UNIVERSITY OF NAIROBI

FACULTY OF SCIENCE AND TECHNOLOGY

DEPARTMENT OF CHEMISTRY

UTILIZATION OF CONCRETE WASTE IN THE MANUFACTURE OF PORTLAND POZZOLANA CEMENT

BY

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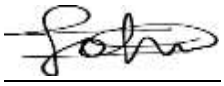
DECLARATION

I confirm that this thesis presented for the degree of Master of Science in Industrial Chemistry has not been submitted for any other degree for research. The work contained here has been acknowleged and referenced according to the University of Nairobi requirements in sections where other people's work has been used.

Signature:  Date: 7th December,2023

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DEDICATION

I dedicate this thesis to my wife Beatrider Mbatha and son Newton Muthui, who have been affected in every way possible.Their quest for unconditional love has been a source of encouragement and support throughout the pursuit of this work. This work is also dedicated to my parents Jeremiah Kioko and Eunice Kioko who have offered constant support throughout my study life. All this is to bring joy to our family.

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ABSTRACT

Concrete waste is a subclass of construction and demolition waste composed of hydrated cement, coarse, and fine aggregates. It bears its origin from the construction and demolition of concrete structures. The purpose of this study was to investigate the utilization of concrete waste as a substitute for natural pozzolana in the manufacture of Portland pozzolana cement(PPC). A total of 3 samples10 Kgs each, were collected in polythene bags from Roysambu, Woodley, and Mowlem all in Nairobi city, Kenya. The samples ware milled in a laboratory ball mill to 5% retention on a 45 µm sieve. Substitution of Ordinary Portland cement (OPC) was done at 10%, 20%,30%,40% and 50%. The compressive strength was determined by breaking mortar prisms in a computerized compression analysis machine type YAW-300, on the 2^{nd},7^{th}, $28^{th,}$ and 56^{th} day of curing according to the Kenya cement standards. The optimum substitution rate required to achieve a compressive strength of 32.5 MPa on the 28^{th} day was determined from the graph of the 28th day curing period compressive strength development data against the curing period. The test cements for pozzolanicity were prepared using the optimum substitution rate determined. The pozzolanicity was evaluated through a gradual comparison of Calcium oxide and hydroxyl ion concentration after a set period of 3,8,15,21 and 28 days of curing as outlined in Kenya cement standard. The chemical composition of the waste concrete was analysed using X-ray fluorescence spectrophotometer model epsilon 3XLE and results were expressed in percent oxides of the respective elements. This study revealed that the compressive strength of all the test cements increased gradually throughout the curing period. Control OPC showed the highest compressive strength in all curing ages ranging from 35.80 MPa on the 2^{nd} day to 57.20 MPa on the 56^{th} day, with a minimal strength change of 0.1 MPa from the 28^{th} to the 56^{th} day of curing. Control PPC showed a strength change from 17.64 MPa on the 2^{nd} day to 37.40 MPa on the 56^{th} day. The waste concrete substituted cements strength development mirrored that of control PPC growing steadily from the 2^{nd} day up to the 56^{th} day of curing. However, an inverse relationship between the rate of substitution and strength development was noted. All the cements achieved the minimum required 32.5 MPa strength on the 28^{th} day except the 50% substitution which achieved 28.73 MPa. An optimum substitution rate of 45.42% waste concrete on OPC was established. The hydroxyl ions and calcium oxide concentration on control PPC and the three formulated cements decreased gradually from an average of 56.43 mmol/l to 40.83 mmol/l and 7.56 mmol/l to 2.65 mmol/l respectively from the 3^{rd} to 28^{th} day indicating the presence of pozzolanic reactions. However, for the OPC the concentrations of hydroxyl ions and calcium oxide increased gradually from 58.4 mmol/l to 67.6 mmol/l and 7.9 mmol/l to 8.8 mmol/l respectively negating pozzolanicity. The chemical composition of waste concrete showed the presence of silica dioxide and aluminum trioxide averaging 36.32% and 9.19% respectively meeting the minimum pozzolana specification of 25% silica dioxide.

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LIST OF ABBREVIATIONS/ACRONYMS & SYMBOLS

ACI	America Concrete Insitute
ACI	American Concrete Institute
ASTM	American Standard for Testing Materials
AU	Africa Union
C&DW	Construction and Demolition Waste
CA	Course Aggregates
CMs	Cementitious Materials
EDTA	Ethylene Diamine Tetra Acetic acid
GDP	Gross Domestic Product
G	Grams
IR	Insoluble Residue
ITZs	Interfacial Transition Zones
LoI	Loss on Ignition
Ml	Milliliter
MPa	Mega Pascal
NEMA	National Environment Management Authority
^{o}C	Degree Celsius
OPC	Ordinary Portland Cement
PC	Portland Cement
pH	Potential of Hydroxide
PPC	Portland Pozzolana Cement
RCA	Recycled Course Aggregates
RFA	Recycled Fine Aggregates
SAI	Strength Concrete Institute
SCMs	Supplementary Cementitious Materials
SE	Standard Error
UHPC	Ultra High Performance Concrete
UHPC	Ultra-High-Performance Concrete
UNEP	United Nations Environment Program

UN	United Nations
US EPA	United States Environmental Protection Agency
US	United States
Wt	Weight
%	Percent
µm	Micrometer

CHAPTER ONE

INTRODUCTION

1.1 Background of the study

The construction and demolition waste C&DW is a composition of various waste streams, comprising inert waste, hazardous and nonhazardous waste produced from the building, repairs, and deconstruction actions on houses, roads, bridges, and other structures (Torgal *et al*., 2020). Renovations and demolitions are noted to constitute the major sources of C&DW (Ng & Engelsen, 2018). The composition of C&DW is generally noted to comprise concrete, building blocks, hydrated mortar, metals, and timber. Although, with the sophistication of the building the composition may vary to include ceramics, polymers, gypsum, fibers, and asphalt(Galvez-Martos *et al*., 2018a; Osmani, 2011). C&DW forms the largest waste stream contributing to 13-30% of global solid waste (de Sousa *et al*., 2021). However, the proportion of C&DW in solid waste (SW) varies drastically from one geographical location to another dictated by the size and the rate of economic growth. For example, in 2016, the proportion of C&DW was 30% in Europe, 23%in Hong Kong in 2014,80% in the UAE in 201, and 59% in Singapore in 2011 (Turkyilmaz *et al*., 2019a).

The current population explosion, urbanization, economic growth, and per capita increase have led to increased demand for infrastructure including; large buildings, road networks, bridges, dams, railways, pipelines, and ports, and demolitions of low-capacity structures to pave the way for high capacity structures(Patel *et al.,* 2014). These structural developments have contributed significantly to the generation of C&DW and specifically concrete waste which forms the primary construction material in the world (Restuccia *et al.,* 2016). Oikonomou in his research on recycled concrete aggregates in Greece noted that concrete waste takes 40% composition of demolition wastes (Oikonomou, 2005).

According to a report by UN habitat out of the 30 fastest-growing cities, 21 of them are in Africa (UN-Habitat, 2020). This translates to an excessive demand for concrete. A report by UNEP on

Eco-efficient cement indicated that developing countries will produce and use most cement implying a huge generation of C&DW and exploitation of natural resources (UNEP, 2017). Different developmental agendas locally and internationally have their success anchored on infrastructural development, including but not limited to; vision 2030 of the Kenyan government, agenda 2063 of the African Union, and the United Nations sustainable development goals (AU, 2017; *Kenya-Vision-2030-Sector-Progress-Project-Updates-June-2018.Pdf*; The Economist Intelligence Unit, 2019). Therefore, there is a need for a more sustainable and reliable means of handling C&DW.

1.2 Concrete Waste

Concrete waste is a subclass of construction and demolition waste, composed of hydrated cement, coarse aggregates, and fine aggregates. It bears its origin from the processes of constructing, renovating, altering, or demolishing concrete structures. The fine aggregates are glued together by hydrated cement, forming mortar that bonds the coarse aggregates together (Torgal *et al*., 2020). An interfacial transition zone exists between the adhered mortar and coarse aggregate which serves as a point of weakness when separating the two, as shown in Figure 1 below.

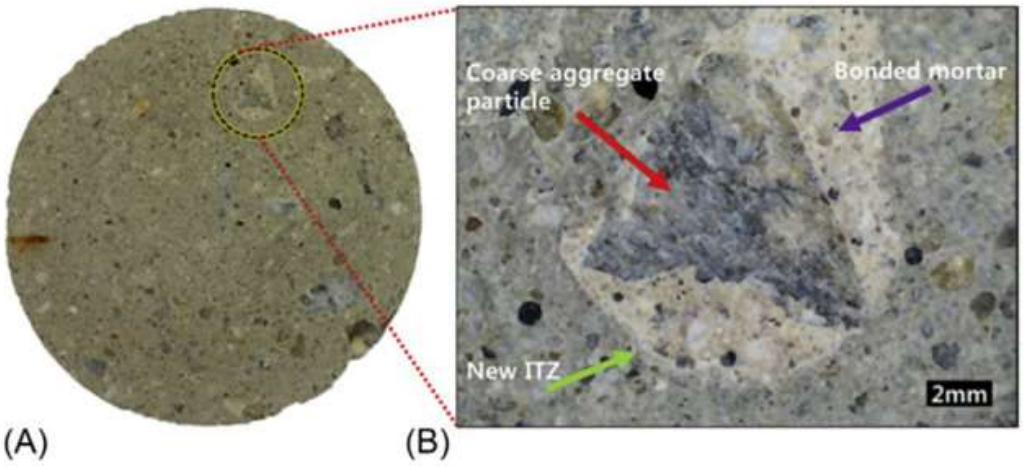

Figure 1: (A) Mortar adhered on coarse aggregate, (B) magnification of adhered mortar on coarse aggregate showing bonded mortar, coarse aggregate particle, and interfacial transition zones (ITZ)
Source:(De Brito & Saikia, 2013)

The interfacial transition zones are associated with the poor structural performance of recycled coarse aggregates due to weak bonding with fresh cement paste/mortar (De Brito & Saikia, 2013). The waste concrete is composed of 70% and 30% aggregates and hydrated cement respectively (Ho *et al*., 2020). Ahmad and co-researchers make a similar observation that waste concrete constitutes 60-70% natural aggregates and 30-40% hydrated mortar(Ahmad *et al.*, 2022). Aggregates are small crushed stones or sand that are chemically inert and used in concrete primarily as a filler and at the same time provide concrete structural stability (Alexander & Mindess, 2005). A hydrated cement paste is a concrete binder resulting from the reaction of cement and water mainly composed of calcium hydroxide and hydrates of silica and alumina. ((Taylor, 1997). The hydrated cement paste is composed of amorphous Ca_2SiO_4, $CaAl_2O_4$, $Ca(OH)_2$, and minor components of $CaCO_3$ and $MgCO_3$ (Gastaldi *et al*., 2015). This chemical structure makes hydrated cement an appealing material in the manufacture of cement. The reaction compounds of hydrated cement are chemically active and can participate in different advantageous chemical reactions which include decarbonization (Kashef *et al.*, 2015; Marangu *et al*., 2019), pozzolanicity, desulfurization(Wu et al., 2008), and calcium hydroxyapatite production (Ho *et al*., 2021). Therefore, concrete waste can undergo mechanical and chemical recycling aiding the re-use of the aggregates and hydrated cement.

1.3 The constituents of construction and demolition waste

The constituents of C&DW differ greatly with the kind of activity taking place at the site. However, sites involving the building and demolition of concrete structures will breed a huge amount of waste concrete. The construction of a new concrete structure is termed to breed between 18-33 kg of concrete waste per m^2 of the build area. Demolition of concrete structures is noted to breed 840 kg of concrete waste per m^2 of demolished concreted structures (Galvez-Martos *et al*., 2018b). The C&DW typically includes a variety of materials as presented in Table 1 below.

Table 1: The constituents of C&DW.

Waste category	% Min-max rage
Concrete mortar and masonry	40-84
Concrete	12-40
Masonry	8-54
Asphalt	4-26
Others(mineral)	2-9
Wood	2-4
Metals	0.2-4
Gypsum	0.2-0.4
Plastics	0.1-2
Miscellaneous	22-36

Source:(Torgal et al., 2020)

Excluding the unearthed material, concrete forms the largest composition of C&DW (Galvez-Martos *et al.,* 2018). Therefore, in the quest for sustainability regarding natural raw material extraction to manufacture construction materials and the management of solid waste disposal proper practices to reduce, reuse, and recycling ought to be practiced. This is what draws the attention of this research focusing on the recycling of waste concrete back in the construction cycle.

1.4 Cement

Cement is defined as an adhesive material of an inorganic origin with the ability to bond particles and then set to a solid mass (Hewlett, 2003). Cement is composed of different phases. The cement phases refer to the distinct crystalline compounds or minerals that are formed during the manufacturing process of ordinary Portland cement. The main cement phases include; Tricalcium silicate, Dicalcium silicate, Tricalcium aluminate, and tricalcium aluminoferrite.Cement is classified into two broad categories based on its setting characteristics; non-hydraulic and hydraulic cement.

In cement chemistry, various notations and abbreviations are used to represent different compounds and reactions. This is shown in Table 2 below.

Table 2: Cement notations and abbreviations

Name	**Actual formula**	**Notation**
Tricalcium Silicate	$3CaO.SiO_2$	C_3S
Dicalcium Silicate	$2CaO.SiO_2$	C_2S
Tricalcium aluminate	$3CaO.Al_2O_3$	C_3A
Tetracalcium alumino ferrite	$4CaO.Al_2O3.Fe_2O_3$	C_4AF
Calcium hydroxide (portlandite)	$Ca(OH)_2$ or $CaO.H_2O$	CH
Calcium silicate hydrate	$CaO.\ SiO_2.\ H_2O$	C-S-H
Calcium aluminate hydrate	$CaO.Al_2O_3.H_2O$	C-A-H
Calcium aluminate silicate hydrate	$CaO.Al_2O_3.SiO_2.H_2O$	C-A-S-H

1.4.1 Non-hydraulic cement

Non-hydraulic cement is the cement that sets fully through carbonation using atmospheric carbon dioxide(CO_2), examples include slaked lime (R. M. Lawrence *et al*., 2007a). The slaked lime is made using relatively pure limestone through burning to yield calcium oxide (CaO) and slaking in water to produce calcium hydroxide($Ca(OH)_2$)which then undergoes carbonation using atmospheric CO_2 to produce calcium carbonate($CaCO_3$) which offers structural strength and has significantly low solubility compared to calcium hydroxide.

1.4.2 Hydraulic cement

America society for testing materials (ASTM), defines hydraulic cement as an inorganic material with the capacity to react with water in the ambient environment to yield a hardened and impermeable solid product (ASTM C150, 2020; Ojovan *et al*., 2019). Hydraulic cements are calcium silicate and calcium aluminate based which include Ordinary portland cement (OPC) and

blended cement (ASTM C595). The hydration process of the hydraulic types of cement takes place in two phases; the first phase involves the hydration of quicklime (CaO) to calcium hydroxide [$Ca(OH)_2$] but with a limited dosage of water limiting the hydration of hydraulic compounds. The second phase involves further hydration of hydraulic compounds by the addition of water to form reactive substances, calcium silicate hydrate and calcium aluminate hydrate which now participate in hydraulic setting (Forster, 2004; R. M. Lawrence *et al*., 2007b).

1.4.3 Ordinary Portland cement

American Concrete Institute defines ordinary Portland cement as a material derived from inter-grinding clinker and calcium sulfate (CT-18, 2018). The clinker is produced by calcining a mixture of clay and limestone at an elevated temperature of about 1450 ^oC. The clinker is composed of different phases namely; alite/tricalcium silicate (Ca_3SiO_5), belite/dicalcium silicate (Ca_2SiO_4), aluminate/tricalcium aluminate ($Ca_3Al_2O_6$), and ferrite/dicalcium alumino ferrite (Ca_2AlFeO_5) constituting of 50-70%, 15-30%, 5-10%, and 5-15% respectively (Taylor, 1997).

Ordinary Portland cement (OPC) is used as a binding agent in concrete production. It binds the ingredients of concrete; water, and fine and coarse aggregates together making concrete a multiphase material. In this regard OPC serves as the key construction material globally (Singh *et al*., 2019), making concrete the second most widely used material after water in the world(PALH *et al*., 2021). The world's production of cement is projected to grow from 3.27 billion metric tons in 2010 to 4.83 billion metric tons by 2030, with China currently taking up to half of the global cement production(*Global Cement Production Top Countries 2019*).

It is approximated that half of the OPC produced globally is used in the production of about 11 billion tons of concrete annually with the rest consumed in other cement applications (Naqi & Jang, 2019a). The demand for concrete is foreseen to increase rapidly in developing countries where the need for infrastructure and buildings is rising, with its demand expected to grow to over 18 billion tons per year by 2050(Mehta, P.K & Monteiro, P.J.M, 2006).

However, the hydration of OPC generates high quantities of calcium hydroxide[$Ca(OH)_2$], which predisposes it to acid attacks hence limiting its applicability. For instance biogenic acid in sewer lines reacts with $Ca(OH)_2$ to yield additional gypsum($CaSO_4.2H_2O$) in the parent concrete which

in turn undergoes a reaction with C_3A forming ettringite, which is an expansive material within the concrete. This leads to interference with the integrity and soundness of the concrete(Munyao *et al.*, 2020).

1.4.4. Manufacture of Ordinary Portland cement

The production of OPC consumes huge quantities of raw materials from quarries posing a great environmental and ecological threat. For example,(Naqi & Jang, 2019b; Rashad, 2015) noted that manufacturing one ton of OPC is estimated to consume 1.5 tons of raw materials. The cement industry is also on the spot for its carbon footprint in the environment. It is noted to emit 7% of the total world's anthropogenic CO_2, (Akhtar & Sarmah, 2018b).(Mehta, P.K & Monteiro, P.J.M, 2006) also stated that to manufacture 1 ton of cement clinker, which is an intermediary material in the manufacture of portland cement, 1 ton of CO_2 is discharged into the atmosphere. Therefore, the cement industry is facing a big challenge in mitigating natural resource depletion, cutting down carbon emissions, and implementing low-energy demand manufacturing practices.

Limestone ($CaCO_3$) and clay form the two principal natural resources for the production of Portland cement. These two are extracted from nature in very large quantities. Limestone provides lime (CaO) and clay provides alumina, silica, and iron. Quartz sand is sometimes used as a source of iron and silica(Hewlett, 2019). These raw materials are extracted in the form of rocks from quarries. They are then crushed to small sizes, analyzed, proportioned, and milled to fine powder, then blended. The blended material is then fed to a kiln and burned, at a temperature of 800^{o}C where limestone undergoes calcination to yield calcium oxide (CaO).

$$CaCO_3 \xrightarrow{Heat(800^oC)} CaO+CO_2 \qquad (0.1)$$

Inside the burning section of the kiln, the temperature rises to between 1350^{o}C and 1450^{o}C, where the Cao reacts with Fe_2O_3, Al_2O_3, and SiO_2 to form dicalcium silicate (Ca_2SiO_4), Tricalcium silicate(Ca_3SiO_5), tricalcium aluminate ($Ca_3Al_2O_6$) and tetracalcium aluminoferrite ($Ca_4Al_2Fe_2O_{10}$) which constitutes the Portland cement clinker. Tricalcium silicate also called the alite phase dominates the cement clinker constituting between 50 and 80% (K. L. Scrivener *et al.*, 2015).

$$2CaO + SiO_2 \rightarrow Ca_2SiO_4 \quad (0.2)$$

$$3CaO + SiO_2 \rightarrow Ca_3SiO_5 \quad (0.3)$$

$$3CaO + Al_2O_3 \rightarrow Ca_3Al_2O_6 \quad (0.4)$$

$$4CaO + Al_2O_3 + Fe_2O_3 \rightarrow Ca_4Al_2Fe_2O_{10} \quad (0.5)$$

From the kiln, the Portland cement clinker is cooled promptly to a temperature of below 1200^{o}C, then allowed to cool slowly to room temperature. It is then ground with calcium sulfate (gypsum) to give Portland cement (Hewlett, 2019; Taylor, 1997).

1.4.5 Hydration of Portland cement

The hydration of OPC refers to the reaction between OPC hydraulic phases which include tricalcium silicate,dicalcium silicate and tricalcium aluminate and water. This reaction leads to the formation of hydrated paste material of the respective phases (calcium silicate hydrate and calcium alumino hydrate). The cement hydration reactions are exemplified by the Equations below (Astin, 1960; H. F. W. Taylor, 1997).

$$3CaO.Al_2O_6 + 6H_2O \rightarrow 3CaO.Al_2O_3.6H_2O \quad (0.6)$$

$$2Ca_2SiO_4 + 4H_2O \rightarrow Ca_3Si_2O_7.3H_2O + Ca(OH)_2 \quad (0.7)$$

$$2Ca_3SiO_5 + 6H_2O \rightarrow Ca_3Si_2O_7.3H_2O + 3Ca(OH)_2 \quad (0.8)$$

1.4.6 Portland pozzolana cement

Portland pozzolan cement, PPC is a blended cement manufactured by inter grinding Ordinary Portland cement/cement clinker together with a pozzolanic material following certain specified proportions (G. Gupta & Pal, 2020). The PPC and OPC are the two main types of cements widely used in the construction industry, however in recent history the advocacy for the use of PPC as a substitute for OPC has been scaled up owing to its low cost of production, low clinker factor, and

its positive impacts on concrete in terms of strength, durability, workability, and resistance towards aggressive chemical attacks (Waghmare *et al.*, 2021).

When PPC is mixed with water, the pozzolanic material reacts with calcium hydroxide emanating from the hydration of OPC hydraulic phases leading to the formation of a further hydrated paste of silicates and alumina as shown in the Equation (1.9). This pozzolanic reaction is what leads to enhanced strength and improved concrete properties of PPC cement (Hewlett, 2019). However, it is worth noting that for the hydration of PPC cement, in the first or so days there are usually very insignificant reactions involving the pozzolanic materials, where the witnessed initial setting is due to clinker hydraulic phases (K. L. Scrivener *et al.*, 2015).

1.4.7 Green cement

Green cement is defined as a type of cement manufactured using carbon offsetting production processes that minimize carbon footprint. The initiatives that have been employed to achieve the realization of green cement include; stepping up energy efficiency, low cement-to-clinker ratios, utilization of substitute material for cement, shifting to alternative fuels, and carrying out carbon capture and storage (Kırgız, 2016; C.-Y. Zhang *et al*., 2021).

The production of traditional cement is facing a huge challenge owing to the price increase and depletion of fossil fuels reserves, inadequacy of natural raw materials, and the global demands to cut down on greenhouse gas emissions contributing to climate change (Naqi & Jang, 2019a). To overcome these challenges coming with traditional cement, the production of green cement has been encouraged due to the precedence they set in terms of consumption of industrial wastes, reduced carbon dioxide emissions, handling in terms of weight per unit volume and workability, reduced energy required in their production, cost-effectiveness in production and the durability and sustainability imposed (Saxena, 2016).

Different industrial wastes have been investigated for their potential to substitute OPC gearing for the production of low-clinker types of cement. These wastes include; fly ash, blast furnace slag, silica fumes, clay bricks wastes, and sugarcane bagasse ash (Imbabi *et al*., 2012). Other wastes are in the research stages for their applicability in green cement production and specifically in the

production of low-clinker factor types of cement. In line with this global objective, this research will investigate the application of waste concrete in the production of green cement.

1.5 Pozzolan

Pozzolans are defined as "natural or manmade inorganic materials which are attributed with toughening in water when combined with $Ca(OH)_2$, or with substances whose reaction can produce $Ca(OH)_2$ such as OPC during its hydration"(Hewlett, 2019). An alternative definition by (Thomas, 2013) pozzolan is termed as "a material composed of SiO_2 or SiO_2 and AL_2O_3 which possesses slight or no cementitious properties, although in its finely milled state and contact with water, undergoes a chemical reaction with $Ca(OH)_2$ at normal temperatures to produce products possessing cementitious behavior".

The pozzolans can be added as a distinct ingredient alongside PC in the mixer yielding concrete or forming a component during the manufacture of PPC (blended cement) (Thomas, 2013). In pursuit of cutting down on cement manufacturing costs and carbon footprint from the cement industry, partial replacement of Portland cement clinker with Pozzolans has been identified as the most effective and widely applied practice (Snellings, 2016).

The use of these pozzolans for partial replacements of PC enhances the behavior of freshly prepared and resultant set concrete, which includes workability, resistance to aggressive environments, lasting strength, and water demand (Saxena, 2016; Thomas, 2013).

1.5.1 Sources of pozzolans

1.5.1.1 Natural Pozzolans

The American body on concrete research (ACI) describes natural pozzolan also referred to as pozzolana as " either unprocessed or heat activated naturally existing materials that bear pozzolanic characteristics like volcanic ash or pumicite, operline chart, and shale, tuff, and diatomaceous earth" (ACI 116, 2000). Hewlett in his book on cement and concrete gives an alternative description of natural pozzolan as "natural materials that do not need additional processing from milling to show pozzolanic properties." This definition excludes any material

requiring calcination or thermal treatment like shale, diatomaceous earth, and clays from the class of natural pozzolans (Hewlett, 2019).

Natural pozzolans have been used in the manufacture of cement since time immemorial. With the increased demand for cement and increase in population exerting pressure on natural resources, the availability of this very important natural resource is threatened therefore the need to explore alternatives to aid in the manufacturing of eco-friendly cement (Pacheco-Torgal *et al*., 2012)

1.5.1.2. Industrial wastes

These are wastes of industrial origin that have been rendered structurally unstable through calcination by having hydroxyl groups exposed for reaction. These include; fly ash which has its origin from coal-fired electric and steam generating plants, silica fume originating from silicon and ferrosilicon alloys smelting process, granulated blast furnace slag from iron and steel manufacturing process, ash originating from rice husk and sewage sludge (Imbabi *et al*., 2012; Pacheco-Torgal *et al*., 2012).

The drive for sustainability in the energy sector has led to realignment towards renewable sources of energy shutting down coal-fired electric and steam-generating plants the principal source of silica fume. Also, the decline in steel and iron manufacturing arising from recycling and substitution by other materials hence decreased ground granulated blast furnace slag. These industrial developments have led to the declining provision of these traditional pozzolanic materials, also referred to as artificial pozzolans. Therefore, the clarion calls for research towards the provision of new pozzolanic materials (Snellings *e*., 2016).

1.6 Supplementary cementitious materials

The SCMs refer to substances applied together with OPC. Through pozzolanic activity or hydraulic reactions, these substances influence the properties of set concrete. Such materials include industrial waste products (artificial pozzolans) such as silica fume (SF), granulated blast furnace slag (GBFS), fly ash (FA), and natural pozzolans which include diatomaceous earth, calcined clays, and volcanic ash (Juenger & Siddique, 2015b). ASTM C618 defines pozzolan as siliceous and aluminous material which have slight or no cementitious value but in its finely divided form and the presence of moisture reacts chemically with calcium hydroxide at normal temperature to form compounds possessing cementitious properties (Seco *et al*., 2012).

The exploitation of pozzolana by the cement industry which is a raw material-intensive process threatens the sustainability of industrial ecology. This calls for the usage of artificial Pozzolans which are by-products or waste streams of other industrial processes. However, in developing countries like Kenya artificial Pozzolans are not available and these countries rely entirely on natural Pozzolans as the sole source of pozzolana (Wahome, 1990). The current advocacy on green

economy and sustainability threatens the availability of artificial Pozzolans which happens to be by-products of coal-powered industries. Therefore, research on potential pozzolanic materials remains essential to the sustainability and greening of the cement industry. C&DW having shown to be a potential source of low-carbon calcium silicates, can be exploited as a possible pozzolan and applied as a substitute for natural Pozzolans (Teklay *et al.*, 2017a).

1.7 Pozzolanic activity

Protus defines pozzolanic activity as the chemical reaction involving a pozzolanic material, hydrated lime, and water to form a solid material possessing cementitious properties at normal temperatures (Protus, 2014). The pozzolanic activity is driven by the content of silica and alumina which are free throughout the hydration process to react with CH forming additional C-S-H cementing gel enhancing the concrete properties. Factors including particle size, temperature, water/solids ratio, and additives intended to speed up the reaction are noted to affect pozzolanic activity(Hewlett, 2019; Skibsted & Snellings, 2019) This reaction of pozzolanic materials with hydrated lime and water gives the same products as those formed during the hydration of PC regarding the comparable chemical composition(Juenger & Siddique, 2015b). The Equation below describes the general overview;

$$nSiO_2 + nCa^+ + 2NOH^- \rightarrow nCaO.nSiO_2.nH_2O \quad (0.9)$$

The silica and alumina from pozzolanic materials react with CH from the hydration of PC forming additional hydration material C-S-H which is the cementitious material responsible for cement bonding.

1.8 Statement of the problem

The quest for sustainability in the current world economy to satisfy the necessities of the rapidly increasing global population, at the same time meeting the environmental and ecological balance, is posing huge pressure on humanity. The construction industry is quintessential for any country's economic progress. The demand for housing in the limited spaces in urban areas has led to the

demolition of old and low-capacity structures to pave the way for modern high-capacity structures. This has caused huge production of C &DW disposed of to dump sites which are limited in space and high dumping costs contributing to illegal dumping resulting in environmental deterioration.

The cement industry on the other had is on the spot for its cabon foot print for it contributes 5-8% if the global anthropogenic carbon dioxide that emanates from the production of high clinker factor cements. To address this challenge production of blended cements has been recommended. However, the current pozzolanic materials in use which include fly ash, silica fume, and ground granulated blast furnace slug emanate from coal-fired power plants which are still under pressure to shut down due to the current advocacy of green energy transition. The mining of natural pozzolana faces depletion and also challenges of environmental deterioration. Therefore, need for research for a more green alternative to pozzolanic materials. For that matter, this study seeks to investigate the application of the waste concrete material as a possible replacement for natural pozzolana. Through this it will address the challenges of environmental deterioration arising from the disposal of concrete waste and extraction of natural pozzolana, yielding to the production of green, low clinker factor cement. This approach will also offer a more affordable pozzolanic material hence reducing the cost of cement.

1.9 Objectives

1.9.1 General objective

To investigate the utilization of concrete waste mortar in the manufacture of Portland Pozzolana cement.

1.9.2 Specific objectives

1. To determine the compressive strength of the Portland Pozzolana Cement.
2. To determine the Pozzolanic activity of concrete waste formulated Portland pozzolana cement.
3. To quantify the optimum amount of concrete waste for use in cement production.
4. To determine the elemental composition of the waste concrete.

1.10 Justification

The disposal of construction and demolition waste is channeled to landfills and dumpsites with limited capacity and high damping cost, a factor which has contributed to the illegal dumping of this waste contributing to environmental challenges (Osmani, 2011).

Previous research focusing on the possible recycling of concrete waste has been conducted. Although much effort has been directed towards the recovery of coarse aggregates which has shown to yield successful recycling to an extent of 100% (Teklay *et al*., 2017b). However, research on fine fractions as a substitute for fine aggregates and a potential origin for raw material in the manufacture of cement clinker has not been fruitful and the majority of this waste ends up in landfills leading to environmental deterioration(Dan & Wang, 2006).

Research by different scientists has shown concrete waste to have potential properties that can point towards a possible replacement for pozzolans in the manufacture of PPC. For instance(Jiji Antony, 2016) in his research on the possibility of using C&DW as pozzolana, showed this raw material to have appreciable pozzolanic activity. The inert quartz (sand) which is a major constituent of concrete waste has shown possible activation upon subjecting it to mechano-chemistry indicating pozzolanic activity(Benezet & Benhassaine, 1999). C&DW is documented as a potential origin of low-carbon calcium silicates and further research is recommended on possible means of recovering this very important mineral from C&DW (Teklay *et al*., 2017b). Through these findings C& DW can be positioned as a possible supplementary cementitious material, hence its possibility as a replacement for pozzolana in PPC production.

The success of this research will yield the recycling of concrete waste as a possible substitute for pozzolans in PPC production. This will be a step in the right direction toward the realization of a more sustainable and reliable means of C&DW management.

CHAPTER TWO

LITERATURE REVIEW

2.1 Sustainability of the cement industry

In the current world, sustainability is a critical issue of discussion in every industry. The UN defines sustainability as "the ability of the current generation to meet its own needs without compromising the ability of the future generation to meet their own needs" (Peake, 2004; Scoones, 2007). Climate change is one of the main factors affecting global sustainability and inflicting high threats to international communities(Gil *et al*., 2019). Anthropogenic carbon dioxide and other greenhouse gases (methane and nitrous oxide) are listed as the main grounds promoting climate change. However, CO_2 is the main contributor (Böhringer, 2003). A linear relationship is noted between the temperature on the earth's surface and the atmospheric concentration of CO_2 (Ramezanianpour, 2014a). Therefore, to mitigate on effects of climate change we ought to cut down on CO_2 emissions.

Various industrialized and industrializing nations, Kenya included have committed to cutting down the emissions of CO_2 through the signing of treaties. This includes; the Kyoto protocol adopted in 1997 and signed in 2005 by 141 countries committing to alleviate greenhouse gas emissions to below 6% of the 1990 quantities by 2012 (Bohringer, 2003). On 12th December 2015 another treaty, the Paris agreement was adopted by 196 countries it was a legally binding international climate policy to enforce the reduction of greenhouse gases by the member countries and keeping global warming to below 2^{o}C (Falkner, 2016; Streck *et al*., 2016).

In follow up and accountability to Paris agreement. United Nations organizes an annual conference of the parties referred to as "COPs".COP 27 was the last one to be held in Sharm El-sheikh, Egypt in November 2022 which was attended by more than 200 countries, including Kenya (https://ec.europa.eu/commission/presscorner/detail/en/ip_21_6021). Among the resolutions passed in COP27 was reaffirming decarbonization of the world's economy by achieving carbon

neutrality by 2050 (net zero) and keeping global warming below 1.5°C (*Sharm El-Sheikh Climate Change Conference - November 2022 | UNFCCC*).

The sustainability of any industry can be gauged through; energy consumption in its production, emissions of CO_2, the extent of pollution of its material at the end of life span, the lifecycle, and the possibility to recycle material at the end of lifetime, the raw materials required and transport logistics required in the mobilization of raw materials and distribution (Ramezanianpour, 2014a).

The cement industry is characterized by high emissions of CO_2, contributing up to 8% of the global anthropogenic CO_2 (Akhtar & Sarmah, 2018b; Ali *et al*., 2011; Gao *et al*., 2015), high embodied energy in its production process(Awoyera *et al*., 2020; Hammond & Jones, 2008), mining and transportation of raw materials and final distribution(Barcelo *et al.*, 2014; Cabeza *et al*., 2013), and is a raw material intensive process (Klee, 2004). Therefore, to achieve sustainability the players in the cement industry have to innovate on techniques of CO_2 emissions reduction, improvements in energy efficiency, and green alternative raw materials.

OPC-based concrete being the most widely used synthetic material globally has dictated the massive production of cement, projected to attain production of 4830 million metric tons by the year 2030 (Deutscher, 2019). This demand has grown gradually due to global population requirements for housing and infrastructure as shown in Figure 2 below.

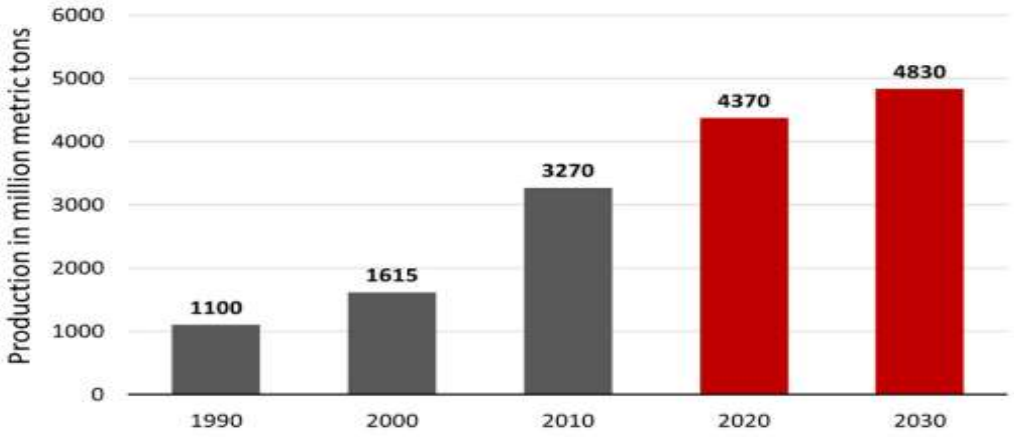

Figure 2: Global cement production and projections up to 2030

Source:(*Deutscher, 2019*).

Research on the application of alternative cementitious materials(Ramezanianpour, 2014a), optimization of cement content to use the minimum possible and application of alternative binders (Adesina, 2020), improving concrete durability(Cheung *et al*., 2018), use of green energy alternatives and researching on possible concrete recyclability are cited as the key pillars to drive sustainability in the cement industry (Aitcin & Mindess, 2014; Bonoli *et al*., 2021)

The raw material intensity of the cement industry ranging to more than 3000 billion tons/year and high waste generation translating to more than 40% of global solid waste of the whole construction industry breeds unsustainability(Elgizawy *et al*., 2016a). Therefore, this calls for more concerted efforts in handling and management of construction and demolition waste towards a zero waste model and at the same time advocating for circularizing of the whole construction industry from the traditional one-way process to reduce intake of the virgin voluminous raw materials (Foster, 2020).

Construction and demolition waste generation have grown in recent years at alarming rates and it continues to intensify. The current population explosion and urbanization are leading to the demolition of old and low-capacity structures to redesign modern high-capacity structures. This has contributed to a huge production of C&DW disposed of at dump sites contributing to environmental challenges(Martinez Molina *et al*., 2015). Waste concrete takes 40% composition of demolition waste (Oikonomou, 2005).

Construction and demolition wastes (C&DW) have grown to be a global subject drawing much attention from scientists and policymakers. For example, the US agency on environmental protection (US EPA) noted that 600 million tons of C&DW wastes were generated in the US in 2018, with C &DW taking 10% and 90% respectively(US EPA, 2019). In the year 2014 C&DW in China was approximated at 1.13B tons, translating to 30-40% of the total waste(B. Huang *et al*., 2018). In Australia, 20.4 metric tons of C&DW were produced from the year 2016 to 2017 translating to 30% of the entire waste produced (Pickin *et al*., 2018).In the EU, 850M tons of C&DW are produced annually (Sáez & Osmani, 2019). According to (Turkyilmaz *et al*., 2019b), the construction industry is responsible for 13-30% of global waste.

The quantification of C& DW has been cited as a key driver to sustainable development in the provision of policy guidance in its handling and regulation for it has grown to be the key waste

steam for solid waste (Islam *et al*., 2019). In this endeavor, different countries have conducted comprehensive studies on the quantification of this waste stream. This includes; china (Ding & Xiao, 2014), Spain (Villoria Saez *et al*., 2012), Thailand (Kofoworola & Gheewala, 2009), Taiwan (R. Y. Huang *et al*., 2011), Greece (Fatta *et al*., 2004) and Malaysia (Mah *et al*., 2016).

2.2 Concrete waste management

Waste management refers to the removal and reduction of waste whenever possible, and the recycling of substances that would otherwise translate to waste (Napier, 2012). The practice of waste management has not been a challenge before the 20th century after which the world's population growth exploded. The amount of space and land decreased abruptly and a huge generation of waste with varying compositions was experienced from the industries, building, and deconstruction sites (Torgal *et al.*, 2020). Since then waste from building and demolition sites has grown to be the main waste stream for solid wastes, hence the call for sustainable management (Elgizawy *et al.*, 2016b). Concrete waste in its management can undergo separation into its coarse fraction and fine fraction, used or disposed of in totality of its wholeness. Different approaches have been employed in the management of concrete wastes, which include;

2.2.1 Disposal in landfills and dumpsites.

Landfills and dumpsite disposals had been practiced before advocacy for more sustainable means of waste disposal (Kaosol, 2009). Landfilling and illegal dumpsites on open land or along the natural drainage systems have been cited as the main means of disposal for much of the concrete wastes produced in the U.S.A. (Napier, 2012). Dumpsites are associated with impacting negative effects on human health, pollution of the environment, and occupying land which could otherwise be used for better economic investments. Egypt employs landfilling as the main concrete waste management practice (Wagih *et al.*, 2013).

The impacts of C&DW are likely to be more severe in developing countries that lag in research on more sustainable means of waste handling. In India, Brazil, and China very little amount of C&DW is reused with a large amount of being sent to landfills for disposal (Torgal *et al*., 2020). Sabai, in his investigation on C&DW characteristics in Tanzania, paints a picture replicable in most African countries, where there isn't even a landfill and open-air dumping is the primary

means of disposal (Sabai, 2020). Research conducted by (Akhtar & Sarmah, 2018a) notes a very low recycling rate in developing and the majority of the waste ends up in dumpsites, citing Crotia, New Zealand, and South Africa where 90%, 80%, and 90% of the waste respectively are landfilled. National Environment Management Authority (NEMA) in its national solid waste management strategy acknowledges the lack of proper C&DW handling citing disposal in open dumpsites as the primary means of dumping (NEMA, 2015).

Landfilling is associated with the pollution of groundwater due to its release of pollutants especially sulfate ions and toxic heavy metals released from waste concrete (Smolka-Danielowska, 2006). This led to the banning of landfilling in European countries and the recommendation of research funding to develop more possibilities of safe disposal on reuse and recycling (BIO Intelligence Service, 2011).

2.2.2 Re-use and recycling.

The advocacy on recycling and the re-use of demolished concrete waste in recent times has been scaled up majorly due to scarcity of natural building materials, increased dumpsites tariffs, and overwhelming demand for construction materials (Jayakody Arachchige *et al.*, 2012). Different modes have been explored and documented for the reusing and recycling of concrete waste material. Applications of concrete waste material are classified into two; structural and non-structural (Gangolells *et al*., 2014).

2.2.2.1 Road base and filling material in road construction.

Open-loop recycling of concrete waste has been practiced exclusively in road civil works as a base and filling material. However, regulations on the protection of groundwater by the State Association of Germany discouraged the use of this open-loop recycling due to associated pollution (Weil *et al*., 2006). Road construction has also been identified as a consumer of waste concrete by (BIO Intelligence Service, 2011).

Applications of C&DW in road base and filling are attributed to the soil stabilization ability of concrete wastes through pozzolanic and hydration reactions (Ho *et al*., 2021). This creates hard soil with decreased shrinking and swelling properties which are fundamental in civil applications.

Cai and his colleagues investigated civil applications of waste concrete aggregates in the design of road bases having permeable characteristics. This material showed ideal behavior in terms of drying, shrinkage, and cracking. However, high water uptake was exhibited which posed the challenge of cement slurry leakage but the research indicated a maximum allowable limit of 30% (Cai *et al.*, 2021).

Gupta and his co-researchers noted that recycled concrete has outstanding mechanical properties and can be used as a substitute for natural aggregates in road construction. However, two setbacks towards this application were identified; this material was established to be a potential pollutant of the underground water due to the leaching of metal ions including aluminum, Lead, Arsenic barium, chromium, Iron, Molybdenum, sodium, Nickel, Antimony, and strontium. The second obstacle was associated with the alkaline leachate of high pH(10.5-12.5) which was seen to corrode the reinforcing metal bars (N. Gupta *et al.*, 2018). Similar observations were also made by (Chen *et al*., 2013; Engelsen *et al*., 2017).

2.2.2.2 Waste concrete recycling into coarse aggregates (CA)

Waste concrete comprises 65-70% original natural coarse aggregates and 30-35% cement mortar (J. Zhang *et al*., 2015). This composition makes these coarse aggregates inhomogeneous, low density, and more permeable due to the adhered cement mortar calling for further treatment before its application in the preparation of fresh concrete (Ohemeng & Ekolu, 2006a).

Recycling CA from demolition waste can be a fundamental drive towards achieving sustainability in the construction and design of infrastructure to meet the current needs (Brandes & Kurama, 2016). Recycling, of course, aggregates in waste concrete to substitute the use of virgin aggregates in fresh concrete has been researched widely by different scientists and has shown practicability for application in structural quality concrete. The utilization of recycled course aggregates has also shown appreciable properties of concrete ranging from compressive strength, tensile strength, modulus of elasticity, and soundness to levels of even 100% substitution. The study also showed a major possibility of decreased concrete cracking when used in high-risk cracking applications (Adams *et al.*, 2016).

The compressive strength of concrete at a given water-cement ratio remains within appreciable levels of up to 30% replacement of recycled coarse aggregates, after which it showed an inverse proportion with an increase in the RCA ratio (Xie *et al.*, 2018). Similar observations are made by (Ngo & Chai, 2004), where the compressive strength of concrete blocks is hardly influenced by the substitution of up to 30% RCA. This decline in strength is attributed to the high w/c ratio required to ensure concrete workability in these increased RCA replacements.

2.2.2.3 Waste concrete recycling into fine aggregates for use in fresh concrete

Fine aggregates (FA) also referred to as recycled sand consists of sand and hydrated cement paste and are defined to be of particle sizes not larger than 5mm (Zhao *et al.*, 2015). The pursuit of sustainability in the building sector has caused a lot of research to be undertaken in exploring the possibility of recycling fine aggregates from demolition waste in replacement of natural fine aggregates. Evangelista and Brito studied the behaviors of concrete made with recycled fine aggregates. They established that replacement ratio can be done up to 30% without affecting compressive and tensile strength. The modulus was observed to decrease with an increase in substitution ratio and abrasion resistance showed a linear proportionality (Evangelista & de Brito, 2007).

Braga, Brito, and Veiga employing European standards studied the effects of incorporating very fine CA in concrete mortar. This study indicated increased bulk density, almost direct proportionality of compressive and flexural strengths with the use of fine aggregates, decreased water absorption coefficient due to high compaction, very low vulnerability to cracking, and decreased shrinkage (Braga *et al*., 2012). In agreement with (Dapena *et al.*, 2011), the application of recycled sand in the manufacture of fresh concrete compromises the most important concrete properties; compressive strength and durability attributed to increased concrete porosity and permeability.

The application of fine aggregates from concrete waste is limited by their physical properties. High water demand translates to poor concrete workability and adhered mortar which renders the material a multiphase affecting the mechanical properties, transport mechanisms within the new concrete setting, and durability. The concept of contamination of the parent concrete through

chlorides and sulfate attacks from sewer systems, seawater, or acid rain also poses a major concern for it affects the structure's durability made from recycled FA (Nedeljkovic *et al*., 2021).

Flexural strength, compressive strength, and firmness of the concrete declined with the increased proportion of RFA. This observation was attributed to interfacial transition zones (ITZs) arising from the multiphase property of RFA which affects the properties of resultant concrete (Ohemeng & Ekolu, 2006b; H. Zhang *et al*., 2018).

2.2.2.4 Application of concrete waste in cement clinker production

In pursuit to maintain the three bases of sustainability; economic growth, social aspects, and environmental protection in the construction industry closed-loop recycling have been advocated (Torgal *et al*., 2020). In line with this endeavor, different scientists have focused their research on the development of 100% recyclable concrete by incorporating C&DW in the raw meal for cement clinker production. Specifically, the fine aggregates are of the attention regarding this application. These aggregates are composed of cement in its hydrated state bearing all the essential elements for clinker production exhibiting low carbon emissions(Zhutovsky & Shishkin, 2021). For instance (Liu *et al*., 2021) produced a cement clinker at different temperatures of 1300^{o}C, 1350^{o}C, 1400^{o}C, and 1450 ^{o}C with alteration admixtures by incorporating 97.78 wt% waste from the demolition site as a raw meal. In comparison with traditional clinker, the clinker made from recycled waste showed improved burnability, calcination temperature reduction, and decreased C_3S energy of formation.

Fine Concrete waste aggregates can be incorporated into cement clinker raw meal. Krour observed that these waste aggregates can be incorporated to a maximum rate of between 10-20% with slight effects on the burnability and composition of the clinker (Krour *et al*., 2020).

Miao and his co-researchers in their research on the production of PC clinker using both the traditional method of "two millings and one burning "where the raw meal (hydrated cement paste) is calcined at between 1400 and 1450^{o}C and OPC clinker synthesis at a lower temperature where the raw meal (hydrated cement paste) is calcined at 650^{o}C for one hour. Using the traditional method this raw meal is observed to exhibit prohibitive crystallinity posing challenges in burning and ability to grind, factors which compromised the quality of the clinker manufactured. The low-

temperature method produced C_2S as the main clinker active ingredient which showed low crystallinity and increased hydration activity. These two methods are noted to mitigate the exploitation of non-renewable sources for clinker manufacturing, however, energy consumption and carbon footprint remain a major concern (Miao *et al*., 2015b).

2.2.2.5 Preparation of alkali-activated cement

Alkali-activated cements also known as geopolymers are manufactured from alkali-activated materials which are subjected to an alkaline medium yielding a cementitious material demonstrating elevated strength and durability (Hewlett, 2019; Miao *et al*., 2015a). Different scientists have sought to investigate the potential of C&DWs as possible alkali-activated materials.

The use of sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$) and sodium sulfate (Na_2SO_4) to regenerate the activity of finely ground concrete waste to cement showed the possibility of restoring the activity of cement in waste concrete by the use of alkali activators. However, the regenerated cement showed low 28-day strength which was attributed to low cementitious phases (Deng, 2011).

The activity of hydrated cement constituents can be restored by the use of NaOH or a solution of sodium or potassium silicate (water glass) as activators. The alkali-activated material realized from this study acquired 7.5 and 45.4 MPa flexural and compressive strength respectively upon 30% substitution on slag residue (Gong *et al*., 2014).

2.2.2.6 Dehydration and rehydration of hydrated cement in concrete waste

Thermal treatment is researched as the primary means of dehydrating hydrated cement. The first stage of dehydration is the evaporation of both chemically and physically bound water, which happens below 120^{o}C. Above 120^{o}C structural alterations start to occur; between 200^{o}C and 400^{o}C calcium silica hydrate (C-S-H) dehydrates, calcium hydroxide breaks down at 450^{o}C and $CaCO_3$ decomposes at 750^{o}C. Therefore, at 800^{o}C the hydrated mortar is completely dehydrated (Castellote *et al*., 2004; Florea *et al.*, 2014; Shui *et al*., 2008a)

Bogas and his co-researchers conducted comprehensive investigations on dehydrating recycled cement waste by use of thermal activation. This research observed that dicalcium silicates (C2S) were the most dominant phase after thermal treatment. Other phases yielded after this treatment

include tricalcium silicates (C_3S) and aluminate ferrite monosulfate (AFm) though in insignificant amounts (Bogas *et al*., 2022).

Research by Shui and colleagues envisioned the reactivation of fine recycled concrete aggregates (FRCA) by use of thermal treatment and subsequent application of it as the key constituent of the construction mortar. The possible rehydration of this material was gauged by the impacts it could have on the mechanical and microstructure properties of the resultant mortar. The findings showed that thermally treated FRCA bears rehydration reactivity and can be applied in mortar preparation (Shui *et al*., 2008b).

2.3 Pozzolanic properties of construction and demolition wastes.

Various scientists have explored possible pozzolanic characteristics of C&DW through the employment of different means to activate them. For instance, (Caneda-Martinez *et al*., 2021) investigated the pozzolanic activity of C&DW after calcining at 150 ^oC for 24 hours and gridding to below 63 µm for which the material showed to have pozzolanic properties. The substitution of OPC by this material at the rate of 5%, 7%, and 10% showed cement paste performance resembling that of OPC. Upon assessing the environmental impact as a result of recycling this C&DW it showed minimal energy demand compared to manufacturing of OPC which showed to be an energy-intensive process. In terms of CO_2 emissions, blended cement showed a 9.9% reduction. Caneda-Martinez and colleagues concluded that C&DW fines can be applied as a supplementary cementitious material owing to its pozzolanic properties and recommended further research to advance application.

A study on "potential of construction and demolished waste as pozzolana" sought to explore the pozzolanic activity of concrete waste by employing the method of lime reactivity and electrical conductivity. This research established appreciable pozzolanic activity implying the possible recycling of concrete waste as SCM which is a "green" method to manage the C&DW which has become a nuisance in the environment (Antony & Nair, 2016).

Mucsi and his fellow scientists explored improvements in pozzolanic activity through mechanical activations of C&DW focusing on fine fractions. The material was subjected to gridding and its pozzolanic activity was determined through the saturated lime test and strength activity index

(SAI) where the material showed pozzolanic properties. This mechanically activated C&DW material attained a 28^{th}-day compressive strength of 53 MPa upon a 30% replacement ratio on cement showing a very viable means of activation (Mucsi *et al.*, 2021).

This research shall seek to apply concrete waste as a substitute for pozzolana in the making of Portland pozzolana cement using Kenyan cement standards. The concrete waste will be activated through a mechanochemical approach through fine grinding, which is a more green and sustainable method that has been shown to improve the surface reactivity of materials compared to calcining which contributes to CO_2 emissions.

2.4 Pozzolanicity

Shvarzman and co-researchers defined pozzolanicity as the ability of a pozzolanic material to undergo a reaction with $Ca(OH)_2$ in the existence of excessive water at ordinary temperature forming cementitious materials (Shvarzman *et al.*, 2003; N. Zhang *et al*., 2011). Another more specific definition by Davraz, pozzolanicity has been defined as the capability of SiO_2-centered pozzolan to react with calcium hydroxide (CH) yielding calcium silica hydrate (C-S-H) binding gel in concrete in the presence of water.(Davraz *et al*., 2018). Cheriaf also defines pozzolanicity as "the ratio between the strength of the mortar containing the blended cement and that of the mortar cast with plain cement" (Cheriaf *et al*., 1999).

Different test procedures can be employed in the determination of pozzolanic activity this includes; the Frattini test which involves chemical titration to determine dissolved $[Ca^{2+}]$ and $[OH^-]$ for a solution containing Portland pozzolana cement (CEM I) and the pozzolan under study (ASTM C 311, 2013; BS EN 196, 2005). The strength activity index (SAI) method is taken as the ratio of the strength of PPC mortar (CEM II) and control mortar of CEM I, Reported as;

$$SAI = \frac{A}{B} \times 100\% \tag{2.1}$$

Where; A is the compressive strength of PPC mortar made with test pozzolan (MPa) and B is the compressive strength of (CEM I) the control mortar (MPa) (ASTM C618-19, 2019; BS 3892-1, 1997).

The saturated lime test is another method applied in pozzolanicity determination, in which the pozzolan is blended with saturated lime in place of CEM I and cured in water. The pozzolanicity of the material is determined by evaluating the residual $Ca(OH)_2$ in the reaction system of the pozzolanic material and OPC hydration products at different ages of curing (Frais *et al*., 2005; García *et al.*, 2008; Li *et al*., 2023).

The pozzolanicity of a material is determined by equating the amount of $Ca(OH)_2$ in a solution interacting with hydrated cement for a set period (8-15 days) with the amount of $Ca(OH)_2$ efficiently to saturate the same solution under the same alkalinity (KS EAS 148-5-2000) The concentration of hydroxyl ions (OH^-) and calcium oxide (CaO) is determined and plotted on pozzolanicity curve shown in Figure 3 below.

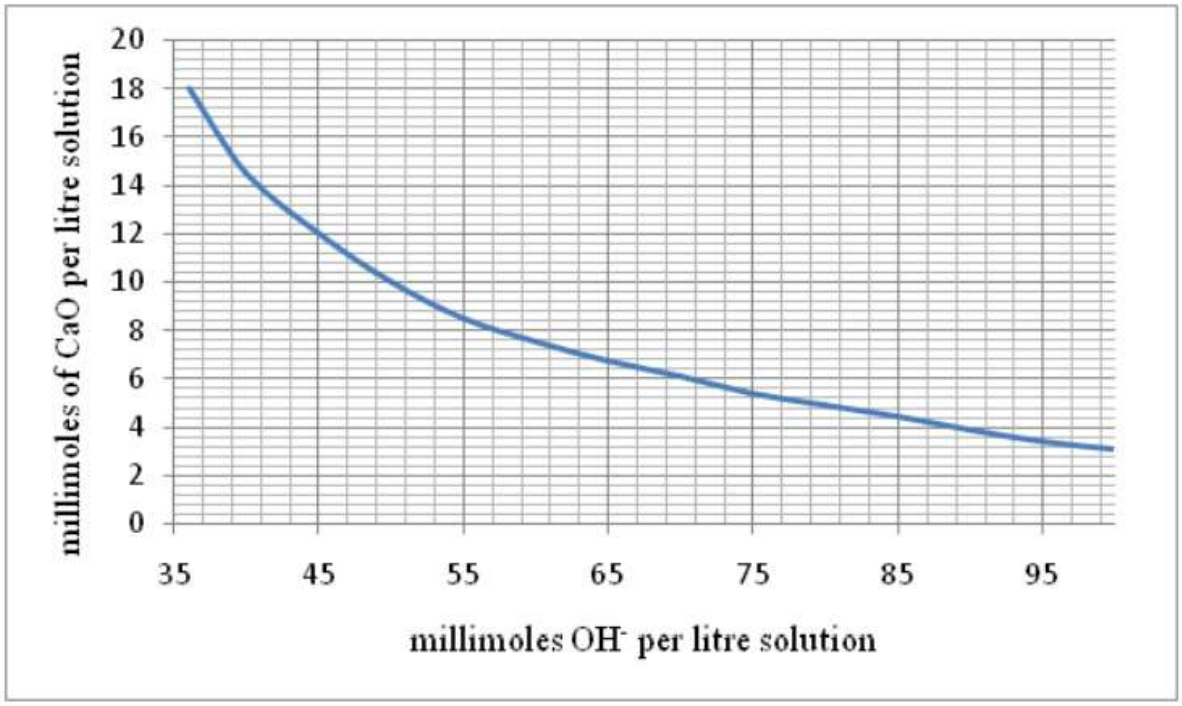

Figure 3: Pozzolanicity test curve

Sourse:*(KS EAS 148-5-2000)*

The cement under investigation is said to satisfy the pozzolanicity test if the mean CaO and OH^- concentration point is below the CaO saturation concentration curve. The lower the CaO ad OH^-

concentration coordinates below the saturation solubility curve the higher the pozzolanicity of the material under investigation.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Introduction.

This chapter describes the materials and methodologies used in the sampling and analysis methods in this research. Analytical grade reagents were employed with distilled water used in their preparation. The glass wares used were washed using detergent and tap water then rinsed using distilled water and oven dried at 50 ^{o}C. The physical and chemical tests undertaken in this study were conducted at Savannah cement Limited research laboratories.

3.2 Determination of the compressive strength development.

3.2.1 Materials

Ordinary Portland cement (OPC), CEM I 42.5N, and Portland pozzolana cement CEM IV 32.5R both complying with KS EAS 18:1-2017 were obtained from Savannah Cement Limited. Standard sand conforming to ISO 679:2009 and EN 196-1 was obtained from Xiamen ISO Standard sand Co.Ltd and Distilled water was obtained from Science Lab Limited.

3.2.2 Equipments

Types of equipment used include; digital planetary orbital mixer model JJ-5, laboratory scale jaw crusher, laboratory scale ball mill,45 µm sieve, computerized compression analysis machine model YAW-300, jolting table apparatus, stainless steel moulds (40 mm × 40 mm ×160mm), moist air cabinet maintained at 25^{o}C ±1 ^{o}C and relative humidity of 90% and curing buckets of more than 160mm depth.

3.2.3 Sampling and sample preparation

The three concrete waste samples used for this study A, B, and C ware collected from demolition sites in Roysambu, Woodley in Dagoretti North, and Mowlem in Embakasi West sites respectively

all within Nairobi city, the capital of Kenya. By use of a chisel and hammer, hydrated cement mortar adhered to the demolished construction blocks and was removed randomly throughout the demolition site. A sample of 10 kg was collected from each site. Laboratory installed jaw crusher was used to reduce the collected concrete waste samples to a size of 2 mm. The samples were further milled in a laboratory ball mill for 6 hours to 5% retention on a 45 μm sieve. The milled concrete was subsequently applied as pozzolan in the formulation of PPC.

The test cement was formulated by substituting Ordinary Portland cement (OPC), CEM I 42.5N complying with KS EAS 18:1-2017 by 10%, 20%, 30%, 40%, and 50% of milled concrete waste which could serve as pozzolana in the formulation of PPC.

3.2.4 Mortar preparation.

The proportion of mortar consists of 1 part cement, 3 parts standard sand, and 0.5 parts water (water/cement ratio=0.5). A batch of 3 test specimens consists of 450±2 g of test cement, 1350±5 g standard sand, and 225±1 g of water. The batch composition of the 5 test cement and control OPC and PPC is illustrated in table 3 below;

Table 3: Batch composition of the control and test cements

Substitution rate (%)	Cement (450±2 g)		Sand(1350±5 g)	Water(225±1 g)
	Waste concrete	OPC Cement		
10	45	405	1350	225
20	90	360	1350	225
30	135	315	1350	225
40	180	270	1350	225
50	225	225	1350	225
Control OPC	450		1350	225
Control PPC	450		1350	225

Using the planetary orbital mixer model JJ-5 as described in (KS EAS 148:1-2000), 225 g of water,450 g of cement, and 1350 g of sand ware mixed to yield mortar.

3.2.5 Preparations of test specimens.

Twelve Samples of test prisms measuring 40 mm× 40 mm×160 mm for each test cement (10%, 20%, 30%, 40%, and 50%), OPC, and PPC control samples were made. Using the mould described in (KS EAS 148:1-2000) casting of the test specimens was undertaken instantly after mortar preparation. This was done by adding the mortar in two layers directly from the mixing vessel to the labeled mold compartments clamped on the jolting apparatus. 60 jolts were done after each layer for compaction.

3.2.6 Curing of the test specimens

The moulds were covered by a plate of 210 mm×185 mm and placed on a horizontal base in a moist air cabinet maintained at 25^{o}C ±1 ^{o}C and relative humidity of at least 90% for 24 hours after which demoulding was done. The demoulded specimens were clearly labeled and submerged either vertically or horizontally in tap water at 25^{o}C ±2 ^{o}C keeping them apart and ensuring not less than 5 mm of water above the faces of the specimens.

The specimens were removed from the water not more than 15 minutes before carrying out the test, and any water deposits on the surface were removed and covered with a damp cloth until testing is carried out.

The age of the specimens was calculated from when the mixing of cement and water took place. The compressive strength development tests were undertaken after the 2^{nd}, 7^{th}, 28^{th}, and 56^{th} days of curing.

3.2.7 Compressive strength determination

This was conducted in agreement with (KS EAS 148:1-2000). The compressive strength of the test specimens for 10%, 20%, 30%, 40%, and 50% OPC replacement, and OPC and PPC control specimens were tested for compressive strength by use of computerized compression analysis machine type YAW-300 at Kenyan based cement manufacturer, Savannah Cement Limited Research Laboratory. Triplicate specimens for each test cement were tested for each curing time and results were averaged.

The test mortar prism was longitudinally centered below the platens of the compressive test machine at an accuracy of ± 0.5 mm in such a way that the end face of the prism (40 mm x 40 mm) overhangs the platen with about 10mm. The load is then increased smoothly at the rate of 2400N/s ± 200 N/s over the entire load application till fracture.

3.3 Quantification of the amount of concrete waste for use in cement production

The Kenyan cement standards demand that PPC cement achieves a minimum compressive strength of 15 MPa and 32.5 MPa at a curing age of 7 days and 28 days respectively. While OPC to attain a minimum compressive strength of 25 MPa and 42.5 MPa for a curing period of 7 days and 28 days respectively (KS EAS 18-1: 2017).

For the production of Portland pozzolana cement also referred to as CEM IV type of cement the Kenyan cement standard and British standards (EN 197-1, 2011; KS EAS 18-1:2017) recommend a substitution rate of at least 35% of natural pozzolan to achieve a compressive strength of 32.5 MPa at 28 days of curing.

3.4 Pozzolanic activity determination of recycled concrete waste.

3.4.1 Materials

Waste concrete formulated cements; A, B, and C, Ordinary Portland cement (OPC), CEM I 42.5N, Portland pozzolana cement CEM IV 32.5R complying with Kenya cement standards.

3.4.2 Reagents

Distilled water, dilute hydrochloric acid(250 ml in 1000 ml water) 0.003M HCl, sodium hydroxide, calcium carbonate dried at 110 ^{o}C, potassium chloride dried at 110 ^{o}C, sodium carbonate dried at 260 ^{o}C, Methyl orange indicator(0.02 g in 1000 ml), murexide indicator(1g of murexide ground with 100gm KCl),0.025M Ethylene diamine tetra acetic acid(EDTA). All the reagents ware of analytical grade.

3.4.3 Standardization of reagents

3.4.4.1 Standardization of EDTA solution

100 g of $CaCO_3$ was weighed into a 250 ml beaker and 100 ml of water and 50 ml of dilute HCl were added maintaining the beaker covered with a watch glass. The solution was then stirred up

to complete dissolution and then transferred into a 500 ml volumetric flask together with the washings of the beaker and watch glass, then filled to the mark using distilled water.

50 ml of the solution was pipetted into a 400 ml beaker and diluted with about 150 ml of water and pH adjusted to 13 using NaOH solution. 50mg of murexide indicator was added to the solution and titrated against EDTA solution until a steady color change from purple to violet was observed.

The factor F1 of the EDTA was then calculated from the EDTA volume used by employing the Equation (3.1) below;

$$F_1 = \frac{M_1}{100.09} \times \frac{1000}{10 \times 0.25 \times V_1} = \frac{M_1}{V_1} \times 39.96 \quad (3.1)$$

Where

$F_{1:}$ EDTA solution factor

$M_{1:}$ mass of $CaCO_3$, in grams

$V_{1:}$ volume of EDTA solution used for the titration

100.09: molar mass of $CaCO_3$

3.4.4.2 Standardization of 0.1M HCl solution

Approximately 0.2 g of Na_2CO_3 was weighed into a 250 ml flask and dissolved into 50 ml of water. In the resulting solution, 5 drops of methyl orange indicator were added and then titrated with 0.1M HCl till the color change from yellow to orange was observed.

F_2 which is the HCl factor shall be computed from the Equation(3.2) below;

$$F_2 = \frac{M_2}{105.989} \times \frac{1000}{0.1 \times V_2} = \frac{M_2}{V_2} \times 188.70 \quad (3.2)$$

Where;

F_2 factor of the HCl acid

M_2 is the mass of Na_2CO_3, in grams

V_2 is the volume of HCl used for the titration in a milliliter

105.989 is the molar mass of Na_2CO_3

3.4.4 Sample preparation

The three test cements were formulated by substituting Ordinary Portland cement (OPC), CEM I 32.5N complying with KS EAS 18:1-2017 at 45.42% substitution (3.3) using milled waste concrete from the three sources A, B, and C and labeled A, B, and C respectively. Curing of the test cement samples was done by use of 100 ml of freshly boiled distilled water in PE containers equilibrated at 40 ± 0.2^{o}C in a thermostatic enclosure. Upon achieving equilibrium in about one hour the containers were removed from the enclosure and (20±0.01) g of the test cement was added to the respective containers by use of a wide stem funnel. The containers were then sealed and shaken vigorously in a revolving motion to avoid the formation of cement lumps for about 20 seconds. The containers were returned to the thermostatic enclosure ensuring it was placed perfectly horizontally on their base so that the deposited cement forms a layer of uniform thickness.

Upon attaining the testing period (3, 8, 15, 21, and 28 days of curing) the containers were removed from the constant temperature enclosure. Immediately the solution was filtered through a dry double layer of Whatman filter paper in a Buchner funnel under a vacuum within a very short time to avoid carbonation. The vacuum flask was then sealed instantly and allowed to cool to room temperature.

3.4.5 Hydroxyl ion concentration determination.

The tests were done in triplicates for each test cement at respective curing times (3, 8, 15, 21, and 28 days). The filtrate obtained in the vacuum flask in section 3.4.4 above was homogenized by shaking, and then 50 ml of the solution was pipetted into a 250 ml beaker. The total alkalinity was then determined by titrating the solution with dilute HCl acid, using a methyl orange indicator with an endpoint color change from yellow to orange.

The hydroxyl ion concentration shall then be determined using the formula (3.3) below;

$$[OH^{-}] = \frac{1000 \times 0.1 \times V_3 \times F_2}{50} = 2 \times V_3 \times F_2 \qquad (3.3)$$

Where;

$[OH^{-}]$ is the hydroxyl ion concentration in mmol per liter

V_3 is the volume of 0.1M HCl used for the titration, in ml

F_2 is the factor of the 0.1M HCl acid solution.

3.4.6 Calcium oxide concentration determination

In the filtrate solution remained after undertaking hydroxyl ion concentration, 5 ml of 2.5M NaOH and about 50mg of murexide indicator were added. The pH of the resulting solution was maintained at a minimum of 13 using NaOH solution it was then titrated against EDTA until a steady color change of purple to violet is observed.

The CaO concentration shall then be computed using the formula (3.4)below;

$$[\mathrm{CaO}] = \frac{1000 \times 0.025 \times V_4 \times F_1}{50} = 0.5 \times V_4 \times F_1 \qquad (3.4)$$

Where;

[CaO] is the concentration of CaO in mmol per litre

V_4 is the volume of EDTA used for the titration in ml

F_1 is the factor of the EDTA solution

Triplicate results obtained from the test cements and control OPC and PPC in both tested parameters were averaged. The averaged results of CaO and OH^- concentrations were then plotted on a graph against the respective curing period.

3.5 Concrete waste, OPC and PPC control cements chemical analysis

3.5.1 X-ray fluorescence background

X-Ray fluorescence (XRF) was applied for elemental analysis. XRF is a non-destructive analytical method applied in the qualitative and quantitative determination of the elemental composition of materials. X-ray fluorescence analysis relies on bombarding the test material with high-energy X-rays. The atoms of the test material absorb the rays ejecting inner shell electrons in terms of photoelectrons leaving the atom in an excited state and having a vacancy in the inner shell.

To return the atom to a stable state, an electron is forced to fall from the outer shell to occupy the vacancy in the inner shell. This transition emits a photon whose energy is equivalent to the energy

difference between the two states. Each element emits a characteristic energy unique to itself, hence it can be qualitatively determined. The intensity of the e-ray emitted is proportional to the concentration of the element understudy and therefore can be quantitatively ascertained.

3.5.2 Sample preparation and analysis

10.0 grams of the milled waste concrete samples A, B, and C, and OPC and PPC control cements were each mixed homogeneously with 1.0 g of starch, which served as a binder. The mixture was pelleted using a pelleting machine. The pellets for each sample were placed into a sample cup of x-ray spectrophotometer model epsilon 3XLE for analysis. The resultant results were calculated and expressed in terms of the percent oxides of the respective elements.

3.6 Loss on ignition

This was determined as outlined in the Kenya cement standard (KS EAS 148-2, 2000).

3.6.1 LoI Test Procedure

19±0.05g of the cement was weighed into a crucible earlier ignited and tared then covered. The crucible was then placed in an electric furnace operated at 975^{o}C ±25^{o}C and heated for 5 minutes. The lid was slid without removing it to allow the escape of gases and moisture. The crucible was further heated for 10 minutes and then cooled in a desiccator to room temperature and weighed. 15-minute ignitions were done successively to determine constant mass when the recorded weighings between two successive ignitions were less than 0.0005g. This procedure was done in triplicate for each sample.

The percent loss on ignition was computed using the Equation below;

$$\text{Loss on ignition} = \frac{M_o - M_1}{M_O} \times 100\% \qquad (3.5)$$

Where;

M_o-Mass of the test portion

M_1-Mass of the ignited test portion

3.7 Determination of insoluble residue

3.7.1 Insoluble Residue test Procedure

1g ±0.05 g of the test material was placed in a porcelain dish and 25 ml of cold water was added, then dispersed using a glass stirring rod. 40 ml of concentrated HCl was added and the solution was heated gently crushing the sample using the glass stirring rod until complete decomposition of the sample. Then evaporated to dryness in a water bath. The above procedure was repeated twice using 20 ml of concentrated HCl acid.

The residue from the above procedure was treated with 100 ml of dilute HCL acid, reheated, filtered through filter paper, and then washed using boiling water until free from Cl^- ions as tested using $AgNO_3$. The filter paper and the adhered contents were transferred in a 250 ml conical flask mounted with a bulb condenser. 100 ml KOH solution was added and left to stand for 16 hours at room temperature and then boiled for 4 hours under reflux.

The mixture was further filtered through a filter paper and washed consecutively with water, 100 ml dilute HCl, and finally boiling water until free from Cl- ions as confirmed by $AgNO_3$. The filter paper together with the residue was placed in an already ignited and tared crucible and then slowly incinerated without flaming in an oxidizing environment until complete combustion. The crucible is ignited in an electric furnace until constant mass.

The percent Insoluble Residue (IR) is computed using the formula below;

$$IR = \frac{M_o}{M_1} \times 100\% \tag{3.6}$$

Where;

M_o-Mass of the test sample

M_1-Mass of the ignited insoluble residue.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

The results and discussion of this study are presented in this chapter. This includes the compressive strength development of the test cement mortars made from waste concrete substituted OPC and control OPC and PPC, pozzolanicity test of the control OPC and PPC, and the waste concrete formulated PPC and elemental composition of the sampled waste concrete and the test cements.

4.2 Compressive strength development

The compressive strength development of the controls (PPC and OPC), and the substituted test cements are presented in Figure 4 below.

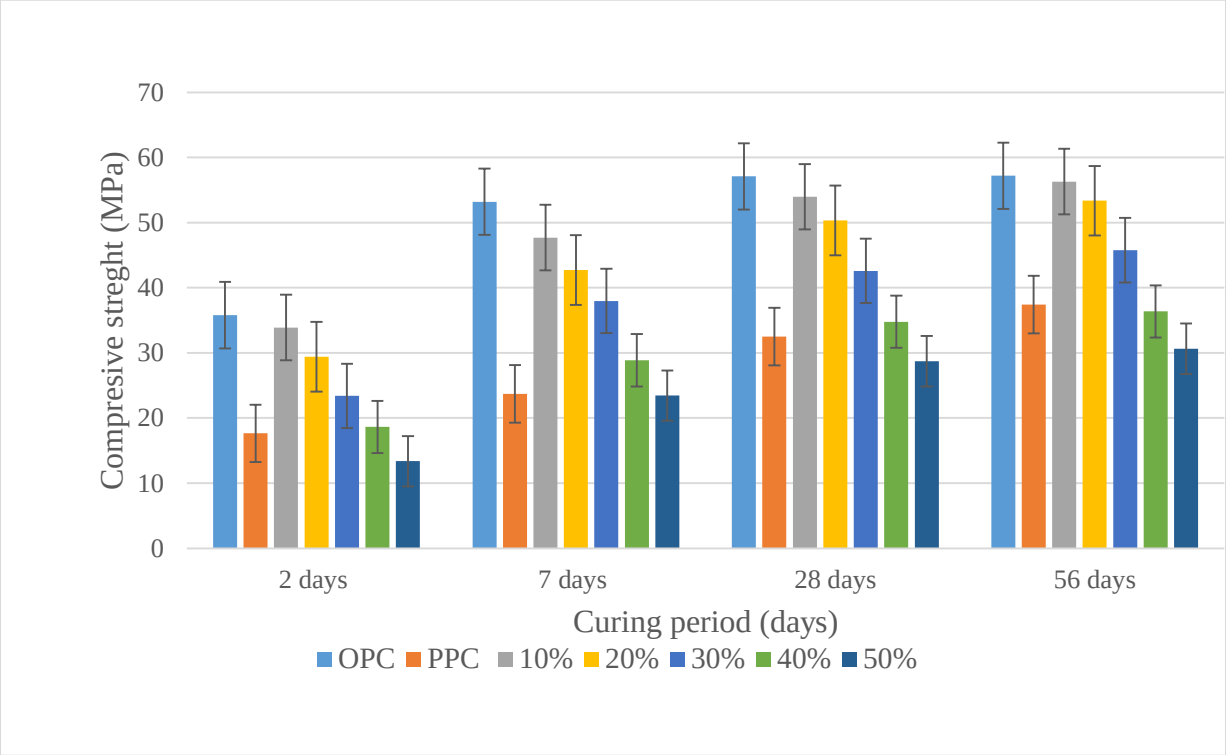

Figure 4: A graph of compressive stregth against curig period

From the results, a general observation is seen that the compressive strength of the control OPC, PPC, and all the test cements increased gradually with the curing period. This was attributed to the hydration of tricalcium silicate and dicalcium silicate that allows the formation of calcium silica hydrate cementing gels. These are responsible for the strength of concrete on the OPC cement and the coupled synergy of these hydration phases and pozzolanic reactions for the PPC cements (Munyao, 2022). This is due to the cement hydration process.

The Control OPC showed the highest compressive strength among all the test cements in all curing ages up to the 56^{th} day. This observation is attributed to the high content of tricalcium silicate(C3S) and tricalcium aluminate (C3A) which influences the setting and early strength development of OPC cement (Barnes & Bensted, 2002; Bertolini *et al*., 2013; Taylor, 1997). Tricalcium silicate is the most significant constituent of OPC and is responsible for controlling the setting, hardening, development, and durability of mortars and concrete strength (John *et al*., 2018). (J. Zhang & Lounis, 2006), showed that C3S exhibited a fast setting, a factor that contributed to the high compressive strength of OPC compared to PPC. However, after the 28^{th} day to the 56^{th} day of curing, OPC compressive strength seemed to level up showing a small change of 0.18%. This is because the hydration of OPC was presumed to be complete.

The waste concrete OPC substituted test cements showed a similar trend in compressive strength development with control PPC. An inverse relationship between the rate of substitution and compressive strength development was observed at each curing age.

The compressive strength at each curing period is observed to decrease with an increase in substitution rate. At a low substitution rate, the test cement has a high content of Ca_3SiO_5 (C3S), Ca_2SiO_4 (C2S), and $Ca_3AL_2O_6$ (C3A) from the OPC portion per unit weight which results in the generation of calcium silica hydrate, the cementing gel at a higher rate and high proportions leading to enhanced strength. As the substitution rate is increased the OPC hydration phases decrease and the strength development is attributed to pozzolanic reaction as per the Equation(0.9). The control PPC and waste concrete substituted OPC showed a gradual increase of the compressive strength development throughout the curing period which is attributed to pozzolanic reactions and expected to grow even beyond the OPC strength with time.

The inert quartz from the finely milled sand is suggested to impact a micro filler effect which can cure some challenges associated with hardened concrete like prolonged setting time, poor early mechanical strength, poor rheology, and penetration of chloride ions (Antoni *et al*., 2012; Cordeiro *et al*., 2009). Other researchers have also observed that the finely milled inert particles could act as nucleation sites of the calcium silica hydrate, hence accelerating the cement hydration process by lowering the hydration energy barrier(Cordeiro *et al.*, 2009; Deschner *et al*., 2012; Garces-Vargas *et al.*, 2022; Juenger & Siddique, 2015a). Through these findings, it can be inferred that the finely ground silica from the sand in the waste concrete mortar contributed to the enhanced hydration reaction and strength development of the formulated cements.

4.3 Pozzolanicity test results

The results of pozzolanic activity test for the control cements OPC and PPC and the waste concrete formulated cements A, B, and C are shown in Figures 5 and 6 below. The results are displayed in terms of CaO and OH^- concentrations as evaluated over a period of time after 3, 8, 15, 21, and 28 days of respective cement curing. As a result of the ongoing cement hydration, the testing gives the progressive residual concentration of $Ca(OH)_2$ after a specific hydration period.

During the hydration of PPC cements, the pozzolanic materials continuously react with calcium hydroxide from the OPC hydraulic phases (1.9), referred to as lime fixation. This implies a decreased concentration of $Ca(OH)_2$ over time in the hydrated PPC cement or its concrete as compared to OPC cement. This gradual comparison of CaO and OH^- concentrations after a set period during hydration is applied as an indication of pozzolanicity of a given PPC cement (International Standards Organization (ISO 863), 2008).

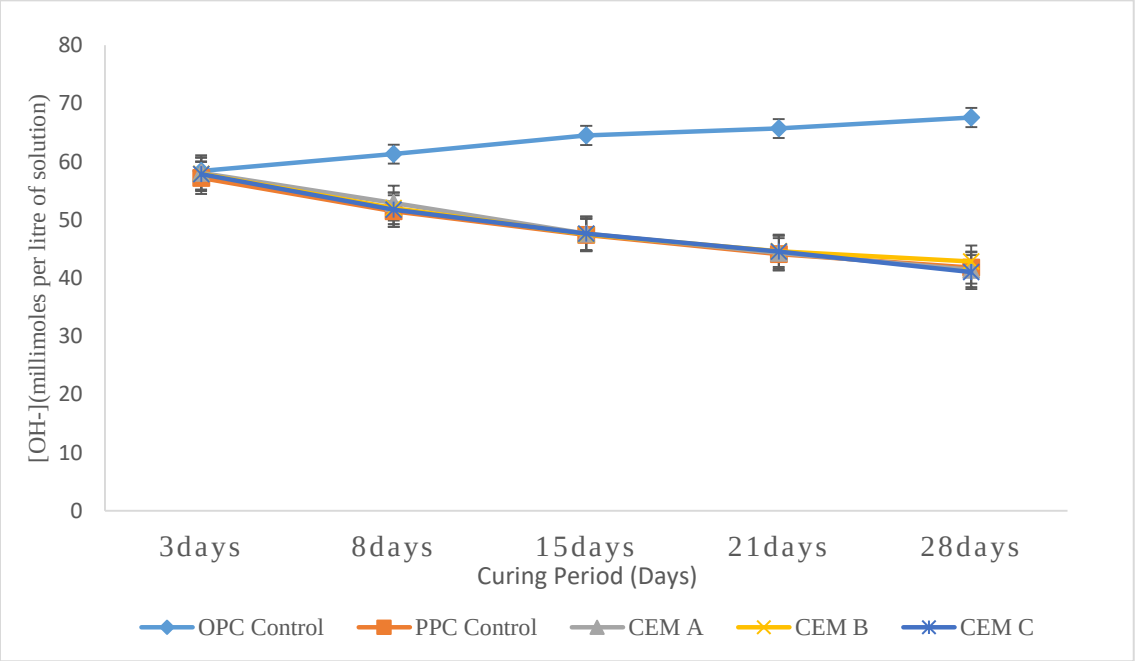

Figure 5: OH- Concentration change as a function of the curing period

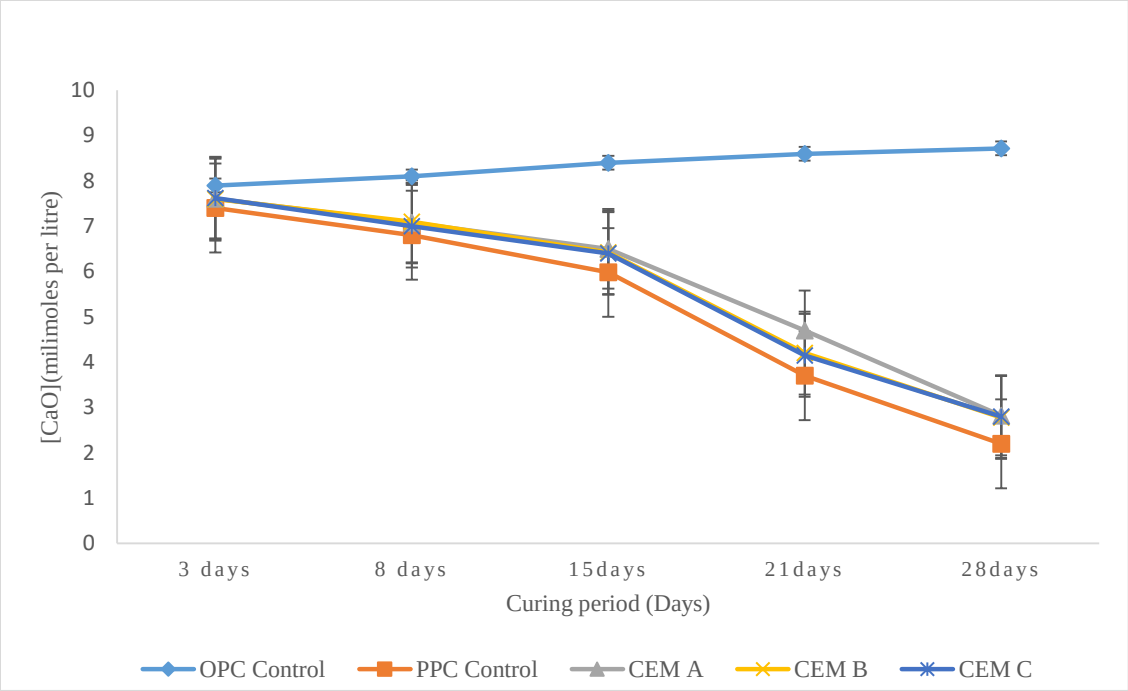

Figure 6: CaO Concentration changes as a function of the curing period.

From the results of this study, it is noted that CaO and OH^- concentrations of the OPC control cement increased gradually throughout the curing period from 7.9 mmol/l to 8.8 mmol/l and 58.4 mmol/l to 67.6 mmol/l respectively negating pozzolanicity as shown in appendices v and vi. This observation is in line with the hydration mechanism of OPC cement where the $Ca(OH)_2$, accumulates in the hydrated material as illustrated in the Equation (0.7). This is because there is no uptake or fixation of the calcium hydroxide.

However, the concentration of CaO and OH^- species in the PPC control cements and the waste concrete formulated cements showed a significant reduction over the curing period. The concentrations decreased gradually from an average of 7.58 mmol/l to 2.65 mmol/l and 57.77 mmol/l to 41.78 mmol/l respectively from the 3rd to 28th day indicating the presence of pozzolanic reactions as shown in appendices v and vi. These findings are in agreement with the behavior of hydration of PPC cements. During pozzolanic reactions, the silicates and aluminate phases of pozzolana undergo reactions with $Ca(OH)_2$ emanating from the hydration of OPC hydraulic phases resulting in additional calcium silica hydrate (Taylor, 1997). The hydroxyl ions accumulated in the OPC concrete structure can undergo an alkali-silica reaction (ASR). This can

lead to the formation of a gel-like substance, causing expansion and cracking in the concrete structure over time.

$$2SiO_2 + 3Ca(OH)_2 + 5H_2O \rightarrow 3CaO.2SiO_2.8H_2O \quad (4.1)$$

$$Al_2O_3 + 4Ca(OH)_2 + 9H_2O \rightarrow 4CaO.Al_2O_3.13H_2O \quad (4.2)$$

This reduction of $Ca(OH)_2$ via pozzolanic reactions is seen to increase the resistance of hydrated cement and concrete to aggressive ions such as sulphates and chlorides (Baghabra Al-Amoudi, 2002; Bellmann & Stark, 2008). Calcium hydroxide reacts with sulfate ions to form gypsum whose formation is expansive and destructive compromising the integrity of concrete structures (Tian & Cohen, 2000). The additional calcium silica hydrate from the pozzolanic reactions increases the cementing abilities, therefore, impacting positively the strength of Portland pozzolana cement (Waghmare *et al*., 2021). Also, this additional cementing material makes the resultant concrete material more compact with low porosity, lowering the diffusivity of deleterious ions such as chlorides hence prolonged durability (Munyao, 2015; K. Scrivener *et al*., 2016; Taylor, 1997).

4.4 Quantification of the amount of concrete waste for use in cement production

This study showed that compressive strength development of all test cement samples achieved the minimum Kenya cement standards requisites except the 50% waste concrete substituted OPC. This implies that the waste concrete can achieve an OPC substitution that meets the Kenyan cement standards requirements. From the compressive strength development data at 28 days of curing shown in Table 3 below, the optimum substitution rate was extrapolated.

From Figure 7 below, compressive strength against the substitution rate of the waste concrete material the amount of concrete waste substitution rate required to achieve 32.5 MPa strength was determined from the trend line.

Table 4: Results of compressive strength development at 28 days of curing

%OPC Substitution	Recycled concrete waste % substitution	28 Days compressive strength (MPa)
100	0	57.1

90	10	53.97
80	20	50.35
70	30	42.6
60	40	34.78
50	50	28.73

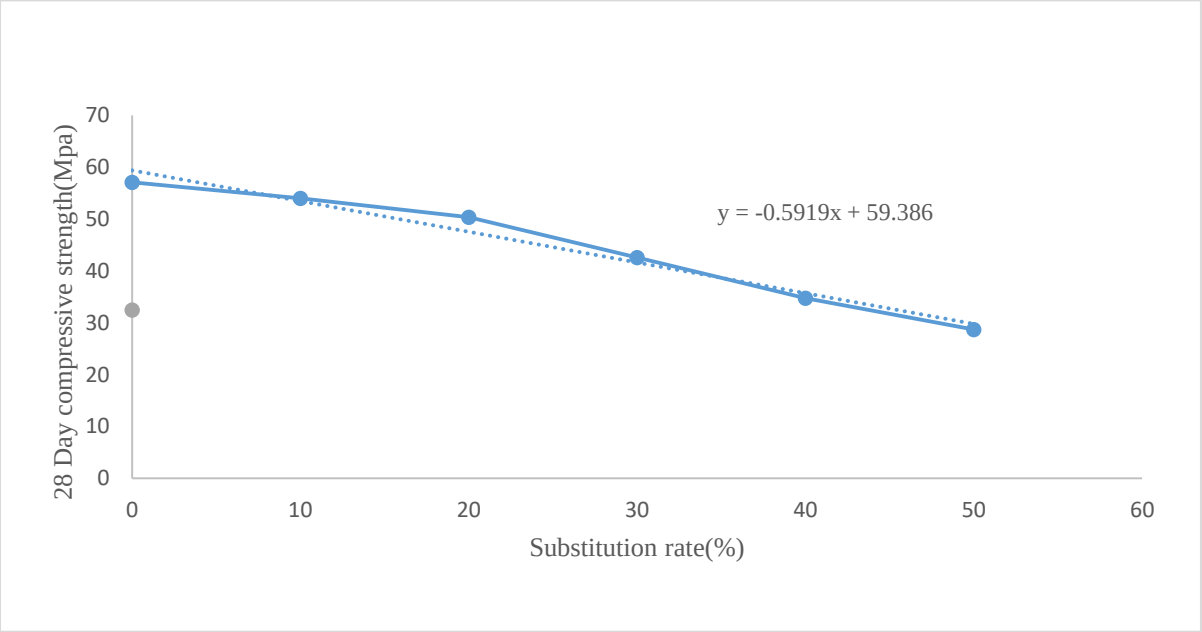

Figure 7: A graph of 28-day compressive stregth against substitution rate.

From the trend line; $y = -0.5919x + 59.386$ (4.3)

Having y at 32.5 MPa, x the substitution rate of waste concrete on OPC is determined to be 45.42%. This implies that to manufacture 1 ton of PPC Cement complying with (KS EAS 18-1: 2017), 454.2 Kgs of waste concrete material will be required, translating to having saved 350 kgs of natural pozzolana.

4.5 Chemical analysis

4.5.1 Cement Chemical Analysis

The findings of the chemical composition of the formulated cements using waste concrete samples A, B, and C and control PPC and OPC are tabulated in Table 5 below.

Table 5: The chemical composition, LoI and IR of the waste concrete formulated PPC cements and control OPC and PPC cements**.**

Metal oxides (%)	**Control OPC** **Mean±SE**	**Control PPC** **Mean±SE**	**CEM A** **Mean±SE**	**CEM B** **Mean±SE**	**CEM C** **Mean±SE**
CaO	65.20 ±0.06	45.8 ±0.06	46.1 ±0.05	45.63 ±0.07	45.83 ±0.04
MgO	1.70 ±0.02	0.96 ±0.01	0.92 ±0.01	1.01 ±0.02	0.83 ±0.01
Fe_2O_3	3.82 ±0.02	5.88 ±0.07	5.43 ±0.01	5.62 ±0.02	5.54 ±0.01
Al_2O_3	5.10 ±0.03	9.63 ±0.01	8.3 ±0.02	8.93 ±0.02	9.08 ±0.02
SiO_2	20.18 ±0.02	32.78 ±0.02	35.68 ±0.02	35.37 ±0.02	35.24 ±0.02
SO_3	2.30 ±0.01	2.10 ±0.02	1.43 ±0.01	1.37 ±0.02	1.28 ±0.02
Na_2O	0.32 ±O.02	1.06 ±0.02	0.94 ±0.01	0.86 ±0.01	0.81 ±0.01
K_2O	0.61 ±0.02	1.50 ±0.02	1.17 ±0.02	1.23 ±0.01	1.36 ±0.01
LOI	1.50 ±0.02	2.20 ±0.01	2.89 ±0.01	3.1 ±0.02	2.68 ±0.01
Insoluble residue(IR)	1.20 ±0.02	29.72 ±0.01	34.01 ±0.02	33.7 ±0.01	32.46 ±0.01

The waste concrete-based cements (CEM A, CEM B, and CEM C) are observed to meet the chemical composition as stipulated in (KS EAS 18-1: 2017). CaO and SiO_2 the determinants of cement strength development are observed to constitute more than 80% of the total oxides. A general observation is made that the OPC cement constitutes less SiO_2 content than the PPC cements, a factor attributed to the addition of pozzolana in PPC cement. OPC is noted to contain high quantities of CaO compared to PPC cements, an observation accredited to the fact that supplementary cementitious materials blended with OPC to yield PPC have less calcium and high silica content (Bach *et al*., 2013). The active silica reacts with calcium hydroxide from the hydration of OPC yielding secondary cementitious material which contributes to the long-term strength and durability of PPC cements. This is what constitutes the basis of the pozzolanic reaction.

The alkali oxides (Na_2O and K_2O) are observed to be relatively high in the control PPC cement and the waste concrete formulated pozzolanic cements compared to control OPC cement. On

hydration, the alkali ions easily dissolve in water and provide an alkaline environment in the hydrated cement and concrete pore structure. This high pH environment is advantageous in the protection of reinforcing metal bars against corrosion (Bertolini *et al*., 2013; Munyao, 2015; Skibsted & Andersen, 2013).

Insoluble residue proportion is high in PPC control cement and waste concrete formulated cements compared to control OPC. This observation is attributed to non-cementing substances which are insoluble in hydrochloric acid present in pozzolana. Probably siliceous and aluminous matter as cited by (Mawardi *et al*., 2021). For the waste concrete formulated cements this insoluble residue (IR) could be accredited to the crystalline silica and alumina portion from the fine aggregates sand. However, the cements under this study comply with Kenyan standards and European standards (BS EN 197-1, 2011; KS EAS 18-1: 2017) which stipulate that PPC and OPC have IR of between 25-35% and ≤ 5% respectively.

The MgO content in all the test cements is observed to meet the standards required of ≤5.00%. MgO is known by cement chemists for its concrete dimensional instability, for it contributes to unsoundness. When subjected to moisture it hydrates yielding magnesium hydroxide [$Mg(OH)_2$], which expands within the concrete leading to unsoundness(Goncalves *et al*., 2019; Taylor, 1997).

$$MgO + H_2O \rightarrow Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \quad (4.4)$$

MgO is also attributed to slowing down the cement initial setting. The $Mg(OH)_2$ precipitates in the form of insoluble tiny crystals on the cement particles developing an inhibiting layer slowing down mass transfer and hence decreasing hydration (Munyao, 2015)

4.5.2 Concrete waste chemical analysis results

The results of the elemental composition of the concrete waste are tabulated in Table 5 below. The elemental components are presented in terms of percent oxides except for the insoluble residue and loss on ignition.

Table 6: The chemical composition, LoI and IR of the waste concrete samples

Metal oxides (%)	Sample A Mean±SE	Sample B Mean±SE	Sample C Mean±SE
CaO	42.80 ±0.06	41.68 ± 0.16	43.10 ±0.25
MgO	0.88 ±0.01	0.94 ±0.02	0.82 ±0.03
Fe_2O_3	5.92 ±0.04	6.98 ±0.97	6.49 ± 0.21
Al_2O_3	9.48 ±0.03	9.42 ±0.04	8.67 ±0.34
SiO_2	35.78 ±0.34	36.43 ±0.44	36.74 ±0.24
SO_3	1.20 ±0.02	1.26 ±0.02	1.30 ±0.04
Na_2O	0.820 ±0.03	0.96 ±0.02	0.87 ±0.03
K_2O	1.38 ±0.04	1.47 ±0.04	1.43 ±0.04
LOI	3.60 ±0.06	3.2 ±0.03	2.78 ±0.04
Insoluble residue (IR)	33.90 ± 0.47	32.37 ±0.51	31.75 ±0.43

The three samples of concrete waste met the minimum specification for pozzolana as stipulated in (KS EAS 18-1: 2017) with SiO_2 composition being above 25% by mass. The chemical composition of the three concrete waste samples compared well with other SCMs in terms of percent oxide composition, sulfur trioxide content, moisture, and loss on ignition (ASTM-C618, 2014; Ramezanianpour, 2014b; Seco *et al.*, 2012; Snellings *et al*., 2012)

The Al_2O_3 and SiO_2 oxides are the main constituents of pozzolana because they are the ones that drive pozzolanic reactions by reacting with $Ca(OH)_2$ from the hydration of OPC or free lime from CMs generating secondary calcium silica hydrate and calcium alumino hydrate cementing gel (MUSYIMI, 2015). The alkali levels and MgO content were below the maximum allowable limits as set out by (KS EAS 18-1: 2017).

The three waste concrete samples; A, B, and C showed to have highly insoluble residue which could be attributed to the crystalline silica from the fine aggregates (sand) and other inorganic matter which could not dissolve in hydrochloric acid.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The compressive strength development of the formulated cements from the three waste concrete waste samples mirrored that of the control Portland pozzolana cement where it increased gradually throughout the curing period. However, it declined with an increase in substitution rate at each curing age. However, for the control Ordinary Portland cement the compressive strength increased and leveled up after 28 days of curing signifying the end of the hydration reaction. This observation implies the presence of pozzolanic reactions on the concrete waste formulated cements.

This study established an optimal substitution rate of 45.42% concrete waste on Ordinary Portland cement in the production of PPC, translating to 454.2 Kgs of concrete waste per 1 ton of Portland pozzolana cement of grade 32.5R complying with the Kenyan cement standards.

The hydroxyl ions and calcium oxide concentration on control Portland pozzolana cement and the three formulated cements decreased gradually from an average of 56.43mmol/l to 40.83mmol/l and 7.9mmol/l to 2.5mmol/l respectively throughout the curing period indicating uptake of $Ca(OH)_2$ signifying pozzolanic reaction taking place. For the control, OPC the concentrations of OH^- and CaO increased gradually from 58.4mmol/l to 67.6 mmol/l and 7.9 to 8.8mmol/l respectively stipulating accumulation of $Ca(OH)_2$ in the system throughout the curing period negating pozzolanicity. This observation indicates the presence of pozzolanic reactions on waste concrete formulated cements, hence a conclusion that this material can be applied as a pozzolana.

The chemical composition of the three concrete waste samples was observed to meet the minimum pozzolana specifications with SiO_2 averaging 36.31% against the minimum recommended 25% by mass, the alkali content, MgO, and loss on ignition were also shown to be within limits as stipulated in Kenya cement standards. However, a high insoluble residue of up to 33.90% was noted which was attributed to the high content of crystalline silica which could not dissolve in HCl. The results of this study suggested the potential application of concrete waste in the manufacture of Portland pozzolana cement.

5.2 Recommendations from this research work

This study has revealed that waste concrete from demolition sites bears pozzolanic properties. The recommendations for this research are listed below.

I. In order to reduce dependence on natural pozzolana waste concrete to be recycled back in the cement industry for the manufacture of Portland pozzolana cement.

II. Develop Kenyan cement standards for PPC Cements formulated from waste materials.

III. Waste concrete formulated PPC cement concrete to be subjected to deleterious ions penetration (Cl- and SO_4^{2-}) and biogenic acid attack tests to determine its resistances.

IV. Enhanced quality control and assurance measures are to be put in place to enable the application of this waste concrete material at an industrial scale.

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APPENDICES

Appendix I: Compressive strength development sor sample A (MPa)

Ordinary portland cement(%)	Recycled concrete % substitution	2 Days	mean	7 Days	Mean	28 Days	Mean	56 Days	Mean
90	10	33.3		46.8		53.1		55.4	
		33.4	33.4	47.1	47.2	53.4	53.2	55.1	55.3
		333.6		47.4		53.1		55.4	
80	20	29.2		42.0		50.7		52.2	
		29.5	29.3	41.8	41.9	51.1	50.9	52.2	52.15
		29.2		41.9		50.8		52.1	
70	30	22		32.9		40.9		44.4	
		21.6	21.8	32.4	33.6	40.6	40.7	44.6	44.7
		21.8		35.5		40.6		45.1	
60	40	18.1		28.7		34.2		34.9	
		18.3	18.1	28.4	28.55	33.9	34.15	33.4	34.2
		17.9		28.6		34.4		34.3	
50	50	13.1		22.1		27.4		29.1	
		12.6	12.8	21.6	21.85	27.6	27.4	28.6	28.7
		12.7		21.9		27.2		28.4	

Appendix II: Compressive strength development data for sample B (MPa)

Ordinary portland cement(%)	Recycled concrete % substitution	2 Days	mean	7 Days	Mean	28 Days	Mean	56 Days	Mean
90	10	34.0		47.2		53.7		56.9	
		33.6	33.7	48.1	47.6	54.2	54.0	56.1	56.4
		33.5		47.5		54.1		56.2	
80	20	29.2		44.0		50.4		52.7	
		29.5	29.2	43	43.5	48.6	49.85	52.4	52.4
		28.9		43.5		50.6		52.1	
70	30	23.9		37.1		43.9		47.1	
		24.4	24.2	37.5	37.3	43.8	44.10	47.8	47.5
		24.3		37.3		44.6		47.6	
60	40	19.3		31		36.8		40.6	
		18.7	18.9	30.4	30.7	37	36.9	40.9	41.0
		18.7		30.7		36.9		41.5	
50	50	13.2		24.7		30.8		33.8	
		13.6	13.5	24	24.3	30.4	30.6	34.1	33.8
		13.7		24.2		30.6		33.5	

Appendix III: Compressive strength development data for sample C (MPa)

Ordinary portland cement(%)	Recycled concrete % substitution	2 Days	mean	7 Days	Mean	28 Days	Mean	56 Days	Mean
90	10	34.8		48.3		54.9		57.4	
		34.6	34.6	48.3	48.3	55	54.7	56.7	57.2
		34.4		48.3		54.2		57.5	
80	20	29.5		42.6		49.5		51	
		30.1	29.7	46.9	42.75	50.6	49.05	50.8	50.8
		29.5		38.8		47.05		50.6	
70	30	24.1		38.4		43.2		45.1	
		23.8	24.1	38.2	38.3	42.7	42.9	44.7	45.1
		24.4		38.3		42.8		45.5	
60	40	18.7		27.9		35.2		36.9	
		18.9	18.9	28.6	27.35	34.7	34.9	36.1	36.5
		19.1		25.55		34.8		36.5	
50	50	13.9		23		27.7		30.3	
		13.7	13.8	23.4	23.2	28.3	28.2	29.7	30.1
		13.8		23.2		28.6		30.3	

Appendix IV: Compressive strength development data for control cements (MPa)

		2 days	Mean	7 days	Mean	28 days	Mean	56 days	Mean
Control PPC		12.5		22.4		32.3		37.1	
		12.6	12.5	22.3	22.3	32	32.25	37.6	37.4
		12.4		22.2		32.5		37.5	
Control OPC		36.1		53.2		56.6		59.6	
		35.7	35.8	53.2	53.2	57.4	57.1	59.4	59.4
		35.6		53.2		57.3		59.2	

Appendix V: Gradual comparison of calcium oxide concentration in millimoles per liter

Curing period	3days	8 days	15 days	21 days	28 days
Control OPC	7.90	8.10	8.40	8.600	8.72
Control PPC	7.40	6.80	5.98	3.700	2.20
CEM A	7.71	7.08	6.50	4.700	2.82
CEM B	7.60	7.10	6.42	4.200	2.78
CEM C	7.62	7.00	6.40	4.150	2.80

Appendix VI: Gradual comparison of hydroxyl ion concentration in millimoles per liter

Curing period	3 days	8 days	15 days	21days	28 days
Control OPC	58.40	61.30	64.5	65.70	67.60
Control PPC	57.20	51.50	47.40	44.10	41.80
CEM A	58.10	52.90	47.46	44.32	41.42
CEM B	57.92	52.02	47.52	44.60	42.86
CEM C	57.87	51.77	47.64	44.53	41.03