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Applications of conduction calorimetry to the setting reaction of zinc phosphate dental cement

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Abstract

The kinetics of the exothermic setting reaction of zinc phosphate dental cement can be successfully investigated by conduction calorimetry. The primary objective of this study is to examine the effects arising from the addition of various additives to the liquid and calcination of cement powder. The rate of heat evolution versus time shows the occurrence of merely one maximum. In the case of unmodified orthophosphoric acid a sharp peak occurs early after onset of mixing due to the formation of crystalline α-hopeite. Commercial cement liquids contain aluminum and zinc. From the calorimetric curves it has been found that these cations act as a setting retarders, and ensure sufficient working time in the surgery in this way. The peak of heat evolution broadens and shifts due to the formation of an amorphous reaction product. When the ingredients of the cement powder are calcined at sufficient temperature the reactivity is further reduced. The setting time proves to be sensitive to changes in specific surface area of cement powder. The observed effects are discussed in terms of chemical reactions taking place during setting. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Conduction calorimetry; Dental cements; Luting cements; Zinc phosphate cement; Hopeite

1. Introduction

Some of the most important materials used in dentistry are dental cements. They are available for the cementation of prefabricated crowns and bridges, for the protection of dental pulp against chemical attack and thermal stresses, and for filling of cavities [1].

Zinc phosphate cements (ZPC) are the strongest among the dental cements. They are principally used as a luting cement for the cementation of inlays and other restorations fabricated outside of the mouth due to easy handling characteristics and adequate retentive properties. The setting and hardening of these cements takes place within 3–5 min after onset of mixing. Although the acid–base type reaction between zinc oxide and orthophosphoric acid is exothermic and rapid, so far no efforts were taken to study the setting reaction of ZPC by the methods of thermal analysis.

In the building industry conduction calorimetry is a well established method for examining the hydration behavior of different types of cement and phenomena such as early stiffening and setting [2]. The influence of accelerating and retarding admixtures on hydration is also clearly indicated by this technique [3,4].

In this paper the application of conduction calorimetry to the setting reaction of ZPC is presented.

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2. Experimental

2.1. Materials

Six commercially available brands of ZPC, designated as C1–C5b, were used for this study. Cement C5 was supplied as normal and fast setting cement, denoted as C5a and C5b, respectively. In addition, two kinds of test cements, C6 and C7, were prepared with the aim of investigating the effects of different additives to the liquid and calcination of the powder.

2.1.1. Powder composition

Chemical compositions of the powders were quantitatively analyzed by WDXRF (Philips PW1404). Chemical analyses of commercial cement powders are given in Table 1. X-ray diffraction spectra were performed using a Bragg–Brentano powder diffractometer (Seiffert XRD 3000 TT). Cement C6 was prepared from plain ZnO (ACS grade, Fluka). MgO (ACS grade, Riedel-De Haen AG) and ZnO, the ingredients of cement C7 were calcined in air at 1473 K for 5 h and subsequently ground and sifted to a fine powder.

The grain size distributions of all cement clinkers were measured using a particle size analyzer (Galai CIS1). BET specific surface area measurements have been performed by gas adsorption using an ASAP 2010 Micromeritics instrument. Surface areas below 1 m^2/g were investigated by krypton adsorption–desorption isotherms at 77 K. Nitrogen was used as analysis adsorptive for pure ZnO and MgO. Mean grain sizes and BET specific surface areas are also given in Table 1.

Table 2
Chemical compositions of commercial cement liquids

Composition (wt%)	C1	C2	C3	C4	C5a	C5b
H_3PO_4	60.00	55.00	50.00	45.00	50.00	50.00
H_2O^a	34.74	38.92	40.96	45.20	44.37	45.25
Al	2.24	2.47	3.61	3.59	2.56	2.49
Zn	3.02	3.61	5.43	6.21	3.07	2.26

[a] Calculated to 100.

2.1.2. Liquid composition

The chemical composition of the liquids supplied for use with the commercial powders are given in Table 2. The principal component is H_3PO_4. Al and Zn are added as modifiers. The acid concentration was given by the manufacturers. The amounts of Al and Zn were determined by FAAS (SpectrAA-300, Varian). The liquids for use with cements C6 and C7 were prepared from 85 wt% H_3PO_4 (ACS grade, Fluka) by dilution using deionized water. The buffered solutions containing 3 wt% Al and 3 wt% Zn were made by thoroughly dissolving Al (ACS grade, Fluka) and ZnO in different concentrated acid solutions. The chemical

Table 1
Chemical compositions (powders, wt%), specific surface areas (ssa, m^2/g) and mean grain sizes (mgs, μm) of commercial and test cements

Composition (wt%)	C1	C2	C3	C4	C5a	C5b	C6	C7
ZnO	83.26	88.23	82.35	79.02	80.62	87.74	100.00	90.00
MgO	11.32	10.65	11.43	–	11.53	9.64	–	10.00
SiO_2	2.24	0.10	2.13	11.36	2.74	1.82	–	–
Al_2O_3	1.41	–	1.12	8.89	0.76	0.44	–	–
CaF_2	1.53	0.07	1.39	0.06	4.03	–	–	–
CuO	0.03	0.03	1.13	–	–	–	–	–
P_2O_5	0.13	0.85	–	–	–	–	–	–
K_2O	–	–	–	0.38	0.29	0.13	–	–
CaO	–	0.07	0.39	–	–	0.19	–	–
Fe_2O_3	0.07	–	–	0.15	0.03	0.01	–	–
Na_2O	0.01	–	0.06	0.14	–	0.03	–	–
ssa (m^2/g)	0.72	0.99	0.32	0.57	0.43	0.80	4.19	0.85
mgs (μm)	2.19	2.80	4.46	3.51	4.48	3.06	3.42	4.25

Table 3
Chemical compositions and designation of test liquids

Additive (wt%)		3 Al	3 Al/3 Zn
30 H_3PO_4	L31	L32	L33
40 H_3PO_4	L41	L42	L43
50 H_3PO_4	L51	L52	L53
60 H_3PO_4	L61	L62	L63
70 H_3PO_4	L71	L72	L73

compositions of these liquids and their designation are listed in Table 3.

2.1.3. Cement preparation

Powder and liquid of the commercial cements were dosed according to the manufacturers instructions. In each of the experiments including cements C6 and C7, 1 ml of the liquid was added to 2 g of the cement clinker, so that the powder to liquid ratio was 2.0 g/ml. The reaction products in all set cements were identified by powder X-ray diffraction and FT–IR (Perkin-Elmer 1760).

2.2. Conduction calorimetry

The heat evolution occurring on cement setting was followed by conduction calorimetry (Tonical 7335, Toni Technik Building Materials Testing Systems GmbH). The instrument employed in this study enables the detection of 0.5 μW effects. For all samples the heat evolution was followed for 2 h at 298 K. Two additional long term studies (298 K/72 h) were performed to ensure that all the thermal events had been observed. All results were processed by an on-line computer.

3. Experimental results and observations

3.1. Commercial cements

One general conclusion to be drawn from XRD data is that the main constituents of the cement powder are present as simple oxides. The principal component is ZnO (Table 1). MgO and minor ingredients as Al_2O_3 affect the working characteristics and final properties, e.g. dimensional stability after setting, compressive and tensile strength, and rheological behavior of the mixed cement [5–7]. Additional components act as inactive filler (SiO_2), and ensure the release of fluoride into dental enamel and dentine (CaF_2). The fluoride containing cements may be particularly suitable for the cementation of orthodontic bands. Fluoride release continues over a long period [8], and fluoride uptake results in reduced enamel solubility and increased hardness [9]. Dental enamel which has acquired fluoride from ZPC is apparently more resistant to caries attack [10]. Further, the biocompatibility of ZPC can be improved by the addition of CuO which shows germicidal properties [10–12]. Thus, the addition of CaF_2 and CuO to ZPC prevents secondary caries and periodontal inflammation to some extent [13,14].

In common for all commercial cements there is a considerable evolution of heat due to cement forming reaction when the cement powder is mixed with the liquid. Additional contributory factors to this exothermic reaction include heats of wetting. Measured curves for the commercial cements are given in Figs. 1 and 2. In Fig. 1(a) and Fig. 2(a) the rate of heat evolution is shown up to 20 min for clarity. In contrast to the well-known calorimetric curves of building cements the rate of heat evolution versus time plot shows merely one maximum, occurring within 3–5 min after mixing. Even after 72 h no further maxima were detectable. After this peak, there is a steady diminution in the evolution of heat, which soon reaches a steady, but low value. In X-ray diffraction spectra the reaction products after 2 h appear to be amorphous. Peaks of residual zinc oxide can be clearly detected. The FT–IR spectra of set cements show a broad featureless band in the phosphate region. Times required for reaching the maxima of heat evolution approximately represent setting times given by the manufacturers for the powder to liquid ratio used in this study.

3.2. Test cements

When the powder of cement C6 reacts with unbuffered liquids L31–L71 a sharp peak occurs at 1.3–1.6 min after mixing, indicating a violent reaction (Fig. 3). Thus, the integral heat after 2 h increases significantly when compared to commercial cements. From X-ray diffraction and FT–IR analyses it becomes evident that a solid, crystalline substance is rapidly formed.

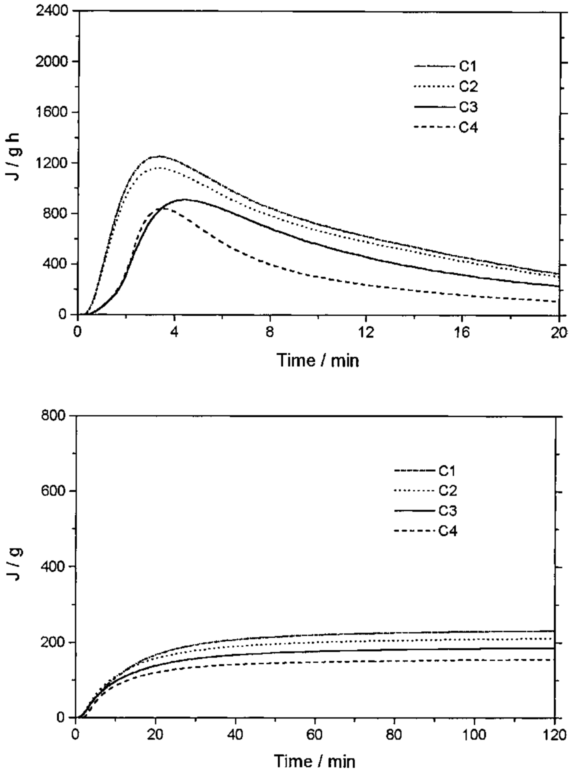

Fig. 1. (a) Rate of heat evolution and (b) integral heat evolution for commercial cements C1–C4.

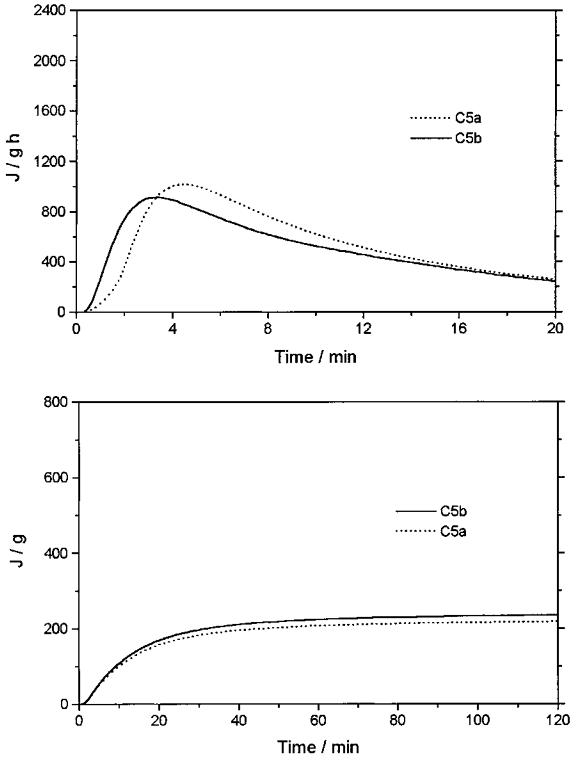

Fig. 2. (a) Rate of heat evolution and (b) integral heat evolution for commercial cements C5a and C5b.

When the powder of cement C6 reacts with liquids L32–L72, modified by the addition of 3 wt% aluminum, reaction products in the cement are amorphous as revealed by X-ray diffraction. In comparison to the commercial cements the FT–IR spectra show the same broad featureless band in the phosphate region. In the case of addition of 3 wt% aluminum to the liquid, the peak, occurring after 1.8–1.9 min, broadens, accompanied by loss of intensity (Fig. 4(a)). The integral heat is effectively reduced (Fig. 4(b)). These effects are continued by further addition of 3 wt% zinc to the solution (L33–L73). For these cements the maximum shifts to 1.9–2.2 min after start of mixing. The continued reduction of both, peak intensity and integral heat, can be clearly recognized (Fig. 5). At least, addition of magnesium oxide and calcination of the cement powder undoubtedly are factors in control of the setting time. When liquids L31–L71 react with the powder of cement C7 the peak occurs within 1.8–2.2 min from the onset of mixing (Fig. 6). For liquids L32–L72 and L33–L73 maxima of heat evolution shift to 2.3–2.8 and 3.1–3.7 min, respectively (Figs. 7 and 8). In the latter case the heat evolved after 2 h is reduced by about 50% compared to the reaction between cement C6 and unmodified orthophosphoric acid. Amorphous products were also formed in set cements of this type. Further the shape of conduction calorimetric curves becomes indistinguishable from the shape of curves obtained from commercial cements. After 2 h X-ray diffraction spectra of all set cements showed the peaks of residual zinc oxide.

4. Discussion

Provided a commercial ZPC is offered for luting and cementation applications, the ISO 9917 specification demands that the setting time for ZPC is in the range of 2.5–6 min [15]. Therefore, the chief problem

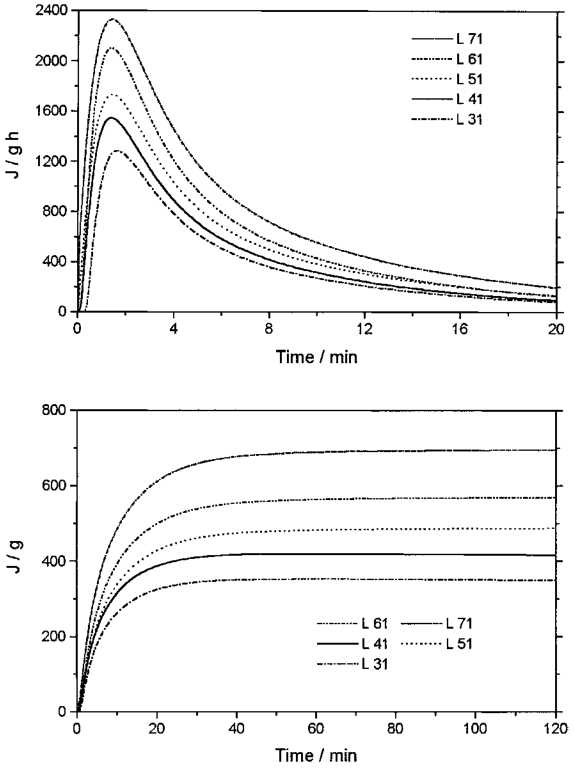

Fig. 3. (a) Rate of heat evolution and (b) integral heat evolution for test cement C6 mixed with liquids L31–L71.

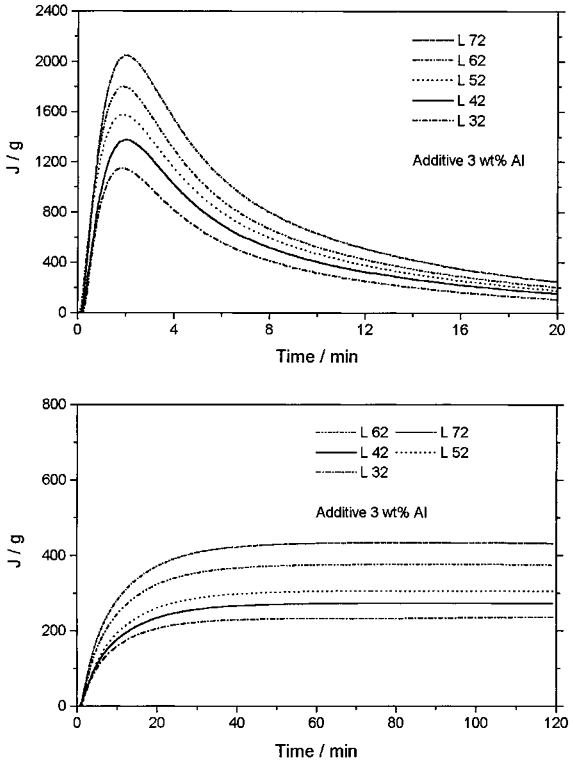

Fig. 4. (a) Rate of heat evolution and (b) integral heat evolution for test cement C6 mixed with liquids L32–L72.

is to moderate the cement-forming reaction. If the reaction is over-vigorous, e.g. in the case of the reaction between pure zinc oxide and unmodified orthophosphoric acid, then a crystalline mass rather than a cement is formed. Hence, the cement powder of ZPC has to be deactivated and densified by sintering. The specific surface areas of pure zinc oxide and magnesium oxide used in this study are 4.19 and 14.30 m^2/g, respectively. After sintering the specific surface area of test cement C7 is reduced to 0.85 m^2/g. A sound understanding of the reactions taking place during roasting of the cement powder is essential.

The ingredients of commercial cement powders are heated together at temperatures ranging from 1273 to 1623 K for approximately 4–8 h, depending on the temperature [16]. The sintering of a non-stoichiometric solid, such as zinc oxide, is affected by its initial physical condition and the surrounding atmosphere. Freshly prepared zinc oxide has a high surface energy because of its preparation in an oxygen-rich atmosphere [17]. Heating of zinc oxide results in the loss of oxygen which creates anion vacancies (V). The structure of such zinc oxides may be represented as $Zn^{2+}e^{-}_{2x}V_xO^{2-}_{1-x}$. The sintering effect was attributed to the diffusion of Zn^{2+} ions consequent on the difference in concentration of excess Zn^{2+} ions between the surface and the bulk [18]. The presence of water can further enhance sintering of zinc oxide particles [17], a procedure that is used in the current state-of-the-art roasting process [19]. Recently it has been shown that the specific surface area of MgO is sufficiently reduced when the calcination temperature is around 1250 K [20]. The calcination temperature of silicon dioxide and aluminum oxide must be greater than or equal to 1073 K to cause a significant decrease of the specific surface area under an oxygen-rich atmosphere [21]. These additional oxides which are added to the zinc oxide prior to ignition improve the sintering process and cements prepared from the mixed oxides are stronger [22]. As a result, the sintering temperature

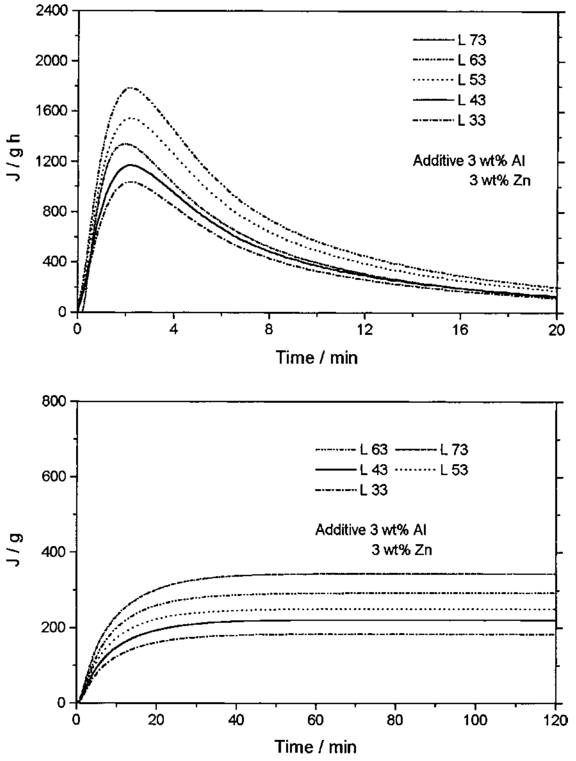

Fig. 5. (a) Rate of heat evolution and (b) integral heat evolution for test cement C6 mixed with liquids L33–L73.

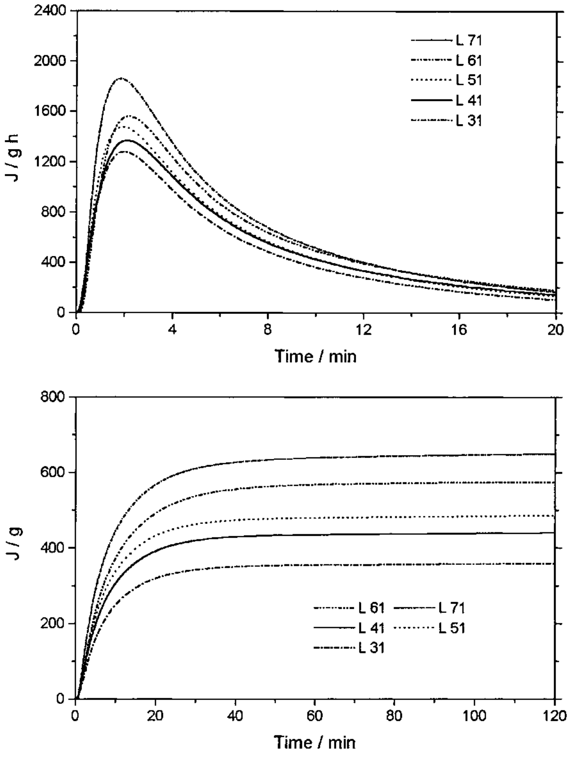

Fig. 6. (a) Rate of heat evolution and (b) integral heat evolution for test cement C7 mixed with liquids L31–L71.

for commercial cement powder can be reduced from 1623 to 1273–1473 K.

The reactivity of a cement is indicated by its calorimetric curve which has three characteristic features. The occurrence of peak after onset of mixing, the maximum heat evolution, and the integrated heat evolution after a given time. For the commercial cements these parameters are given in Table 4. The specific surface area is a factor responsible for faster or slower setting. Plotting of specific surface area versus peak time yields a linear correlation (R=−0.95(9)) with a negative slope (Fig. 9). Thus, the lower the surface area the later the peak occurs after onset of mixing, indicating a prolonged setting time. When the integrated heat evolution after 2 h is plotted versus a parameter of potential reactivity X_{PL}, an approxi-

Table 4

Occurrence of peak after onset of mixing (P_t, (min)), maxima of heat evolution ($H_{\max}$, (J/gh)), integrated heat evolution after 2 h (I_{2h}, (J/g)), specific surface area (ssa, (m^2/g)), and reactivity factor X_{PL} for commercial cements

Cement	C1	C2	C3	C4	C5a	C5b
P_t	3.40	2.98	4.30	3.47	4.25	3.37
$H_{\max}$	1253	1164	912	841	1017	915
I_{2h}	230	221	186	155	217	234
ssa	0.72	0.99	0.32	0.57	0.43	0.80
X_{PL}	4996	4853	4118	3556	4031	4387

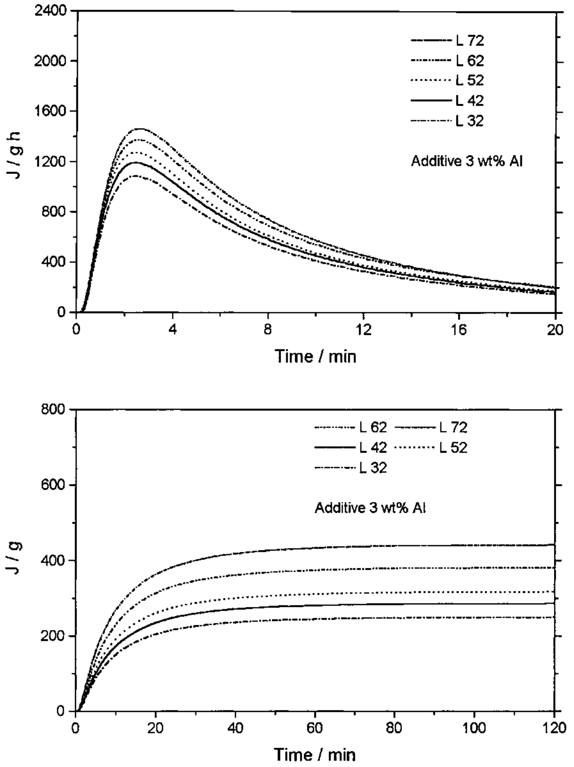

Fig. 7. (a) Rate of heat evolution and (b) integral heat evolution for test cement C7 mixed with liquids L32–L72.

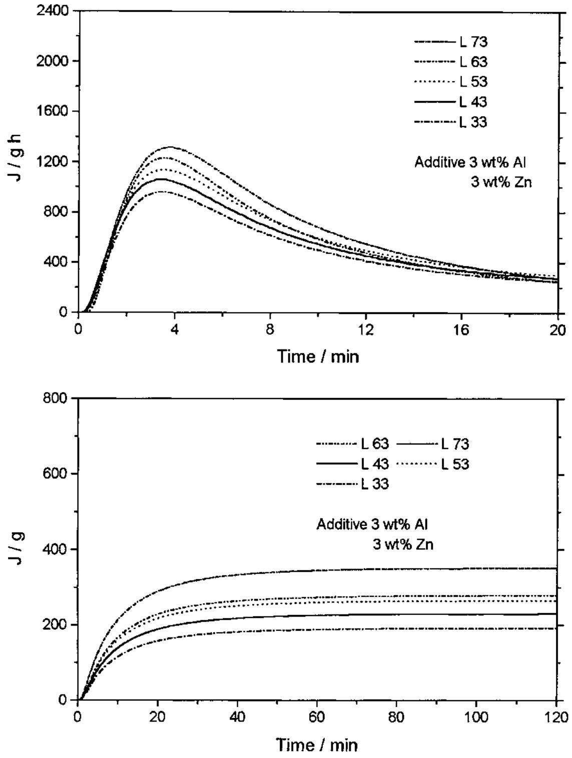

Fig. 8. (a) Rate of heat evolution and (b) integral heat evolution for test cement C7 mixed with liquids L33–L73.

mately positive correlation can be derived (Fig. 10). The parameter is defined as

$$X_{\mathrm{PL}} = (\text{wt\% ZnO in powder})\,(\text{wt\% H}_3\text{PO}_4 \text{ in liquid}).$$

Thereby X_{PL} represents the potential reactivity of a cement (Fig. 4). At least, from Figs. 3–8 one notices that peak intensities of the heat evolution curves correlate with the acid concentration. This holds for all of the cements examined in this investigation. Further, the addition of aluminum and zinc into the cement liquid leads to a continued setting prolongation. A detailed knowledge of the chemical reactions during setting of ZPC is essential for the interpretation of these observations.

When plain zinc oxide is mixed with unmodified orthophosphoric acid a solid, crystalline substance is rapidly formed due to the following reaction:

$$3\mathrm{ZnO} + 2\mathrm{H_3PO_4} + \mathrm{H_2O} \rightarrow \mathrm{Zn_3(PO_4)_2} \cdot 4\mathrm{H_2O}$$

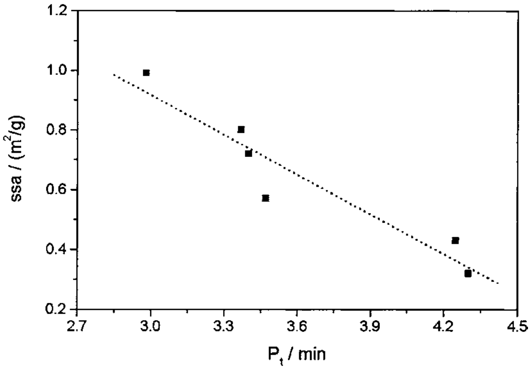

Fig. 9. Plot of specific surface area (ssa, (m^2/g)) versus peak time (P_t, (min)) for commercial cements.

The crystal structure of the reaction product, named hopeite, is well-known [23]. Although uncertainties in X-ray diffraction arise from the existence of some polymorphs, involving identical non-hydrogen atom frameworks but marked differences concerning the

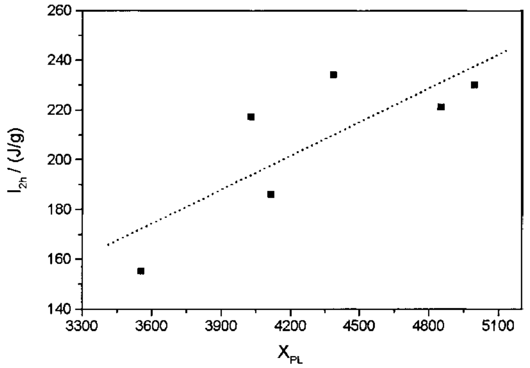

Fig. 10. Plot of integral heat evolution (I_{2h}, (J/g)) versus factor of reactivity (X_{PL}) for commercial cements.

hydrogen atom positions [24], the product obtained here could be unambiguously identified as α-hopeite from the FT–IR spectra. Under the given conditions this is the thermodynamically stable phase in the ternary system $ZnO–P_2O_5–H_2O$ [25,26]. By use of isoperibol solution–reaction calorimetry and batch microcalorimetry Al-Maydama et al. [27,28] determined the molar enthalpy of formation of α-hopeite to be −4094(3) kJ/mol at 298.15 K. It becomes evident that the above reaction is driven by a sufficient negative change in Gibb's free energy. This simple form of cold- setting cement has little value for dental application as it suffers from pronounced brittleness [29]. Further the rapid kinetic of this reaction, as indicated by the sharp maximum occurring after 1.3–1.6 min, prevents adequate working time in the surgery.

Bondforming reactions of oxides with orthophosphoric acid are quite general, but require certain definite properties from the cation involved. Oxides of an acidic nature and chemically inert oxides of a very stable nature show no reaction with orthophosphoric acid at room temperature. Zinc oxide, lanthanum oxide and the alkaline earth oxides react so violently with orthophosphoric acid that the structure is effectively torn apart, and no cohesion is possible. This effect is caused by the strongly basic nature of these oxides [30].

When zinc oxide reacts with orthophosphoric acid, modified by the addition of amphoteric aluminum in sufficient concentration, reaction products in the cement are amorphous and cannot be identified by X-ray diffraction. The FT–IR spectra show a broad featureless band in the region of orthophosphates, indicating the formation of an amorphous zinc orthophosphate and magnesium orthophosphate, respectively. The calorimetric curves of this test cement and of commercial cement are of similar shape, due to the same chemical reaction taking place during setting. Judging from our results, it is concluded that Al^{3+} in the cement liquid precipitates amorphous aluminum phosphate due to increasing pH of liquid when it is mixed with the basic oxides. The formation of amorphous phosphates in commercial cements and in our test cements is assumed to arise from the complexation behavior of aluminum in orthophosphoric acid. Experimental evidence from ^{27}Al- and ^{31}P-NMR shows that in orthophosphoric acid with concentrations from 50 to 65 wt%, modified by the addition of 0.5–5 wt% aluminum, complexes are present corresponding to the formulae $Al(H_3PO_4)^{3+}$, $AlH_2PO_4^{2+}$, $Al(H_2PO_4)_2^{+}$ and multiligand $Al(H_3PO_4)_n^{3+}$, where n is ≥ 2 [31]. Zinc in orthophosphoric acid solution forms only simple phosphates [32] and remains uncomplexed but its addition leads to a considerably higher compressive strength of hardened cements [33]. The metal ions Al^{3+} and Zn^{2+} are small ions of high ionic potential having some glass forming ability [34,35]. Since the same may be said of the phosphate group [36] a plausible hypothesis is that gelation occurs when these species join together leading to a continuous glassy network.

5. Conclusion

Conduction calorimetry proves to be a powerful method that provides valuable information about the setting reaction of ZPC by estimating both the amount of heat evolved and the instantaneous rate of heat liberation at any time. Variation of acid concentration leads to considerable differences in the peak intensities of heat evolution curves. The effect of additives to the cement liquid can be derived from the calorimetric curves. Aluminum and zinc act as setting retarders when these cations are added to the cement liquid. The incorporation of aluminum to the cement liquid leads to the precipitation of an amorphous reaction product. Calcination of cement powder and addition of basic magnesium oxide are contributory factors of setting prolongation. Calcination of cement powder has the effect of consolidating the powder to a denser form of reduced surface area and reactivity. The peak occurrence after onset of mixing proves to be sensitive to the specific surface area of the cement powder. Beside these effects the peak shape is a significant parameter. When a sharp peak is observed early after onset of mixing this can be ascribed to the formation of crystalline α-hopeite, whereas a broadening of the peak, combined with loss of intensity, indicates the formation of an amorphous phase. Taken into account the easy handling of a conduction calorimeter, this method is powerful for quality control and research or development related to dental cements. Process parameters, i.e. sintering temperature of the cement powder, as well as the indispensable amount of various additives, can be optimized using conduction calorimetry. The technique is fast and reliable and gives additional information not readily available from other analytical methods. However, the results and interpretations should be substantiated by those of other techniques such as WDXRF, FAAS, XRD, FT–IR and gas adsorption in the case of this study.

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