



Synthesis and characterization of ionomer-type cements from alkaline-activated kaolinite

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ABSTRACT

The objective was to synthesize ionomer-type cements from alkaline-activated kaolinite and describe their setting characteristics, compressive strength and fluoride ion releasing properties. Aluminosilicate phases were visible on XRD spectra with minimal difference between raw and alkaline-activated kaolin. D50 range of sieved powders was 8.10–9.07 μm . Characteristic bands of polyacrylates and tartrates were identifiable in the cements on FTIR. Cements were hydrolytically stable with mixing and setting times of 60s and 135–240 s, respectively. Mean compressive strength increased over time, highest value 3.24 MPa recorded for Kaolin100 after 28 days, and significantly different within the group ($F = 76.64$, $p = 0.000$). Cement containing fly ash (FA) exhibited fluoride ion release capabilities with Kaolin80FA20 having the highest 0.69 mmol/L at 60 min. Mechanically weak but hydrolytically stable ionomer cements can be formulated from alkaline-activated kaolin geopolymers.

1. Introduction

In the era of a global phase down of usage of dental amalgam following the Minamata Convention on Mercury in 2013, there has been an emphasis on research on tooth-coloured alternatives such as resin composites and glass ionomer cements. Moreover, advances in adhesive dentistry have resulted in a paradigm shift from traditional management of dental caries to promotion of preventive and minimal intervention dentistry [1].

Glass ionomer or polyalkenoate cements (GICs) were developed in 1971 by Wilson and Kent [2] following a commission to improve dental silicate cements and are a product of merging dental silicate and zinc polycarboxylate cements. They are presented as powder and liquid components where the powder is calcium or strontium fluoroaluminosilicate glass, like in silicate cements, whereas the liquid is poly (acrylic acid) as is used in zinc polycarboxylate cements [3,4]. GICs overcome disadvantages of their predecessors, notably by reduced solubility and acidity, reduced pulpal irritation, and improved optical and mechanical properties [5–7]. Moreover, two salient properties of GICs are chemical adhesion to tooth structure and fluoride release following acid attack of the glass particles. Therefore, GICs currently have a myriad of dental restorative applications that include bases,

intermediate restorations, permanent restorations in deciduous dentition, cementation of indirect restorations and sandwich restorations with resin composites [2–4,7]. Their adhesive property makes them the preferred material for minimally invasive techniques such as the atraumatic restorative treatment approach [1,3,4].

The fluoroaluminosilicate glasses used in GICs are different from everyday glasses such as those used in windows and bottles, which are mainly soda-lime-silica based. The difference arises from the fact that everyday glasses comprise a chemically stable unreactive structure because of a highly cross-linked O-Si-O network formed from individual $[\text{SiO}_4]$ tetrahedra, while ionomer glasses are highly reactive and susceptible to acid decomposition because of disruption of the oxygen bonds through the introduction of glass modifiers such as CaO and CaF_2 within the composition [3,4]. Glass modifiers are necessary for balancing the net negative charge following addition of alumina as a glass intermediate to replace some of the $[\text{SiO}_4]$ tetrahedra [6,7]. The glasses are prepared by melting alumina, silica, and other metal oxides, fluorides and phosphates at temperatures ranging from 1100 °C to 1500 °C following which the melt is quenched in cold water. Components such as sodium, potassium, aluminium, barium and silver may be incorporated to provide specific properties. The glass is then ground to fine powder, with the particle size dependent on the intended clinical

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application [2–4,7].

The original liquid was aqueous poly (acrylic acid) (PAA), which is still widely used in commercial glass ionomer formulations. Co-polymers are also used, all of which are based on acrylic acid but with maleic acid itaconic or 2-methylene butanedioic acid [8,9]. Tartaric acid was yet another important additive; it prolongs and sharpens the setting time and increases the compressive strength of the cement. To maintain the molecular weight of PAA it may, together with tartaric acid, be freeze-dried and included in the powder. This presentation is to be mixed with distilled water or, if tartaric acid is not in the freeze-dried form, with an aqueous solution of tartaric acid [2,6,8,9].

GICs are classified as acid-base cements because of their setting reaction [2,9]. The reaction results in the release of metal cations such as Al^{3+} and Ca^{2+} through surface dissolution of the glass particles; thereafter, the ions crosslink the poly-acid network to form a rigid poly-salt matrix [6,7,10]. Furthermore, an inorganic component comprising silicon and phosphorus is also thought to contribute to the increasing strength of these cements with age, as concluded by Zainuddin et al. [11] from a long-term study of the setting reaction of GICs using MAS-NMR spectroscopy. Nicholson [12] had earlier reviewed this aspect and reiterated the inorganic component existed because of the glass component and contributed to the insolubility of GICs as well as the gradual increase in compressive strength with time. Therefore, the fully set cement is a composite of residual glass particles embedded in a siliceous hydrogel and bonded in a metal-polyacrylate matrix [5,6,13].

There are documented reports where, instead of a typical fluoroaluminosilicate glass, other silicate minerals have been used to form cements. One of the earliest efforts include that by Wilson [14] who, while experimenting with precursors of the aluminosilicate poly (acrylic acid) (ASPA) cements, described formation of polyalkenoate-like cements derived from mixtures of naturally occurring aluminosilicates and PAA. These naturally occurring silicates, whose reactions with organic acids were first investigated by Murata in 1943 [15], are categorized as: orthosilicates, pyrosilicates, cyclic or chain metasilicates and aluminosilicates. Further reports on their reaction with polycarboxylic acids were made by Crisp et al. [16], who concluded that cements from these materials arose from an acid-base reaction characterized by acidic attack of the mineral phases to form ionic polymer (ionomer) complexes. Just like is observed in GICs, the reactivity was dependent on the ratio of aluminium to silicon which determines the basicity following acid attack. Among the promising silicate materials, they further observed that cement stability, particularly in aqueous media, was dependent on the nature of the cations in the matrix. For example, zinc based cements were found to be more stable and to demonstrate compressive strength as high as 34 MPa, faring better than calcium-based aluminosilicates [14,16]. Kaolin and silica sand together with other additives have been used to form variable sintered glasses capable of forming glass ionomer cements for luting applications [17].

Alkaline-activated aluminosilicates or geopolymers are cementitious materials synthesized through a low temperature reaction (typically below 100 °C) between aluminosilicate precursors and alkaline sodium silicate solution [18,19]. 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. Alkaline activation of these powdery aluminosilicates produces pastes capable of setting within a short period while gaining considerable strength. This has been attributed to their reactive amorphous phases undergoing a process of dissolution, polycondensation and hardening on exposure to the alkaline activator [18,20–25]. Kaolin or kaolinite is a clay-based material which may be used as a precursor for alkaline-activation; however, its high crystalline content renders it less reactive hence it characteristically produces weak cements. As such, it is usually transformed via thermal treatment to metakaolin, which is more amorphous. Geopolymers derived from metakaolin generally set and harden within 24 h [26].

The low-temperature alkaline-activation reaction is attractive for

production of low-cost materials associated with lower energy consumption and reduced CO₂ emissions. Naturally occurring aluminosilicates and glasses have been evaluated extensively in GICs but not alkaline-activated aluminosilicates. Therefore, the aim of this study was to synthesize and characterize ionomer-type cements derived from alkaline-activated kaolinite.

2. Materials and methods

2.1. Sourcing, alkaline-activation, composition and particle size analysis of kaolinite

The sampling and sourcing of kaolinite was previously described [19]. Briefly, 1 kg of raw kaolinite was obtained from a ceramic manufacturing company in Kenya: Saj Ceramics. In addition, FA (pozzolana) was obtained from a Portland cement manufacturing company in Kenya: Bamburi Cement. Approximately 100 g of kaolinite and a mixture of kaolinite and FA (80 g:20 g) were weighed separately and activated in 55 mL of Na₂SiO₃ solution with a final constitution of 9.1% Na₂O, 27.5% SiO₂ and 63.4% H₂O and SiO₂/Na₂O ratio of 3.02, at 85°C for 24 h. After 24 h, the dried products were removed from the oven, bench cooled and left at ambient temperature for 90 days. Thereafter, the products were sprayed with ethanol to stop further activation, pulverized and stored in sealed, labelled, airtight sample bags. They were then subjected to composition analysis by X-ray diffraction (XRD), energy dispersive X-ray fluorescence (EDXRF) and fluoride ion selective electrode (FISE), and particle size distribution analysis by laser diffraction. Alkaline-activated materials were sieved through a 120 μm analytical sieve (Endecotts Ltd., London, UK) prior to cement preparation.

2.2. Cement preparation

Experimental ionomer-type cement pastes were prepared by mixing various ratios of alkaline-activated kaolinite powder, PAA (mw 35KDa) (S & C Polymer GmbH, Elmshorn, Germany) and aqueous tartaric acid (Sigma Aldrich, Gillingham, UK). Several ratios were attempted to attain a promising mixture with reasonable mixing and setting time, and which exhibited a workable dough consistency.

2.3. Cement mixing and setting time

Cement mixing time (MT) was recorded as the time in seconds required to obtain a homogenous dough consistency by combining all the components dispensed on a glass slab using a stainless-steel spatula with continuous long strokes. Cement initial setting time (ST) was recorded in seconds using a Gillmore needle apparatus (Humboldt Mfg, Elgin, Illinois, USA) at ambient temperature as specified in ISO 9917-1:2007 for hydraulic dental cements [27]. Once the desired cement consistency was obtained, samples were condensed in preformed cuboids, 8mm² by 10 mm, made from modelling wax. Three specimens were prepared for each cement sample. The initial set needle was held in a vertical position and applied lightly to the surface of the cement. This was repeated until the Gillmore needle did not cause an appreciable indentation on the cement surface.

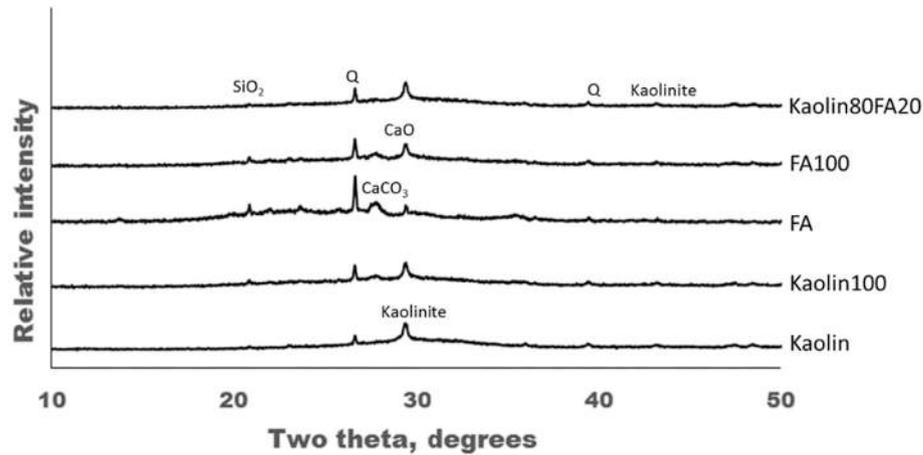
2.4. Cement setting characteristics

FTIR spectroscopy (Cary 630, Agilent Technologies, Ratingen, Germany) was used to evaluate the setting characteristics of the experimental cements. Kinetic measurements were conducted on cement pastes 30s after mixing and followed up to 25 min after mixing. The kaolinite and FA, freeze-dried PAA and tartaric acid powders were also scanned as reference materials. Data was collected in the IR region between 3600 cm⁻¹ to 500 cm⁻¹.

Table 1

Composition of raw and alkaline-activated kaolinite and FA by EDXRF (%wt).

Sample name	CaO	SiO ₂	Al ₂ O ₃	P ₂ O ₅	S	Cl	K ₂ O	MgO	Fe	Sr	Others	Total
Kaolin	0.65	62.88	27.69	0.03	0.00	0.08	3.95	2.72	1.68	0.01	0.30	100.00
Kaolin100	0.61	68.44	23.45	0.03	0.08	0.09	3.84	1.91	1.29	0.01	0.25	100.00
Kaolin80FA20	1.02	70.77	20.71	0.00	0.03	0.07	3.89	1.03	2.11	0.01	0.35	100.00
FA100	3.18	74.65	10.32	0.00	0.12	0.14	5.18	0.00	5.58	0.01	0.82	100.00

**Fig. 1.** Powder X-ray diffraction patterns of raw and alkaline-activated kaolinite and FA.

2.5. Compressive strength testing of cements

Compressive strength tests were performed on cement cylinders 4.0 mm in diameter by 6.0 mm in height, according to ISO 9917-1:2007 [27]. Cylindrical specimens were fabricated by condensing freshly mixed cement pastes into Teflon moulds containing three bores of the above dimensions. Thereafter, the moulds were clamped between two steel plates and placed in a preheated oscillating oven at 37 °C for 24 h (after one hour, the cements had not obtained final set necessitating the extension). After 24 h, they were removed from the moulds, placed in centrifuge bottles at 100% humidity achieved by damp tissues and incubated at 37 °C for 24 h, 3d, 7d and 28d. The specimen dimensions as well as weight before incubation and prior to testing was recorded. A 30kN load cell was used to load the samples using a compression cage on a Universal Testing machine (ProLine Z050TN, ZwickRoell, Ulm, Germany) at a crosshead displacement speed of 1 mm min⁻¹. Six cement cylinders were fabricated and tested for the two types of alkaline-activated kaolinite cement sample. Compressive strength was calculated using the formula: $\sigma_c = F \div \pi r^2$ where: σ_c is compressive strength (MPa); F is applied load at failure (N); and, r is the sample radius as measured prior to testing (mm).

2.6. Cement fluoride ion release profile

Fluoride ion release measurements were conducted in deionized water and artificial saliva at 37 °C and pH 7. The elution media were selected based on their neutral pH as well as few elemental contents which may form complexes hence interfere with the ion release processes of the cements. Cement cylinders like those for compressive strength tests were fabricated for ion release measurements, three specimens for each cement sample. On retrieval from the incubator after 24 h, they were stored in a 15 mL centrifuge bottle containing 10 mL of each elution medium and returned to storage at 37 °C. Fluoride ion release in the elution media was measured at specified time points of 10, 20, 40 and 60 min. Prior to use, the electrode tip was flushed with deionized water and then calibrated using standard solutions of 0.5, 1 and 10 ppm fluoride and TISAB II. TISAB II was also added to the samples to ensure uniform pH and ionic strength values with the

Table 2

Particle size distribution of raw and alkaline-activated kaolinite and FA (µm).

Sample name	D10	D50	D90	D10	D50	D90
<i>Before alkaline-activation and sieving</i>				<i>After alkaline-activation and sieving</i>		
FA	2.25	19.70	393.80	Kaolin 80FA 20	1.51	9.07
Kaolin	3.29	20.61	1050.33	Kaolin100	1.36	8.10
				FA100	1.47	8.86

standards. Fluoride concentration in the samples was recorded in ppm with a corresponding RmV, then converted to mmol/L. The stable reading for each sample specimen was recorded, and the average value taken as the amount of fluoride ion content released by the material.

3. Results

3.1. Composition and particle size analysis

Table 1 summarizes the major constituents (%wt) of the materials as analyzed by EDXRF. The materials had low proportions of CaO, ranging from 0.61%wt to 3.18%wt. All the materials contained SiO₂ ranging from 62.88%wt to 74.65%wt, and Al₂O₃ ranging from 10.32%wt to 27.69%wt. FA had previously been reported to contain fluoride (43.33 µg/g ± 5.77) [19].

Fig. 1 shows the diffraction patterns of raw and alkaline-activated kaolinite and FA with peaks corresponding to the aluminosilicate, kaolinite and calcite phases. There was little difference in the kaolinite spectra, suggesting little alteration in the structure by alkaline activation.

Table 2 shows the particle size distribution of raw and alkaline-activated kaolinite and FA before and after sieving. D50 of sieved powders ranged between 8.10 and 9.07 µm.

Table 3
Experimental cement preparation ratios and outcomes.

Sample name	Powder (gm)	PAA (gm)	10% tartaric acid (mL)	Outcome – MT(s), initial ST(min), consistency
1. Kaolin100	1.0	0.2	0.25	30s, 30s, paste
2. Kaolin100	0.7	0.2	0.25	60s, 3.41min, paste
3. Kaolin100	0.7	0.1	0.20	60s, 2.15min, paste
4. Kaolin80FA20	0.7	0.1	0.20	60s, 2.40min, paste

3.2. Cement preparation, mixing and setting time

The various cement preparation ratios and outcomes are presented in Table 3. Table 4 summarizes the final acceptable cement mixing ratios, mixing and initial setting times. Geopolymers (0.7–1.0 g) were mixed

Table 4
Final acceptable experimental cement mixing ratios, MT and initial ST.

Sample name	Si:Al ratio	Ca:Al ratio	Powder (gm)	PAA (gm)	10% tartaric acid (mL)	MT (s)	Initial ST (s)
Kaolin100	2.92	0.03	0.7	0.1	0.2	60	135
Kaolin80FA20	3.42	0.05	1.0	0.1	0.25	60	135–240

with 0.1 g of PAA and 0.2 mL of aqueous tartaric acid. The mixing and setting times ranged between 60s and 135–240 s, respectively.

3.3. Cement setting characteristics

Fig. 2 (2.1) shows the kinetic setting characteristics of cement derived from alkaline-activated Kaolin100. Prominent bands were identified at 1636 cm^{-1} , 1375 cm^{-1} , 1095 cm^{-1} , 1028 cm^{-1} , 1010 cm^{-1} and 909 cm^{-1} . Smaller bands were also visible at 1558 cm^{-1} , 1455 cm^{-1} and 935 cm^{-1} . Fig. 2 (2.2) shows the kinetic setting characteristics of cement derived from alkaline-activated Kaolin80FA20. Prominent bands were identified at 1625 cm^{-1} , 1371 cm^{-1} , 1095 cm^{-1} , 1028 cm^{-1} , 1006 cm^{-1} and 909 cm^{-1} . Smaller bands were also visible at 1556 cm^{-1} , 1453 cm^{-1} , 939 cm^{-1} .

Fig. 3 (3.1) shows the kinetic setting characteristics of alkaline-

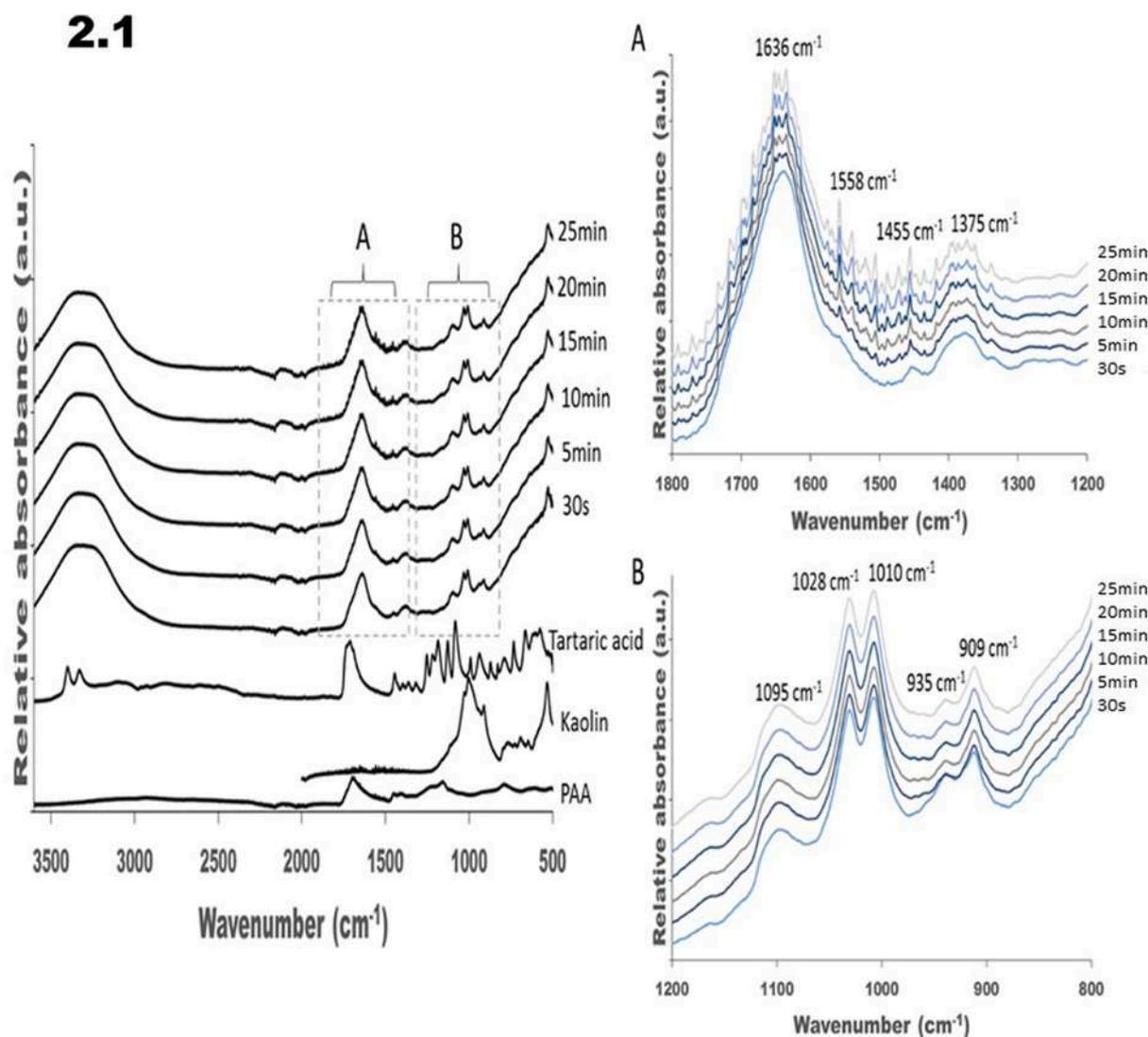


Fig. 2. (2.1): Setting characteristics of cements derived from alkaline-activated Kaolin100. (2.2): Setting characteristics of cements derived from alkaline-activated Kaolin80FA20.

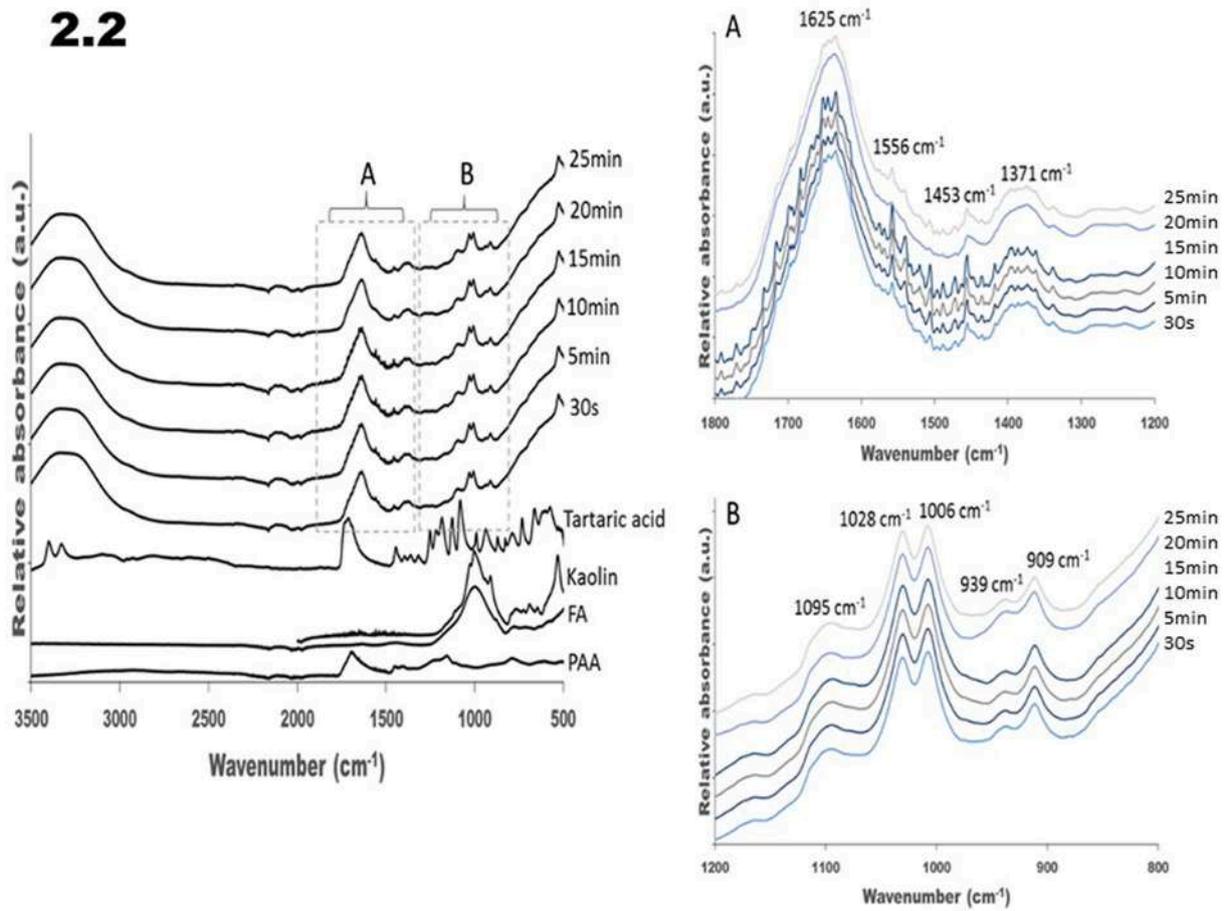


Fig. 2. (continued).

activated Kaolin100 on mixing with either 10% aqueous tartaric acid (A, C) or PAA (B, D). On mixing with tartaric acid, prominent bands were identified at 1634 cm⁻¹, 1373 cm⁻¹, 1025 cm⁻¹, 1000 cm⁻¹ and 909 cm⁻¹ while smaller bands were visible at 1110 cm⁻¹ and 935 cm⁻¹ and. On mixing with PAA, prominent bands were identified at 1645 cm⁻¹, 1369 cm⁻¹, 1095 cm⁻¹, 1028 cm⁻¹, 1004 cm⁻¹ and 909 cm⁻¹ while smaller bands were visible at 1558 cm⁻¹, 1455 cm⁻¹ and 937 cm⁻¹. Fig. 3 (3.2) shows the kinetic setting characteristics of alkaline-activated Kaolin80FA20 on mixing with either 10% aqueous tartaric acid (A, C) or PAA (B, D). On mixing with tartaric acid, prominent bands were identified at 1632 cm⁻¹, 1382 cm⁻¹, 1025 cm⁻¹, 1000 cm⁻¹ and 909 cm⁻¹ while smaller bands were visible at 1110 cm⁻¹ and 935 cm⁻¹. On mixing with PAA, prominent bands were identified at 1632 cm⁻¹, 1558 cm⁻¹, 1455 cm⁻¹, 1401 cm⁻¹, 1028 cm⁻¹ and 1006 cm⁻¹ while smaller bands were visible at 1095 cm⁻¹ and 909 cm⁻¹.

3.4. Cement compressive strength

Fig. 4 shows the mean compressive strength of Kaolin100 (A) and Kaolin80FA20 (B) cements after 1, 3, 7 and 28d. The cements increased in strength between 1d and 28d, except for a dip on day 7 for Kaolin100 cements. The highest compressive strength value was 3.24 MPa recorded for Kaolin100 after 28 days.

Table 5 presents a descriptive summary and results of analysis of variance (ANOVA) test of individual cement compressive strengths. There was a statistically significant difference at the various time points for both cement samples further confirmed by Tukey's post hoc test ($p \leq 0.01$).

3.5. Cement fluoride ion releasing profile

Fig. 5 shows the fluoride ion release profile of the cements in artificial saliva (A) and deionized water (B), both at 37 °C and pH 7. The fluoride release had a linear relationship to square root of time ($t^{1/2}$), with $R^2 > 96$ (except K100 in artificial saliva) but low intercept values. Kaolin100 cements showed no fluoride release (< 0.1 mmol/L) in both media. Kaolin80FA20 cements released more fluoride in artificial saliva than deionized water, up to 0.69 mmol/L after 60 min.

4. Discussion

To the best of our knowledge, this is the first report of ionomer-type cements prepared by mixing alkaline-activated kaolinite powders with various ratios of freeze-dried PAA and aqueous tartaric acid. The selection of the materials was based on the compositional analysis which showed a similarity to GIC glass powders. Moreover, experiments conducted on natural silicate materials had shown their ability to form ionomer-type cements [14,16]. Although alkaline-activated kaolinite has less amorphous phase than metakaolin [26], it was expected that the high ratios of alumina and silica but low CaO content would still result in a reaction similar to that observed between PAA and natural aluminosilicate materials. This was observed but we must acknowledge that despite the potential of these ionomer-type cements derived from alkaline-activated kaolinite geopolymers, they do not meet the ISO specifications for water-setting dental cements [27] due to their extremely low compressive strength and opacity.

The mixing ratios were guided by those established for restorative dental cement applications usually mixed to dough consistency. It is recommended to have higher powder to liquid ratio in GICs to confer

3.1

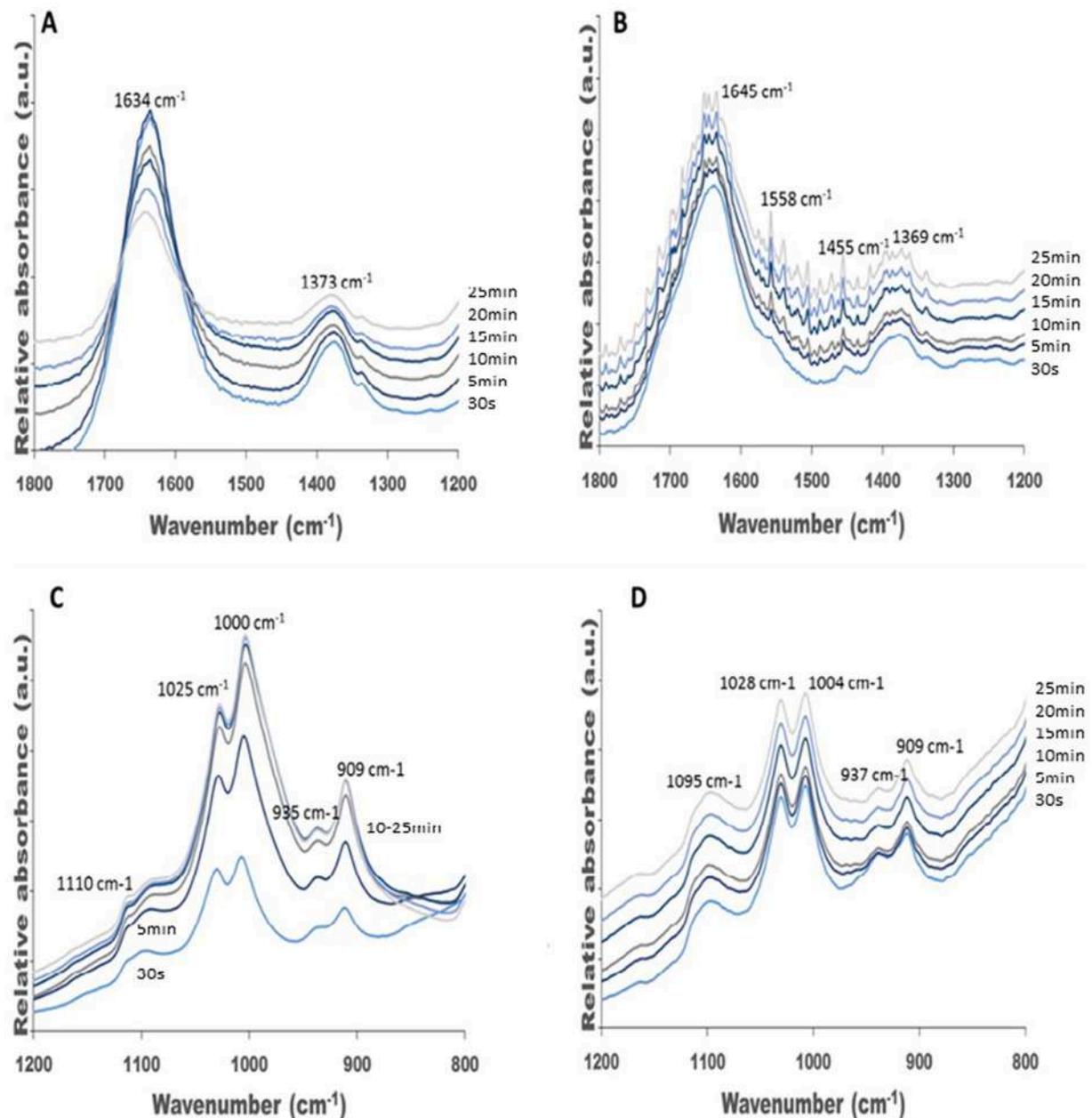


Fig. 3. (3.1): Setting characteristics of alkaline-activated Kaolin100 on mixing with aqueous tartaric acid (A, C) or PAA (B, D). (3.2): Setting characteristics of alkaline-activated Kaolin80FA20 on mixing with aqueous tartaric acid (A, C) or PAA (B, D).

strength [2,5,7,12]. Nonetheless, variations in mixing and setting times were observed with several attempts before a reasonable powder/liquid ratio was determined. One gram of alkaline-activated kaolinite powder resulted in a rapid set that made it impossible to manipulate the cements further after mixing. Reducing the amount of powder to 0.7 g resulted in a paste/ dough consistency with a more reasonable working time. It is hypothesized that the amorphous nature of alkaline-activated aluminosilicate materials made them reactive with PAA and enhanced their ability to form ionomer-type cements [18,22,25,26,28]. Further, these cements demonstrated hydrolytic stability after 24 h likely due to crosslinking of Al³⁺ ions and PAA, a reaction similar to that occurring in GICs. The mixing and setting time of the experimental cements were found to be reasonable. The mixing time ranged between 30s and 60s

while the setting time ranged between 135 s and 240 s. As visualized by FTIR, the setting reaction of these cements showed an acid-base reaction similar to GICs and characterized by production of carboxylates and tartrates [29,30]; therefore, this may explain the hastened setting reaction.

There was little difference in the setting characteristics of the two alkaline-activated kaolinite-derived cements. Their powders comprised of high aluminosilicate ratios but low CaO content, similar to natural silicate materials evaluated by Wilson and co-workers [14,16]. This, coupled with the presence of an amorphous phase in FA [31–33] and the fact that there is no formation of any new crystalline phases following alkaline-activation, may provide a plausible explanation as to the setting characteristics of these materials. Further, the role of PAA as a dominant

3.2

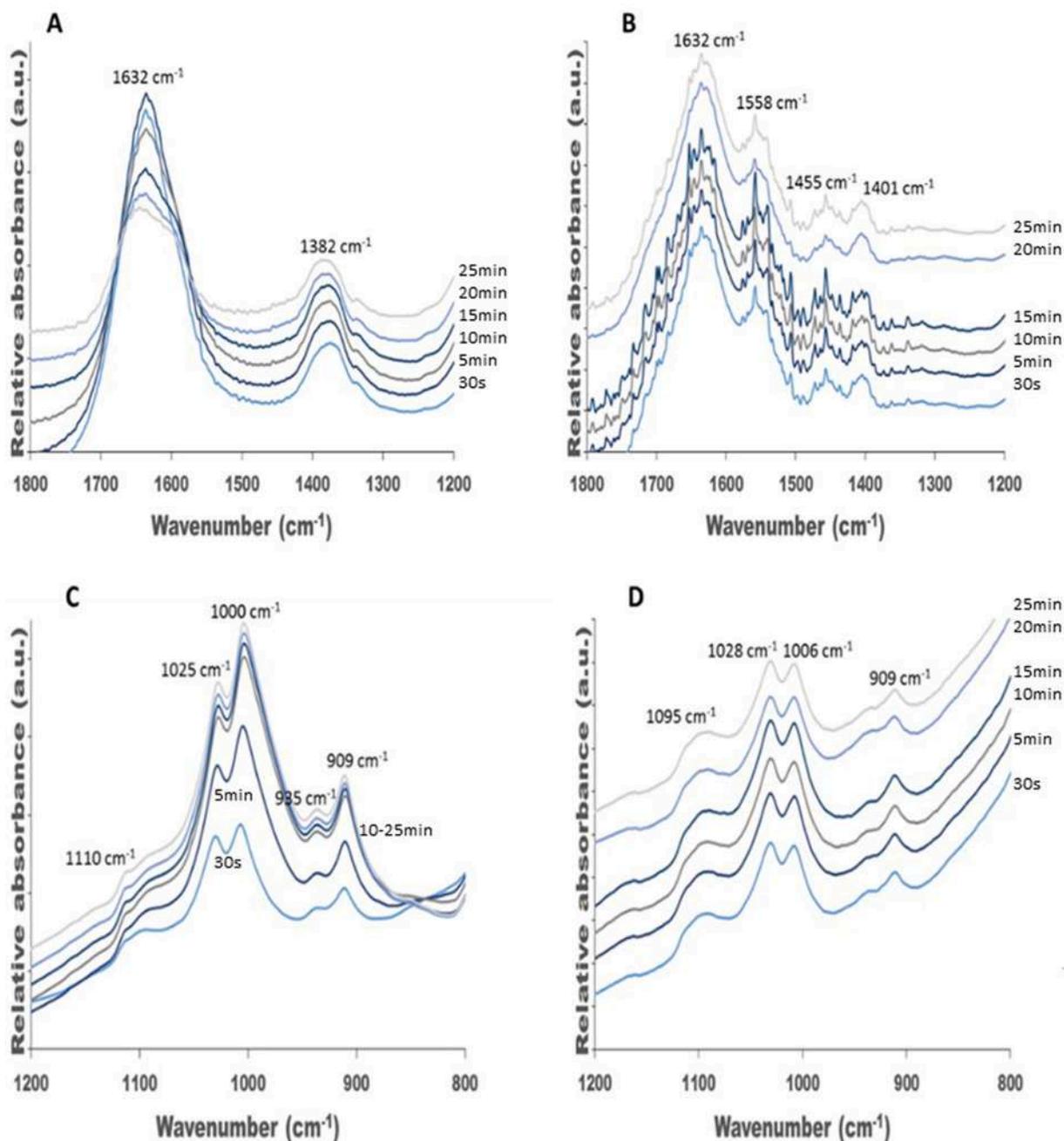


Fig. 3. (continued).

reactant was reinforced by the visibility of more symmetric and asymmetric bands with PAA than tartaric acid as well as prominence of the band associated with the glass powder and diminishing of the same for reactions with tartaric acid and PAA, respectively. Although not all the identified bands were typical of those expected in GICs, the resemblance suggests that these materials set in a similar fashion to GICs, with polyacrylates and tartrates as the major reaction products. Moreover, the low calcium content may have been quickly depleted leading to formation and observation of bands at 1600 cm^{-1} typically associated with aluminium salts sooner than would be expected for GICs.

It is particularly worthwhile to consider that alkaline-activated aluminosilicates or geopolymers are inorganic polymers [18], the exact description for which ‘ionomers’ are christened [2,14,16]. In fact, the

widely accepted setting reaction of geopolymers involves dissolution of the aluminosilicates, followed by polycondensation and hardening [18,26]. Seemingly, the findings discussed above suggest that the 3-dimensional aluminosilicate geopolymer framework can participate in an acid-base reaction to form new salts, likely due to the presence of an amorphous phase. The similarity to the behaviour of a charge balanced aluminosilicate glass on exposure to polycarboxylic acids is not lost, and for the kaolinite-based geopolymers which had very low calcium content, it is hypothesized that this was highly likely achieved by Na^+ from the sodium silicate activating solution to maintain the basicity of the powders [6,34].

Wilson [14] and Crisp et al. [16] reported that while naturally occurring aluminosilicates were capable of forming cements on mixing

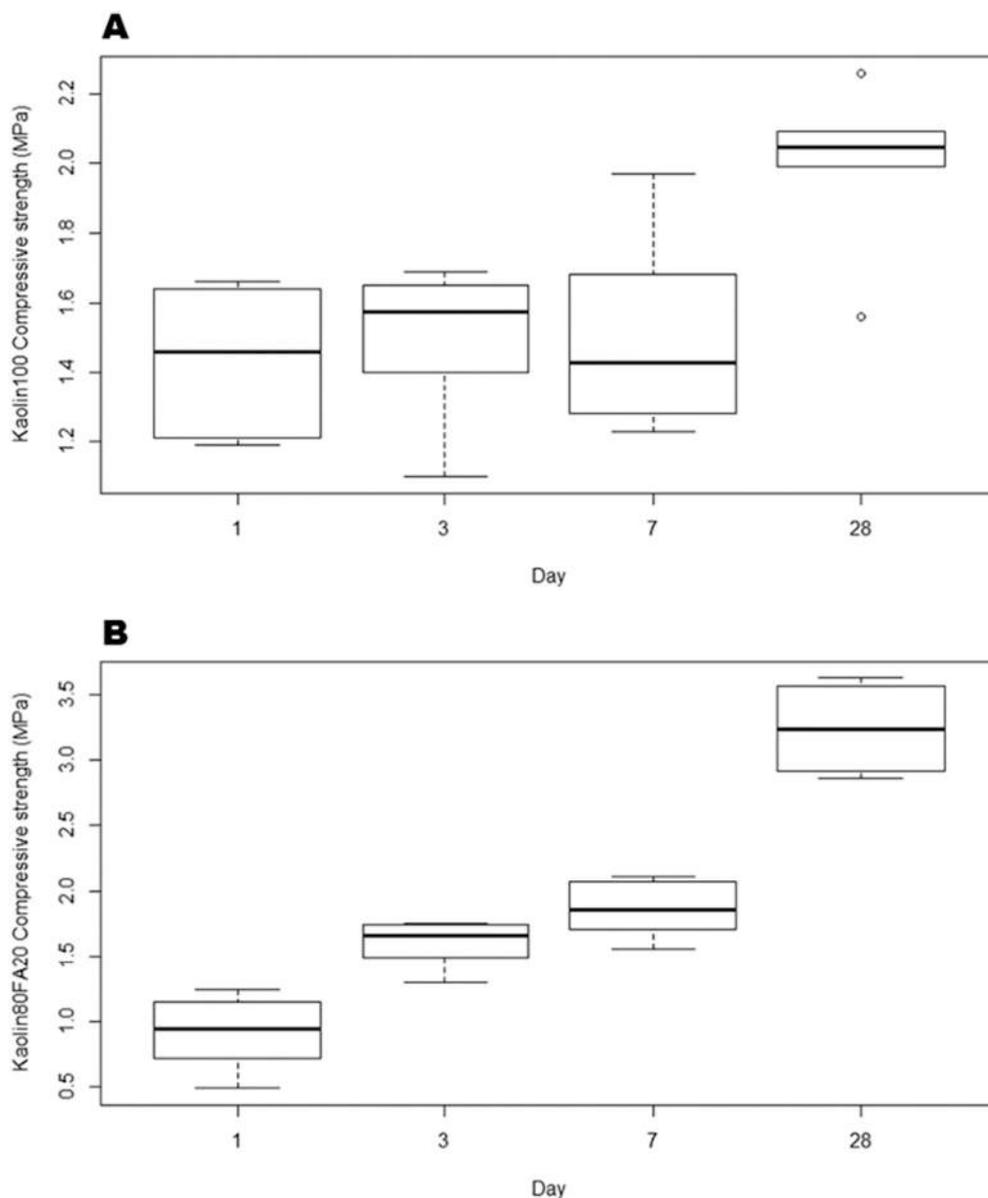


Fig. 4. Mean compressive strength of Kaolin100 (A) and Kaolin80FA20 (B) cement samples after 1, 3, 7 and 28d.

Table 5
Descriptive summary and ANOVA of cement compressive strength (MPa).

Sample name	Time	Mean (SD)	Min	Max	F statistic, df, p-value	Tukey's post hoc adjusted p-value	Diff (95% CI)
Kaolin80FA20	1 (n=6)	0.92 (0.29)	0.49	1.24	76.64, 3df $p < 0.0001^{***}$	1:3 = 0.002** 1:7 = 0.000*** 1:28 = 0.000*** 3:28 = 0.000*** 7:28 = 0.000***	0.69 (0.25, 1.13) 0.94 (0.50, 1.38) 2.32 (1.88, 2.76) 1.63 (1.19, 2.07) 1.38 (0.94, 1.82)
	3 (n=6)	1.61 (0.19)	1.30	1.76			
	7 (n=6)	1.86 (0.22)	1.56	2.11			
	28 (n=6)	3.24 (0.36)	2.86	3.63			
Kaolin100	1 (n=6)	1.44 (0.21)	1.19	1.66	7.09, 3df $p = 0.002^{**}$	1:28 = 0.003** 3:28 = 0.01** 7:28 = 0.01**	0.56 (0.17, 0.95) 0.50 (0.11, 0.89) 0.50 (0.11, 0.88)
	3 (n=6)	1.50 (0.22)	1.10	1.69			
	7 (n=6)	1.50 (0.29)	1.23	1.97			
	28 (n=6)	2.00 (0.23)	1.56	2.26			

** $p \leq 0.01$.
*** $p \leq 0.0001$.

with polycarboxylic acids, the resultant cements exhibited low compressive strength of 30 MPa or less. Furthermore, among clay-based materials for alkaline-activation, the highly crystalline structure of kaolinite renders it less reactive hence the thermally converted metakaolin is preferred for being more amorphous and reactive. Cements

from alkaline-activated kaolinite typically have compressive strength of 2-10 MPa while those derived from metakaolin may achieve strength of 25 MPa or more [26]. This is similar to what was observed in this study. Although the alkaline-activated kaolinite is capable of forming ionomer-type cements, classical glass ionomers derive their strength from the

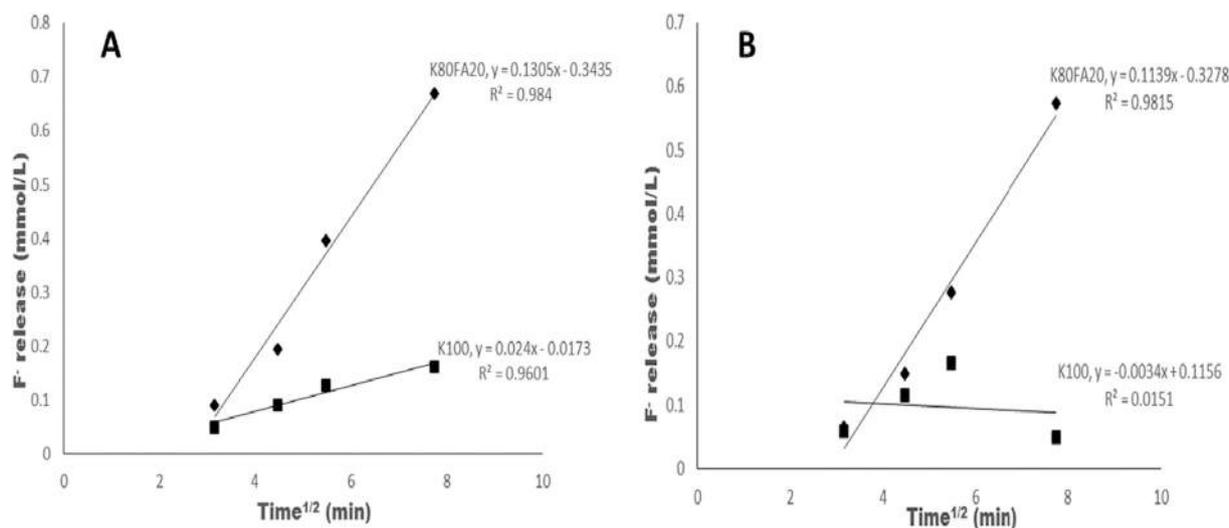


Fig. 5. F⁻ release profile of Kaolin100 and Kaolin80FA20 cements in artificial saliva (A) and deionized water (B), pH 7, 37 °C.

reactivity of the glass phase, ideally a factor of the ratio of glass formers and modifiers [5–7,9]. For example, for optimum properties in earlier GICs, percentage of SiO₂:Al₂O₃:CaF₂ was 21:16.6:34.2. This may be varied to increase basicity and translucency or opacity but despite the complexity of these glass systems, it is generally accepted that they are principally composed of silica (SiO₂), alumina (Al₂O₃) and lime (CaO), with addition of fluoride (CaF₂) for fluoride release [5–8,12,34]. The importance of the Si:Al and Ca:Al ratios for optimal glass dissolution and development of compressive strength has also been shown [7,10]. A Si:Al ratio of one or more and Ca:Al ratio of 1:2 or more is preferable as this enables aluminium to adopt a fourfold coordination to enter the glass network as a tetrahedron (AlO₄) like the silicon tetrahedron (SiO₄). In this state, the glass network is negatively charged and is balanced by the positively charged network dwelling cations. However, the bridging oxygen between the aluminium and silicon tetrahedra is susceptible to acid attack which is desirable in glass ionomers. A low Ca:Al ratio forces the aluminium to adopt a sixfold coordination for charge balancing thus reducing the reactivity of the glass [7,10]. The Si:Al ratio of the materials investigated in this study was greater than one, ranging from 2.92 to 3.42, but the Ca:Al ratio was much less than half (0.03–0.05). Thus, the low Ca:Al ratio probably impaired the reactivity and consequently, the cement mechanical properties. On the other hand, the strength of geopolymers is dependent on the amount and strength of the gel phase as well as reactivity of the amorphous phase [26].

Nevertheless, it is noteworthy that the strength of the experimental cements increased on aging, like the behaviour of GICs, and that this difference was statistically significant among the various time points. This may further explain the finding that the setting behaviour of these cements was also similar to GICs, characterized by dissolution, gelation and hardening leading to formation of polyacrylates and tartrates [11,29]. This maturation of GICs is responsible for the increase in strength with time as the larger Al³⁺ react with carboxylic end groups of poly (acrylic acid) in a delayed reaction [5–7,11]. Observations by FTIR showed that this was the setting mechanism of the cements.

The results of the fluoride ion release characteristics of the cements suggest a diffusion-controlled process as shown by the linear relationship to square root of time rather than to time; a linear relationship to time would suggest a dissolution-controlled process. Moreover, the linear correlation was further evidenced by $R^2 > 0.96$ while the increasing cumulative behaviour suggested a sustained release over the period of study. These findings are similar to the behaviour of GICs as reported by Luo et al. [35]. However, the low intercept values suggest a lack of ‘initial burst’ of fluoride ion release. It has been shown that this phenomenon is characteristic of glasses that contain monovalent Na⁺,

which was minimal in these materials [34–36]. Further, the fluoride ion release profile also suggests that it was primarily dependent on the quantity of the fluoride in the materials rather than the type of media and the pH; only the Kaolin80FA20 demonstrated fluoride ion release, presumably from the FA component.

5. Conclusions

Alkaline-activated kaolinite geopolymers can be used to form quick-setting, hydrolytically stable ionomer-type cements on mixing with predetermined ratios of PAA and aqueous tartaric acid. The mean compressive strength of the cements increased over time but was less than 5 MPa after 28 days. Addition of FA, a fluoride-containing material, resulted in fluoride ion release of 0.69 mmol/L after 1 h through a diffusion-controlled process dependent on the amount of fluoride in the cements.

Credit author statement

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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