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Development of Portland cement for orthopedic applications, establishing injectability and decreasing setting times

Gareth Wynn-Jones, Richard M Shelton, Michael P Hofmann

Biomaterials, School of Dentistry, University of Birmingham, St Chad's Queensway, Birmingham, B4 6NN, UK

Abstract: The injectability of Portland cement (PC) with calcium chloride and calcium nitrate additives was investigated using a syringe with a 2 mm aperture for potential clinical applications such as vertebroplasty. Addition of either additive at 10 wt % increased the quantity of cement extruded through the syringe from approximately 25 wt % for the PC standard, to over 95 wt %. 10 wt % additions of either additive also decreased setting times from over 2 h to below 25 min. The compressive strength of the modified cements was all greater than the compressive strength of a human vertebral body. Decreasing either additive to 5 wt % generated compressive strengths after 24 h setting equal to polymethylmethacrylate, the cement used for the majority of vertebroplasty procedures. An initial early exotherm in the chloride cements was coupled with an X-ray diffraction (XRD) peak that indicated the early formation of the ettringite cement phase. In contrast, Fourier transform infrared (FTIR) spectroscopy and XRD data indicated that calcium nitrate may have stimulated early calcium silicate hydrate (C—S—H) production (the main strength producing phase of PC). Combining the two additives produced a synergistic effect with cements having increased injectabilities and compressive strengths compared with either addition used individually. This study has demonstrated that by modifying PC with nonproprietary chemicals it was possible to significantly increase cement injectability and reduce setting times whilst maintaining compressive strengths, making PC suitable for potential orthopedic applications. © 2012 Wiley Periodicals, Inc. J Biomed Mater Res Part B: Appl Biomater 100B: 2213–2221, 2012.

Key Words: Portland cement, orthopedic, injectability, compressive strength, setting times, surface charge, infrared spectroscopy, X-ray diffraction, calorimetry

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INTRODUCTION

Portland cement (PC) is known for its numerous applications in the construction industry.[1] However, as mineral trioxide aggregate (MTA), a PC-based root filling material, obtained FDA approval in the late 90s there has been an increased interest in the use of the cement for other *in vivo* applications.[2–4] For example, fibroblasts have been reported to demonstrate enhanced proliferation in the presence of PC[5] while PC-based materials placed *in vivo* have also been reported to promote calcification serving as a nidus for ossification.[6]

As PC possesses high compressive strengths and has demonstrated biocompatibility as an endodontic filling material when in contact with soft and hard tissue in the form of MTA, so its potential to stabilize vertebral compression fractures (VCFs) has been investigated as another potential application.[7] VCFs are caused by the collapse of a vertebra due to diseases such as osteoporosis or vertebral myelomas.[8–12] Vertebroplasty is the minimally invasive surgical procedure which stabilizes a fractured vertebral body by the injection of bone cement into the fracture.[13] At present, the cement used in the majority of these procedures is polymethylmethacrylate (PMMA).[14] PMMA has a compressive strength in the region of 79 MPa and a setting time of approximately 12 to 20 min, which permits complete immobilization of vertebrae while the patient is in the operating theatre and allows the patient to be discharged on the same day.[15] However, the use of PMMA is associated with several disadvantages including the highly exothermic polymerization of the methyl methacrylate monomer which may lead to localized tissue necrosis.[16] In contrast, PCs setting reaction is only weakly exothermic and has been shown not to increase localized tissue temperature during setting.[17] The toxic PMMA monomer has also been shown to diffuse from the site of application and has been linked to increased morbidity for patients through pulmonary embolism.[18] PCs allow the incorporation of radiopacifiers enabling monitoring of the cement during placement and postoperatively as is the case for PMMA.[19]

Calcium silicate-based PC is composed of at least two-thirds by mass of calcium silicates alite (Ca_3SiO_5) and belite (Ca_2SiO_4), the remainder consisting of aluminum- and iron-containing clinker phases.[20] Multiple reactions occur simultaneously during the cements hydraulic setting; the calcium

silicate groups hydrate to become the main strengthening phase of the cement calcium-silicate-hydrate (C—S—H), the aluminate phase reacts with calcium sulfate hydrate to form ettringite (an alumina, ferric oxide, tri-sulphate (Aft) phase) and the ferric phases react to form aluminoferrite-based phases.[21] This complex set of reactions contrasts with other ceramic cements such as calcium phosphates which set according to one major reaction.[22]

There are two key challenges that need to be overcome before PCs can be considered as suitable cements for vertebroplasty. First, the freshly mixed cement needs to be made injectable through the aperture of an orthopedic syringe with a diameter of approximately 2 mm. Second, the long setting time needs to be decreased to allow early stabilization of the vertebrae. Low cement injectabilities can be overcome by the addition of liquefiers to the cement powder. The setting time of PC is 3–4 h at a typical powder-to-liquid ratio (PLR) of 3 g mL^{-1}.[23] Setting times can be decreased by the addition of setting accelerators and there are many types available from building industry sources.[24–28] However, these additives were not developed for *in vivo* use and often contain biologically harmful chemicals such as formaldehyde.[29] The chloride and nitrate anions have both demonstrated PC setting acceleration to around 20 min which would be suitable during the vertebroplasty procedure.[30] Chloride and nitrate additions to MTA have also generated similar relatively low levels of inflammatory responses compared with MTA alone when used *in vivo*.[31] To date the effects of chloride and nitrate ions as liquefiers for PC cement systems has not been documented. The aim of this study was to investigate the suitability of chloride and nitrate anions in modifying the extrusion, setting times, and compressive strengths of PC.

EXPERIMENTAL
Materials
PC (Lafarge, UK) was prepared by sieving through a 250 μm steel mesh to minimize the presence of agglomerates in the powder. Calcium chloride and calcium nitrate (Sigma, UK) were added at either 5 or 10 wt % into the powder phase. Double distilled water was added to the cement at a PLR of 4.5 g mL^{-1} and samples were hand mixed for 1 min to produce cement slurries. This particular PLR was chosen as it combined high compressive strength of the set cement with good workability of the cement paste.

Injectability studies
Five grams of prepared PC slurry were transferred into a 5 mL disposable syringe and extruded through an outlet diameter of 2 mm (for each admixture at 5 or 10 wt % $n = 4$). A mechanical testing machine (Instron 1185, High Wycombe Bucks, UK) was used to apply a cross-head speed of 30 mm min^{-1} and a maximum force of 100 N to the syringe plunger. The force and crosshead speed were selected to mimic the maximum force and typical rate of extrusion used during manual injection. Any remaining cement within the syringe was weighed and the injectability (I) was calculated according to Eq. (1):

$$I(\text{wt \%}) = \frac{\text{mass of cement paste infected through syringe} \times 100}{\text{original mass of cement in syringe}} \quad (1)$$

Initial cement setting time, compressive strengths, and density measurements
The initial setting times of the cements were measured in a normal laboratory atmosphere (20–23°C and 50–60% humidity) using the Gilmore needles test with a needle of 113.9 g and 2.11 mm diameter according to the ASTM standard.[32]

For the compressive mechanical testing, the hand mixed slurries were placed into polytetrafluoroethylene molds producing cylindrical samples of 12 mm height and 6 mm diameter. After 24 h and 30-days immersion in water at 37°C the wet compressive strength of the cement samples ($n \geq 30$) was measured using a universal testing machine (Instron 5544, High Wycombe Bucks, UK) at a crosshead speed of 1 mm min^{-1}. The strut densities of the dried set cement sample fragments were determined using helium pcynometry (10 runs; Accupyc 1330, Micromeritics, UK). The relative porosity (RP) of each cement variation was obtained from calculations using the dry density (mass / volume) and measured strut densities according to the formula: RP = 1– (dry density/ strut density).

### Surface charge investigations by zeta potential measurements
The effective surface charge of PC with various additives was measured using a Zeta-Sizer 3000 (Malvern Instruments, UK). Suspensions of 0.1 g L^{-1} solid to liquid ratio of PC were hydrated just prior to the zeta potential measurements. Calcium chloride and nitrate were added at 0.2 g L^{-1} resulting in an excess of chloride and nitrate anions to bind with the PC particles. The Zeta-Sizer calculated zeta potential by determining electrophoretic mobility using Henry's equation. For each suspension, the average zeta potential value was obtained from five measurements.

Cement enthalpy changes investigations by differential scanning calorimetry
After sample preparation between 80–120 mg of material was transferred to an aluminum crucible before being inserted into the sample compartment of a differential scanning calorimeter (DSC 7, Perkin-Elmer,UK). The enthalpy change of the cement was then recorded for the next 2 h and calculated by integrating the DSC-curves from the heat capacity base line using the Pyris$^{\text{TM}}$ DSC software ($n = 3$ for each variation).

Infrared spectroscopy (IR) via attenuated total reflectance
After the PC samples were prepared 1 g of was placed on the diamond window of an attenuated total reflectance FTIR (Nicolet 6700, Thermo scientific) at 23°C and covered with a glass slide with spectra recorded at 0 and 120 min. At each time point the samples were scanned 32 times with a resolution of 2.0 cm^{-1}. The calcium hydroxide peaks were assigned according to established reference spectra.[33,34]
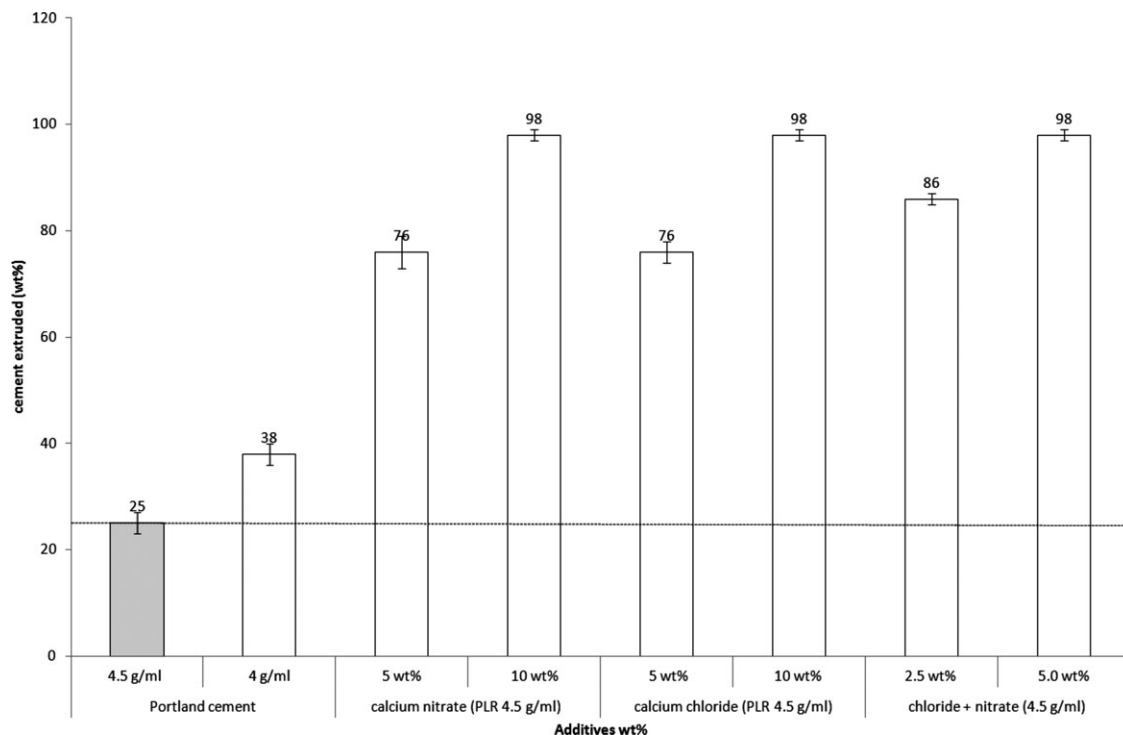
FIGURE 1. Graph demonstrating the significant increase in cement extrusion (injectability) when calcium chloride, calcium nitrate or a combination of the two was added to PC. There was a significant increase in extrusion with a 5 wt % addition of any additive to PC, there was also a significant increase in injectability when the additions were increased to 10 wt %.

Phase analysis using X-ray diffraction (XRD)

Data sets were collected from $2\theta = 5–30°$ with a step size of 0.02 and the count time was normalized to 1 s/step. The phase compositions of the cements were determined according to the inorganic crystal structure database, calcium hydroxide (PDF Ref. 04-010-3117), calcium silicate $18°\theta$ (PDF Ref. 04-011-1393), calcium sulfate anhydrous $25°\theta$ (PDF Ref. 00-037-1496), and ettringite 9 and $16°\theta$ (PDF 00-041-1451). The calcium silicate hydrate standard was described by Chang et al.[35]

Statistical analysis

Data was analyzed for statistical significance using 1-way Analysis of Variance (ANOVA) at a significance of $p < 0.001$ using SPSS statistics v19, IBM, UK).

RESULTS

Injectability studies

Both calcium chloride and calcium nitrate acted as liquefying agents for PC. A 5 wt % addition of either salt or an equal 2.5 wt % combination of the two significantly increased cement extrusion compared with the PC standard ($p < 0.001$) (Figure 1). There was a further significant increase in extrusion when the total additive wt % was increased to 10 wt % ($p < 0.001$). Combining the additives also had a positive effect on the injectability of the cement increasing extrusion by 10 wt %. The apparent limit on injectability was 98 wt % extrusion with 2 wt % of the cement remaining in the tip of the syringe.

For cements containing calcium chloride and/or calcium nitrate either individually or in combination addition of the liquefiers only a relatively low initial force of between 3 to 30 N was required to extrude the majority of the cement from the 2 mm syringe aperture. An increase in force was required only when the syringe was nearly empty (Figure 2). In contrast, PC without a liquefier demonstrated
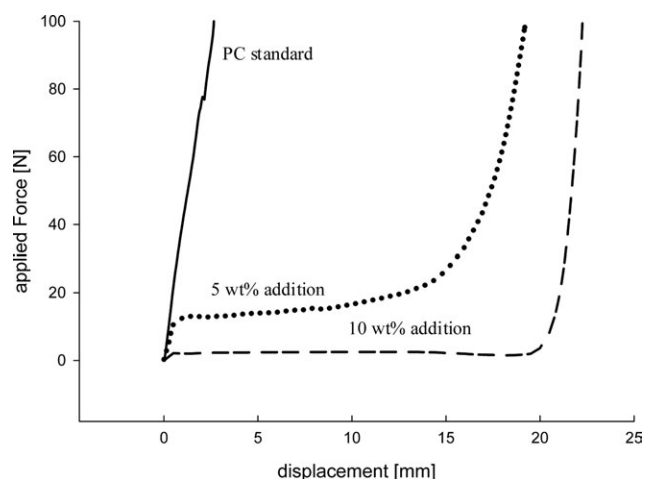
FIGURE 2. A typical force/displacement graph recorded during the injectability experiments. Adding 5 wt % of calcium chloride, calcium nitrate or a 2.5 wt % combination of the two reduced the force required to displace the syringe plunger during cement injection. Increasing the additive content to 10 wt % further reduced the force to a point where less than 5 N was required to extrude over 90 wt % of the cement.
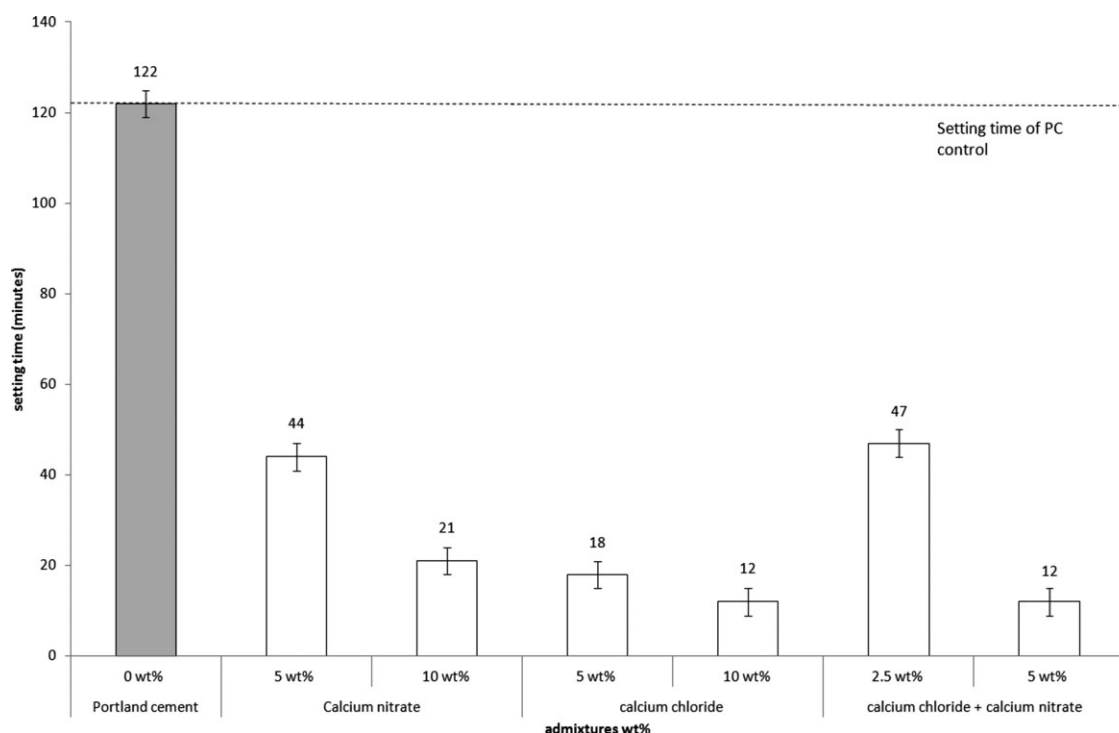
FIGURE 3. Graph showing the influence of different admixtures on the setting time compared with PC. The addition of 5 wt % calcium chloride, calcium nitrate or a combination of the two significantly decreased cement setting times compared with the PC standard. There was also a decrease in setting times when increasing additive addition to 10 wt %

no characteristic force plateau but exhibited a sharp increase in force necessary for displacement as the cement failed to be extruded from the syringe.

Initial cement setting time, compressive strength, and density measurements

The two additives both acted as setting accelerants when added individually or in combination. The addition of calcium chloride or calcium nitrate significantly decreased setting times from over 2 h to below 60 min with 5 wt % additions and to below 22 minutes for the 10 wt % additions ($p < 0.001$) (Figure 3).

After 24 h setting cements containing 5 wt % additions of calcium chloride, calcium nitrate or 2.5 wt % combination of the two produced compressive strengths which were comparable or higher than the PC standard. In contrast, cements containing 10 wt % additions had significantly lower compressive strengths ($p < 0.001$). After 30 days cements 5 wt % additions all possessed significantly higher compressive strengths than the standard cements ($p < 0.001$). The compressive strengths of the 10 wt % additions of calcium chloride and nitrate were still lower than the standard cements but the 5 wt % combination of the two produced comparable values with the standard.

After both 1 and 30-days the relative porosities of the cements containing 5 wt % calcium chloride or nitrate or a 2.5 wt % combination of the two all possessed lower relative porosities than the PC standard. In contrast, after 24 h cements containing a total of 10 wt % additive addition all had lower porosities, but after 30-days the porosities were

comparable with the standard cement. The specific density of the cement in the presence of chloride and nitrate was consistently lower than the standard regardless of the wt % used. As the specific density of cement decreases with adsorption of water this indicated that in the presence of chloride and nitrates the cements were more hydrated (Table 1).

Surface charge investigations by zeta potential measurements

The surface charge of the standard cement particles was approximately −12 mV. Calcium nitrate and calcium chloride addition reduced the negative charge of the cement resulting in charge neutralization of the cements (Figure 4).

Cement enthalpy changes investigations by DSC

An addition of 5 wt % calcium chloride to PC produced a similar overall exotherm with the standard cement, 25 and 29 J g^{-1} cement, respectively. The profile of the chloride cements heat signature indicated that the exotherm was predominantly generated within the first 10 min of setting, which coincided with the setting time of the cement as determined via the Gilmore needles test. On closer inspection the peak appeared to be composed of three distinct shoulders. The PC standard and cements containing 5 wt % calcium nitrate both possessed similar heat signatures where the exotherm was released in a single asymmetric peak over 2 h. However, addition of calcium nitrate produced a significantly higher exotherm, 50 J g^{-1} cement,

TABLE I. Compressive Strength, Relative Porosities, and Specific Densities for Cements Containing Additions of Either Calcium Chloride, Calcium Nitrate, or a Combination of the Two

Admixture	wt % of admixture added	Compressive strength/MPa (1-day)	Compressive strength/MPa (30-day)	Relative porosities % (1-day)	Relative porosities % (30-day)	Specific densities g/cm^3 (1-day)	Specific densities g/cm^3 (30-day)
PC standard		56 ± 4	73 ± 7	23 ± 1	20 ± 1	2.55 ± 0.05	2.44 ± 0.05
Calcium chloride	5	57 ± 7	88 ± 8	19 ± 1	15 ± 1	2.45 ± 0.05	2.38 ± 0.05
	10	43 ± 6	63 ± 7	25 ± 1	19 ± 1	2.43 ± 0.05	2.32 ± 0.05
Calcium nitrate	5	66 ± 7	89 ± 8	18 ± 1	13 ± 1	2.47 ± 0.05	2.37 ± 0.05
	10	45 ± 6	62 ± 6	26 ± 1	22 ± 6	2.43 ± 0.05	2.33 ± 0.05
Calcium chloride/nitrate combination	2.5	67 ± 7	99 ± 6	17 ± 1	13 ± 1	2.47 ± 0.05	2.36 ± 0.05
	5	44 ± 7	73 ± 7	27 ± 1	19 ± 1	2.43 ± 0.05	2.32 ± 0.05

After both 1 and 30-days setting, cements containing 5 wt % calcium nitrate or 2.5 wt % combinations of calcium chloride and calcium nitrate possessed significantly higher compressive strengths than the PC standard. In contrast, cements containing a total additive addition of 10 wt % possessed significantly lower compressive strengths than the PC standard. The relative porosities of the cements containing 5 wt % additions were lower than the PC standard, whereas the cements containing 10 wt % additions were consistently higher. Adding 5 or 10 wt % of any additive reduced the specific densities of the set cements. Standard deviation (compressive strength) and minimum error of method (specific density, porosity) are given as error.

compared with the PC standard of 23 J g^{-1} cement ($p <$ 0.001) (Figure 5)

FTIR analysis

The absorbance peak at 3640 cm^{-1} appears to correspond with calcium hydroxide the major by-product of the hydration phase C—S—H. Therefore, this peak may indicate the early presence of this essential setting phase in the cements containing calcium nitrate (Figure 6).

Phase analysis using XRD

After 2 h setting cements containing 5 wt % calcium chloride possessed peaks at 9° and 16°θ corresponding with the set cement phase ettringite. Whereas, cements containing 5 wt % calcium nitrate had a small peak at 18°θ corresponding with calcium hydroxide. The only noticeable PC standard peak was at 25°θ corresponding with anhydrous calcium sulfate. After 24 h all of the cements contained ettringite and calcium hydroxide peak in addition to a small peak at 29°θ corresponding with C—S—H formation. After 30-days of setting the calcium hydroxide peak in all the cements
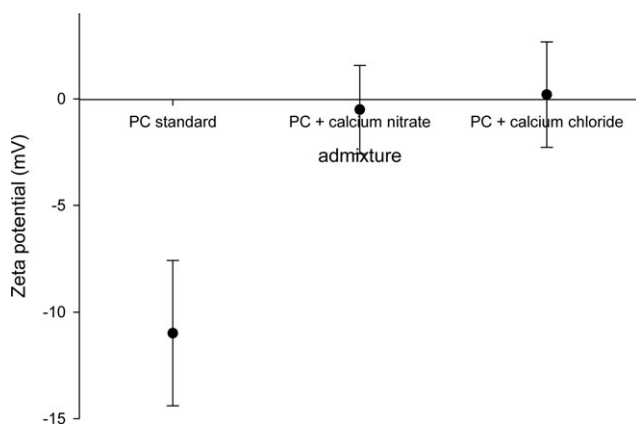
FIGURE 4. Zeta potential measurements of hydrating PC in the presence of calcium chloride and calcium nitrate. Inclusion of the additives to PC caused an inflection in the surface charge of the hydrating cement.
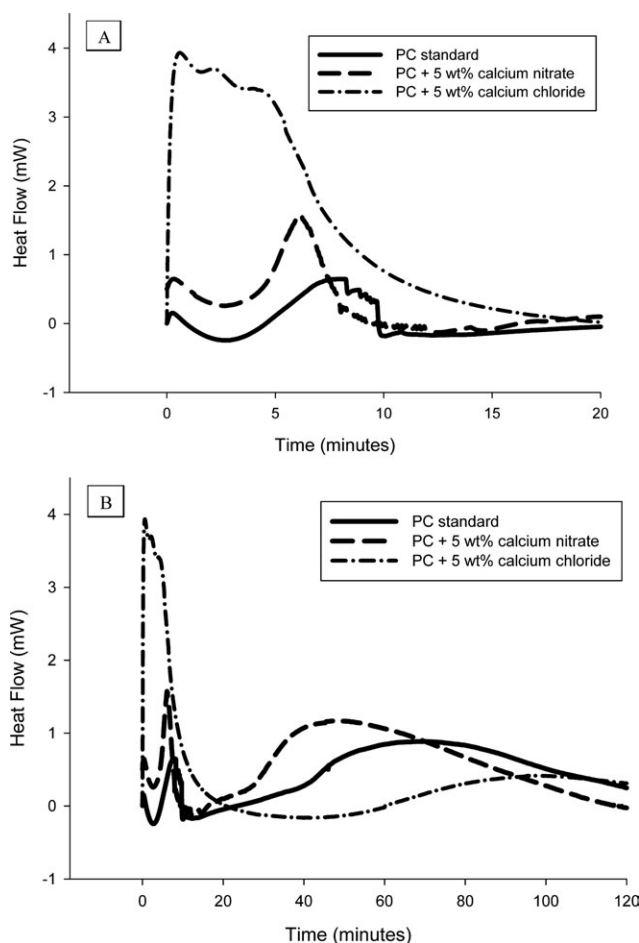
FIGURE 5. (a) Graphs illustrating the isothermal calorimetry traces of PC standard and cements containing either 5 wt % calcium nitrate or 5 wt % calcium chloride during the first 120 minutes of cement setting. The addition of calcium chloride produced a similar overall energy release with the standard cement except that the majority of energy with the chlorides was released early during the setting reaction. In contrast, cements containing nitrate had a similar trace profile with the standard cements but released significantly more energy. (b) When the chloride exotherm was investigated more closely the trace appeared to comprise three distinct exotherms which all occurred within the first 10 minutes of the start of the setting reaction.
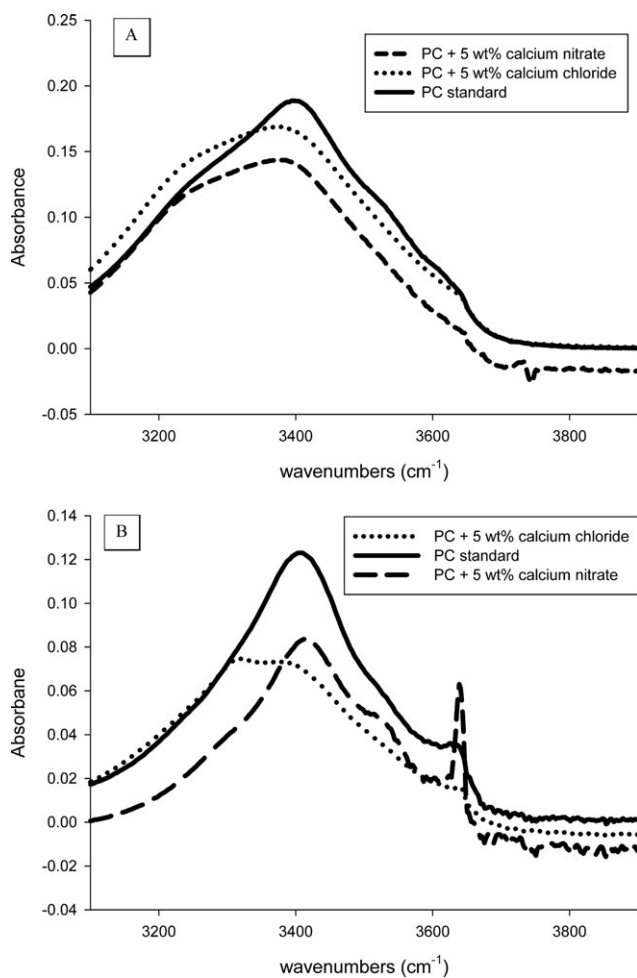
FIGURE 6. (a) FTIR of PC standard and cements containing either 5 wt % calcium chloride or calcium nitrate 2 minutes after cement mixing. 6 (b) After 120 min the calcium nitrate cements had developed a peak at 3640 cm^{-1} indicating the presence of calcium hydroxide.

appeared significantly higher than the 1-day set cements (Figure 7).

DISCUSSION

Injectability studies

Each hydrated phase of PC carries a different surface charge with Portlandite and Friedel salts being positive whereas ettringite and monosulfate possess negative surface charges.[36] The final charge is a combination of all of the various cement phases. However, the overall slight negative surface charge can be explained by ionization of the silanol groups of C—S—H, the major hydration product of PC [Eq. (2)].[36-39]

$$> SiOH \rightarrow SiO^- + H^+ \tag{2}$$

The -12 mV value observed for the PC standard was close to the theoretical surface charge range for C—S—H (-9.2 to -12.7 mV) in a low calcium environment.[38,39] This may have been an indication that the surface charge of the hydrating PC was also determined by the calcium silicate phase. Cement agglomerates which reduce cement flowability and possibly injectablity of cement pastes are caused by attraction of oppo-

sitely charged surface particles.[40] Typically, commercial liquefiers are large negatively charged polyvalent compounds which function by binding to the surface of PC creating an electrostatic repulsion force between the cement particles which disperses the aggregates, leading to the liquefying effect.[41-43] In contrast, chloride in the presence of Ca^{2+}, appeared to neutralize the cement surface through a series of reactions. First, neutralization occurs through the adsorption of Ca^{2+} onto dissociated silanol groups [Eq. (3) and (4)].[35,36]

$$> SiOH + Ca^2 \rightarrow SiOCa^+ + H^+ \tag{3}$$

$$> SiOH + Ca^{2+} + Cl^- \rightarrow SiOCaCl + H^+ \tag{4}$$
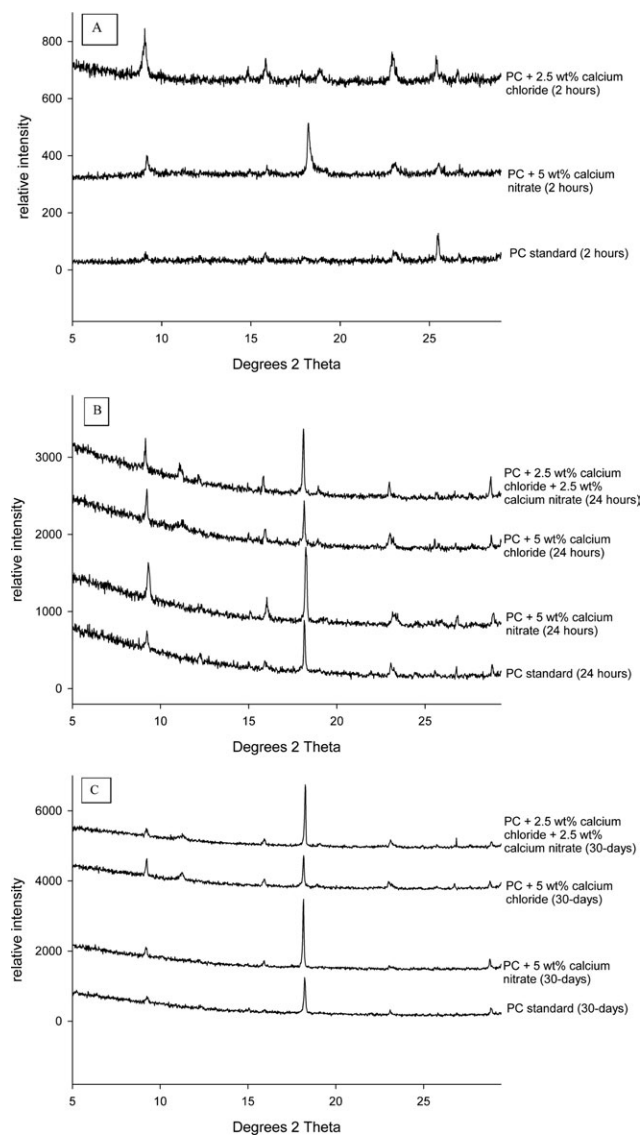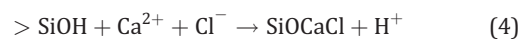
FIGURE 7. X-ray diffraction patterns of set cements after 2 h (a), 24 h (b) and 30-days (c). After 2 h calcium chloride developed peaks at 9° and 16°θ corresponding with the set cement phase ettringite. Cements containing calcium nitrate possessed a calcium hydroxide peak at 18°θ. In contrast, after 2 h the only discernable peak for the PC standard was calcium sulfate dihydrate at 25°θ. After 24 h all of the cements had developed ettringite peaks in addition to those corresponding with C-S-H formation at 29°θ. After 30-days setting the peaks corresponding with calcium hydroxide were significantly higher.

Second, chloride has also been shown to neutralize positively charged Portlandite [Eq. (5)].[36]

$$[CaOH]^+ + Cl^- \rightarrow CaOHCl \qquad (5)$$

Last, both chloride and nitrate neutralize the forming Friedel salts of the hydrating aluminate phase [Eq. (6) and (7)].[36,44]

$$[Ca_2Al(OH)_6]^+ + CaCl_2 + 2H_2O \rightarrow [Ca_2Al(OH)_6]Cl.2H_2O + Ca^{2+} \qquad (6)$$

$$2[Ca_2Al(OH)_6]^+ + 2Ca(NO_3)_2 + 6H_2O$$
$$\rightarrow [Ca_2Al(OH)_6](NO_3)_2.6H_2O + Ca^{2+} \qquad (7)$$
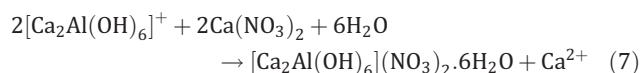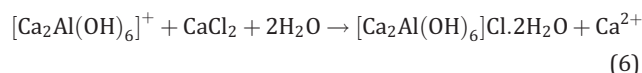
This leads to a neutralization of the cement particles that may reduce agglomeration as there are less oppositely charged particles.[36] Therefore, the liquefying effect of chloride and nitrate may be based on charge neutralization as opposed to other liquefiers which function through charge and steric repulsion of cement particles.[45]

Acceleration of the setting reaction

Previous calorimetry studies have indicated that the accelerating effect of calcium chloride on PC setting may be due to an increased early rate of heat evolution in the presence of the additive.[46] The heat signature obtained during this study indicated that the accelerating effect of chloride may be due to early energy generation that was not present in the PC standard. This initial exotherm appeared to be composed of three distinct sections which may have corresponded with three unique reactions, or, a single reaction with multiple exotherm stages. The early presence of the set cement phase ettringite within the first 2 h of cement setting indicated that at least a portion of this initial exotherm in cements with the chloride additive was due to early ettringite formation. It has been inferred from previous infrared spectroscopy studies that calcium chloride modified PCs also demonstrated increased silicate polymerization to produce a more structured C—S—H bond formation compared with standard PCs leading to the increased cement strength in the presence of the additive.[47] The presence of a peak corresponding with C—S—H in the XRD phase analysis studies indicated that C—S—H was present within the first 24 h of setting. However, as the peak was not present after the first 2 h of setting the primary mode of acceleration by calcium chloride appeared to be ettringite formation which is a known cause for early cement strength.[48] In civil engineering, early formation of ettringite is minimized in order to avoid the ettringite reacting under sulfate attack leading to expansion and subsequent crumbling of the cement.[49] However, for an orthopedic application sulfate attack is not an issue.

The rate of the setting reaction for cements containing calcium nitrate has previously been linked to the belite (C_2S) content in the clinker phase.[24] Belite dissolves slowly to form short C—S—H fibers which provide long term strength for the cement and the short C—S—H bonds possibly contributed to the high cement strengths for the 5 wt %

nitrate modified cements.[50] The early presence of calcium hydroxide was observed in both the XRD and FTIR studies as a by-product of C—S—H formation, possibly indicating calcium silicate dissolution that led to early C—S—H development.[22,33] Even though the heat signatures of the PC standard and cements containing 5 wt % calcium nitrate were similar, the exotherms for nitrate containing cements were significantly higher ($p < 0.001$). This may have indicated an increased rate of reaction of PC in the presence of 5 wt % calcium nitrate. After 24 h, both the PC standard and calcium nitrate possessed crystalline peaks corresponding with C—S—H.

Decreased cement strength with increasing addition of supplements correlated with increased cement porosities. Increased porosity may have been an indication of a higher proportion of nitrate and chloride being washed out from the pores of the forming cements as additive addition increased.[19] As water became adsorbed into the structure of cement the specific density of the material decreased.[51] Therefore, the decreased strut densities of PC in the presence of chloride and nitrate compared with standard PC indicated the additives may have been accelerating the cement hydration reaction.

When combining additives a synergistic effect could be achieved with cements being more injectable and possessing higher compressive strengths. Increased injectability may be due to a degree of complementary surface binding of the two additives leading to a greater degree of surface charge neutralization. The increased compressive strength may have been as a result of chloride stimulating ettringite formation, whereas nitrate enhances C—S—H production.

PMMA is the bone cement used in the majority of vertebroplasty operations.[52] However, the material possesses several major disadvantages, it cures at temperatures up to 90°C,[53] the methylacrylate monomer is toxic and has been shown to damage osteocytes[54] and leakage of the monomer has also been linked to pulmonary embolism.[18] Viable alternatives are actively being researched and several calcium phosphate cements have been approved for clinical use.[55] For PC ceramic materials this is first study to fully address all the issues associated with using the material for vertebroplasty, i.e., poor injectability and long setting time. With addition of simple organic chemicals the material is now injectable, has setting times and compressive strengths equivalent to PMMA. The material also demonstrates clinical equivalence as it is the major constituent of MTA, a material used for dental applications.[3] After clinical trials it may therefore be a viable alternative cement for use in the vertebroplasty procedure.

CONCLUSIONS

Calcium chloride and calcium nitrate both acted as liquefying agents and setting accelerants producing cements which had compressive strengths equal to or greater than the PC standard. Calcium chloride appeared to accelerate the setting reaction through an early exotherm which was responsible for early ettringite formation. In contrast, calcium nitrate stimulated early C—S—H formation. Combining the

additives had a synergistic effect increasing injectabilities while also improving compressive strengths.

ACKNOWLEDGMENTS

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