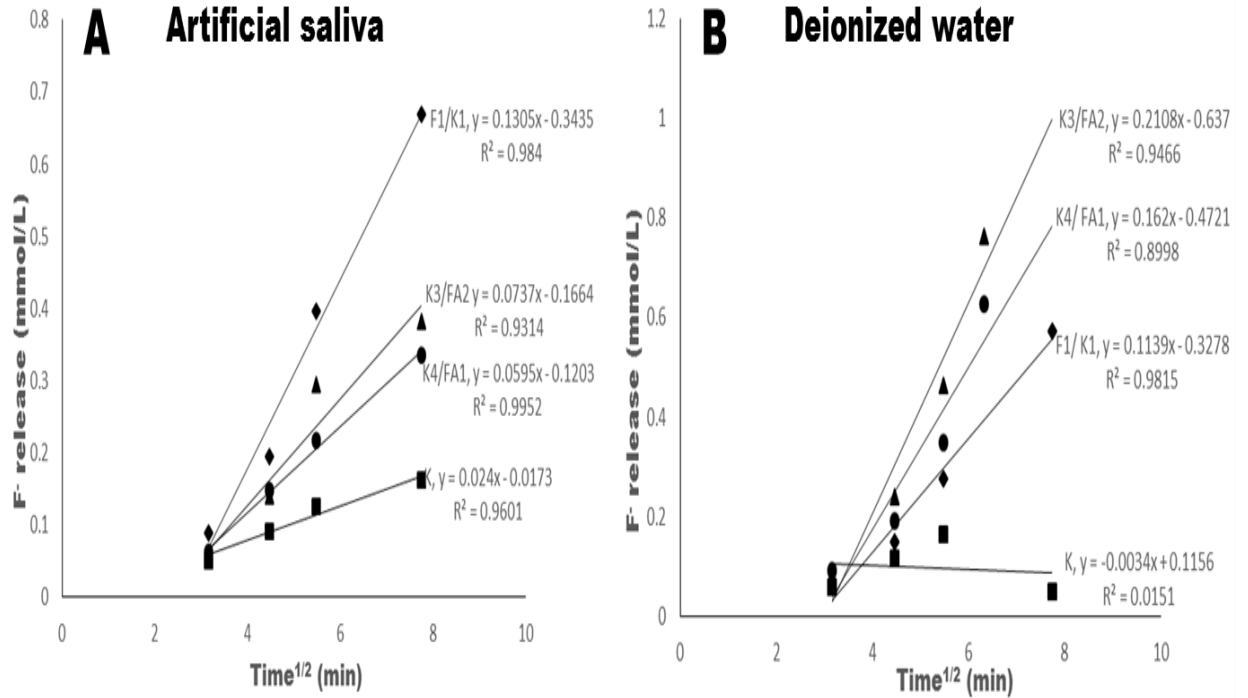
Figure 5.3.24: F⁻ release profile of geopolymer-based cements in artificial saliva (A) and deionized water (B), pH 7

5.3.4 Assessment of cost of production of experimental cements

Table 5.3.6 presents an assessment of cost of production of experimental dental cements in comparison to market brands. Other than the initial investment costs, local production of dental cements has the potential to cost less than imported materials.

Table 5.3.6: Assessment of cost of production of experimental cements

Material	Cost of production, including initial investment	Local purchase price /gm	Development and evaluation, including initial investment	Cost-benefit analysis
MTA Cem	Unknown	USD 30	Unknown	Purchase price USD 30
ProRoot MTA	Unknown	USD 50	Unknown	Purchase price USD 50
Fuji IX GIC	Unknown	USD 9	Unknown	Purchase price USD 9
PC clinker (ground)	Unknown	<USD 0.10	Cost of outsourcing lab facilities, PAA and tartaric acid for testing approximately USD 10,000 for two years	Excluding cost of initial investment, unit cost of locally available materials is cheaper in the long run
AS materials	Raw materials available at no cost from manufacturers	-		

CHAPTER SIX

6. DISCUSSION

The aim of this study was to develop a prototype for a restorative dental cement in Kenya. PC clinker and aluminosilicate materials for production of PC clinker were collected from three PC and one ceramic manufacturing companies in Kenya and evaluated in a laboratory-based study in three phases.

In the first phase, the composition and particle size of the materials were described. In the second phase, experimental ionomer-type dental cement formulations were prepared and in the third phase, some properties of the said cements were evaluated. A discussion of the findings of the study is presented in this chapter, commencing with an assessment of the methodology employed.

6.1 Overview of the methodology

This study was *in vitro*, laboratory-based in design as is always employed in the initial phases of biomaterial development. Although inference of *in vitro* study findings to *in vivo* studies or even actual clinical settings is difficult and far-fetched, *in vitro* studies remain crucial to this process. This is because they are cheaper to conduct, contribute to elimination of unsatisfactory products and help to navigate ethical issues in research involving human and animal subjects.

This was one of the first studies in Kenya to attempt to develop a prototype for use as a restorative dental material. Despite the limitations of lack of reference to similar studies

conducted locally, the study was designed similarly to others conducted globally. The experimental techniques employed have been utilized in numerous other studies and have been shown to be suitable for obtaining the results as documented in this study. The principles of operation of the techniques employed as well as their advantages and disadvantages were reviewed in detail in Chapter 2, section 2.13.

The study evaluated a population of materials that are readily available in Kenya; however, while the original intention was to study white Portland cement and related materials due to their aesthetic potential, regrettably, the companies included did not produce their own white PC clinker and those which did used imported raw materials. Therefore, the study was limited to gray PC clinker and related raw materials to satisfy the inclusion criteria.

Nonetheless, random sampling and conducting experiments according to ISO and ASTM standards minimized errors and bias and ensured validity of results within reasonable limits. There was a need to modify the standards in only one instance (during compressive strength testing) to overcome some challenges associated with the setting behaviour of the materials.

6.2 Phase I: Evaluation of Kenyan Portland cement and raw materials for Portland cement production

6.2.1 Compositional analysis

The composition of three clinker and three aluminosilicate material samples obtained in Kenya were analyzed and compared to the composition of two commercial brands of MTA. The three groups of materials were found to be composed of similar constituents in different proportions but mostly within a similar range. The constituents also formed different phases

as visualized by XRD, specifically di-calcium and tri-calcium silicate for MTA and PC, and quartz, calcite and mullite for raw and alkaline-activated aluminosilicates.

There was no statistically significant difference between MTA and PC except with regards to bismuth (Bi) and lead (Pb). This finding is not surprising given the established fact that MTA is a derivative of PC. Several studies have reported the similarity in composition between MTA and PC, with the only difference being presence of radiopacifiers, commonly Bi_2O_3, in MTA and their absence in MTA [21,22,31-33,37,165-167,169,186,189,190]. The composition of Kenyan PC has never been analyzed to assess its potential for use in a dental material. This study found similar results regarding the composition and article size of Portland cements as has been reported from other parts of the world.

Local aluminosilicate materials in Kenya as well as geopolymers derived from the same have also never been evaluated in comparison to PC and MTA for biomedical purposes. The similarity in the constituents of these materials warrants further investigations in the search for an affordable locally-produced alternative dental material.

Additionally, the clinker, aluminosilicate materials and MTA samples did not contain any detectable amounts of arsenic (As). Small quantities of Pb were detected in both MTA samples using EDXRF; however, using GFAAS, two clinker samples and both MTA samples were found to contain small amounts of Pb. While the Pb content in three of these samples was below the ASTM recommendation of <2mg/kg for PC, it is noteworthy that one clinker sample (Bamburi) contained Pb levels >2mg/kg (3.57µg/g). Studies that have reported on levels of potentially toxic elements such as As and Pb in MTA and PC had

varying results although most of the materials studied were found to have low levels of As [195-197]. Monteiro Bramante [197] found that one brand of MTA contained 5.91mg/kg of As. Continuous research in this area may shed more light in the inconsistencies obtained.

Among the materials evaluated in this study, fly ash was found to contain fluoride. The review of literature reported on evaluation of fluoride release in glass ionomer cements [92,130-132]. Topical fluoride is necessary to enhance remineralization and inhibit demineralization of initial caries lesions, as documented by Featherstone [126], and a key characteristic of anti-cariogenic materials such as GICs. Therefore, the presence of high levels of fluoride in fly ash is an interesting finding that warrants further research on how this may be harnessed in a locally-produced restorative dental material.

6.2.2   Particle size distribution analysis

The particle size distribution of the materials was also analyzed and results presented in Section 5.1.5. Prior to sieving, a variation was observed in the 10th, 50th and 90th percentile in the particle size distribution of the various materials. This finding was consistent with that reported by other studies [172-178] and may be explained by the differences in production methods in relation to the intended application, that is, endodontic material and construction material for MTA and clinker and alkaline-activated aluminosilicates, respectively.

However, after sieving, the particle size distribution was found to be comparable among the materials. Moreover, sieving was found to be an effective method of controlling the particle size to that recommended for dental cements (45µm) as documented in other studies [92]. Additionally, it was shown in the literature review (Section 2.10) that particle size above

50µm remained largely unreacted in PC and could compromise the overall quality of the set cement [33]. Nonetheless, there was no statistically significant difference in the particle size distribution of the materials either before or after sieving.

Although the scope of this study did not extend to assess the specific influence of particle size and shape on the properties of materials under investigation as was done by Ha *et al.* [173,175], Torabinejad *et al.* [176] and Komabayashi and Spangberg [177,178], the similarity in particle size is an advantage when seeking alternative biomedical applications of these materials.

6.3 Phase II: Formulation of experimental ionomer-type dental cements from Portland cement clinker or synthetic geopolymer

6.3.1 Formulation sequence of experimental cements

Experimental ionomer-type restorative dental cements were prepared by mixing clinker and geopolymer powders with various ratios of freeze-dried PAA, CaF_2 and aqueous tartaric acid. The selection of the materials was based on the compositional analysis which showed a similarity of the materials to silicate MTA and GIC glass powders. A previous study by Lovschall *et al.* [171] sought to expand the applications of MTA from endodontic to restorative material by mixing Portland cement with PAA. Moreover, experiments conducted on natural silicate materials had shown their ability to form cements [105,106]. Glass polyalkenoate cements derived from waste gasifier slags had also been investigated [108,109].

The mixing ratios were guided by published similar ratios for dental cements for restorative dental applications which are usually mixed to dough consistency. It is recommended to

have higher powder to liquid ratio in cements such as GICs and those derived from zinc oxide in order to confer strength [92,97,105,106,121,122].

Nonetheless, it is noteworthy that the actual materials under investigation have never been evaluated for this purpose before and this study was the first attempt to utilize materials locally produced in Kenya to develop an affordable alternative dental restorative material. Therefore, variations in mixing and setting times were observed before a reasonable ratio was determined.

For the clinkers, large amounts of clinker powder resulted in a grainy mixture instead of a pliable dough, on mixing with PAA and aqueous tartaric acid. However, addition of CaF_2 and reduction of the powder improved the consistency to a sticky dough. This may be explained by the fact that the clinkers were not pure glass but contained a considerable amount of crystalline phases. This has been shown by several studies that have employed XRD to describe the phase structure of MTA and Portland cement [32,165,166,170,186-188,191-193,206]. The crystalline powder may therefore not have been as reactive as a glass powder which is readily dissolved following acidic attack [92,98].

In glass ionomer cements, glass degradation is typically the initiation of the setting reaction. The glass phase in materials has a higher potential energy than the equivalent crystalline phase. Moreover, variations of bond angles and distances makes it easier to break the bonds in glass [160]. This determines the reactivity of the glass following acidic attack and subsequently the series of events that lead to a hardened cement from a paste [105,106]. Although it has been considered difficult to quantify the amorphous phase in clinker, several

studies have employed Rietveld refinement to do so and its existence is now widely accepted [138-140]. However, this was beyond the scope of the present study.

Furthermore, the importance of the Si: Al and Ca: Al ratios in formation of glass polalkenoate cements have been specified by Hill and co-workers [97,108,109,116]. For optimal glass dissolution with resultant cements having adequate mechanical properties, they specify a Si: Al ratio of one or more and Ca: Al ratio of 1:2 or more. It is notable that the Si: Al ratio of all materials investigated in this study was greater than one, ranging from 3.42 to 7.23 while the Ca: Al ratio of the clinkers was much greater than half, at least 10. These ratios may provide an explanation as to the failure of these cements to demonstrate classical setting characteristics of glass ionomer cements, which can elicit reasonable crushing strength within one hour of setting and remain hydrolytically stable. In fact, their hydrolytic instability is similar to the so-called 'macro defect free cements' which are derived from clinker and polyacrylamide [108,109].

The aim of including CaF_2 in the cements was to provide a source of fluoride. Inadvertently, this resulted in better handling by improving the cement consistency to a sticky paste. CaF_2 has low solubility; however, the solubility increases slightly in low pH. This behaviour makes it one of the preferred additives for fluoride delivery in dentifrices. Studies on mechanism of caries prevention of topical fluoride have concluded that a low oral pH facilitates release of fluoride ions from NaF or CaF_2 which can subsequently form fluoroapatite in the demineralizing tooth structure. Moreover, for this to be effective, the process should be extended and continuous which is achieved by such fluoride molecules with low reactivity [127,128]. Likewise, this may provide an explanation for the clinker-based

cement consistency on addition of CaF_2. On exposure to PAA and aqueous tartaric acid, it was capable of participating in an acid-base reaction as did the clinker.

Unlike in the clinker-derived cements, for the BF slag/ fly ash geopolymer cements, a higher powder/ liquid ratio was required to produce a mixture with a dough consistency. Otherwise, a lower powder/ liquid ratio resulted in a fluid cement mixture having a consistency of a luting cement. The high water by-product content of the polycondensation setting reaction of these cements proposed by Davidovits [148,150] may provide an explanation as to the fluid consistency when low powder/ liquid ratios were used for cement formation. The XRD patterns showed a more amorphous structure for the geopolymers than the clinkers, identifiable by an amorphous halo and peaks for specific mineral phases, respectively. It is highly likely that these materials had a higher amorphous content hence tended to be more reactive or readily soluble in aqueous tartaric acid and poly (acrylic acid). In fact, polyalkenoate cements derived from waste gasifier slags have been investigated [108,109]; however, it is important to note that their aluminosilicate composition may vary from blast furnace slags.

As presented in the review of literature, geopolymers are derived from aluminosilicate precursors [145,150]. Additionally, the glass phase in fly ash has been modelled using the network connectivity theory [160-162]. Further, XRD [148] and NMR [163] evaluation of FA geopolymers have found that alkaline-activation does not result in formation of new crystalline phases other than the original content in the aluminosilicate precursor. Therefore, it is unsurprising that they would react similarly to aluminosilicate glass under acidic attack, as has been shown in other studies that mixed naturally occurring silicates

with polycarboxylic acids to form cements during the early experiments by Wilson and co-workers while developing GICs [105,106].

For the Kaolin geopolymers, an amount of aluminosilicate powder as high as that used for the BF slag/ fly ash derived cements (1gm) resulted in a rapid set that made it impossible to manipulate the cements further after mixing. Reducing the amount of powder to 0.7gm resulted in a paste/ dough consistency with a more reasonable working time. Just like for the BF slag/ fly ash geopolymers, this finding suggests that the amorphous nature of these aluminosilicate materials made them reactive with PAA and enhanced their ability to form cements, as discussed above [105,106,145,164].

Nonetheless, on exposure to distilled water, it is notable that the cements based on BF slag/ fly ash geopolymer disintegrated while those based on clinker softened apparently due to water sorption. This may be explained by the fact that despite the ability of these materials to form cements on mixing with PAA, and as has been reported by Wilson [105] and Crisp *et al.* [106] regarding naturally occurring silicates, the generic formulation of their natural amorphous content, together with impurities, was not adequate to ensure an optimum setting reaction for a stable cement product. Just as was explained for the clinker-derived cements, the Si: Al and Ca: Al ratios of these cements was far off from the recommendation for polyalkenoate cements by Hill and co-workers [97,108,109,116] hence the hydrolytic instability and poor mechanical properties.

On the other hand, the cements from Kaolin geopolymers demonstrated better stability and this may be attributed to the fact that among all the materials tested, these geopolymers showed the greatest resemblance to GIC powder with regards to the aluminosilicate content.

6.3.2 Setting reaction characteristics of experimental cements

As discussed in Section 6.3.1, addition of PAA and aqueous tartaric acid to the clinker and geopolymer materials led to a reaction which resulted in a cement material with a reasonable setting time. The kinetic setting reaction was followed using FTIR, 30 seconds to 25 minutes after mixing.

For the cements derived from clinker, on mixing with both PAA and aqueous tartaric acid (Figures 5.2.2 to 5.2.5), prominent bands were identified at 1321 cm^{-1}, 1403 cm^{-1} and 1539 cm^{-1} together with a range of smaller bands. On mixing with only PAA (Figure 5.2.11-B), prominent bands were identified at 1321 cm^{-1}, 1403 cm^{-1} and 1537 cm^{-1}, together with several smaller bands, while on mixing with only aqueous tartaric acid (Figure 5.2.11-A), one prominent band was identified at 1632 cm^{-1}.

These findings suggest an acid-base reaction between the clinker powders, freeze-dried PAA and aqueous tartaric acid, resulting in the formation of polyacrylate and tartrate salts in a setting reaction similar to that of glass ionomer cements. FTIR studies of the setting reaction of GICs have identified specific representative bands associated with these calcium and aluminium salts due to symmetric and asymmetric stretching of C-O bonds (Tables 2.9.2 and 2.9.3) [100-102,105].

This finding was somewhat surprising considering that the composition and structural phases of the clinker powders was predominantly crystalline and similar to MTA, a calcium silicate material. Nonetheless, it is expected that clinker would contain a glass phase because although it is not quenched in cold water as is typical for glass production, the rapid cooling enables some content to solidify without crystallization. The presence of glass in clinker has been shown as well as its advantages in the setting reaction and overall cement properties [137-140]. In addition, the overall composition of the calcium aluminosilicate in the clinkers was similar to that in GICs as stated by Wilson and McLean [89].

Furthermore, the band at 1632 cm^{-1} which was prominent when the clinker powder was mixed with only aqueous tartaric acid (Figure 5.2.11-A) and is associated with the C-O asymmetric stretch for Al-tartrate, diminished when the clinker powder was mixed with only PAA Figure 5.2.11-B), and when the clinker powder was mixed with both acids (Figure 5.2.4). This suggests that PAA is the dominant reactant, a similar occurrence as in GICs [91,92,94,96]. Nicholson's review of the effect of additives on the setting reaction of GICs also showed that the presence of tartaric acid led to a variation in the time of polyacrylate formation, characterized by slower formation of the calcium polyacrylates and more rapid formation of the aluminium ones [92]. In fact, tartaric acid was a later addition during the development of GICs with the effect of prolonging their working time while sharpening their setting time to improve the sluggish behavior which was characteristic of original ASPA materials and its actual contribution to the setting reaction still remains unclear [91,92,94].

For the cements derived from BF slag and fly ash geopolymer (80:20), on mixing with both PAA and aqueous tartaric acid (Figure 5.2.8), prominent bands were identified at 1537 cm^{-1}, 1403 cm^{-1} and 1321 cm^{-1}. On mixing with only PAA (Figure 5.2.14-B & D), the prominent bands were identified at 1643 cm^{-1}, 1541 cm^{-1}, 1405 cm^{-1} and 995 cm^{-1}, while on mixing with only aqueous tartaric acid (Figure 5.2.14-A & C), prominent bands were identified at 1626 cm^{-1}, 1384 cm^{-1}, 1121 cm^{-1} and 1064 cm^{-1} only within 30s of mixing.

These findings also seem to suggest an acid-base reaction characterized by the formation of polyacrylates and tartrates. Moreover, Wilson [105] associated bands 940 cm^{-1} and 1050 cm^{-1} with unreacted ASPA glass and silica gel, respectively. In these cements, the band closest to the unreacted glass (995 cm^{-1}) was diminishing by the 25th minute. Although the prominent bands were not classically those associated with GICs, they are similar. The calcium aluminosilicate composition of this geopolymer was also similar to the GIC glass hence a similar setting reaction is not surprising [89]. Furthermore, Bijen [137] has also shown that BF slag and fly ash contain a glass phase which influences the setting reaction and is beneficial to the properties of Portland cements that are mixed with these materials. Nonetheless, little information exists on the reaction of such materials with PAA and aqueous tartaric acid for dental material applications hence these results must be interpreted with caution.

On adjusting the ratio of BF Slag and fly ash, a shift in the prominent bands was observed. For the cements derived from BF slag and fly ash geopolymer (60:40 and 20:80), on mixing with both PAA and aqueous tartaric acid (Figures 5.2.9 and 5.2.10), prominent bands were identified at 1539 cm^{-1}, 1403 cm^{-1}, 1321 cm^{-1}, 1004 cm^{-1} and 872 cm^{-1}. On mixing with only

PAA (Figures 5.2.15-B & D and 5.2.16-B & D), the prominent bands were identified at approximately 1640 cm^{-1}, 1543 cm^{-1}, 1405 cm^{-1}, 1000 cm^{-1} and 872 cm^{-1}, while on mixing with only aqueous tartaric acid (Figures 5.2.15-A & C and 5.2.16-A & C), prominent bands were identified at 1632 cm^{-1}, 1585 cm^{-1}, 1385 cm^{-1}, 985 cm^{-1} and 870 cm^{-1}. However, the peak associated with the powder (870 cm^{-1}) appeared to be diminishing with PAA by the 25th minute.

Although these findings still suggest an acid-base reaction resulting in formation of polyacrylates and tartrates, it further suggests that the ratios of BF slag and fly ash influence the reactivity and products of the geopolymer powder. Given the little information that exists on this research area, it is difficult to provide a concrete explanation for the specific role of BF slag and fly ash in the setting reaction of these cements. However, Towler *et al.* [160], Stanton *et al.* [161] and Henry *et al.* [162] have shown that fly ash contains a mixture of amorphous and crystalline phases . As the ratio of fly ash in the geopolymer increases, it is observed that the relevant bands are more prominent and are present 30s to 25 minutes after mixing, unlike in the cement with less fly ash, suggesting a continuous dissolution of the amorphous phase in the geopolymer powder with more fly ash. On the other hand, the increasing calcium content with increasing BF slag/ FA ratio may also explain why the bands observed shift closer to those classically associated with GICs.

For the cements derived from Kaolin geopolymer (100%), on mixing with both PAA and aqueous tartaric acid (Figure 5.2.6), the prominent bands were identified at 1636 cm^{-1}, 1375 cm^{-1}, 1095 cm^{-1}, 1028 cm^{-1}, 1010 cm^{-1} and 909 cm^{-1}. On mixing with only PAA (Figure 5.2.12-B & D), the prominent bands were identified at 1645 cm^{-1}, 1369 cm^{-1}, 1095 cm^{-1},

1028 cm^{-1}, 1004 cm^{-1} and 909 cm^{-1} while on mixing with only aqueous tartaric acid (Figure 5.2.12-A & C), prominent bands were identified at 1634 cm^{-1}, 1373 cm^{-1}, 1025 cm^{-1}, 1000 cm^{-1} and 909 cm^{-1}.

For the cements derived from Kaolin and fly ash geopolymer (80:20), on mixing with both PAA and aqueous tartaric acid (Figure 5.2.7), the prominent bands were identified at 1625 cm^{-1}, 1371 cm^{-1}, 1095 cm^{-1}, 1028 cm^{-1}, 1006 cm^{-1} and 909 cm^{-1}. On mixing with only PAA (Figure 5.2.13-B & D), the prominent bands were identified at 1632 cm^{-1}, 1558 cm^{-1}, 1455 cm^{-1}, 1401 cm^{-1}, 1028 cm^{-1} and 1006 cm^{-1}, while on mixing with only aqueous tartaric acid (Figure 5.2.13-A & C), prominent bands were identified at 1632 cm^{-1}, 1382 cm^{-1}, 1025 cm^{-1}, 1000 cm^{-1} and 909 cm^{-1}.

There was little difference in the setting characteristics of the two Kaolin-based geopolymer cements (100% and 80:20). Wilson [105] and Crisp *et al.* [106] reported that naturally occurring silicate materials could react with PAA to form cements. Among all the materials selected for further evaluation, the powders of the Kaolin-based materials comprised the highest aluminosilicate ratios but lowest CaO content, similar to natural silicate materials evaluated by Wilson and co-workers [105,106]. This, coupled with the presence of an amorphous phase in fly ash [160-162] and the fact that geopolymers do not form any new crystalline phases following alkaline-activation [148,163,164], may provide a plausible explanation as to the setting characteristics of these materials. Further, the role of PAA as a dominant reactant is reinforced by the visibility of more symmetric and asymmetric bands with PAA than tartaric acid as well as prominence of the band associated with the glass powder and diminishing of the same for reactions with tartaric acid and PAA, respectively.

Although not all the identified bands were typical of those expected in GICs, the resemblance suggests that these materials also set in a similar fashion to GICs, with polyacrylates and tartrates as the major reaction products. Moreover, the low calcium content may be quickly depleted leading to formation and observation of bands at 1600 cm^{-1} typically associated with aluminium salts sooner than would be expected for GICs. Nonetheless, additional research is needed to verify these findings.

It is particularly worthwhile to consider the fact that geopolymers are already inorganic polymers [145] the exact description for which 'ionomers' are christened [105,106]. Seemingly, the findings discussed above suggest that the 3-dimensional aluminosilicate geopolymer framework is capable of participating in an acid-base reaction to form new salts. The similarity to a charge balanced aluminosilicate glass is not lost, and for the Kaolin-based geopolymers which had very low calcium content, this was highly likely achieved by Na^+ from the sodium silicate activating solution to maintain the basicity of the powders.

6.4 Phase III: Evaluation of experimental cements' properties and cost assessment

6.4.1 Mixing and setting time of experimental dental cements

The mixing and setting time of the cements was found to be reasonable for dental applications. The mixing time ranged between 30s and 90s while the setting time ranged between 135s and 480s (Table 5.3.1). It is recommended that a dental cement should set almost immediately after placement [30]. This enables adequate time for manipulation of the material while also ensuring that the patient not only spends a reasonable time on the dental chair without tiring but is also discharged with a hardened restoration to avoid fracture.

The mixing and setting times of the experimental cements were similar to that of glass ionomer cements (<10min) but markedly less than calcium silicate cements such as MTA (2 – 4hr). This may be explained by the fact that while calcium silicate cements are hydraulic in nature and set through a hydration reaction that takes hours [33,165,170,192,193], glass ionomer cements set through an acid-base reaction that progresses rapidly through dissolution, gelation and hardening on exposure of the glass powder to the polycarboxylic acids [92,96]. As visualized by FTIR, the setting reaction of these cements suggest an acid-base reaction similar to GICs and characterized by production of carboxylates and tartarates [100-102]; therefore, this may provide a plausible explanation for the hastened setting reaction.

A similar finding was reported by Lovschall *et al.* [171] who patented an accelerated calcium silicate cement for restorative applications. They reported that addition of superplasticizers resulted in a faster setting time and a dough-like consistency suitable for restorative applications like GICs.

Although it has been shown that the setting time of accelerated calcium silicate cements such as Biodentine® has been shortened by addition of accelerators such as 10% $CaCl_2$ [21,22,167,181,182], such additives were not incorporated in the experimental cements under investigation. This observation further suggests that their setting reaction was hastened in an acid-base reaction and not a hydration reaction.

The influence of the particle size on the setting time of dental cements has also been shown. It is expected that smaller particles would be more reactive hence the recommendation of an ideal average particle size of 45μm [92]. Moreover, Ha *et al.* [175] have suggested that D90

is the greatest determinant in the setting time of calcium silicate and Portland cements. However, in this study, there was no correlation between particle size and setting time of the experimental cements (Figures 5.3.2, 5.3.4 and 5.3.6). There was a moderate positive and strong positive correlation between D10 and the type of material, respectively, to cement mixing time (Figure 5.3.1). Nonetheless, the novelty of this experiment limits reference to other studies in seeking an explanation for this finding thus necessitating further studies on the same.

6.4.2 Compressive strength of experimental dental cements

Cements based on clinker and Kaolin geopolymer were selected for further evaluation of their properties. Although the Kaolin-based cements were stable in distilled water, the clinker-derived cements became soft and rubbery while those based on BF slag/ fly ash disintegrated. On this basis the first two were selected for evaluation of compressive strength under 100% humidity. Furthermore, clinker with and without gypsum were selected for comparison to elucidate any observable role of gypsum in the experimental cements.

The compressive strength of the experimental cements was much lower than that of both MTA and GIC. Wilson [105] and Crisp et al. [106] reported that while naturally occurring aluminosilicates were capable of forming cements on mixing with polycarboxylic acids, the resultant cements exhibited low compressive strength of 30MPa or less. This is similar to what was observed in this study and may be explained by the fact that glasses for ionomer cements are specially formulated with ideal ratios of oxides and fluorides to optimize the acid-base reaction and resultant cement properties [92,105]. Conversely, this reaction would be

difficult to control and optimize in naturally occurring aluminosilicates. For example, for optimum properties in earlier GICs, percentage of $SiO_2:Al_2O_3:CaF_2$ was 21:16.6:34.2 [89]. This may be varied to increase basicity and translucency or opacity but generally, Nicholson [92] states that this general formula is ideal for optimum setting and compressive strength higher than 200MPa. The importance of the Si: Al and Ca: Al ratios for optimal glass dissolution and development of compressive strength has also been shown by Hill and co-workers [97,108,109,116].

Nevertheless, it is noteworthy that the strength of the experimental cements increased on aging, similar to the behavior of GICs, and that this difference was statistically significant among the various time points. This may explicate the finding that setting behaviour of these cements was also similar to GICs, characterized by dissolution, gelation and hardening leading to formation of polyacrylates and tartrates [100-102,104]. This maturation of GICs is responsible for the increase in strength with time as the larger Al^{3+} react with carboxylic end groups of poly (acrylic acid) in a delayed reaction [92,96,98,99]. Observations by FTIR (Section 5.2.3, Figures 5.2.2 to 5.2.16) suggest that this was the setting mechanism of the cements.

At 1d and 3d, some of the cements derived from clinker were not completely 'set', subsequently difficult to crush the samples to assess compressive strength; instead they seemed to behave in a rubbery fashion, compressing rather than breaking. It is difficult to explain why these cements behaved in this manner. It is possible that the crystalline content of these powders limited the setting reaction which seemed to be through glass dissolution. As such, the reaction was slower and by the time the samples were tested, they had not

developed adequate cross-linking of the Ca^{2+} and Al^{3+} with the carboxylic groups of the acid to sustain compressive forces. This may also be an explanation as to why these cements demonstrated water sorption.

Perhaps, better results may have been observed had these cements been given adequate time to complete the setting reaction before exposure to moisture. In fact, after 28d under 100% humidity, the highest compressive strength was observed in clinker-based cements. This further suggests that these cements continued to mature with time and that protection from moisture during the initial phases of their setting reaction was crucial to development of strength. This is also characteristic of glass ionomer cements which should be protected from moisture within the first few hours for optimal gelation and hardening [89,100].

Kaolin geopolymer cements contained the highest amount of aluminosilicates and lowest CaO content but were more stable in distilled water than the other cements. Nonetheless, they demonstrated the lowest strength values. This may be explained by the fact that these geopolymers did not contain an actual glass but an alkaline-activate aluminosilicate. A proper glass, designed and synthesized from Kaolin may have performed better in terms of stability and compressive strength, attributed to the role of the glass in the setting reaction and the interaction with the PAA and tartaric acid [92,105].

6.4.3 Fluoride ion releasing profile of experimental dental cements

The results of the fluoride ion release characteristics of the cements suggest a diffusion controlled process as shown by the linear relationship to square root of time rather than to time (Section 5.3.3, Figures 5.3.21 to 5.3.24). A linear relationship to time would suggest a

dissolution controlled process. Moreover, the linear correlation was further evidenced by $R^2 > 0.9$ while the increasing cumulative behavior suggested a sustained release over the period of study. These findings are similar to the behavior of glass ionomer cements as reported by Luo *et al.* [124].

However, the low intercept values suggest a lack of 'initial burst' of fluoride ion release. As shown by Hill *et al.* [125], this phenomenon is characteristic of glasses that contain monovalent Na^+, which was minimal to nil in these materials. Further, the fluoride ion release profile also suggests that it was primarily dependent on the quantity of the fluoride in the materials rather than the type of media and the pH.

As discussed in Section 6.3.1, the clinker-based cements softened to a rubbery consistency while the FA/ slag-based geopolymers disintegrated in aqueous media. However, the Kaolin-based cements remained stable. Therefore, only the clinker-based and Kaolin-based cements were evaluated for fluoride ion release with promising findings. Overall, the fluoride ion release behavior of these cements further reinforce their similar tendency towards glass ionomer cements.

6.4.4 Cost assessment of experimental dental cements

Excluding the cost of initial investments, which also covers that of PAA and tartaric acid, the findings from the study suggest that the cost of local production of experimental dental cements are potentially lower than cost of importing market brands.

However, because the production costs of the commercial materials were unknown, this must be interpreted with caution and further studies detailing an itemized budget would be more conclusive. Nonetheless, the local availability of raw materials as well as their low cost presents an avenue for a cost-effective collaboration with manufacturers, who in addition, have already made initial investment in form of equipment and laboratory testing facilities.

6.5 Scope, limitations and assumptions of the study

- The study was designed to comprise three phases to address the specific objectives. The original intention was that the second and third phases would majorly utilize white cement clinker produced in Kenya. Regrettably, none of the companies from which the materials were sourced were producing white clinker at the time of the study hence restricting the project to gray clinker.

- Only kaolin was available locally as a potential tooth-coloured material.

- Obtaining permission to source the materials as well as to utilize research facilities in some of the laboratories outside the University of Nairobi resulted in delays in time as well as restrictions to further processing of the materials. Specifically, obtaining a glass from kaolin for further assessment required additional access to these facilities yet permission was not obtained in time.

- Elemental analysis by GFAAS was limited to only those which could be conducted at our facilities while EDXRF quantified the percentage composition of all major compounds in the materials. Therefore, findings from EDXRF were considered to be more conclusive.

- Development of biomaterials is an expensive, long-term exercise thus limited funding as well as time restricted the scope of the study.

CHAPTER SEVEN

7. CONCLUSION AND RECOMMENDATIONS

7.1 Conclusion

The aim of this study was to develop a prototype for an ionomer-type restorative dental cement in Kenya. PC clinker and aluminosilicate materials for production of PC clinker were collected from three PC and one ceramic manufacturing companies in Kenya and evaluated in a laboratory-based study in three phases. In the first phase, the composition and particle size of the PC clinker and geopolymers synthesized by alkaline-activation of the aluminosilicates for clinker production, in comparison to MTA, was evaluated. In the second phase, an ionomer-type experimental dental cement was formulated by mixing PC clinker or geopolymer powders with CaF_2, freeze-dried PAA and aqueous tartaric acid following which the cements' setting characteristics were described. In the third phase, the experimental cements' initial setting time, mechanical properties and fluoride ion releasing profile was evaluated, and a costing assessment conducted. The conclusions from the study are presented in this chapter.

7.1.1 Phase I: Evaluation of Kenyan Portland cement and raw materials for Portland cement production

Regarding the composition, the following conclusions are made:

- Phase identification by XRD showed that PC and MTA comprised primarily of dicalcium silicate and tricalcium silicate. On the other hand, the geopolymers comprised mainly of aluminosilicates, specifically quartz and mullite, as well as calcite.

- The major compounds in the three groups of materials, as determined by EDXRF, were CaO (PC = 59.50%wt, sd 7.41, MTA = 46.07%wt, sd 10.24, AS = 18.35%wt, sd 17.85), SiO_2 (PC = 25.65%wt, sd 5.68, MTA = 19.02%wt, sd 0.91, AS = 58.10%wt, sd 13.65) and Al_2O_3 (PC = 5.49%wt, sd 0.491, MTA = 2.65%wt, sd 1.07, AS = 15.31%wt, sd 6.25). Bi was present only in MTA (24.72%wt, sd 11.92).

- The major element in the three groups of materials, as determined by GFAAS, was Ca (PC = 51623.00μg/g, sd 5182.00, MTA = 77083.00 μg/g, sd 4612.00, AS = 16328.00μg/g, sd 18110.00).

- Only fly ash contained fluoride, as determined by FISE (43.33μg/g, sd 5.77).

- Although none of the materials contained detectable As levels, Pb was detected in both brands of MTA and two brands of clinker by GFAAS, and in one brand of MTA by EDXRF. Using GFAAS, only Bamburi clinker was found to contain Pb levels beyond the ASTM recommendation of 2mg/kg (3.57μg/g, sd 0.00).

- There was no major significant difference in the mean composition of Kenyan Portland cement and ProRoot MTA and MTA Cem except the presence of Bi in MTA and its absence in Portland cement, as determined by EDXRF (F-statistic=44.29, df=2, adjusted p<0.0001, difference=2.47, 95% CI 16.30, 33.14%wt). Likewise, the mean Pb content in MTA was statistically significantly different from PC (F-statistic=164.40, df=2, adjusted p=0.000, difference=1.74, 95% CI 1.43, 2.05%wt).

- The difference in mean content of alumina and silica was statistically different among the three groups of materials, as determined by EDXRF: (F-statistic=6.98, df=2, unadjusted p<0.01, adjusted p≤0.04) and (F-statistic=14.33, df=2, unadjusted p<0.001, adjusted p≤0.004), respectively.

- Similarly, the aluminosilicates contained neither Bi nor Pb hence statistically significantly different from MTA: (F-statistic=44.29, df=2, adjusted p<0.0001, difference=-2.47, 95% CI -31.87, -17.57%wt) and (F-statistic=164.4, df=2, adjusted p=0.000, difference=-1.75, 95% CI -2.01, -1.48%wt), respectively.

Regarding the particle size, it is concluded that:

- After sieving through a 120µm mesh sieve, mean D50 for PC was 12.46µm, sd 3.18, for MTA was 7.23µm, sd 3.43 and for AS was 12.74µm, sd 3.79.

- There was no significant difference in the mean particle size distribution of the various groups of materials, based on the D10, D50 and D90: (F-statistic (before sieving) = 1.29, 2.38, 0.93, df=2, unadjusted p>0.05) and F-statistic (after sieving) = 1.46, 1.87, 0.08, df=2, unadjusted p>0.05).

- Sieving was effective in controlling the mean particle size distribution of the materials.

7.1.2 Phase II: Formulation of experimental dental cements from Portland cement clinker or geopolymers

Regarding the formulation of the dental cements, the following conclusions are made:

- Addition of 0.1 – 0.2gm of poly (acrylic acid) and 0.15 – 0.25mL of aqueous tartaric acid to Portland cement clinker (0.3 – 0.4gm) or geopolymers (0.7 – 1.0gm) in pre-determined ratios resulted in a cement paste which set in <8 minutes.

- Addition of CaF_2 (0.2gm) to the clinker-derived cements improved the consistency of the mixture from grainy to a paste.

- Exposure to moisture by immersion in distilled water resulted in disintegration of all the geopolymer cements except those based on Kaolin. The cements derived from clinker softened and became rubbery.

Regarding the setting characteristics of the cements, the following conclusion is made:

- Addition of poly (acrylic acid) and aqueous tartaric acid to Portland cement clinker and geopolymers resulted in a setting reaction similar to that of glass ionomer cements, characterized by formation of acrylates and tartrates identifiable by FTIR bands associated with C-O asymmetric and C-O symmetric stretches.

7.1.3 Phase III: Evaluation of experimental cements' properties and economic assessment

Regarding the cement properties, the following conclusions are made:

- The mixing and initial setting times of the experimental cements ranged between 30s – 60s and 90s – 480s, respectively. These times were found to be satisfactory and reasonable (MT = 30s – 60s and ST <10min) for dental cement applications.

- On average, the mean compressive strength of all cements increased over time (1d = 0.41MPa, sd 0.08, 3d = 1.69MPa, sd 0.49, 7d = 4.31, sd 0.66, 28d = 5.90MPa, sd 1.06), similar to the behaviour of glass ionomer cements, with a statistically significant difference between means at different time points (F-statistic = 82.39, df=3, unadjusted p<0.0001, adjusted=0.000).

- The cements exhibited low mean compressive strength of less than 15MPa after 28d (EAPC, 7d – 11.10MPa, sd 2.00). Some of the clinker-derived cements did not achieve a complete set during the earlier time points of 1d (ARM, Bamburi and EAPC+5%

Gypsum) and 3d (EAPC+5% Gypsum) hence could not record compressive strength, instead behaving like compressible rubbers.

- Although cements based on Kaolin recorded lowest mean strength values, their behavior was most consistent between 1d and 28d, with all samples breaking. Cements based on Kaolin/FA recorded a statistically significant difference between means at all the time points within the group (F-statistic=76.64, df=3, unadjusted p<0.0001, adjusted p=0.000).

- The cements containing fly ash demonstrated fluoride ion release, specifically, Kaolin/FA cement demonstrated the highest fluoride ion release (1mmol/L at 28d). Moreover, addition of CaF_2 to clinker-based and Kaolin-based cements also resulted in fluoride ion release.

- The fluoride ion release profile of the cements was a diffusion controlled process (R^2>0.9) dependent on the amount of fluoride in the cements rather than the elution medium or its pH. This behavior was found to be similar to that of glass ionomer cements.

Regarding the costing assessment, the following conclusion is made:

- Excluding the initial investments (approximately USD 10,000), the cost of local production of experimental dental cements are potentially lower than cost of importing market brands (Fuji IX – USD 9/gm, MTA Cem – USD 30/gm, ProRoot MTA – USD 50/gm) .

7.2 Recommendations

1. The similarity of Kenyan Portland cement and related materials to a commercial dental product (MTA), specifically the absence of toxic elements, make Portland cement a potentially affordable substitute.

2. Locally available aluminosilicate materials have demonstrated cement forming capabilities which should be explored further for use in low-cost dental restorations in ART procedures.

3. Specifically, the cements based on Kaolin have been identified as a hydrolytically stable prototype. Instead of alkaline-activation, a simple pure glass derived from Kaolin should be investigated further to yield a cement with better mechanical properties than what was recorded in the study.

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BUDGET

1. Development of Proposal

No.	Activity	Units	Unit cost (Kshs)	Total (Kshs)
1.	Travelling costs while conducting feasibility assessment	5	1,000	5,000
2.	Travelling costs to prospective labs where the project will be conducted	5	1,000	5,000
3.	Airtime consumed during development of the proposal (supervisors and suppliers)	10	100	1,000
4.	ISO standards 9917-1:2007 and 7405	2	13,500	27,000
5.	Typing, printing, photocopying and internet services	12	1,000	12,000
	Sub-total			**50,000**

2. Registration and tuition fees

No.	Item	Units	Unit cost (Kshs)	Total (Kshs)
1.	Fees (Year 1)	1	158,200	158,200
2.	Fees (Year 2)	1	141,200	141,200
3.	Fees (Year 3)	1	141,200	141,200
	Sub-total			**440,600**

3. Data collection

3.1 Phase I

No.	Item description	Units	Unit cost (Kshs)	Total (Kshs)
1.	Kenyan Portland cement (gray, 50kg bags)	10	1,000	10,000
2.	Kenyan Portland cement (white, 25kg bags)	10	1,000	10,000
3.	X-ray diffractor (Available KIRDI Labs)	1	-	-
4.	Laser diffractor (Available ICRAF)	1	-	-
5.	Inductively coupled plasma/ Optical emission spectroscope (Available ICRAF)	1	-	-
6.	Fluoride ion measurements at Laboratory of Government Chemist	20	500	10,000
7.	Arsenic and lead level determination at Laboratory of Government Chemist	20	1,000	20,000
8.	Specimen containers	100	100	10,000
9.	Travelling costs to various lab facilities	20	1,000	20,000
10.	Airtime and internet costs	10	1,000	10,000

No.		Units		Total (Kshs)
11.	Research assistants	2*3 months	10,000 (each, per month)	60,000
	Sub-total (phase I)			**150, 000**

3.2 Phase II

No.	Item	Units	Unit cost (Kshs)	Total (Kshs)
1.	Special formulation of white Portland cement (batch)	2	100,000	200,000
2.	Freeze-dried poly (acrylic acid)	2kg	10,000	20,000
3.	Deionized water	500lts	50	25,000
4.	X-ray diffractor (Available KIRDI Labs)	1	-	-
5.	Laser diffractor (Available ICRAF)	1	-	-
6.	Arsenic and lead level determination at Laboratory of Government Chemist	10	1,000	10,000
7.	Mechanical vibrator	1	150,000	150,000
8.	Micro sieves (25µm)	2	20,000	40,000
9.	Gilmore needle apparatus (Available School of Dental Sciences, University of Nairobi)	1	-	-
10.	Specimen containers	100	100	10,000
11.	Glass slabs and mixing spatulas	5	1,000	5,000
12.	Metal or Perspex moulds for specimen fabrication	10	1,500	15,000
13.	Weighing scales (Available Department of Chemistry, University of Nairobi)	2	-	-
14.	Weighing bottles	10	1,000	10,000
15.	Travelling costs to various lab facilities	20	1,000	20,000
16.	Airtime and internet costs	10	1,000	10,000
17.	Research assistants	2*3 months	10,000 (each, per month)	60,000
	Sub-total (phase II)			**575,000**

3.3 Phase III

No.	Item	Units	Unit cost (Kshs)	Total (Kshs)
1.	Mechanical testing at KEBS labs	100	1,000	100,000
2.	Inductively coupled plasma/ Optical emission spectroscope (Available ICRAF)	1	-	-
3.	Fluoride ion measurements at Laboratory of Government Chemist	20	500	10,000
4.	Cell culture studies	20	2,000	40,000
5.	Travelling costs to various lab facilities	20	1,000	20,000
6.	Airtime and internet costs	10	1,000	10,000

7.	Research assistants	2*3 months	10,000 (each, per month)	60,000
	Sub-total (phase III)			**240,000**

4. Report writing

| No.	Item	Units	Unit cost (Kshs)	Total (Kshs)
1.	Airtime and internet costs (monthly)	6	5,000	30,000
2.	Printing and photocopying (paper, ink and toner)	15	2,000	30,000
3.	Travelling costs (completion of pending work, meetings with supervisors)	10	1,000	10,000
	Sub-total			**70,000**

5. Dissemination of research findings

| No.	Item	Units	Unit cost (Kshs)	Total (Kshs)
1.	Preparation of presentations and manuscripts	6	2,500	15,000
2.	Conference attendance (travelling and conference registration)	3	50,000	150,000
3.	Journal publications	6	15,000	90,000
	Sub-total			**255,000**
	GRAND TOTAL			**1,780,600**

APPENDICES

Appendix A: GFAAS and FISE standard plots and comparative box plots

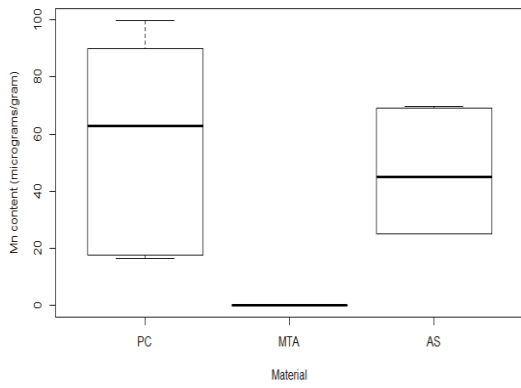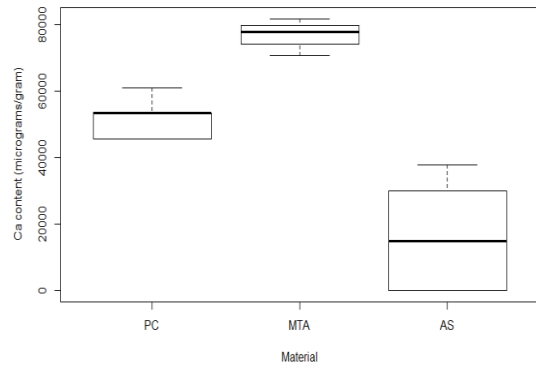### A1: Standard plots (µg/g)
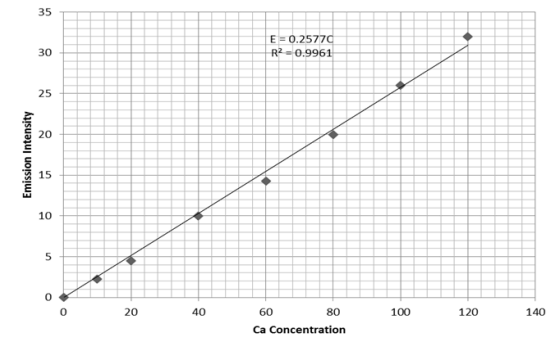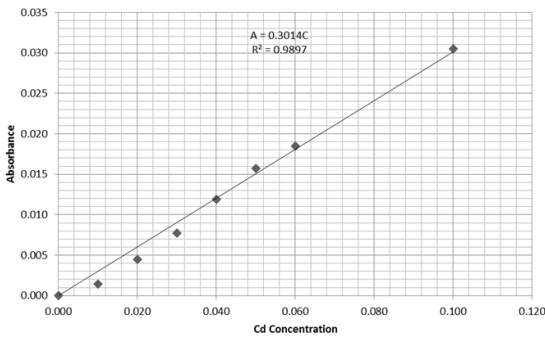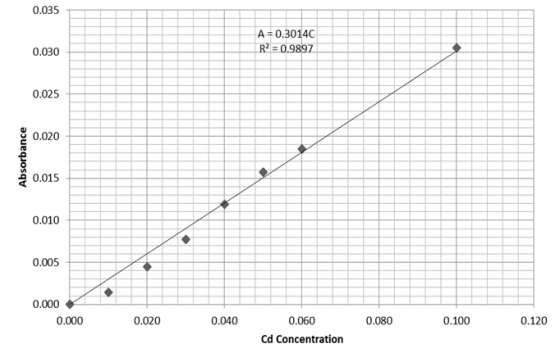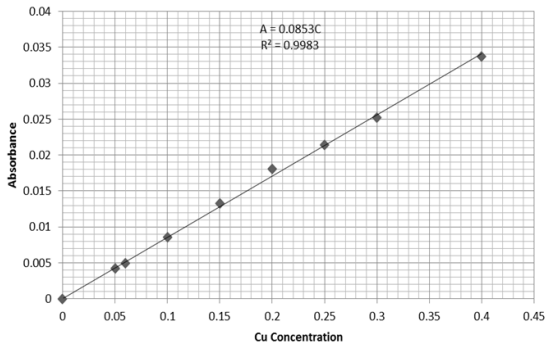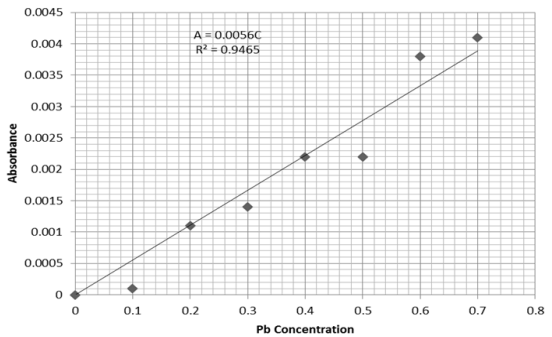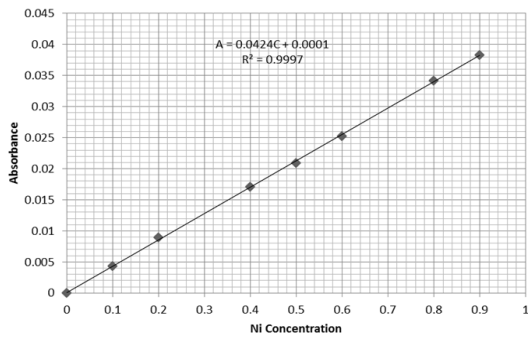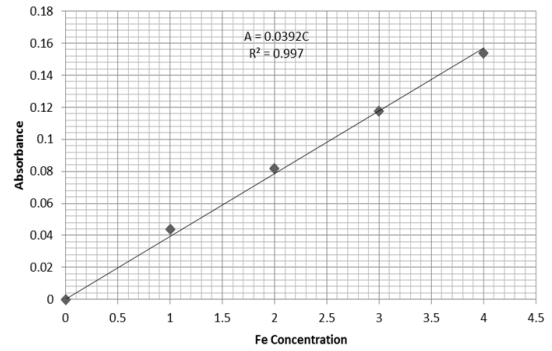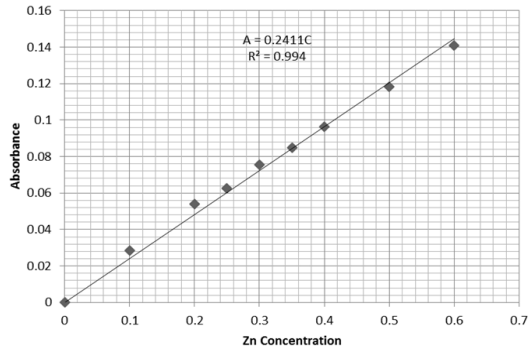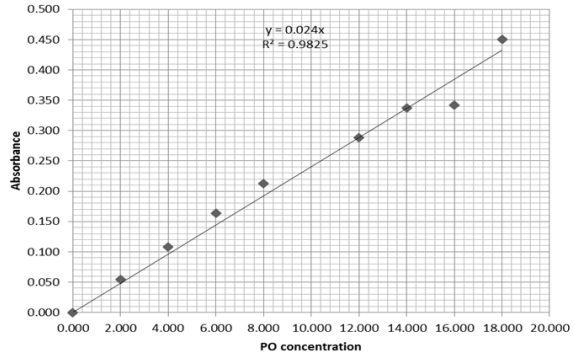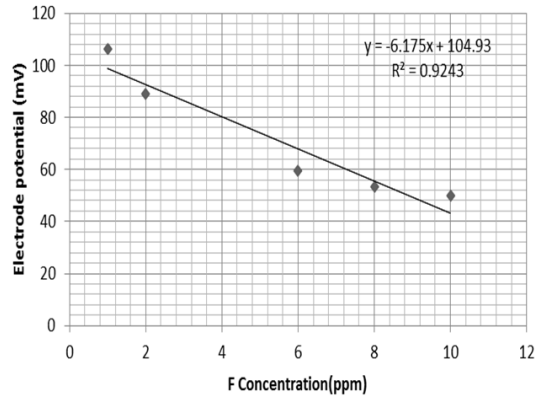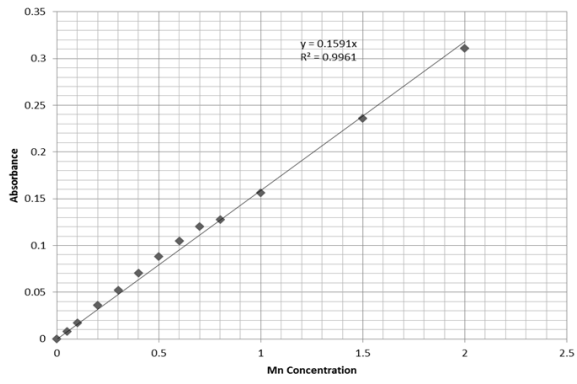
A2: Comparative box plots
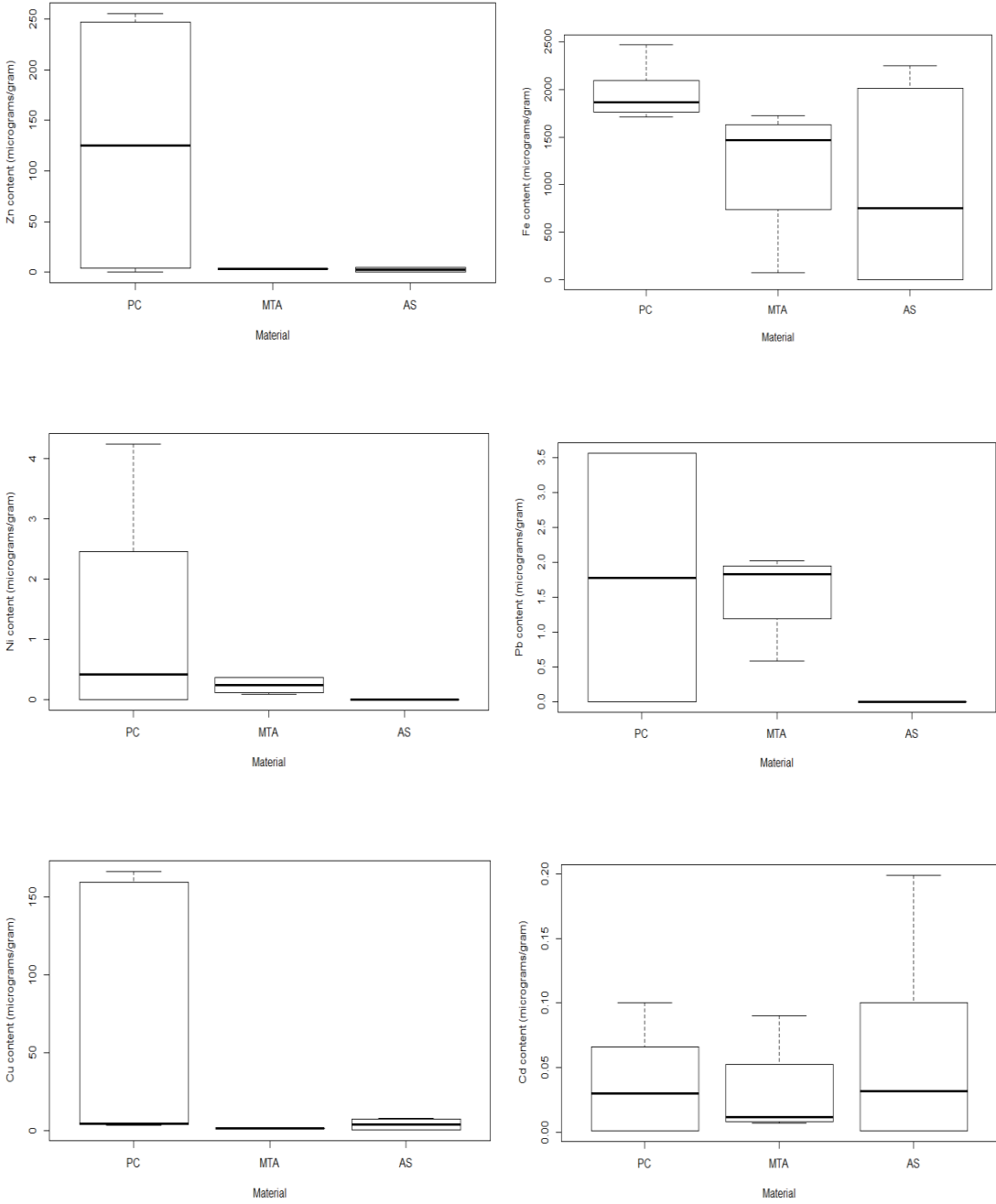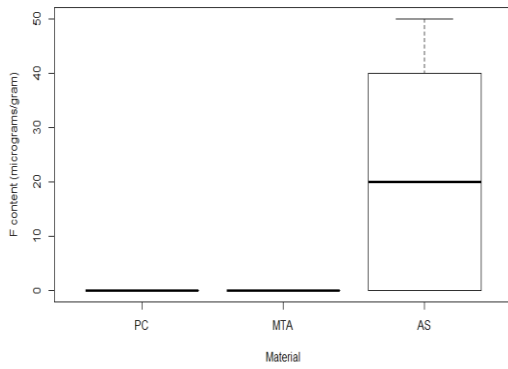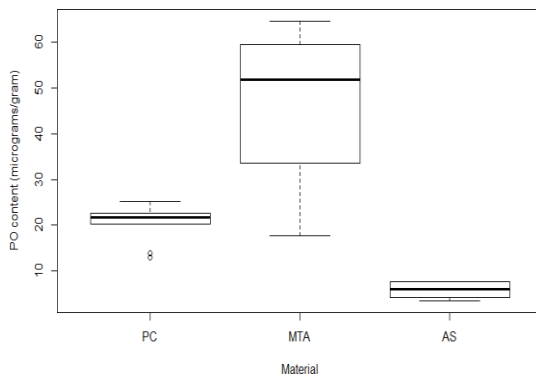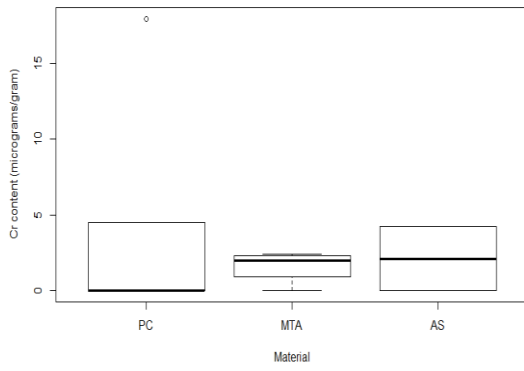
Appendix B: XRF Box plots
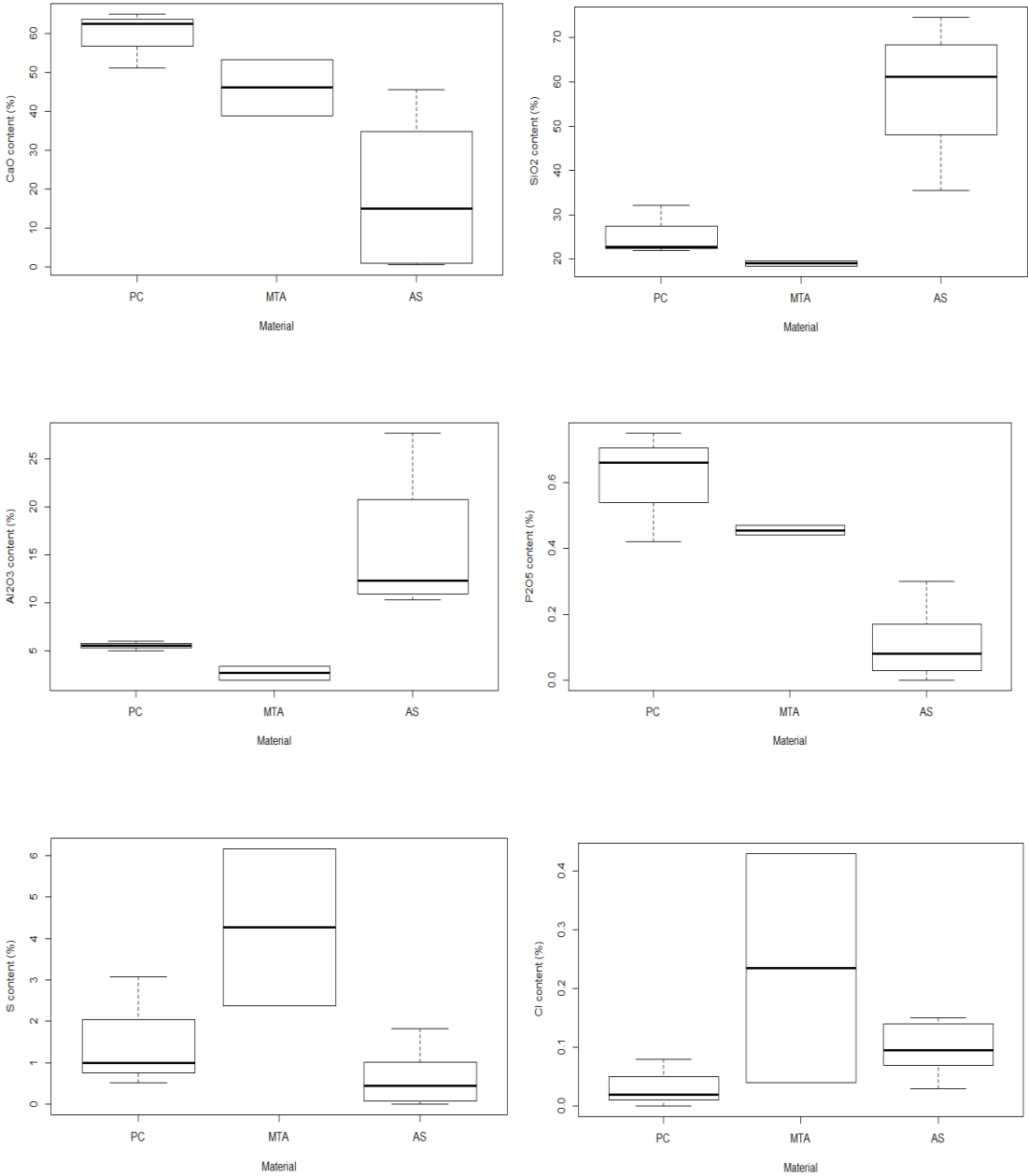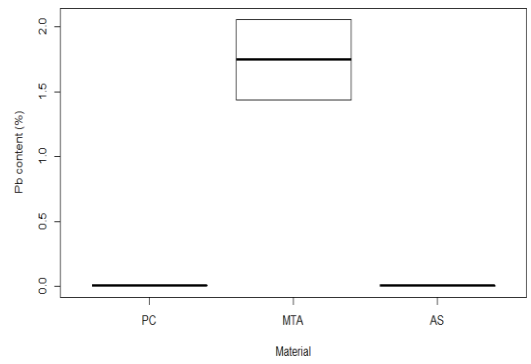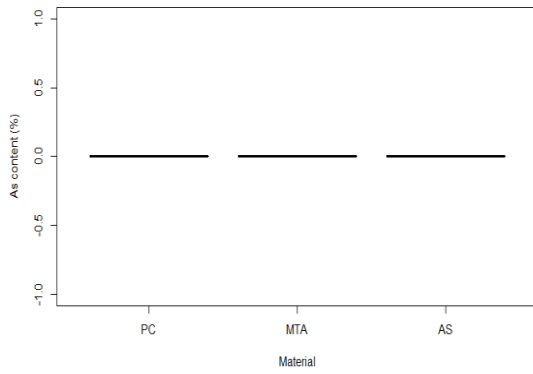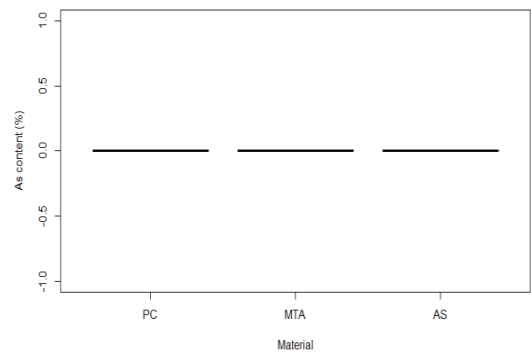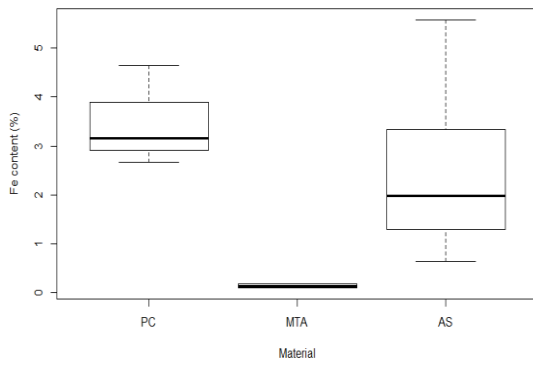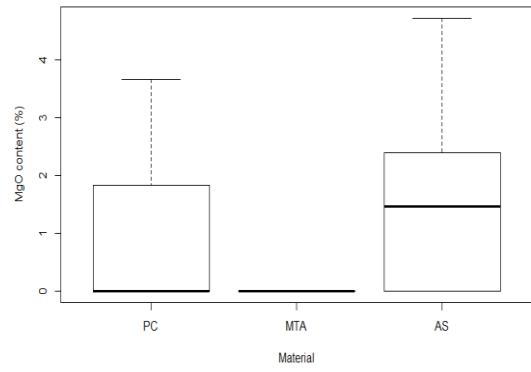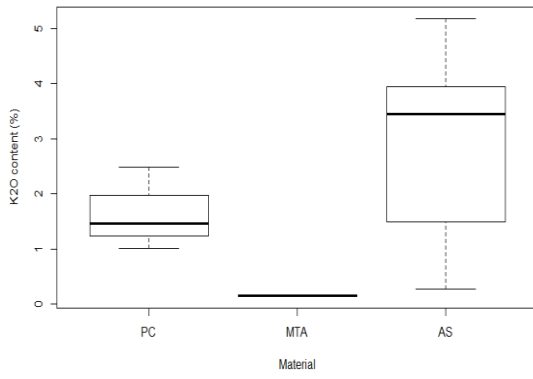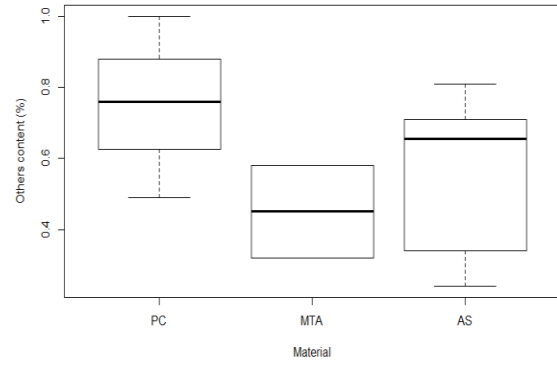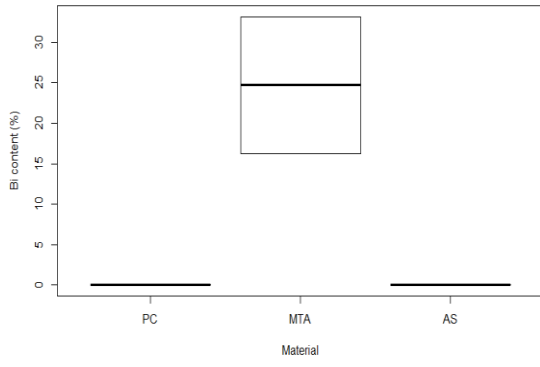
Appendix C: Particle size distribution histograms and box plots

C1: Particle size distribution histograms
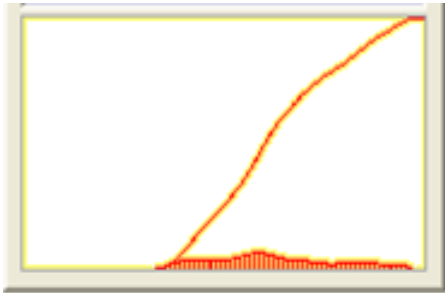
FA (not sieved)
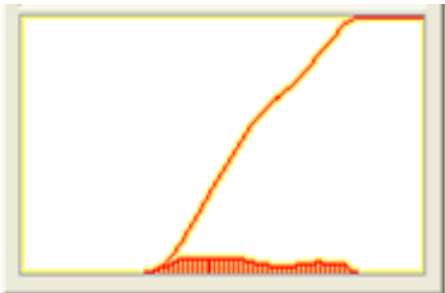
MTA Cem
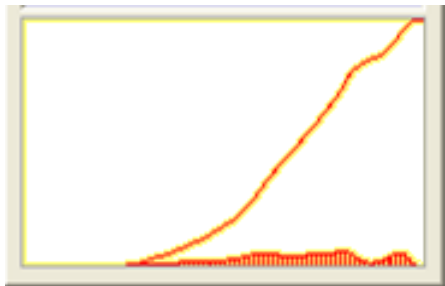
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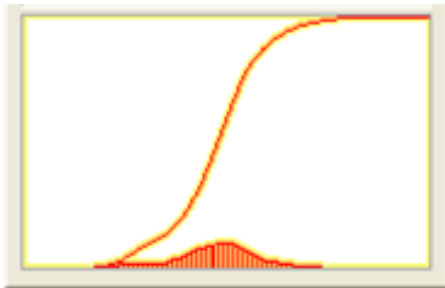
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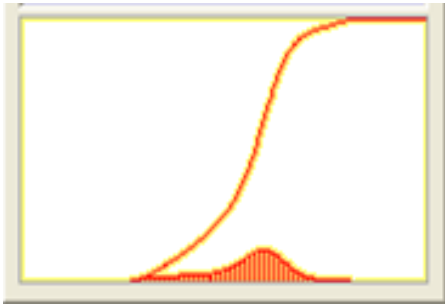
ARM clinker (not sieved)
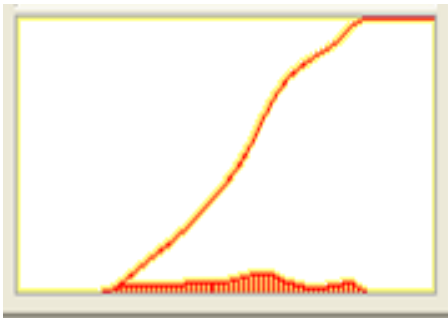
EAPC clinker (sieved)
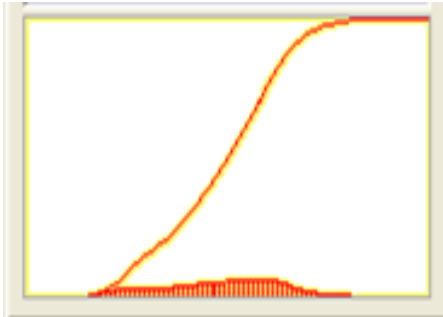
EAPC clinker + 5% Gypsum (sieved)
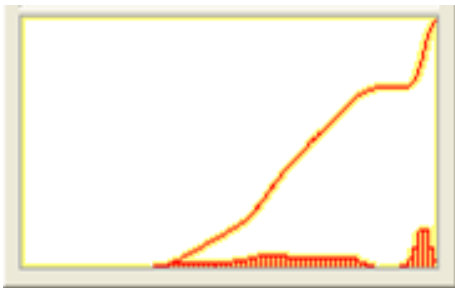
Slag (not sieved)
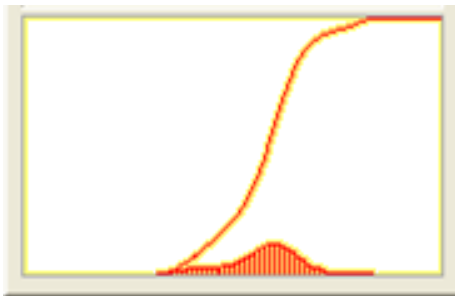
Slag (sieved)
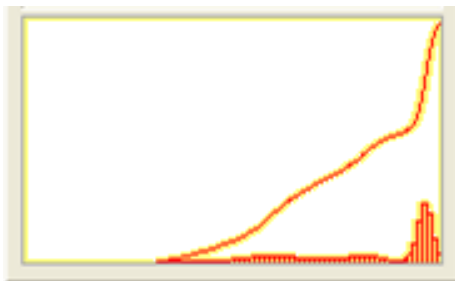
Bamburi (not sieved)
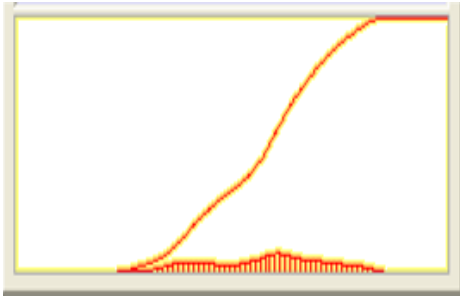
Activated slag100 (sieved)
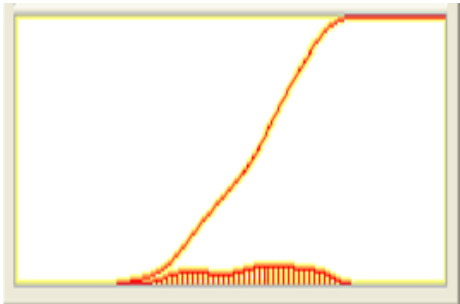
Activated slag80 (sieved)
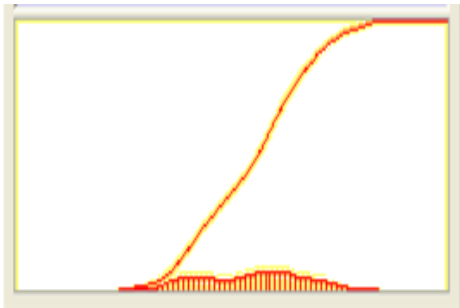
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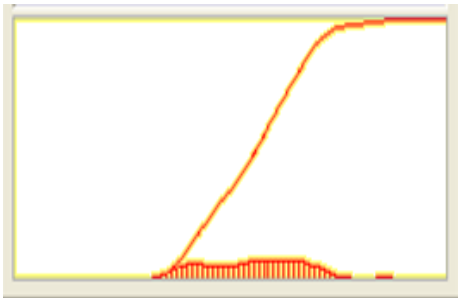
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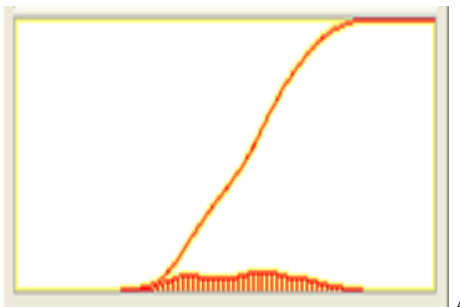
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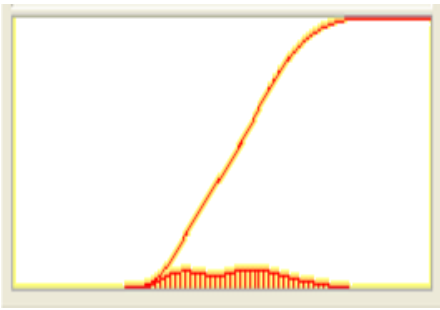
Activated FA100 (sieved)
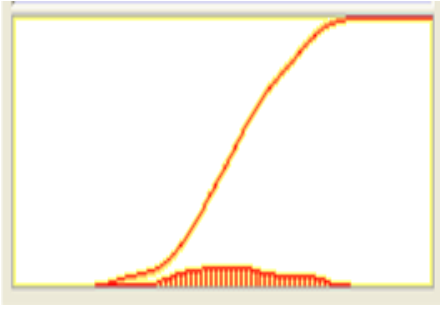
Activated Kaolin00 (sieved)
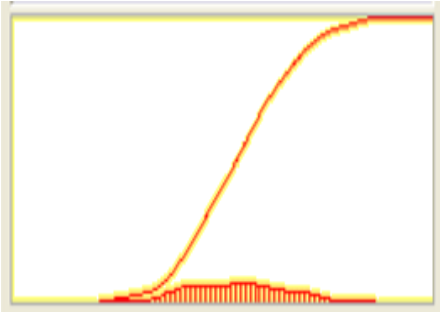
Activated Kaolin80 (sieved)
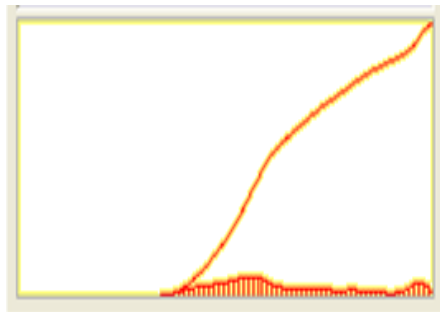
Kaolin (not sieved)

C2: Particle size distribution box plots

Not sieved
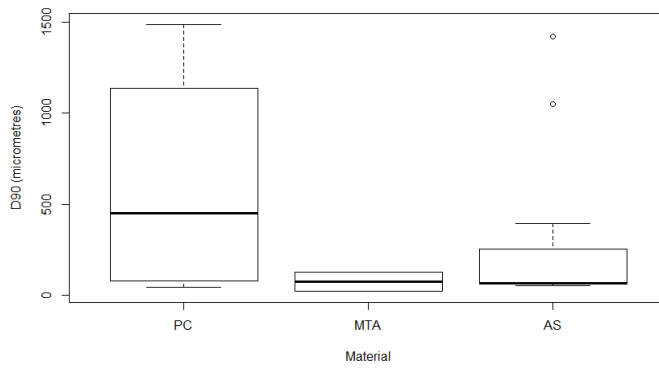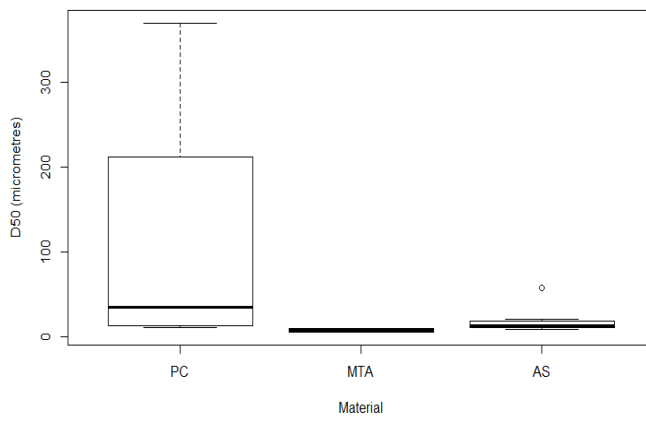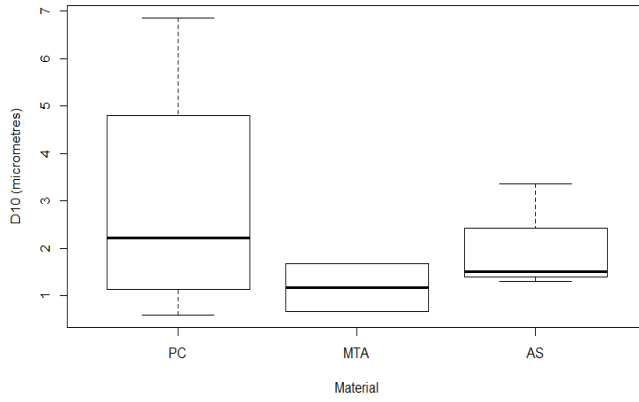
Sieved
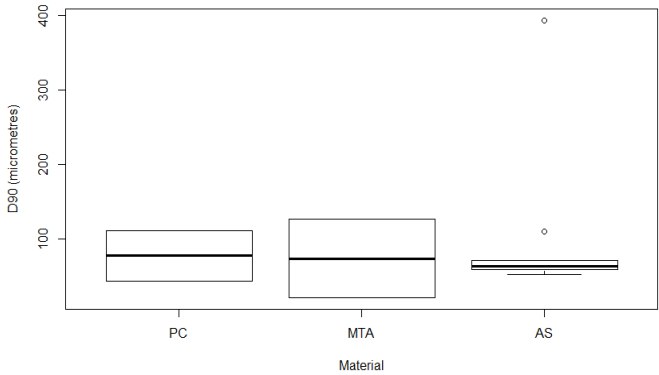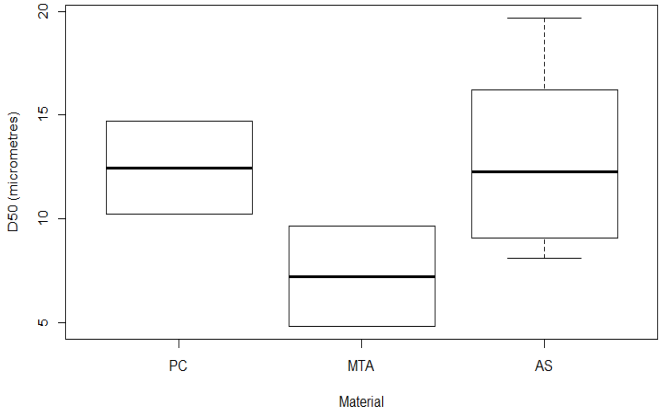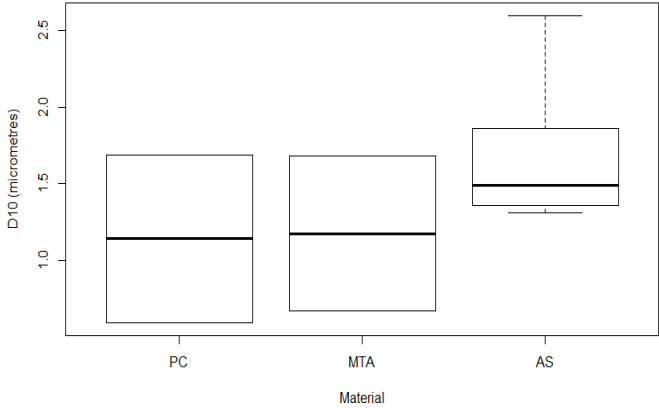
Appendix D: Work plan

Period \ Activity	Jun-Dec '15	Jan-May '16	Jun-Sep '16	Oct-Dec '16	Jan-Apr '17	May-Aug '17	Sep-Dec '17	Jan-Apr '18	May-Jun '18	Jul-Sep '18	Oct-Dec '18	Jan-Apr '19	May-Jul '19	Jul-Dec '19
Finalize feasibility assessment	■													
Finalize proposal development		■												
1. Defend proposal 2. Ethical approval 3. Register for PhD			■											
1. Data collection: Characterization of raw materials				■										
2. Data collection: Formulation/ production of clinker					■									
3. Data collection: Preparation of cements and evaluation of setting rheology						■								
4. Data collection: Evaluation of cement biocompatibility							■							
5. Data collection: Evaluation of cement mechanical and ion releasing properties								■	■					
Data analysis									■	■	■			
Completion of any pending work & write-up											■	■		
Submission & defense													■	
Corrections & graduation														■

Appendix E: Source of funding

E1: Letter of Award – Consortium for Advanced Research Training in Africa (CARTA)

Consortium for Advanced Research Training in Africa
Building a vibrant multidisciplinary African Academy thát is able to lead world class research that makes positive impact on Population and Public Health.
Email: carta@aphrc.org Website: www.cartafrica.org

December 15, 2015

Dear Applicant,

The Consortium for Advanced Research Training in Africa (CARTA) has finalized the selection of candidates for its 2015/2016 Doctoral Fellowships. The CARTA Secretariat is very pleased to inform you that you have been selected as one of the 25 recipients of its Fellowship award. Congratulations on being selected for this highly competitive award!

Your home institution is a member of the CARTA consortium. Our main goal is to produce the next generation of academic and research leaders. In addition to an outstanding international faculty, we also provide an internationally-benchmarked PhD level program to ensure that you will graduate with a world-class doctorate.

A key element of the CARTA program is our compulsory series of four residential Joint Advanced Seminars (JAS). In these seminars, you will be exposed to key theories and concepts, seminal readings, and research methods of disciplines relevant to public and population health. Prior to attending the first JAS, you will be required to undertake Pre-JAS Part 2 Tasks. The details about the tasks will be sent to you in due course. The first JAS will be held from February 29, 2016, in Nairobi. The second JAS will be held at University of the Witwatersrand, South Africa in November 2016, the third will be held at University of Ibadan, Nigeria in mid-2018, and the fourth in Nairobi in early 2019. The cost of your participation in these seminars will be covered by the CARTA program as part of your award.

During the tenure of your fellowship, CARTA will be paid a modest monthly stipend. Further, CARTA will provide small grants for research activities, a laptop loaded with relevant software, and funds for travel to selected scientific conferences. Fellows studying outside their home country will receive a supplementary stipend, one round trip ticket each year, tuition fees, and health insurance cover. A detailed fellowship agreement that clarifies disbursement plans, milestones, timelines, and reporting requirements will be shared with you in due course.

Please complete the **Acceptance Form** and return to the Program Manager (carta@aphrc.org) as soon as possible but not later than **18th December 2015.** We recommend that you keep a copy for your records.

Once again, congratulations on your achievement and we wish you every success as you embark on your doctoral studies.

Sincerely,

Alex Ezeh
CARTA Director

African Population and Health Research Center
That the people of Africa enjoy the highest possible quality of life through policies and practices informed by robust scientific evidence

APHRC Campus, 2nd floor, Manga Close off Kirawa Rd P.O. Box 10787 – 00100 GPO, Nairobi, Kenya
Tel: +254-20-400-1000. Cell: +254-722-205933/720-098388/733-410102. Fax: +254-20-400-1101
Email: info@aphrc.org Website: www.aphrc.org

FELLOWSHIP ACCEPTANCE FORM

I, **OLIVIA MILLICENT AWINO OSIRO** (name, please print) accept the offer of the CARTA Fellowship award. I understand that the annual renewal of this award is based on my satisfactory academic progress, continued stay as a full-time staff at my home university, and attendance and completion of JAS assignments as well as the recommendation of my supervisor and the availability of funds at CARTA.

_____

Awardee Signature

18|12|2015

Date

E2: Letters of Award – DAAD

DAAD Deutscher Akademischer Austauschdienst
German Academic Exchange Service

Letter of Award

Name:	Dr. Olivia Millicent Awino Osiro
Date of birth:	18/01/82
Personal ref. no.:	91636519
Funding programme/-ID:	In-Country/In-Region Programme CARTA, 2016 (57300485)
Nationality:	Kenya

You are being granted a DAAD-Scholarship for the PhD programme at CARTA. The scholarship includes the following benefits:

Start of funding	End of funding	Destination country	Institution
01/09/16	31/08/17	Kenya	CARTA - University of Nairobi, Kenya

Scholarship and supplementary benefits

Benefit	Destination country	Amount	Payment	From	To
Scholarship instalment	Kenya	1,700.00 EUR	01/09/16	01/09/16	30/09/16
Scholarship instalment	Kenya	1,700.00 EUR	01/03/17	01/03/17	31/03/17
Health insurance allowanc	Kenya	500.00 EUR	01/09/16	01/09/16	01/09/16
Research allowance	Kenya	920.00 EUR	01/09/16		

For months with a funding period of less than 23 days, the scholarship payment will be calculated on a daily basis and the exact number of funding days paid. The payments listed above are subject to possible changes.

The enclosed booklet „Ihr DAAD-Stipendium/Your DAAD-scholarship" is an integral and complimentary part of this Letter of Award.

Conditions and requirements
Please hand in the Admission Letter from the University of Nairobi.

Other comments
University registration and tuition fees = 2,500.00 Euro; Research and Academic Monitoring and all other Research costs (incl. additional costs for field work, lab facilities, books, thesis, travel cost etc.) = 4,080.00 Euro; Lump sum for student service(s) = 240.00 Euro; Total Fees: 6,820.00 Euro per year

The scholarship granted as part of the above funding programme is financed entirely from federal public funds.
This letter of award only becomes effective if you are admitted to the above university.

Bonn, 19/09/16

Secretary General of the German Academic Exchange Service

Personal ref. no.:	91636519
Section in charge:	Section ST32
Head of Section:	Cay Etzold
Person in charge:	Melanie Wolf
Telephone number:	+49 228 882-8861

DAAD

Deutscher Akademischer Austauschdienst
German Academic Exchange Service

Letter of Award

Name:	Dr. Olivia Millicent Awino Osiro
Date of birth:	18/01/82
Personal ref. no.:	91636519
Funding programme/-ID:	In-Country/In-Region Programme CARTA, 2016 (57300485)
Nationality:	Kenya

This Letter of Award confirms your DAAD-scholarship (PhD) extension.

Start of funding	End of funding	Destination country	Institution
01/09/17	31/08/18	Kenya	CARTA - University of Nairobi, Kenya

The scholarship includes the following benefits:

Scholarship and supplementary benefits

Benefit	Destination country	Amount	Payment	From	To
Scholarship instalment	Kenya	283.33 EUR	monthly	01/09/17	31/08/18
Health insurance allowance	Kenya	500.00 EUR	01/09/17	01/09/17	01/09/17
Research allowance	Kenya	920.00 EUR	01/09/17		

For months with a funding period of less than 23 days, the scholarship payment will be calculated on a daily basis and the exact number of funding days paid. The payments listed above are subject to possible changes.

The enclosed booklet „Ihr DAAD-Stipendium/Your DAAD-scholarship" is an integral and complimentary part of this Letter of Award and therefore legally binding.

Other comments
University registration and tuition fees = 2,500.00 Euro; Research and Academic Monitoring and all other Research costs (incl. additional costs for field work, lab facilities, books, thesis, travel cost etc.) = 4,080.00 Euro; Lump sum for student service(s) = 240.00 Euro; Total Fees: 6,820.00 Euro per year

The scholarship granted as part of the above funding programme is financed entirely from federal public funds.

Bonn, 28/07/17

Secretary General of the German Academic Exchange Service

Personal ref. no.:	91636519
Section in charge:	Section ST32
Head of Section:	Cay Etzold
Person in charge:	Melanie Wolf
Telephone number:	+49 228 882-8861

DAAD

Deutscher Akademischer Austauschdienst
German Academic Exchange Service

Letter of Award

Name:	Dr. Olivia Millicent Awino Osiro
Date of birth:	18/01/82
Personal ref. no.:	91636519
Funding programme/-ID:	Short Term Research Scholarship for In-Country/In Region Scholarship Holders, 2018 (57399477)
Nationality:	Kenya

You are being granted a DAAD Short Term Research Scholarship under the In-Country/In-Region Scholarship Programme.

Start of funding	End of funding	Destination country	Institution
01/03/18	30/04/18	Germany	Universität Jena

The scholarship includes the following benefits:

Scholarship and supplementary benefits

Benefit	Destination country	Amount	Payment	From	To
Scholarship instalment	Germany	1,000.00 EUR	monthly	01/03/18	30/04/18
Travel allowance	Germany	700.00 EUR	01/03/18		

For months with a funding period of less than 23 days, the scholarship payment will be calculated on a daily basis and the exact number of funding days paid. The payments listed above are subject to possible changes.

Insurance benefits

- Primary health insurance (fully comprehensive insurance)

  Unless you hear otherwise, you will be automatically registered for health insurance by the DAAD with Continentale for the duration of your scholarship. You are required to inform yourself about the conditions of your health insurance cover in Germany by reading chapter 1.5.1. „General information" and Point II in the brochure „Ihr DAAD-Stipendium/Your DAAD-scholarship".

- Insurance for accident and personal liability

The enclosed booklet „Ihr DAAD-Stipendium/Your DAAD-scholarship" is an integral and complimentary part of this Letter of Award and therefore legally binding.

Other comments
The scholarship cannot be extended

§ 34 of the Ordinance Governing Residence applies to this scholarship. According to this, the visa for academics and scientists and dependants (spouses or partners, if the marriage or civil partnership already existed upon arrival in Germany, and minor, unmarried children) accompanying

- 1 -

or subsequently joining them is not subject to the approval of the foreigners' authorities if the scientists are assigned a place by German scientific organisations or a German public body and in this connection are receiving a publicly funded scholarship in Germany.

The scholarship granted as part of the above funding programme is financed entirely from federal public funds.
This letter of award only becomes effective if you are admitted to the above university.

Bonn, 24/01/18

Secretary General of the German Academic Exchange Service

Personal ref. no.:   91636519
Section in charge: Section ST32
Head of Section: Cay Etzold
Person in charge: Melanie Wolf
Telephone number: +49 228 882-8861

E3: National Research Fund (2016/2017)

2.0 SIGNATURES

The student, supervisors, Graduate school/faculty and the Head of University (VC or DVC) must sign this application. It should bear official stamp of the institution.

Student's Signature: .... Date: 3 November 2016.

SUPERVISORS: (*This is to confirm that the student is under my supervision and will facilitate project timely implementation*)

i). Name: PROF. DAVID K. KARIUKI .... Signature ....

ii). Name: PROF. LOICE.W. GATHECE .... Signature ....

iii). Name: .... Signature ....

DIRECTOR GRADUATE STUDIES/SCHOOL: (*This is to certify that the said Student is currently fully registered in this University and His/her research work has been approved and/or is ongoing*).

Name: PROF LYDIA W. NJENGA .... Signature & Stamp ....

HEAD OF THIS UNIVERSITY:

Declares:

- That this University supports this application and will ensure the project is implemented as scheduled in the postgraduate programme if he/she receive the Grant;

- **This page to be endorsed by (*VC or DVCs or Principal in case of University Constituent Colleges*)**

Signature: .... Date: 8/11/2016

Title, Name, Official position:

............PROF LUCY W IRUNGU DEPUTY VICE CHANCELLOR (RPE)............

UNIVERSITY OF NAIROBI
DEPUTY VICE CHANCELLOR

Official stamp:

0 8 NOV 2016

RESEARCH PRODUCTION & EXTENSION
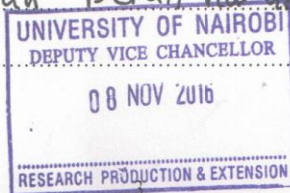
Appendix F: Publications and conference presentations

F1: Citable abstract presented at the 5th IADR (AMER) Regional Congress &

Exhibition, 26th to 28th September, 2017, Addis Ababa, Ethiopia.

Properties of clinker and alkali-activated aluminosilicates for experimental restorative cements

Olivia Osiro, David Kariuki, Loice Gathece

Journal of Dental Research; 96 (Spec Iss B): AMER. (2017) Available: www.iadr.org.

Aim: To evaluate the physical properties of Kenyan Portland cement clinker and alkali-activated aluminosilicates (geopolymers) with potential for use in developing an experimental restorative dental cement for atraumatic restorative treatment (ART).

Materials and methods: Clinker samples were obtained from three production companies in Kenya while geopolymers were synthesized through alkali activation of aluminosilicates used as raw materials for clinker production. Properties were compared to mineral trioxide aggregate (MTA). X-ray fluorescence and Graphite Furnace Atomic Absorption Spectroscopy were used for compositional and elemental analysis. Fluoride ion selective electrode was used for fluoride ion measurements. The setting time of experimental cements, prepared by mixing the clinker or synthetic geopolymers with poly (acrylic acid) and tartaric acid, was evaluated.

Results: Kenyan Portland cement clinker was found to have a similar composition and physical properties to MTA. Addition of poly (acrylic acid) and tartaric acid to the clinker or synthetic geopolymer yielded a cement mass with reasonable setting time.

Conclusions: In light of the imminent phase-down of dental amalgam, low- and middle-income countries can consider translational science in seeking affordable, alternative materials. These experimental cements may provide a viable solution to reduce the burden of dental caries in under-privileged settings through minimally invasive, low cost techniques such as ART. Further investigations of their properties are necessary.

F2: Citable abstract presented at 97th IADR General Session & Exhibition, 25th to 28th July, 2018, London, England.

Composition, Particle Size, Setting Time of Clinker and Geopolymer Cements

Olivia Osiro, David Kariuki, Loice Gathece

Journal of Dental Research; 97 (Spec Iss B): 0236. (2018) Available: www.iadr.org.

Aim: To evaluate composition, particle size and setting time of Portland cement clinker and alkali-activated aluminosilicates (geopolymers) for development of experimental restorative cements for atraumatic restorative treatment (ART).

Materials and methods: Clinker samples were obtained from three companies in Kenya while geopolymers were synthesized through alkali-activation of blast furnace slag, fly-ash, pumice and kaolin. Compositional analysis was by X-ray diffraction (XRD), X-ray fluorescence (XRF), Graphite furnace atomic-absorption spectroscopy (GFAAS) and F^- selective electrode while Laser diffraction was used for particle size analysis (LDPSA). Cements were prepared by mixing clinker or geopolymer with freeze-dried poly(acrylic-acid) and aqueous tartaric acid in pre-determined ratios; setting time (ST) was assessed using Gilmore needle apparatus. Commercial MTA and glass ionomer cements were controls. Analyses were conducted in triplicates and means reported.

Results: XRD and XRF showed similar spectra with characteristic $CaCO_3$, $2CaO.SiO_2$, $3CaO.SiO_2$ (XRD), SiO_2, CaO_2 (XRF) peaks in clinker, geopolymer and MTA. Bi_2O_3 was seen only in MTA. Low Pb levels were detected in one MTA (1.57µg/g, 0.66SD) and two clinkers (1.9µg/g, 1.6SD, 3.57µg/g, 0SD) but marked in pumice (79.14µg/g, 5.76SD). Fly-ash had marked levels of F^- (43.33µg/g, 5.77SD) while pumice had 5.99µg/g, 1SD. LDPSA confirmed an average particle size of <45µm for all samples although D90 was comparatively less for MTA (9.9µm). Mean ST of clinker cements was 1.28min, 0.18SD, while for slag, fly-ash, slag/fly-ash mixture and kaolin geopolymer cements was 1.57min, 6.30min, 2.82min (0.72SD) and >7min, respectively.

Conclusions: Experimental clinker and geopolymer cements were similar in composition and particle size to commercial dental materials, and with reasonable ST. Further investigations of mechanical and biological properties are necessary to evaluate their potential for use in minimally-invasive, low-cost caries treatment techniques such as ART, in the era of dental amalgam phase-down.

F3: Abstract presented at the 1st International Inorganic Chemistry Conference, 22nd to 24th May 2018, Best Western Plus Meridian, Nairobi, Kenya

Characterization of experimental dental cements derived from locally available aluminosilicate materials in Kenya

Olivia Osiro[1], David Kariuki[2] and Loice Gathece[1]

School of Dental Sciences[1] and Department of Chemistry, School of Physical Sciences[2], University of Nairobi

Abstract

An evaluation of locally available alkali-activated aluminosilicates (geopolymers) and clinker was carried out for the purpose of establishing a substitute material for development of atraumatic restorative treatment (ART) cements. Materials were obtained from local Portland cement manufacturers. Compositional analysis was carried out by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS), X-ray Fluorescence (XRF), X-ray diffraction (XRD) and Fluoride Selective Electrode meter while Laser diffraction was used for particle size analysis (LDPSA) after sieving through a 53μm sieve. Geopolymers and clinker (0.5-1g) were mixed with freeze-dried poly(acrylic-acid) (0.1-0.2g) and aqueous tartaric acid (0.15-0.25mL) to produce cements whose setting time and compressive strength in 100% humidity was assessed after 1, 3 and 7d. Mineral trioxide aggregate (MTA) and glass ionomer cements (GIC) were used as controls. Geopolymers, clinker and MTA were found to contain varying ratios of SiO_2 (18-74wt%), CaO (1-65wt%), Al_2O_3 (2-27wt%) and similar diffraction peaks of $CaCO_3$, $2CaO.SiO_2$ and $3CaO.SiO_2$. MTA was found to contain Bi_2O_3 (16-33wt%) and Pb (1-2wt%), while geopolymers and clinker contained <0.001wt% Pb. Two geopolymers contained F^- (5.99- 43.33μg/g). LDPSA reported an average particle size of 45 μm or less. The average mixing time was 1min while setting time ranged from 1.5-8min. All cements except those based on kaolin softened in distilled water at earlier time points but seemed to harden again after 28d. However, the kaolin cements exhibited the lowest CS (<5MPa) while one of the clinkers had CS of 14MPa after 28d.

Keywords: Clinker, Geopolymer, Atraumatic Restorative Treatment, Cement formulation

F4: Published Journal articles.

The Minamata Convention on Mercury and its implication for management of dental caries in low- and middle-income countries.

Osiro OA, Kariuki DK, Gathece LW

Abstract

Dental caries is one of the most prevalent oral diseases and a ubiquitous public health problem. It is a major cause of tooth mortality consequently associated with reduced quality of life. The disease burden emanating from dental caries is dire in low- and middle-income countries because of the high cost of treatment and lack of preventive strategies. In most cases, extraction is the cheaper and readily available option, providing immediate symptomatic relief but often followed by regrettable aftermath. Limited resources render advanced restorative treatment inaccessible to many. Moreover, dental amalgam, the preferred direct restorative material in developing countries is subject to a global phase-down in line with the Minamata Convention on Mercury. It is anticipated that this will have a great impact on these countries. A number of the envisioned challenges are presented and possible solutions to the same suggested. There is a need to find an affordable viable replacement for dental amalgam that can be utilized even in underprivileged regions. Additionally, policy should advocate for oral health promotion and disease prevention together with dental training curriculum revision aimed at embracing low cost, minimally invasive techniques.

Background

Dental caries has become a ubiquitous public health problem despite overwhelming evidence that it is preventable[1,2]. Petersen reported that virtually all populations are affected globally, with 60 – 90% of school-going children and most adults affected by this condition1. Dental caries is a disease of the dental hard tissues characterized primarily by demineralization following acid production of fermentable carbohydrates by oral bacteria, as described in Keyes' triad. Left untreated, caries progresses to pulpitis, a painful condition warranting emergency intervention. Conventionally, the treatment modality for caries has been through elimination of affected tooth structure and placement of direct and indirect restorations[3].

An ideal restorative material should be biocompatible, resistant to fracture, demonstrate longevity, be affordable and easy to manipulate even in a resource-strained environment[4]. In low- and middle-income (LMI) countries, lack of prioritization of oral health due to its often morbid but not fatal nature, and in the face of limited resources, typically means minimal investment in the infrastructure necessary for advanced restorative treatment. In such countries, conventional caries treatment is not readily available and the ensuing alternative is extraction to provide immediate relief of symptoms; the partially dentate or completely edentulous state following tooth mortality is associated with reduced quality of life[1,2].

Dental amalgam is one of the oldest direct dental restorative materials, its use spanning more than a century. Amalgam is an alloy of a powder comprising silver, tin and copper triturated with triple distilled mercury into a soft pliable mass which is condensed into a cavity and carved prior to setting to a rigid solid. Dental amalgam has several advantages. It has adequate compressive strength of more than 400MPa, it is inexpensive and easy to manipulate. It is also radiopaque and exhibits a self-sealing ability due to corrosion products. However, its disadvantages include its metallic appearance as well as its tendency to corrode in the oral cavity that renders it unaesthetic. Additionally, dental amalgam is brittle in tension and is not adhesive and thus requires extensive tooth preparation to ensure mechanical retention and adequate bulk to prevent fracture.

Moreover, silver-mercury amalgam is a mercury-based product and is now scheduled to be phased down following the Minamata Convention on Mercury in 2013. The Convention is a global treaty whose agenda seeks to reduce environmental impact from mercury waste through phase-out of mercury-based products and cessation of manufacture of mercury. Although there is no proof of any adverse reactions in humans from dental amalgam, mercury is a well-known toxic substance and precaution is mandatory when handling it in the dental surgery. The looming phase-down of dental amalgam by 2020 presents a challenge to the dental profession[5]. Apart from its remarkable compressive strength, silver-mercury amalgam is one of the simplest to use and affordable restorative materials making it readily accessible. The phase-down of dental amalgam is likely to further hinder access to affordable restorative dental treatment in LMI countries[3]. Therefore, there is an urgent need to find an alternative with minimal adverse environmental impact that offers the excellent properties that characterize amalgam[4].

This commentary addresses the global burden of dental caries and inequalities that exist in LMI countries such as Kenya. It highlights the challenges of disease management, which are expected to worsen during the imminent phase-down of dental amalgam, and proposes practical and cost-effective solutions. The intent is to increase awareness by urging a paradigm shift that requires curriculum review in dental schools to promote disease prevention and further research on restorative alternatives. The articles included were accessed through a systematic search on Pubmed and Google Scholar using the specified keywords. A manual search of gray literature was also performed for additional articles.

Current concepts for managing dental caries

Restorative, or conservative, dentistry traditionally involves placement of restorations to prevent tooth loss by extraction; however, despite advances in restorative dentistry, the greatest challenge remains to find the ideal biomimetic material that can match the properties of hard dental tissues[4,6]. Navigating biocompatibility and environmental impact concerns in the quest for equivalence or superiority to established materials renders the process of biomaterial development tedious and costly. This financial burden is eventually transferred to patients, restricting access to advanced restorative treatment options.

Further, prevention and minimal intervention dentistry are widely accepted concepts for the management of dental caries. Preventive dentistry programmes focussing on risk factors have proven effective in industrialized countries[1,2]. However, the majority of developing countries do not have preventive dentistry programmes[2]. This is mostly due to financial constraints in an environment where public health agendas of various stakeholders often conflict. Despite the fact that disease prevention is ultimately more economical than treatment, limited resources have led to a scenario in which oral health is largely ignored when tackling other chronic non-communicable and communicable diseases perceived to have a higher risk of mortality[1,2]. There is a lack of strategies and goodwill to invest in and implement oral health promotion and disease prevention. In Kenya, healthcare consumes only 8% of total Government expenditure; oral health falls under the umbrella of general health, receiving a meagre 0.0016% of overall healthcare budgetary allocation.

Minimal intervention dentistry (MID) is a more recent, patient-specific treatment. It is a comprehensive longitudinal approach towards prevention through risk assessment while minimizing operative intervention[7]. Proponents of MID suggest that 'extension for prevention' should be replaced by 'prevention of extension', arguing that the conservative goals of the former are questionable because of the surgical approach to remove diseased tissue prior to placement of a restoration. Preventive dentistry, atraumatic restorative treatment (ART) and adhesive dentistry are practical aspects of MID, with the ultimate goal of preventing or halting progression of disease[8].

Minimizing the need for intervention by arresting disease progression is cost-effective; a key advantage of approaches such as ART and silver diamine fluoride is their simplicity as well as affordability, making them practical in resource-strained settings. However, in Kenya, the dental education curriculum focuses on curative rather than preventive training. Often, these techniques are considered intermediary interventions until the patient can access definitive treatment. Dental amalgam is still the preferred posterior restorative material in LMI countries such as Kenya; therefore, it is anticipated that its phase-down will present challenges in oral health care service delivery.

Challenges presented by the Minamata Convention regarding amalgam utilization and possible solutions for LMI countries

Kenya and a number of LMI countries are signatories to the Minamata Convention on Mercury[5,6]. The consequence of this policy in regard to restorative dentistry in these countries should be a matter of concern. Faced with rising caries prevalence due to a number of factors (Figure 1), they are neither economically positioned nor in terms of infrastructure prepared to adopt alternative materials and procedures, majority of which require a reliable source of electricity or technology not available in these resource-poor countries[4].
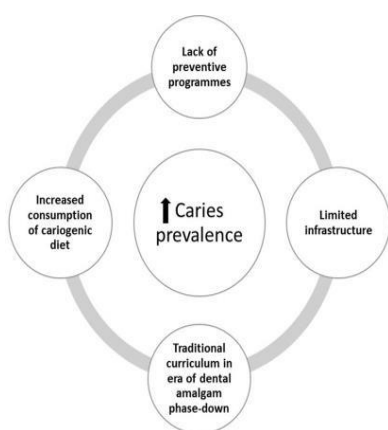
Fig. 1: Challenges faced by LMI countries in addressing the burden of dental caries

The first challenge presented by the dental amalgam phase-down is the lack of caries prevention initiatives in LMI countries which, coupled with a corresponding rise in the prevalence of dental caries, has increased the need for restorative treatment. Economic and infrastructural limitations demand that immediate efforts should be channelled towards disease prevention. The consensus is that prevention is the best approach to address the burden of dental caries[2]. Data from industrialized countries have led to the conclusion that while the disease prevalence may remain high among adults, it is declining among children. Future generations in these countries could witness an overall significant reduction in caries prevalence as a result of preventive measures[2]. On the contrary, there is a rise in caries prevalence in LMI countries and suggested attributable factors include increased consumption of refined sugar as well as changing lifestyles[9]. Unfortunately, in these countries, implementation of preventive measures has been limited, and prevalence is likely to remain high or even increase. Therefore, stakeholders in Kenya and other LMI countries should urgently push for policy adoption and implementation of preventive oral health programmes. Where middle-level colleges exist to train auxiliary dental professionals, as is the case in Kenya, they may bolster this preventive agenda particularly in school-based oral health programmes.

In LMI countries, rural electrification remains a challenge, impacting availability of advanced restorative treatment. Apart from the high cost of contemporary aesthetic restorative materials as well as the established advantages of dental amalgam, this may further explain why the usage of amalgam in LMI countries far surpasses that of resin composites and resin ionomers[3,6]. Cross-sectional surveys conducted among dentists in Kenya have found that amalgam is the preferred direct posterior restorative material (50% in 2003, 76% in 2010, 49% in 2014). The Dental Amalgam Project in East Africa in 2013 also reported that dental amalgam was routinely used (91.2%) for direct restorations10. Industrialized countries have found alternatives in indirect restorations; however, these are impractical in developing countries due to the technical needs and associated expense[3]. It is proposed that simple techniques such as ART should be actively promoted to minimize the need for extractions. High viscosity glass ionomer cements have been extensively examined and have been shown to survive for up to 10 years as ART restorations[11]. This can be done in addition to other techniques aimed at arresting caries progression, for example, use of silver diamine fluoride[12].

Most dental schools, especially those in LMI countries, still rely on traditional curricula focussed on curative management of dental caries. Resource limitations have contributed to disparities in the provision of oral healthcare, and oral healthcare professionals are trained only to provide very basic services.

Another survey in Kenya found that most dentists were aware of the Minamata Convention on Mercury and while 57% were in favour of their country being a signatory, 43% were not. The greatest concern was that adoption of the policy might negatively impact the quality of dental training and consequently provision of oral healthcare as a result of increasing costs.

Nonetheless, Kenya developed a national environmental action plan in 2016 and is at an advanced stage in becoming a party to the Convention. The solid waste policy was reviewed to include a clause on best management practice for dental amalgam waste and there has been intense lobbying by the Kenya Dental Association seeking projects to support the installation of separators and to promote recycling among dental practitioners. Advocacy for a curriculum change intended to encompass prevention, as well as emphasize innovative research to equip the dental workforce in LMI countries, is also necessary to adapt to the phase-down of amalgam.

Contemporary practice in these countries should advocate for MID. Moreover, extraction should not be regarded as treatment per se, but rather as treatment failure6. As illustrated by Banerjee[13], successful minimal intervention requires a treatment plan including four elements: identify, prevent, restore and recall. The identification phase involves diagnosis using modern caries detection techniques when available, along with caries risk assessment of the patient. Prevention involves control of disease progression by employing recognizable approaches on the individual and community level. Restoration involves tissue replacement via minimally invasive techniques and adhesive materials. Recall phase involves return visits with frequency determined by the susceptibility of the patient. Therefore, in order to prevent disease progression, which would increase the likelihood of extraction, restorations should be placed as soon as possible; the smaller the restoration, the better the prognosis. Additionally, smaller restorations may employ adhesive materials8. Such guidelines may form the basis for a standard curriculum that is easy to implement, encompassing practical aspects of MID including prevention and simple techniques such as ART, silver diamine fluoride, fissure sealants, preventive resin infiltration while encouraging repair instead of replacement of defective restorations.

The final challenge presented by the amalgam phase-down is the need for innovative research aimed at finding alternative restorative materials that mimic enamel and dentine. Indeed, it has been said that *'the ideal material is no material'*[4]. On the basis of clinical performance, the crucial factors when considering the ideal material include: resistance to fracture; ease of placement; and, service life of at least 10 years. Other concerns include operator skill, available infrastructure, patient expectations, cost-effectiveness, global challenges in manufacture and supply, and environmental impact4. Infrastructure is important because it may limit the application of some materials on the basis of what is available in resource-poor settings. The ideal material should also be able to be being utilized anywhere in the world without compromising standards[4-6]. It will be difficult to develop a single material that can serve all restorative applications[4].

We recognize that the development of biomaterials is an expensive and time-consuming process, and decades may elapse before new products are availed in the market. Nonetheless, the time has come for Kenya and other LMI countries to make their contribution by using locally available resources and industries to find solutions specific to local needs; locally available materials may be utilized in simple and inexpensive restorative procedures. An example of translational science is the derivation of mineral trioxide aggregate from Portland cement. A more recent approach involves alkaline-activation of naturally occurring silicate materials such as kaolin to produce geopolymers with potential bioactivity[14]. Such materials should be readily available and inexpensive, with minimal adverse environmental impact compared to dental amalgam and other mercury-based products. They may be used to reduce or arrest progression of caries, relieving symptoms, with low cost and applicable for minimally invasive techniques such as ART.
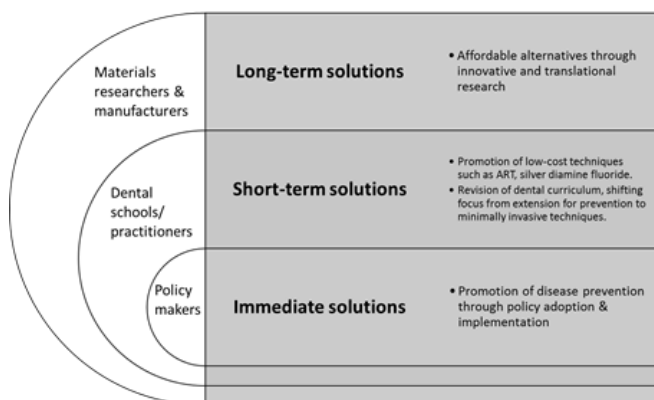
Fig. 2: Conceptual framework model to tackle burden of caries in LMI countries in line with the imminent phase-down of dental amalgam

Conclusions

Figure 2 summarizes the proposed solutions and stakeholders. The impending phase-down of dental amalgam presents a challenge to addressing the burden of dental caries in LMI countries. Development of suitable alternatives is a long-term solution. In the immediate and short-term, efforts should aim at prevention. Beyond policy, aspects of contemporary preventive dentistry such as MID should be incorporated in curricula of dental schools to promote practice by present-day dental workforce. The FDI Vision 2020 statement seeks to shape the future of oral healthcare by shifting focus from a curative to

preventive approach[15]. LMI countries may find it a useful guide in seeking local and practical solutions to address challenges arising from the burden of dental caries in the face of dental amalgam phase-down.

List of abbreviations
ART – Atraumatic Restorative Treatment, GIC – Glass ionomer cement, LMI – low- and middle-income, MID – Minimal intervention dentistry

Declaration of competing interests
The authors declare no competing interests.

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Composition and particle size of mineral trioxide aggregate, Portland cement and synthetic geopolymers

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ABSTRACT

Objective: To describe the composition and particle size of Portland cement (PC) and geopolymers in comparison to mineral trioxide aggregate (MTA).

Design: A quantitative, laboratory-based exploratory study.

Setting: Schools of Dental Sciences and Physical Sciences, University of Nairobi; World Agroforestry Centre (ICRAF); Ministry of Mining, all in Nairobi, Kenya.

Materials and methods: Grey PC clinker, Kaolin, Fly ash (FA) and blast furnace (BF) slag, together with alkaline-activated aluminosilicates (AS) or geopolymers derived from them, were evaluated in comparison to two brands of MTA (MTA Cem and ProRoot MTA). The materials were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), graphite furnace atomic absorption spectroscopy (GFAAS) and Fluoride ion selective electrode (FISE) for compositional analysis, and laser diffraction for particle size distribution analysis. Continuous data was subjected to analysis of variance (ANOVA) for hypothesis testing at α level of 0.05.

Results: There was no statistically significant difference in the composition of MTA and PC except in the Bismuth content (PC = 0%wt, MTA = 24.72%wt, sd 11.92, $p \leq 0.0001$). While MTA and PC comprised mainly of dicalcium and tricalcium silicate phases, geopoymers contained aluminosilicate phases such as quartz and mullite. Only FA contained fluoride (43.33µg/g, sd 5.77). There was no statistically difference in the mean particle size distribution of MTA, PC and geopolymers (D50 for PC = 12.46µm, sd 3.18, MTA = 7.23µm, sd 3.43, aluminosilicates = 12.74µm, sd 3.79, $p > 0.05$).

Conclusion: Composition of PC was similar to MTA while particle size of PC and geopolymers was similar to MTA.

INTRODUCTION

Portland cement (PC) is the product of grinding clinker to a fine powder. It is hydraulic due to its hydration setting reaction on addition of water. The primary constituents of PC are calcium carbonate or calcite ($CaCO_3$, 65%), silica (SiO_2, 20%), alumina (Al_2O_3) and ferric oxide (Fe_2O_3, 10%). Other compounds such as heavy metals like lead (Pb) and arsenic (As) constitute the remaining 5%[1]. Calcination of these oxides produces physical and chemical changes, resulting in clinker that is finally ground to the desired particle size. For optimum setting reaction and strength, it is desirable that at least 90% of the particles should be 50µm and below; particles larger than this tend to remain unreacted and may compromise the cement properties. Small amounts of gypsum are added during the grinding process to retard the setting reaction and enable adequate working time during construction techniques. The two principal phases in PC are tricalcium silicate (C_3S, $2CaO.SiO_2$) or alite and dicalcium silicate (C_2S, $3CaO.SiO_2$) or belite[1].

Alkaline-activated aluminosilicates (AS) or geopolymers are cementitious materials synthesized through a low temperature reaction (typically below 100°C) between aluminosilicate precursors and a friendly sodium silicate (Na_2SiO_3) solution. This is a potentially irritant alkaline solution different from the corrosive ones and having a SiO_2:Na_2O ratio >1.45. The aluminosilicate precursors are usually clay-based materials such as calcined clays, metakaolin and volcanic rocks as well as industrial by-products, commonly fly ash (FA) and blast furnace (BF) slag. These materials are used extensively in the construction industry as a substitute for PC due to the high energy costs and carbon footprint associated with production of clinker. Additionally, they set within a shorter time while gaining considerable strength within the first 24 hours[2-5]. Until recently,

research on geopolymers has focused on their primary application in the construction industry where they have been found to be comparable to PC. However, there is paucity of data on their biological properties and potential as biomaterials.

Calcium silicate cements (CSCs) are a group of hydraulic or water-setting cements presented as powders comprising mainly C_2S and C_3S[6-9]. It is well established that these cements are derived from PC which is the main provider of the calcium silicate elements, with the addition of a radiopacifier such as bismuth oxide (Bi_2O_3)[1, 9-11]. However, the commercial versions are highly purified and manufactured through strict regulatory standards by ethical medical material manufacturers[12]. Several categories of calcium-based cements have been utilized in medical and dental restorative techniques for decades. They include those based on calcium phosphate such as bioglasses, calcium aluminate such as glass ionomer cements and calcium silicate[7]. The first CSC for dental applications, mineral trioxide aggregate (MTA), was introduced by Torabinejad in the early 1990s and marketed as an endodontic material in collaboration with Tulsa Dental Products, a branch of Denstply in Tulsa, Oklahoma in 1995[8, 13]. Several other brands of these cements have since been developed and marketed as rivals to the original MTA. They include Biodentine®, Bioaggregate®, Endosequence®, Calcium-enriched mixture cement® and TheraCal®[6].

Presently, there is a heated debate on whether ordinary PC can be a substitute for commercial CSCs. Earlier reviews discouraged substitution of PC intended for the construction industry for a medical or dental application on ethical grounds as well as the fact that these specific cements were relatively new biomaterials[10, 12]; however, this presented a dilemma for developing countries because these materials are very expensive. On the other hand, more recent reviews have concluded that there are no compelling reasons not to use PC as a cheaper alternative, going further to state that more clinical trials should be conducted using pure PC[1]. Others have emphasized that more studies are required to evaluate the parent compound in order to increase understanding of the same as a precursor for expanded medical and dental applications[14-16].

PCs are classified as Type I to V according to the ASTM standards; CSCs are comparable to Type I PC. Estrella *et al.* were the first to report the similarity between MTA and PC stating that the only difference was the presence of Bi_2O_3 in MTA and its absence in PC[17]. Several other studies have compared the two materials, investigating aspects of their composition[8, 14, 16, 18, 19], setting reaction[20, 21] and biocompatibility[17, 22] and most of these found the two to be quite similar. The particle size of MTA is a little researched area. A few studies have compared the particle size of MTA and PC and how this influences their properties[16, 23-25]. On this basis, several reviews have concluded that more studies utilizing PC are required to evaluate the possibility of substituting it for the expensive commercial calcium silicate versions[1, 15, 16].

Kenya has a vibrant PC manufacturing industry that also utilizes precursors of geopolymers. However, there is no documented study comparing these products to MTA despite the expense incurred in importing the latter for dental treatment. Therefore, the aim of this study was to describe the composition and particle size of PC manufactured in Kenya, geopolymers synthesized from aluminosilicate precursors obtained in Kenya, and two commercial brands of MTA.

MATERIALS AND METHODS
Ethical approval for this study was obtained from the Kenyatta National Hospital/University of Nairobi Ethical Research Committee. To minimize errors and bias, experiments were conducted in triplicate. R-studio version 3.4.4 and Microsoft Excel 2013 were used for descriptive data analysis as well as for hypothesis testing. Continuous data was subjected to analysis of variance (ANOVA) at α level of 0.05, to test the hypothesis that there was no difference in the composition and particle size of PC, alkaline-activated AS and MTA.

Sampling and sourcing of materials
A descriptive summary of the materials is presented in Table 1. PC clinkers and aluminosilicate materials for clinker production were obtained from three PC manufacturing companies in Kenya: East African Portland Cement (EAPC), Athi River Mining (ARM) and Bamburi. One aluminosilicate material was obtained from a ceramic manufacturing company in Kenya: Saj Ceramics. Two commercial brands of MTA were purchased in Nairobi, Kenya: MTA Cem (NexoBio, Chungcheongbuk-do, Korea) and ProRooT MTA (Dentsply Sirona, York, Pennsylvania, USA). Samples of PC clinker were obtained from random batches

within the three identified companies, as specified by ASTM C183 – Standard Practice for sampling and the amount of testing of hydraulic cements. At least 1kg samples were collected from the companies' Nairobi Grinding Plants storage bins prior to packaging, and placed in sealed, labelled, moisture-proof and air-tight containers.

Table 1: Summary of study population

No.	Material description	Source	Ref no. / Lot no. / Expiry date	Collection date
1	PC clinker	EAPC, Athi River, Kenya	Unavailable	April, 2017
2	PC clinker	ARM, Athi River, Kenya	Unavailable	July, 2017
3	PC clinker	Bamburi, Athi River, Kenya	Unavailable	November, 2017
4	BF Slag	ARM, Athi River, Kenya	Unavailable	July, 2017
5	FA/ Pozzolana	Bamburi, Athi River, Kenya	Unavailable	November, 2017
6	Kaolin	Saj Ceramics, Athi River, Kenya	Unavailable	December, 2017
7	MTA Cem	NexoBio, Chungcheongbuk-do, Korea	1013/ MC160516/ 2019.02 1013/ MC150817/ 2018.05	September, 2017
8	ProRoot MTA	Dentsply Sirona, York, Pennsylvania, USA	A040500000400/ 0000108513/ 2018.02.02	September, 2017

Synthesis of alkaline-activated aluminosilicates (geopolymers)
As described in previous studies[3, 5], approximately 100g of various ratios of BF Slag/ FA (0:100, 20:80, 40:60, 60:40, 80:20 and 100:0) and Kaolin/ FA (100:0 and 80:20) were weighed separately. One litre of the alkaline activation solution was prepared by adding 85% 14M NaOH to 15% Na_2SiO_3. Laboratory grade reagents, 98% NaOH pellets and Na_2SiO_3 (both Sigma Aldrich, Gillingham, UK) with a final constitution of 9.1% Na_2O, 27.5% SiO_2 and 63.4% H_2O and SiO_2/Na_2O ratio of 3.02, were used. Approximately 55ml of the alkaline activation solution was placed in eight 250ml capacity glass beakers and the weighed out powders added to each corresponding labelled beaker. The powder/ liquid ratio was approximately 0.55. The solutions were stirred vigorously for a few minutes then transferred to an oven set at 85°C for 24 hours. After 24 hours, the dried product was removed from the oven, bench cooled and left at ambient temperature for 90 days. Thereafter, the products were retrieved from the beakers, sprayed with ethanol to stop further activation, pulverized, stored in sealed, labelled, airtight sample bags and characterized.

Composition analysis
The compositional analysis of powder specimens of MTA, PC clinker, raw and alkaline-activated aluminosilicates (geopolymers) was conducted by X-ray diffraction (XRD) and X-ray fluorescence (XRF), and filtrates of acid-digested specimens of MTA, PC clinker and raw aluminosilicates by Graphite furnace atomic absorption spectroscopy (GFAAS) and Fluoride ion selective electrode (FISE).

1. XRD

XRD (XRD; D2 Phaser, Bruker Corporation, Billerica, MA, USA) was used to identify the compositional phases of MTA, PC clinkers as well as the raw and alkaline-activated aluminosilicates (geopolymers), on the basis of their crystallographic patterns. Approximately 1gm of each powder sample was gently pressed flush into the XRD sample holder using a glass slide to ensure a smooth surface. Excess powder was removed from the edges of the sample holder before it was carefully placed in the appropriate XRD slot. Readings were taken at ambient temperature using CuK□ radiation at 40kV voltage and 40mA current, within a scan range of 10–80° 2θ and a scan speed of 2° 2θ per minute. Diffraction patterns were matched to the International Centre for Diffraction Data database (International Centre for Diffraction Data, Newton Square, PA, USA).

2. XRF

XRF (XRF; Rigaku NEX CG, Rigaku Corporation, Tokyo, Japan) was used to identify the pure elemental and simple oxide composition of MTA, PC clinkers as well as the raw and alkaline-activated aluminosilicates (geopolymers). Approximately 1gm of powder sample was placed in plastic XRF sample holders, suspended on the appropriate slot and readings performed at ambient temperature at 30kV voltage and 1.0mA current.

3. GFAAS

GFAAS (iCE 3000, Thermo Fisher Scientific, Waltham, MA, USA) was used to identify the pure elemental composition of MTA, PC clinkers as well as the raw and alkaline-activated aluminosilicates (geopolymers). Acid digestion of approximately 1gm of dry samples was conducted by moistening with 20ml of deionized water, dissolving in 20ml of 1M HCl and heating to evaporation on a hot plate. The residue was then treated with 20ml of hot water and filtered and dried then the process of acid digestion was repeated. The filtrate was topped up to 100ml using hot water and preserved in labelled bottles. At least five standard aqueous solutions of elements of interest were prepared and used to produce calibration plots. Thereafter, sample readings were performed on the GFAAS at ambient temperature, using argon as a purge gas. Flame photometry was used to quantify the major elements.

4. FISE

FISE (Orion 9609BNWP, Thermo Fisher Scientific, Waltham, MA, USA) was used to determine the F-content of MTA, PC clinkers as well as the raw and alkaline-activated aluminosilicates (geopolymers). The sample filtrate specimens prepared for GFAAS were analyzed for F- content. Prior to measurement, the electrode tip was flushed with deionised water and then calibrated using standard solutions of 0.5, 1 and 10ppm fluoride and TISAB II. Fluoride concentration in the samples was recorded in ppm with a corresponding RmV, then converted to $\mu g/g$.

Particle size analysis
Particle size distribution (PSD) analysis of powder specimens was conducted by laser diffraction (LD).

1. LD-PSD

Laser diffraction particle analysis (Partica, LA-950, Horiba Scientific, Kyoto, Japan), which can determine particle size between 0.022–2000μm, was used to determine the particle size of MTA, PC clinkers as well as the raw and alkaline-activated aluminosilicates (geopolymers). Powder samples were dispersed in 200ml of a solution of deionized water and Calgon (refractive index-1.478 *n*), and sonicated for 10min at ambient temperature to ensure the complete dispersion before running through the LD-PSD analyzer. Tests were performed before and after sieving through a 120μm mesh sieve (Endecotts Ltd, London, UK).

RESULTS

Composition analysis
1. XRD

Figure 1A shows the diffraction patterns of PC and MTA, with similar peaks of C_2S and C_3S in both materials. They also show peaks of Bi2O3 unique to MTA. Figure 1B shows the diffraction patterns of raw and alkaline-activated AS (geopolymers). The spectra show peaks of quartz, calcite and mullite within the various materials. Following alkaline-activation, the quartz and mullite peaks were markedly enhanced in 100% BF slag, and mixtures of BF slag and FA (80:20 and 60:40).
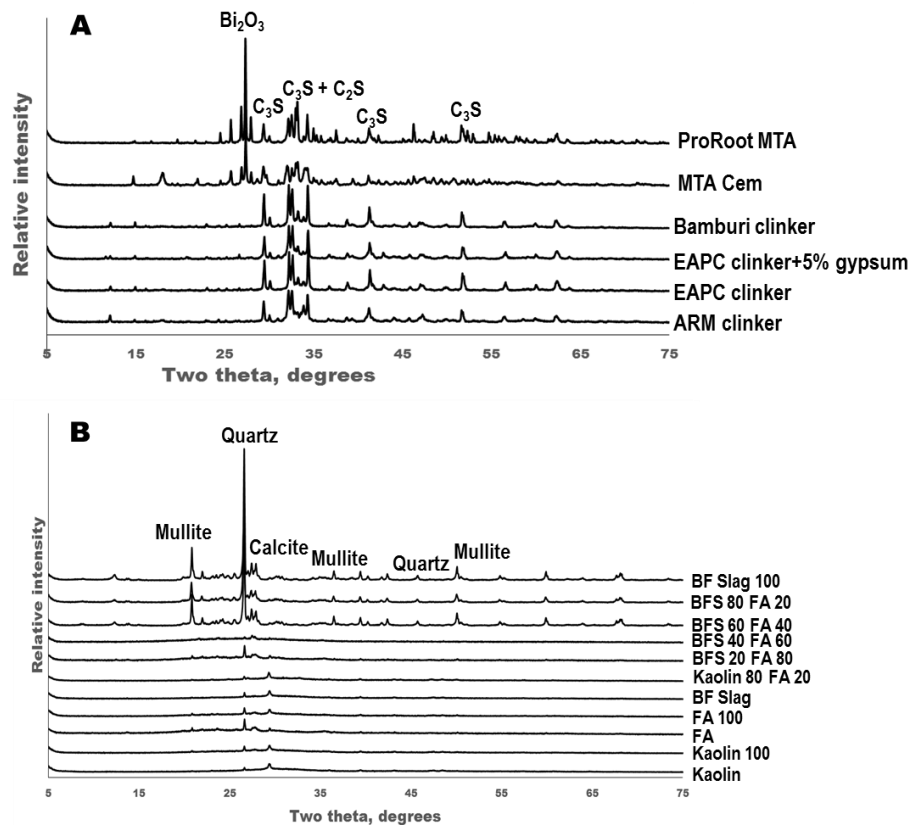
Figure 1: Powder XRD patterns of PC clinker and MTA (A), and raw and alkaline-activated AS (B)

2. XRF

Table 2 is a descriptive summary as well as results of ANOVA of the major constituents (%wt) of the three groups of materials as analysed using XRF. There was a statistically significant difference for CaO, SiO_2, Al_2O_3, P_2O_5, S, Pb and Bi content among all materials. However, Tukey's post hoc test returned no statistically significant difference between PC and MTA except for Pb (p=0.000) and Bi (p<0.0001). For PC and aluminosilicate materials, Tukey's post hoc test returned statistically significant difference for CaO (p=0.006), SiO_2 (p=0.004), Al_2O_3 (p=0.04) and P_2O_5 (p<0.0001) while for MTA and aluminosilicates, Tukey's post hoc test returned statistically significant difference for SiO_2 (p=0.003), Al_2O_3 (p=0.03), P_2O_5 (p=0.003), S (p=0.003), Pb (p=0.000) and Bi (p<0.0001). MTA Cem, ProRoot MTA, ARM and Bamburi clinkers were found to have some levels of lead (Pb); however, none of the materials contained Arsenic (As).

3. GFAAS and FISE

Table 3 is a descriptive summary as well as results of ANOVA of compositional analysis as determined by GFAAS and FISE (μg/g). F^- was detected only in FA (43.33μg/g, sd 5.77). There was a statistically significant difference for Ca, Zn, Fe, Pb, Mn, PO and F among all materials. However, Tukey's post hoc test returned no statistically significant difference between PC and MTA except for Ca (p=0.004), Zn (p=0.04), Mn (p=0.01) and PO (p<0.001) content. For PC and aluminosilicate materials, Tukey's post hoc test returned statistically significant difference for Ca (p<0.0001), Zn (p=0.02), Pb (p=0.04), PO (p=0.03) and F (p=0.02). For MTA and aluminosilicate materials, Tukey's post hoc test returned statistically significant difference for Ca (p<0.0001) and PO (p<0.001).

Table 2: Descriptive summary and ANOVA of composition of PC, AS and MTA as determined by XRF (%wt)

Compound	Material category	Mean (SD)	Min	Max	F statistic, df, p-value	Tukey's post hoc adjusted p-value
CaO	PC (n=3)	59.50 (7.41)	51.09	65.04	8.73, 2 df	PC:MTA = 1.00
	MTA (n=2)	46.07 (10.24)	38.83	53.31	$p \leq 0.01$**	PC:AS = 0.006*
	AS (n=10)	18.35 (17.85)	0.61	45.57		MTA:AS = 0.14
SiO$_2$	PC	25.65 (5.68)	21.99	32.19	14.33, 2df	PC:MTA = 1.00
	MTA	19.02 (0.91)	18.38	19.66	$p \leq 0.001$**	PC:AS = 0.004*
	AS	58.10 (13.65)	35.54	74.65		MTA:AS = 0.003*
Al$_2$O$_3$	PC	5.49 (0.49)	4.99	5.96	6.98, 2df	PC:MTA = 1.00
	MTA	2.65 (1.07)	1.89	3.40	$p \leq 0.01$*	PC:AS = 0.04
	AS	15.31 (6.25)	10.32	27.69		MTA:AS = 0.03*
P$_2$O$_5$	PC	0.61 (0.17)	0.42	0.75	29.5, 2df	PC:MTA = 0.44
	MTA	0.46 (0.02)	0.44	0.47	$p \leq 0.0001$***	PC:AS $\leq$ 0.0001**
	AS	0.10 (0.01)	0.00	0.30		MTA:AS = 0.004*
S	PC	1.53 (1.36)	0.52	3.08	9.33, 2df	PC:MTA = 0.05
	MTA	4.27 (2.69)	2.37	6.17	$p = 0.004$**	PC:AS = 0.68
	AS	0.61 (0.63)	0.00	1.82		MTA:AS = 0.003*
Cl	PC	0.03 (0.04)	0.00	0.08	3.12, 2df	PC:MTA = 0.09
	MTA	0.24 (0.28)	0.40	0.43	$p = 0.08$	PC:AS = 0.92
	AS	0.10 (0.04)	0.30	0.15		MTA:AS = 0.2
K$_2$O	PC	1.65 (0.75)	1.01	2.48	3.2, 2df	PC:MTA = 0.86
	MTA	0.16 (0.02)	0.14	0.17	$p = 0.08$	PC:AS = 0.68
	AS	2.88 (1.66)	0.28	5.18		MTA:AS = 0.1
MgO	PC	1.22 (2.12)	0.00	3.67	0.71, 2df	PC:MTA = 1.0
	MTA	0.00 (0.00)	0.00	0.00	$p = 0.5$	PC:AS = 1.0
	AS	1.49 (1.8)	0.00	4.73		MTA:AS = 0.77
Fe	PC	3.49 (1.03)	2.67	4.64	3.12, 2df	PC:MTA = 0.09
	MTA	0.14 (0.06)	0.10	0.18	$p = 0.8$	PC:AS = 0.94
	AS	2.46 (1.65)	0.64	5.58		MTA:AS = 0.2
As	PC	0.00 (0.00)	0.00	0.00	-	-
	MTA	0.00 (0.00)	0.00	0.00		
	AS	0.00 (0.00)	0.00	0.00		
Sr	PC	0.06 (0.04)	0.03	0.1	3.06, 2df	PC:MTA = 1.0
	MTA	0.09 (0.09)	0.02	0.15	$p = 0.08$	PC:AS = 0.4
	AS	0.03 (0.02)	0.01	0.07		MTA:AS = 0.16
Pb	PC	0.01 (0.01)	0.00	0.01	164.4, 2df	PC:MTA = 0.000
	MTA	1.75 (0.44)	1.44	2.06	$p \leq 0.0001$***	MTA:AS = 0.000
	AS	0.01 (0.01)	0.00	0.01		
Bi	PC	0.00 (0.00)	0.00	0.00	44.29, 2df	PC:MTA $\leq$ 0.0001***
	MTA	24.72 (11.92)	16.25	33.19	$p \leq 0.0001$***	PC:AS = 1.0
	AS	0.00 (0.00)	0.00	0.00		MTA:AS $\leq$ 0.0001***
Others	PC	0.75 (0.26)	0.49	0.88	1.3, 2df	PC:MTA = 0.44
	MTA	0.45 (0.18)	0.32	0.52	$p = 0.31$	PC:AS = 0.73
	AS	0.58 (0.21)	0.24	0.73		MTA:AS = 1.0

**$p < 0.05$, **$p \leq 0.01$, ***$p \leq 0.0001$

Table 3: Descriptive summary and ANOVA of composition of PC, AS and MTA as analyzed by GFAAS and FISE (µg/g)

Element	Material category	Mean (SD)	Min	Max	F statistic, df, p-value	Tukey's post hoc adjusted p-value
Ca	PC (n=3)	51623.00 (5182.00)	45555.00	61118.00	39.33, 2 df	PC:MTA = 0.004**
	MTA (n=2)	77083.00 (4612.00)	70772.00	81860.00	p≤0.0001***	PC:AS ≤ 0.0001***
	AS (n=2)	16328.00 (18110.00)	0.00	37835.00		MTA:AS ≤0.0001***
Zn	PC	127.80 (107.50)	0.41	255.50	6.4, 2 df	PC:MTA = 0.04*
	MTA	3.45 (0.27)	3.06	3.66	p≤0.01**	PC:AS = 0.02*
	AS	2.42 (2.35)	0.25	4.60		MTA:AS = 1.0
Fe	PC	1978.00 (258.50)	1709.00	2472.00	4.17, 2df	PC:MTA = 0.24
	MTA	1185.00 (750.60)	77.26	1726.00	p=0.04*	PC:AS = 0.04*
	AS	960.80 (1079.00)	0.001	2245.00		MTA:AS = 1.0
Ni	PC	1.19 (1.54)	0.001	4.25	2.45, 2df	PC:MTA = 0.5
	MTA	0.24 (0.15)	0.09	0.37	p=0.12	PC:AS = 0.16
	AS	0.001 (0.00)	0.001	0.001		MTA:AS = 1.0
Pb	PC	1.83 (1.74)	0.001	3.57	3.96, 2df	PC:MTA = 1.0
	MTA	1.57 (0.66)	0.59	2.02	p=0.04*	PC:AS = 0.04*
	AS	0.001 (0.00)	0.001	0.001		MTA:AS = 0.22
Cu	PC	57.30 (79.76)	3.63	166.40	2.19, 2df	PC:MTA = 0.36
	MTA	1.50 (0.03)	1.46	1.52	p=0.14	PC:AS = 0.28
	AS	4.06 (3.60)	0.47	7.97		MTA:AS = 1.0
Cd	PC	0.04 (0.04)	0.001	0.10	0.46, 2df	PC:MTA = 1.0
	MTA	0.03 (0.04)	0.007	0.09	p=0.64	PC:AS =1.0
	AS	0.06 (0.08)	0.001	0.20		MTA:AS = 1.0
Cr	PC	3.44 (5.84)	0.001	17.97	0.31, 2df	PC:MTA = 1.0
	MTA	1.61 (1.10)	0.00	2.43	p=0.74	PC:AS = 1.0
	AS	2.12 (2.32)	0.001	4.23		MTA:AS = 1.0
Mn	PC	58.15 (33.72)	16.34	99.84	6.46, 2df	PC:MTA = 0.01**
	MTA	0.00 (0.00)	0.00	0.00	p≤0.01**	PC:AS = 1.0
	AS	46.50 (23.27)	25.10	69.74		MTA:AS = 0.05
PO$_4^{3-}$	PC	20.46 (4.23)	13.00	25.08	23.04, 2df	PC:MTA≤0.001**
	MTA	46.53 (20.23)	17.75	64.67	p≤0.001***	PC:AS = 0.03*
	AS	5.78 (1.87)	3.42	7.58		MTA:AS ≤0.001**
F	PC	0.00 (0.00)	0.00	0.00	5.35, 2df	PC:MTA = 1.0
	MTA	0.00 (0.00)	0.00	0.00	p=0.02*	PC:AS = 0.02*
	AS	21.67 (24.01)	0.00	50.00		MTA:AS = 0.07

*p<0.05, **p≤0.01, ***p≤0.0001

Particle size distribution analysis
1. LD-PSA

Table 4 shows a descriptive summary as well as results of ANOVA of particle size distribution by LD-PSA (µm). There was no statistically significant difference of the particle size of the materials, both sieved and not sieved (p>0.05).

Table 4: Descriptive summary and ANOVA of particle size distribution of MTA, PC and AS (µm)

Descriptive summary LDPSA (not sieved) (µm)

Percentile	Material category	Mean (SD)	Min	Max	F statistic, df, p-value
D10	PC (n=2)	2.97 (2.74)	0.59	6.86	1.29, 2 df
	MTA (n=2)	1.18 (0.71)	0.67	1.68	p = 0.30
	AS (n=3)	1.94 (0.76)	1.31	3.36	
D50	PC	112.50 (173.30)	10.22	370.70	2.38, 2 df
	MTA	7.23 (3.43)	4.80	9.65	p = 0.13
	AS	17.15 (13.44)	8.10	57.80	
D90	PC	607.70 (676.10)	44.05	1489.00	0.93, 2df
	MTA	74.27 (74.47)	21.61	126.90	p = 0.42
	AS	960.80 (1079.00)	52.45	1424.00	

Descriptive summary LDPSA (sieved) (µm)

Percentile	Material category	Mean (SD)	Min	Max	F statistic, df, p-value
D10	PC (n=2)	1.14 (0.78)	0.59	1.69	1.46, 2 df
	MTA (n=2)	1.18 (0.71)	0.67	1.68	p = 0.28
	AS (n=9)	1.67 (0.44)	1.31	2.60	
D50	PC	12.46 (3.18)	10.22	14.71	1.87, 2 df
	MTA	7.23 (3.43)	4.80	9.65	p = 0.2
	AS	12.74 (3.79)	8.10	19.70	
D90	PC	78.08 (676.10)	44.05	112.10	0.08, 2df
	MTA	74.27 (74.47)	21.61	126.90	p = 0.92
	AS	99.84 (104.60)	52.45	393.80	

DISCUSSION

The composition and particle size of PC and geopolymers synthesized by alkaline-activation of AS for clinker production in Kenya was described in comparison to MTA. The information from this study contributes to the knowledge base on the properties of PC and MTA and the potential of PC as a cheaper substitute in resource-strained settings common in low- and middle-income countries. Additionally, an aspect of geopolymers is also presented to highlight the properties of these materials that serve as alternatives to PC.

PC and MTA were found to be composed of similar constituents in different proportions but within a similar range. These findings are not surprising given the established fact that MTA is a derivative of PC. Several studies have reported the similarity in composition between MTA and PC, with the only difference being presence of radiopacifiers in MTA and their absence in MTA[1, 6-11, 14-19, 26]. The composition of PC produced in Kenya has never been evaluated to assess is potential as an alternative material for dental applications. This study found similar results as have been reported for PC from other parts of the world. However, to the best of our knowledge, there is no documentation of a comparison of MTA and geopolymers. Given that the precursors of geopolymers are aluminosilicate materials[2-5], it is not surprising that these materials were found to be comprised primarily of quartz, mullite and calcite while PC and MTA were mainly comprised of belite (C_2S) and alite (C_3S).

Moreover, the clinker, geopolymers and MTA samples did not contain any detectable amounts of As. Small quantities of Pb were detected in both MTA samples using XRF; however, using GFAAS, two clinker samples and both MTA samples were found to contain small amounts of Pb. While the Pb content in three of these samples was below the ASTM recommendation of <2mg/kg for PC, it is noteworthy that one clinker sample (Bamburi) contained Pb levels >2mg/kg (3.57µg/g). Studies that have reported on levels of potentially toxic elements such as As and Pb in MTA and PC had varying results although most of the materials studied were found to have low levels of As[27-29].

Admittedly, the greatest concern in direct substitution of an ethically manufactured biomaterial with a cheap version intended for the construction industry is the potential danger of toxicity from impurities, justly

attributed to the fact that PC has not been proven to be clinically safe[10, 12]. However, a few studies to evaluate the level of such impurities have reported variable results. A study of two grey and one white PC, and two grey MTA cements by Duarte *et al.* found that all of these materials released similar low amounts of As. The values were below those considered to be harmful; therefore, it was concluded that all the cements tested would be safe for clinical applications[29]. A comparison of the levels of As in some brands of MTA and PC by De-Deus *et al.* detected negligible amounts of type III As; surprisingly, the highest and lowest values of As were detected in two different brands of MTA while the PC and two other MTA cements contained intermediate values or none[28]. Yet another study to determine whether the levels of As in MTA and PC complied with the ISO recommended limit for water-based cements of 2mg per kilogram of cement found that all the materials tested contained As; furthermore, one of the MTA cements had levels as high as 5.91mg/kg while one of the white PC contained 0.52mg/kg[27]. It is difficult to draw plausible conclusions on such few studies with varied results hence further research is necessary to assess the actual effects of these potentially toxic elements.

Among the materials evaluated in this study, only FA was found to contain F^-. There is paucity of data on fluoride release in CSCs and related materials such as PC. Considering that the main application of these materials in dentistry is for endodontic applications, it is not surprising that the role of fluoride at this stage of treatment may not be crucial. Indeed, topical fluoride is necessary to enhance remineralization and inhibit demineralization of initial caries lesions, and not advanced disease such as pulpitis[30]. Nonetheless, the presence of high levels of fluoride in FA is an interesting finding that warrants further research on this material.

The particle size distribution of the materials was also analyzed. Prior to sieving, a variation was observed in the 10th, 50th and 90th percentile in the particle size distribution of the various materials. This finding was consistent with that reported by other studies[16, 23-25, 31-33] and may be explained by the differences in production methods in relation to the intended application, that is, endodontic material and construction material for MTA and clinker and geopolymers, respectively. However, after sieving, the particle size distribution was found to be comparable among the materials. Moreover, sieving was found to be an effective method of controlling the particle size to that recommended for dental cements (45μm) as documented in other studies[34]. Additionally, it has been shown that particle size above 50μm remained largely unreacted in PC and could compromise the overall quality of the set cement[1].

A few studies have reported on the particle size of MTA and PC but not geopolymers. Khan *et al.* investigated the chemical composition and particle morphology of white MTA and white PC. They concluded that the materials were similar in composition and that they had irregular particles, although the particles in the MTA were of finer morphology than those of PC[16]. Ha *et al.* assessed the influence of atmospheric moisture on unsealed MTA packages. They found that after two years, there was a 6-fold increase in the particle size of ProRoot MTA left in a folded over open package as compared to a 2-fold increase in MTA Angelus left in a jar with a twistable lid. The increase in particle size was attributed to clumping together following absorption of atmospheric moisture and was thought to affect the material properties negatively hence the manufacturers' recommendation for single use packages[24]. In a different study, they attempted to deconvolute the distribution of the particles contributed by PC and bismuth oxide in MTA. They found that, generally, PC component contributed larger particle sizes while bismuth oxide contributed smaller particle sizes in MTA[25].

In yet another study, Ha *et al.* assessed the influence of particle size on the setting time of MTA and PC. They concluded that despite variations in particle size between MTA and PC, smaller particle size was associated with faster setting times. However, among the three percentiles of particle sizes (D10, D50 and D90), D90 showed the highest positive linear correlation to setting time in both MTA and PC[23]. However, a recent in vivo animal study failed to show the influence of reduction in particle size of MTA on dento-alveolar and osseous healing following root-end fillings[33]. Two earlier studies had attempted to describe the particle shape and aspect ratio of the two materials, speculating that smaller particles may penetrate open dentinal tubules and may be clinically useful in bioactive materials[31, 32]. Nevertheless, the scope of this study did not extend to assess the specific influence of particle size and shape on the properties of materials under investigation.

CONCLUSION

In conclusion, this study found that the composition of PC clinker manufactured in Kenya and MTA were similar except the presence of Bi_2O_3 in MTA. However, while PC and MTA comprised primarily of C_2S and C_3S, geopolymers were aluminosilicate-based and composed of quartz, mullite and calcite. The particle size of the materials was also similar, with most of the materials having a mean of <45μm. Moreover, sieving was found to be effective in controlling the particle size distribution.

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