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COMPOSITION AND PARTICLE SIZE OF MINERAL TRIOXIDE AGGREGATE, PORTLAND CEMENT AND SYNTHETIC GEOPOLYMERS

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# COMPOSITION AND PARTICLE SIZE OF MINERAL TRIOXIDE AGGREGATE, PORTLAND CEMENT AND SYNTHETIC GEOPOLYMERS

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## ABSTRACT

*Objective:* **To describe the composition and particle size of Portland cement (PC) and geopolymers in comparison to mineral trioxide aggregate (MTA).**
*Design:* **A quantitative, laboratory-based exploratory study.**
*Setting:* **Schools of Dental Sciences and Physical Sciences, University of Nairobi; World Agroforestry Centre (ICRAF); Ministry of Mining, all in Nairobi, Kenya.**
*Study population:* **Grey PC clinker, Kaolin, Fly ash (FA) and blast furnace (BF) slag, together with alkaline-activated aluminosilicates (AS) or geopolymers derived from them, were evaluated in comparison to two brands of MTA (MTA Cem and ProRoot MTA).**
*Methods:* **The materials were characterized by x-ray diffraction (XRD), energy dispersive X-ray fluorescence (EDXRF), graphite furnace atomic absorption spectroscopy (GFAAS) and fluoride ion selective electrode (FISE) for compositional analysis, and laser diffraction for particle size distribution analysis. Continuous data was subjected to analysis of variance (ANOVA) and Tukey's post hoc test for hypothesis testing at α level of 0.05.**
*Results:* **While MTA and PC comprised mainly of dicalcium and tricalcium silicate phases, geopolymers contained aluminosilicate phases such as quartz and mullite. Only FA contained fluoride (43.33μg/g, sd 5.77). There was no statistically significant difference in the composition of MTA and PC as determined by EDXRF except in the Bi (F-statistic=44.29, df=2, adjusted $p<0.0001$, difference=2.47, 95% CI 16.30, 33.14%wt) and Pb content (F-statistic=164.40, df=2, adjusted p=0.000, difference=1.74, 95% CI 1.43, 2.05%wt). There was no statistically significant difference in the mean particle size distribution of MTA, PC and geopolymers (D50 for PC = 12.46μm, sd 3.18, MTA = 7.23μm, sd 3.43, aluminosilicates = 12.74μm, sd 3.79, $p>0.05$).**
*Conclusion:* **Composition of PC was similar to MTA while particle size of PC and geopolymers was similar to MTA.**

## INTRODUCTION

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

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

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

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

PCs are classified as Type I to V according to the ASTM standards; CSCs are comparable to Type I PC. Estrella *et al.* were the first to report the similarity between MTA and PC stating that the only difference was the presence of $Bi_2O_3$ in MTA and its absence in PC[17]. Several other studies have compared the two materials, investigating aspects of their composition[8, 14, 16, 18, 19], setting reaction[20, 21] and biocompatibility[17, 22] and most of these found the two to be quite similar. The particle size of MTA is a little researched area. A few studies have compared the particle size of MTA and PC and how this influences their properties[16, 23-25]. On this basis, several reviews have concluded that more studies utilizing PC are required to evaluate the possibility of substituting it for the expensive commercial calcium silicate versions[1, 15, 16, 26].

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

## MATERIALS AND METHODS

Ethical approval for this study was obtained from the Kenyatta National Hospital/University of Nairobi Ethical Research Committee. To minimize errors and bias, experiments were conducted in triplicate. R-studio version 3.4.2 (2017) and Microsoft Excel (2016) were used for descriptive data analysis as well as for hypothesis testing. Continuous data was subjected to analysis of variance (ANOVA) followed by Tukey's post hoc test at $\alpha$ level of 0.05, to test the hypothesis that there was no difference in the composition and particle size of PC, alkaline activated AS and MTA.

***Sampling and sourcing of materials:*** A descriptive summary of the materials is presented in Table 1. PC clinkers and aluminosilicate materials for clinker production were obtained from three PC manufacturing companies in Kenya: East African Portland Cement (EAPC), Athi River Mining (ARM) and Bamburi. One aluminosilicate material was obtained from a ceramic manufacturing company in Kenya: Saj Ceramics. Two commercial brands of MTA were purchased in Nairobi, Kenya: MTA Cem (NexoBio, Chungcheongbuk-do, Korea) and ProRooT MTA (Dentsply Sirona, York, Pennsylvania, USA). Samples of PC clinker were obtained from random batches within the three identified companies, as specified by ASTM C183 – Standard Practice for sampling and the amount of testing of hydraulic cements. At least 1kg samples were collected from the companies' Nairobi Grinding Plants storage bins prior to packaging, and placed in sealed, labelled, moisture-proof and air-tight containers.

**Table 1**
*Summary of study population*

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

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

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

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

(International Centre for Diffraction Data, Newton Square, PA, USA).

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

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

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

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

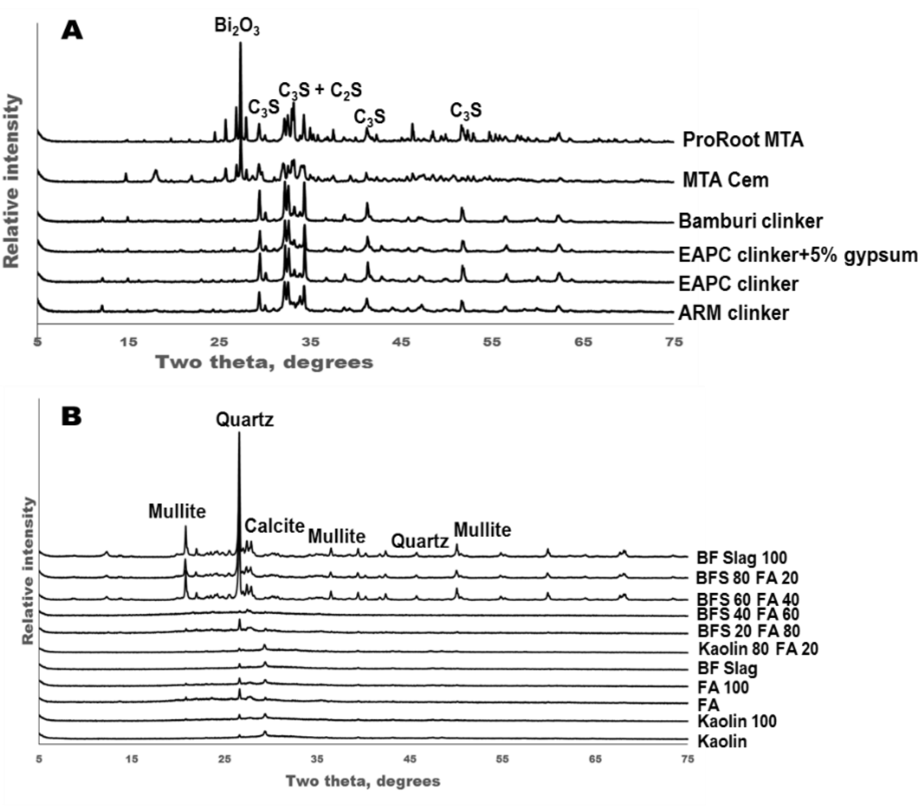
**LD-PSA:** Laser diffraction particle analysis (Partica, LA-950, Horiba Scientific, Kyoto, Japan), which can determine particle size between 0.022–2000μm, was used to determine the particle size of MTA, PC clinkers as well as the raw and alkaline-activated AS (geopolymers). Powder samples were dispersed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

## RESULTS

***Composition analysis:***

**XRD:** Figure 1A shows the diffraction patterns of PC and MTA, with similar peaks of $C_2S$ and $C_3S$ in both materials. They also show peaks of $Bi_2O_3$ unique to MTA. Figure 1B shows the diffraction patterns of raw and alkaline-activated AS (geopolymers). The spectra show peaks of quartz, calcite and mullite within the various materials. Following alkaline-activation, the quartz and mullite peaks were markedly enhanced in 100% BF slag, and mixtures of BF slag and FA (80:20 and 60:40).

**Figure 1**
*Powder XRD of PC clinker and MTA (A), and raw and alkaline-activated AS (B)*



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

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

**Table 2**

*Descriptive summary and ANOVA of composition of PC, AS and MTA as determined by EDXRF (%wt)*

| Compound | Material category | Mean (SD) | Min, Max | F statistic, df, p-value | Tukey's post hoc adjusted p-value | Diff (95% CI) |
|---|---|---|---|---|---|---|
| **CaO** | PC (n=3) | 59.50 (7.41) | 51.09, 65.04 | 8.73, 2df | PC:MTA = 1.00 | |
| | MTA (n=2) | 46.07 (10.24) | 38.83, 53.31 | p≤0.01** | PC:AS = 0.006* | -41.16 (-69.30, -13.01) |
| | AS (n=10) | 18.35 (17.85) | 0.61, 45.57 | | MTA:AS = 0.14 | |
| **$SiO_2$** | PC | 25.65 (5.68) | 21.99, 32.19 | 14.33, 2df | PC:MTA = 1.00 | |
| | MTA | 19.02 (0.91) | 18.38, 19.66 | p≤0.001** | PC:AS = 0.004* | 32.45 (11.29, 53.61) |
| | AS | 58.10 (13.65) | 35.54, 74.65 | | MTA:AS = 0.003* | 39.08 (14.19, 63.98) |
| **$Al_2O_3$** | PC | 5.49 (0.49) | 4.99, 5.96 | 6.98, 2df | PC:MTA = 1.00 | |
| | MTA | 2.65 (1.07) | 1.89, 3.40 | p≤0.01* | PC:AS = 0.04* | 9.82 (0.30, 19.34) |
| | AS | 15.31 (6.25) | 10.32, 27.69 | | MTA:AS = 0.03* | 12.67 (1.46, 23.87) |
| **$P_2O_5$** | PC | 0.61 (0.17) | 0.42, 0.75 | 29.5, 2df | PC:MTA = 0.44 | |
| | MTA | 0.46 (0.02) | 0.44, 0.47 | p≤0.0001*** | PC:AS ≤ 0.0001** | -0.51 (-0.70, -0.32) |
| | AS | 0.10 (0.01) | 0.00, 0.30 | | MTA:AS = 0.004* | -0.36 (-0.58, -0.13) |
| **S** | PC | 1.53 (1.36) | 0.52, 3.08 | 9.33, 2df | PC:MTA = 0.05 | |
| | MTA | 4.27 (2.69) | 2.37, 6.17 | p=0.003** | PC:AS = 0.68 | |
| | AS | 0.61 (0.63) | 0.00, 1.82 | | MTA:AS = 0.003* | -3.66 (-5.93, -1.39) |
| **Cl** | PC | 0.03 (0.04) | 0.00, 0.08 | 3.12, 2df | PC:MTA = 0.09 | |
| | MTA | 0.24 (0.28) | 0.40, 0.43 | p=0.08 | PC:AS = 0.92 | |
| | AS | 0.10 (0.04) | 0.30, 0.15 | | MTA:AS = 0.2 | |
| **$K_2O$** | PC | 1.65 (0.75) | 1.01, 2.48 | 3.2, 2df | PC:MTA = 0.86 | |
| | MTA | 0.16 (0.02) | 0.14, 0.17 | p=0.08 | PC:AS = 0.68 | |
| | AS | 2.88 (1.66) | 0.28, 5.18 | | MTA:AS = 0.1 | |
| **MgO** | PC | 1.22 (2.12) | 0.00, 3.67 | 0.71, 2df | PC:MTA = 1.0 | |
| | MTA | 0.00 (0.00) | 0.00, 0.00 | p=0.5 | PC:AS = 1.0 | |
| | AS | 1.49 (1.8) | 0.00, 4.73 | | MTA:AS = 0.77 | |
| **Fe** | PC | 3.49 (1.03) | 2.67, 4.64 | 3.12, 2df | PC:MTA = 0.09 | |
| | MTA | 0.14 (0.06) | 0.10, 0.18 | p=0.8 | PC:AS = 0.94 | |
| | AS | 2.46 (1.65) | 0.64, 5.58 | | MTA:AS = 0.2 | |
| **As** | PC | 0.00 (0.00) | 0.00, 0.00 | - | - | |
| | MTA | 0.00 (0.00) | 0.00, 0.00 | | | |
| | AS | 0.00 (0.00) | 0.00, 0.00 | | | |
| **Sr** | PC | 0.06 (0.04) | 0.03, 0.10 | 3.06, 2df | PC:MTA = 1.0 | |
| | MTA | 0.09 (0.09) | 0.02, 0.15 | p=0.08 | PC:AS = 0.4 | |
| | AS | 0.03 (0.02) | 0.01, 0.07 | | MTA:AS = 0.16 | |
| **Pb** | PC | 0.01 (0.01) | 0.00, 0.01 | 164.4, 2df | PC:MTA= 0.000*** | 1.74 (1.43, 2.05) |
| | MTA | 1.75 (0.44) | 1.44, 2.06 | p≤0.0001*** | MTA:AS=0.000*** | -1.75 (-2.01, -1.48) |
| | AS | 0.01 (0.01) | 0.00, 0.01 | | | |
| **Bi** | PC | 0.00 (0.00) | 0.00, 0.00 | 44.29, 2df | PC:MTA≤0.0001*** | 2.47 (16.30, 33.14) |
| | MTA | 24.72 (11.92) | 16.25, 33.19 | p≤0.0001*** | PC:AS = 1.0 | |
| | AS | 0.00 (0.00) | 0.00, 0.00 | | MTA:AS≤0.0001*** | -2.47 (-31.87, -17.57) |
| **Others** | PC | 0.75 (0.26) | 0.49, 0.88 | 1.3, 2df | PC:MTA = 0.44 | |
| | MTA | 0.45 (0.18) | 0.32, 0.52 | p=0.31 | PC:AS = 0.73 | |
| | AS | 0.58 (0.21) | 0.24, 0.73 | | MTA:AS = 1.0 | |

***p<0.05, **p≤0.01, ***p≤0.0001***

**Table 3**

*Descriptive summary and ANOVA of composition of PC, AS and MTA analysed by GFAAS and FISE (μg/g)*

| Element | Material category | Mean (SD) | Min, Max | F statistic, df, p-value | Tukey's post hoc adjusted p-value | Diff (95% CI) |
|---|---|---|---|---|---|---|
| **Ca** | PC (n=9) | 51623.0 (5182.0) | 45555.0, 61118.0 | 39.33, 2df | PC:MTA=0.004** | 25460.28 (8480.93, 42439.62) |
| | MTA (n=4) | 77083.0 (4612.0) | 70772.0, 81860.0 | p≤0.0001*** | PC:AS≤0.0001*** | -35294.29 (-50186.16, -20402.42) |
| | AS (n=6) | 16328.0 (18110.0) | 0.00, 37835.0 | | MTA:AS≤0.0001*** | -60754.57, (-78993.31, -42515.83) |
| **Zn** | PC | 127.80 (107.50) | 0.41, 255.50 | 6.40, 2df | PC:MTA=0.04* | -124.31 (242.19, -6.43) |
| | MTA | 3.45 (0.27) | 3.06, 3.66 | p≤0.01** | PC:AS=0.02* | -125.35 (-228.74, -21.96) |
| | AS | 2.42 (2.35) | 0.25, 4.60 | | MTA:AS=1.0 | |
| **Fe** | PC | 1978.00 (258.50) | 1709.00, 2472.00 | 4.17, 2df | PC:MTA=0.24 | |
| | MTA | 1185.00 (750.60) | 77.26, 1726.00 | p=0.04* | PC:AS=0.04* | -1017.03 (-1981.73, -52.33) |
| | AS | 960.80 (1079.00) | 0.001, 2245.00 | | MTA:AS=1.0 | |
| **Ni** | PC | 1.19 (1.54) | 0.001, 4.25 | 2.45, 2df | PC:MTA=0.5 | |
| | MTA | 0.24 (0.15) | 0.09, 0.37 | p=0.12 | PC:AS=0.16 | |
| | AS | 0.001 (0.00) | 0.001, 0.001 | | MTA:AS=1.0 | |
| **Pb** | PC | 1.83 (1.74) | 0.001, 3.57 | 3.96, 2df | PC:MTA=1.0 | |
| | MTA | 1.57 (0.66) | 0.59, 2.02 | p=0.04* | PC:AS=0.04* | -1.82 (-3.54, -0.10) |
| | AS | 0.001 (0.00) | 0.001, 0.001 | | MTA:AS=0.22 | |
| **Cu** | PC | 57.30 (79.76) | 3.63, 166.40 | 2.19, 2df | PC:MTA=0.36 | |
| | MTA | 1.50 (0.03) | 1.46, 1.52 | p=0.14 | PC:AS=0.28 | |
| | AS | 4.06 (3.60) | 0.47, 7.97 | | MTA:AS=1.0 | |
| **Cd** | PC | 0.04 (0.04) | 0.001, 0.10 | 0.46, 2df | PC:MTA=1.0 | |
| | MTA | 0.03 (0.04) | 0.007, 0.09 | p=0.64 | PC:AS=1.0 | |
| | AS | 0.06 (0.08) | 0.001, 0.20 | | MTA:AS=1.0 | |
| **Cr** | PC | 3.44 (5.84) | 0.001, 17.97 | 0.31, 2df | PC:MTA=1.0 | |
| | MTA | 1.61 (1.10) | 0.00, 2.43 | p=0.74 | PC:AS=1.0 | |
| | AS | 2.12 (2.32) | 0.001, 4.23 | | MTA:AS=1.0 | |
| **Mn** | PC | 58.15 (33.72) | 16.34, 99.84 | 6.46, 2df | PC:MTA=0.01** | -58.15(-100.3,-16.04) |
| | MTA | 0.00 (0.00) | 0.00, 0.00 | p≤0.01** | PC:AS=1.0 | |
| | AS | 46.50 (23.27) | 25.10, 69.74 | | MTA:AS=0.05 | |
| **PO** | PC | 20.46 (4.23) | 13.00, 25.08 | 23.04, 2df | PC:MTA≤0.001** | 26.07 (11.63, 40.51) |
| | MTA | 46.53 (20.23) | 17.75, 64.67 | p≤0.001*** | PC:AS=0.03* | -14.68 (-27.35, -2.01) |
| | AS | 5.78 (1.87) | 3.42, 7.58 | | MTA:AS≤0.001** | -40.75(-56.26,-25.24) |
| **F** | PC | 0.00 (0.00) | 0.00, 0.00 | 5.35, 2df | PC:MTA=1.0 | |
| | MTA | 0.00 (0.00) | 0.00, 0.00 | p=0.02* | PC:AS= 0.02* | 2.17 (3.41, 39.92) |
| | AS | 21.67 (24.01) | 0.00, 50.00 | | MTA:AS=0.07 | |

***p<0.05, **p≤0.01, ***p≤0.0001***

***Particle size distribution analysis:***

**LD-PSA:**

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

**Table 4**

*Descriptive summary and ANOVA of particle size distribution of MTA, PC and AS (µm)*

*Descriptive summary LDPSA (not sieved) (µm)*

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

*Descriptive summary LDPSA (sieved) (µm)*

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

## DISCUSSION

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

PC and MTA were found to be composed of similar constituents in different proportions but within a similar range. These findings are not surprising given the established fact that MTA is a derivative of PC. Several studies globally have reported the similarity in composition between MTA and PC, with the only difference being presence of radiopacifiers in MTA and their absence in MTA[1, 6-11, 14-19, 27]. We found only one recent study that employed EDXRF to compare the composition of Kenyan PC and MTA to assess the potential of PC as an alternative material for dental applications[28]. However, to the best of our knowledge, there is no documentation of a comparison of MTA and geopolymers. Given that the precursors of geopolymers are aluminosilicate materials[2-5], it is not surprising that these materials were found to be comprised primarily of quartz, mullite and calcite while PC and MTA were mainly comprised of belite ($C_2S$) and alite ($C_3S$).

Moreover, the clinker, geopolymers and MTA samples did not contain any detectable amounts of As. Small quantities of Pb were detected in both MTA samples using EDXRF; however, using GFAAS, two clinker samples and both MTA samples were found to contain small amounts of Pb. While the Pb content in three of these samples was below the ASTM recommendation of <2mg/kg for PC, it is noteworthy that one clinker sample (Bamburi) contained Pb levels >2mg/kg (3.57μg/g). Studies that have reported on levels of potentially toxic elements such as As and Pb in MTA and PC had varying results although most of the materials studied were found to have low levels of As[29-31].

Admittedly, the greatest concern in direct substitution of an ethically manufactured biomaterial with a cheap version intended for the construction industry is the potential danger of toxicity from impurities, justly attributed to the fact that PC has not been proven to be clinically safe[10, 12]. However, a few studies to evaluate the level of such impurities have reported variable results. A study of two grey and one white PC, and two grey MTA cements by Duarte *et al.* found that all of these materials released similar low amounts of As. The values were below those considered to be harmful; therefore, it was concluded that all the cements tested would be safe for clinical applications[31]. A comparison of the levels of As in some brands of MTA and PC by De-Deus *et al.* detected negligible amounts of type III As; surprisingly, the highest and lowest values of As were detected in two different brands of MTA while the PC and two other MTA cements contained intermediate values or none[30]. Yet another study to determine whether the levels of As in MTA and PC complied with the ISO recommended limit for water-based cements of 2mg per kilogram of cement found that all the materials tested contained As; furthermore, one of the MTA cements had levels as high as 5.91mg/kg while one of the white PC contained 0.52mg/kg[29]. It is difficult to draw plausible conclusions on such few studies with varied results hence further research is necessary to assess the actual effects of these potentially toxic elements.

Among the materials evaluated in this study, only FA was found to contain $F^-$. There is paucity of data on fluoride release in CSCs and related materials such as PC. Considering that the main application of these materials in dentistry is for endodontic applications, it is not surprising that the role of fluoride at this stage of treatment may not be crucial. Indeed, topical fluoride is necessary to enhance remineralization and inhibit demineralization of initial caries lesions, and not advanced disease such as pulpitis[32]. Nonetheless, the presence of high levels of fluoride in FA is an interesting finding that warrants further research on this material.

The particle size distribution of the materials was also analyzed. Prior to sieving, a variation was observed in the 10th, 50th and 90th percentile in the particle size distribution of the various materials. This finding was consistent with that reported by other studies[16, 23-25, 33-35] and may be explained by the differences in production methods in relation to the intended application, that is, endodontic material and construction material for MTA and clinker and geopolymers, respectively. However, after sieving, the particle size distribution was found to be comparable among the materials. Moreover, sieving was found to be an effective method of controlling the particle size to that recommended for dental cements (45µm) as documented in other studies[36]. Additionally, it has been shown that particle size above 50µm remained largely unreacted in PC and could compromise the overall quality of the set cement[1].

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

In yet another study, Ha *et al.* assessed the influence of particle size on the setting time of MTA and PC. They concluded that despite variations in particle size between MTA and PC, smaller particle size was associated with faster setting times. However, among the three percentiles of particle sizes (D10, D50 and D90), D90 showed the highest positive linear correlation to setting time in both MTA and PC[23]. However, a recent in vivo animal study failed to show the influence of reduction in particle size of MTA on dento-alveolar and osseous healing following root-end fillings[35]. Two earlier studies had attempted to describe the particle shape and aspect ratio of the two materials, speculating that smaller particles may penetrate open dentinal tubules and may be clinically useful in bioactive materials[33, 34]. Nevertheless, the scope of this study did not extend to assess the specific influence of particle size and shape on the properties of materials under investigation.

## CONCLUSION

In conclusion, this study found that the composition of PC clinker manufactured in Kenya and MTA were similar except the presence of $Bi_2O_3$ in MTA and its absence in PC. However, while PC and MTA comprised primarily of $C_2S$ and $C_3S$, geopolymers were aluminosilicate-based and composed of quartz, mullite and calcite. The particle size of the materials was also similar, with most of the materials having a mean of <45µm. Moreover, sieving was found to be effective in controlling the particle size distribution.

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