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SETTING REACTION AND RESULTANT STRUCTURE OF ZINC PHOSPHATE CEMENT IN VARIOUS ORTHOPHOSPHORIC ACID CEMENT-FORMING LIQUIDS

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ABSTRACT

The setting reactions and resultant structure of zinc phosphate cements are largely based on the formation of hopeite ($Zn_3(PO_4)_2 \cdot 4H_2O$) and/or zinc phosphate hydrate ($Zn_2P_2O_7 \cdot 3H_2O$) when using orthophosphoric acid (OPA) cement-forming liquids. OPA solutions buffered with aluminum and zinc ion produced better mechanical properties than nonbuffer OPA solutions because of the formation of hopeite and an amorphous phase. Development of the crystalline forms of the phosphate hydrates of zinc and magnesium were retarded and/or prevented by the incorporation of aluminum and zinc ion in the cement-forming liquid. *© 1998 Elsevier Science Ltd*

Introduction

Some of the most important materials used in dentistry are dental cements. These materials, which are prepared directly in the office or surgery, are used for many purposes, and, depending on their formulation, they may be used to attach prefabricated crowns and inlays to teeth, to line cavities for the protection of dental pulp against chemical attack and thermal stresses, and even for the direct filling of cavities (1).

Zinc phosphate cements are the strongest among the dental cements, and probably afford the best protection against mechanical trauma to the pulp, resulting in use principally for the cementation of inlays and other restorations fabricated outside of the mouth.

Zinc phosphate cements, in various formulations, have been used in dentistry for a long time because of their excellent properties, such as good manipulative properties in the fresh state, and good mechanical properties and resistance to intraoral change in the hardened state (1,2). The setting and hardening of these cements take place within 10 min after onset of mixing, and a very high early strength, 10,000 psi, is developed in 24 h. This setting reaction is considered to be an acid-base reaction. Therefore, the reaction is extremely exothermic and rapid when zinc oxide powder with amphoteric property and an acid liquid are mixed, resulting in a reaction-product salt, zinc phosphate hydrate.

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TABLE 1
Chemical compositions of dental zinc phosphate cement-forming liquids synthesized.

Symbol or No.	Chemical Composition (wt.%)			
	H_3PO_4	Al	Zn	H_2O
	Non-buffer solutions			
H55	55.0	0	0	45.0
H65	65.0	0	0	35.0
	Buffer solutions			
1	55.0	0	0	45.0
2	55.0	1.5	4.0	39.5
3	55.0	3.0	8.0	34.0
4	60.0	0	4.0	36.0
5	60.0	1.5	8.0	31.5
6	60.0	3.0	0	37.0
7	65.0	0	8.0	27.0
8	65.0	1.5	0	33.5
9	65.0	3.0	4.0	28.0

Although many reports (1,3) on the properties of zinc phosphate cements have appeared, comparatively little attention has been paid to their setting reaction and resulting cement structure.

In the current study, setting reaction and resultant microstructure of zinc phosphate cement formed in different concentrations of orthophosphoric acid and different inorganic ion buffer solutions of cement-forming liquids were studied. In addition, physico-mechanical properties were investigated.

Experimental

Cement Powders

ZnO, CaO, and MgO (products of Johnson Matthey Co., ACS grade), the powder ingredients of zinc phosphate cement, were calcined in the range of temperature from 950 to 1350°C for 6 h, and were used for studying setting mechanisms of individual components.

Cement-Forming Liquids

Two kinds of cement liquid, orthophosphoric acid and a buffer solution containing aluminum and/or zinc ions in addition to this acid, were used as cement-forming liquids. The cement-forming liquids are made from 85% orthophosphoric acid (product of Johnson Matthey Electronics Co., ACS grade) by dilution of orthophosphoric acid liquid using deionized water. Compositions of cement liquids are shown in Table 1. The buffer solutions were made by thoroughly dissolving aluminum and/or zinc (product of Johnson Matthey Electronics Co., ACS grade, aluminum and zinc metals) in different concentrated orthophosphoric acid solutions.

Mixing and Curing

The mixing of all test specimens was conducted on a clean glass slab by hand with a stainless steel spatula at room temperature and at a relative humidity (RH) between 55 and 76%.

Cement powder and cement-forming liquid were put on the glass slab together. The cement powder was divided into 6 portions as shown below, and then the first part (1/16th of the powder) was mixed with liquid in 10 s. Then each addition was thoroughly mixed during successive additions of powder to liquid in the total mixing time, 1 min and 30 s, according to the ADA Spec. 8 mixing rule as below (4).

Amount of powder	1/16	1/16	1/8	1/4	1/4	1/4
Time (s)	10	10	10	15	15	30

The final mixture of the cement powder and cement-forming liquid was cast and cured in a curing cabinet at 90% RH and 38°C. The specimens for strength measurement were cured for 1 day.

Setting Time

Setting time measurements were conducted using a Vicat needle forfinal set. A plastic cylinder mold (4.8 mm high and 9.5 mm diameter) was placed on a flat glass plate and filled with a mixture of solid and cement-forming liquid. A specimen was transferred to a curing cabinet held at 38°C and 90% RH 3 min after starting the mix. A Vicat needle was gradually lowered onto the surface of the specimen. The setting time is the time elapsed from the start of mixing to the time when the needle failed to make a perceptible circle on the surface of the specimen.

Compressive Strength

A plastic mold (12 mm high and 6 mm diameter) was placed on a flat plastic surface and was slightly overfilled with a mixture of solid and cement-forming liquid within 3 min after starting the mix. A second flat plastic plate was pressed on the top of the mold, and then the plates were held firmly together with a small C clamp. The mold was transferred to the curing cabinet held at 38°C and 90% RH One day after starting the mix, the compressive strength was tested.

pH

pH measurements of dental zinc phosphate cement powder and ingredients were performed using an Orion pH meter. The pH electrode was put into the specimens and the pH values were read up to 250 min after the electrode was standardized. The specimens were prepared using a ratio of solid to liquid = 2.0 g/mL.

TABLE 2
Results of X-ray diffraction analysis for ZnO, which is sintered at 1150°C for 6 h, and then mixed with different cement-forming liquids at solid/liquid = 4.0 g/mL. The cement-forming liquids are non-buffer solutions (H55 and H65) and buffer solutions (No. 3 and No. 9).

Time Sol'n	Phases	10 min	2 h	5 h	1 day	3 days	7 days
H 55	Major	Zincite Hopeite	Zincite Hopeite	Zincite Hopeite	Zincite Hopeite	Zincite Hopeite	Zincite Hopeite
	Minor	-	-	-	-	-	-
No. 3	Major	#	Zincite	Zincite	Zincite	Zincite	Zincite
	Minor	#	Amorp	Amorp	Amorp Hopeite	Amorp Hopeite	Amorp Hopeite
H 65	Major	Zincite Hopeite	Zincite Hopeite ZPH	Zincite Hopeite ZPH	Zincite Hopeite ZPH	Zincite Hopeite ZPH	Zincite Hopeite ZPH
	Minor	ZPH	-	-	-	-	-
No. 9	Major	#	Zincite	Zincite	Zincite	Zincite	Zincite
	Minor	#	Amorp	Amorp	Amorp	Amorp	Amorp

#, Not set in No. 3 and No. 9; Amorp, Amorphous phase; ZPH, $Zn_2P_2O_7 \cdot 3H_2O$

Results

X-ray Diffraction Analysis

The starting materials ZnO, MgO, and CaO were each sintered at 1150°C for 6 h. Tables 2 to 4 show results of X-ray diffraction analysis for the ZnO, MgO, and CaO mixed with various phosphate solutions. H55 and H65 are orthophosphoric acid solutions with H_3PO_4 concentration of 55 and 65 wt.%, respectively. No. 3 and No. 9 (refer to Table 2) are buffer solutions containing both buffer solution agents, Al and Zn.

The oxides reacted more slowly with the buffer solutions (No. 3 and No. 9) than with the non-buffer solution, with no hardening occurring within 10 min after mixing, for zinc and magnesium oxides. However, an amorphous phase formed in all specimens prepared with the buffer solutions aged for 7 days.

For ZnO mixed with buffer solutions, (Table 2) the major crystalline hydrate formed is hopeite, which had always appeared by one day after the onset of mixing. Buffer solutions with higher orthophosphoric acid concentration, e.g., No. 9, do not form any crystalline hydrates up to 7 days. In non-buffer solutions, crystalline hopeite formed as a major phase for high (65%) and low (55%) orthophosphoric acid concentration, and zinc phosphate hydrate ($Zn_2P_2O_7 \cdot 3H_2O$) was also formed in only the high concentration orthophosphoric acid.

The reaction products of MgO with No. 9 buffer solution (Table 3) are an amorphous magnesium phosphate hydrate phase plus unreacted periclase. The non-buffer solution, H65, develops an unidentifiable crystalline phase, which is believed to be a magnesium phosphate hydrate, and unreacted periclase. The amorphous phase is detected only in runs containing the buffer solution.

TABLE 3
Results of X-ray diffraction analysis for MgO, which was sintered at 1150°C for 6 h in different cement-forming liquids at solid/liquid = 4.0 g/mL. The cement-forming liquids are non-buffer solution (H65) and buffer solution (No. 9).

Sol'n	Phases/ Time	10 min	2 h	5 h	1 day	3 days
H65	Major	Periclase	Periclase	Periclase	Periclase	Periclase
	Minor	U	U	U	U	U
No. 9	Major	#	Periclase	Periclase	Periclase	Periclase
	Minor	#	Amorphous	Amorphous	Amorphous	Amorphous

U, unidentified; #, Not set in No. 9

The No. 9 buffer solution with CaO (Table 4) shows evidence of calcium phosphate ($Ca_2P_2O_7$), calcium phosphate hydrate ($Ca_2P_2O_7 \cdot 2H_2O$), portlandite ($Ca(OH)_2$) and an unidentified crystalline phase as major phases in specimens hydrated for 2 h. The calcium phosphate phase and portlandite form at early reaction times. An amorphous phase appeared as a minor phase. The non-buffer solution reacts to form only crystalline phases; calcium phosphate and calcium phosphate hydrate are major phases, and an unidentified phase and portlandite are formed as minor phases.

pH Measurements

The present study included three ZnO samples, each sintered at a different temperature (950, 1150, and 1350°C). The acidity of the cement paste is quite high at early hydration ages due to the presence of the phosphoric acid. The results of pH measurements (Figure 1) indicate that the pH of the cement paste at the start of mixing is approximately in the range of 3 to 3.5 depending on the reactivity of the zinc oxide. The pH then increases rapidly, ultimately approaching neutrality.

TABLE 4
Results of X-ray diffraction analysis for CaO, which is sintered at 1150°C for 6 h, and reacted in different cement-forming liquids at solid/liquid = 4.0 g/mL. The cement-forming liquids are a non-buffer solution (H65) and a buffer solution (No. 9).

Sol'n	Phases/ Time	10 min	2 h	5 h	1 day	3 days
H65	Major	CP, CPH	CP, CPH	CP, CPH	CP, CPH	CP, CPH
	Minor	Lime, U, Portlandite	Lime, U, Portlandite	U, Portlandite	U, Portlandite	U, Portlandite
No. 9	Major	CPH, Lime	CPH, U, Lime, CP, Portlandite	CPH, U, CP, Portlandite	CPH, U CP, Portlandite	CPH, U CP, Portlandite
	Minor	CP, Portlandite	Amorphous	Amorphous	Amorphous	Amorphous

CP, Calcium phosphate ($Ca_2P_2O_7$); CPH, Calcium phosphate hydrate ($Ca_2P_2O_7 \cdot 2H_2O$); U, Unidentified phase

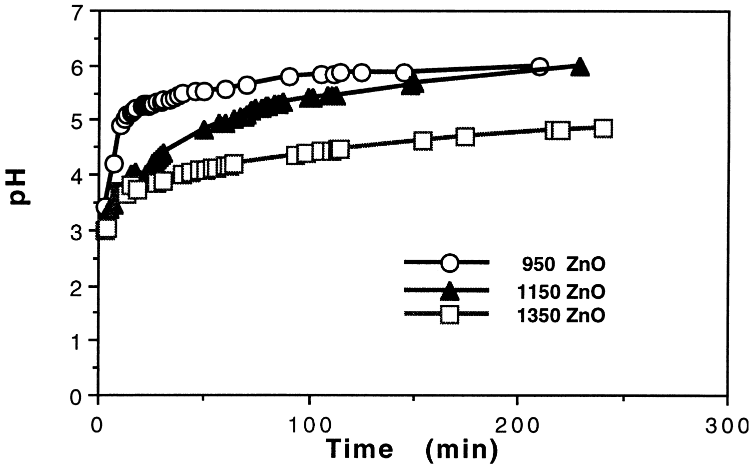

FIG. 1.

pH values of various zinc oxides (sintered at 950, 1150, and 1350°C for 6 h) reacted with No. 9 buffer solution (65% H_3PO_4 + 3% Al + 4% Zn + 28% H_2O) at S/L = 2.0 g/mL.

The mixture with low-temperature-treated zinc oxide shows a low pH at the start, which abruptly increases to about 5.5 in 15 min, and then slowly reacts with the remaining acid. High-temperature-treated zinc oxide maintains a high acidity over the entire time of measurement, 250 min, because the high-temperature heat-treatment decreases the reactive specific surface area of zinc oxide. The pH of this zinc oxide mixture remains at 4.5 up to 250 min. The 1150°C heat-treated zinc oxide is intermediate in behavior. It increases its pH up to 100 min and then the rate of change reduces. The pH of the 1150°C-treated zinc oxide approaches 6.0, the same as that of the 950°C-treated zinc oxide sample in 200 min.

Setting Time and Compressive Strength Measurements

Table 5 shows the results of setting time and compressive strength measurements for the 1150°C-sintered ZnO mixed with various phosphate solutions. These measurements have been conducted at S/L (solid/liquid) = 2.5 g/mL.

Cement-forming liquids have a significant influence on properties of zinc phosphate cement. Liquids without aluminum and zinc metal ions rapidly react with amphoteric zinc oxide, with the liberation of much hydration heat. This heat affects the hydration reaction between the liquid and the zinc oxide powders, accelerating it so that reactions occur partially on the surfaces of the cement powders that contact the liquid during mixing. As a result of this, the reaction product includes much unreacted zinc oxide, which can cause disintegration during curing. Liquids containing one metal ion (zinc or aluminum) show the above situation even though the reaction rates are slower than those of the liquids that do not contain both metal ions. The liquids with one metal ion lengthen setting time, but the resultant materials are not stable because they are heterogeneous due to the partial reaction. Therefore, these two kinds of liquid do not form strong specimens. The liquids containing both metal ions stabilize the pH and slow the reaction initially. As phosphoric acid is consumed the acidity is reduced and the reaction rate also diminishes. Therefore, these liquids react with zinc oxide powders

TABLE 5
Setting time and compressive strength of mixtures with ZnO sintered at 1150°C for 6 h at S/L = 2.5 with phosphate acid solutions.

	Solution (wt. %)					
No	H_3PO_4	Al	Zn	H_2O	Setting time (min)	1 day compressive strength (psi)
1	55	0	0	45.0	1:30	-
2	55	1.5	4.0	39.5	8:00	2400 (105)
3	55	3.0	8.0	34.0	8:00	5280 (108)
4	60	0	4.0	36.0	7:00	-
5	60	1.5	8.0	30.5	9:30	3280 (118)
6	60	3.0	0	37.0	24:00	-
7	65	0	8.0	27.0	13:00	-
8	65	1.5	0	33.5	8:30	-
9	65	3.0	4.0	28.0	45:00	5890 (89)

Standard deviation is noted in parentheses ($n = 6$).

slowly enough that they can be mixed homogeneously resulting in a hydrated structure that can be cured in water without disintegration. The liquids with high aluminum content (No. 3 and No. 9), among the liquids containing both metal ions, show high strength development of zinc oxide phosphate paste.

Figure 2 shows the setting time of the 1150°C-sintered zinc oxide mixed with various cement-forming liquids containing different water contents. The water content in the liquid influences the reaction rate. A high content of water causes rapid reaction, resulting in shortening of the setting time.

Table 6 illustrates the setting time and strength of the mixtures with zinc oxide powders sintered at different temperatures. The setting time of zinc oxide mixtures increases as the

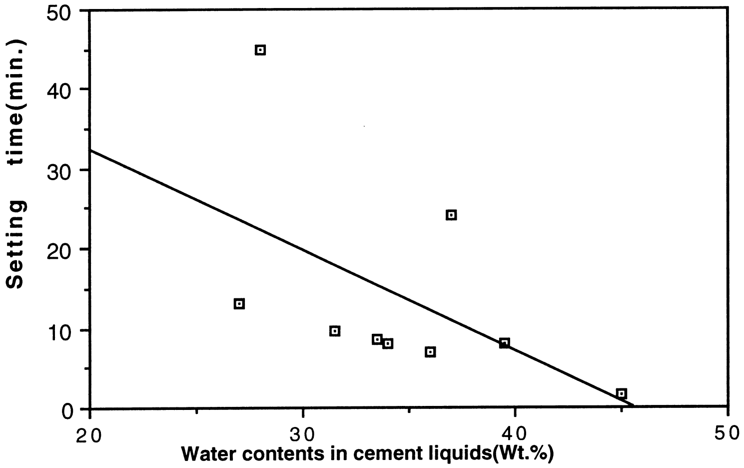

FIG. 2.
Setting time of zinc oxide mixed with various cement-forming liquids with different water contents.

TABLE 6
Setting time and strength development of zinc oxides sintered at different temperatures (950, 1150, and 1350°C) mixed with No. 9 buffer solution.

	Setting time (min)			One day compressive strength (psi)		
S/L (g/mL)	ZnO 950	ZnO 1150	ZnO 1350	ZnO 950	ZnO 1150	ZnO 1350
2.50	35:00	45:00	67:00	6,730 (280)	5,900 (201)	2,070 (130)
3.00	10:30	14:00	21:00	10,880 (213)	6,320 (224)	6,720 (163)
3.50	4:30	5:30	9:00	6130 (150)	8,090 (203)	9,600 (157)
4.00	3:00*	3:00	5:30	5,420 (305)	11,000 (298)	10,190 (204)

Standard deviation is noted in parentheses ($n = 6$).
*, very stiff.

heat-treatment temperature increases. In the case of the 950°C-heated zinc oxide, it is very difficult to make a homogeneous paste because of the fast reaction at a high S/L ratio. The attainment of maximum strength depends on good workability; lower temperature-treated zinc oxide needs more liquid and higher temperature heated zinc oxide requires less liquid to maintain good consistency. The maximum strengths of the zinc oxides heated at different temperatures show a shift toward the high S/L ratio with increasing heat-treatment temperature.

Table 7 presents setting times measured for both magnesium oxide and calcium oxide sintered at 1150°C and mixed with No. 9 buffer solution. The setting reaction for both oxides is so fast that the setting occurs in as little as 10 s when the powder contacts large quantities of liquid. Calcium oxide shows a more rapid reaction than magnesium oxide.

Discussion

The cement-forming reaction of zinc phosphate cement is essentially an acid-base interaction between zinc oxide and the acidic liquid. When the zinc oxide powder and the liquid contact each other, H^+ ions released from the H_3PO_4 attack the zinc oxide. Then, the Zn^{2+} ions released migrate through the aqueous acid solution where they come together with $H_2PO_4^-$,

TABLE 7
Setting time measured in specimens prepared with MgO and CaO both sintered at 1150°C and mixed with No. 9 buffer solution.

	Setting time (min)	
S/L (g/mL)	MgO	CaO
1.0	12:00	3:40
1.5	5:00	1:30
2.0	2:30	0:10

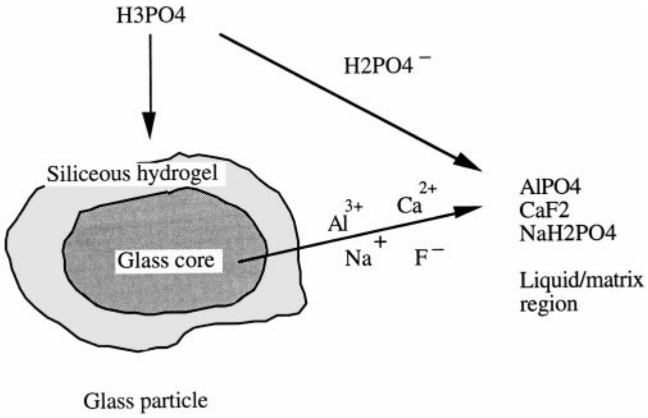

FIG. 3.
Schematic diagram of cement-forming reaction of a dental silicate cement (1).

Zn^{2+}, and Al^{3+} ions already present in the liquid, and react to form insoluble crystalline and non-crystalline phosphate solids. As reaction proceeds the pH of the system increases. Similar work was reported by Wilson (1), who, in his dental silicate cement work, presented a mechanism of reaction represented here as Figure 3. When H^+ ions attack the glass powder, Al^{3+}, Ca^{2+}, Na^+, and F^- are liberated from the glass, leaving behind an ion-depleted layer of silicate gel at the surface of the glass particles. The liberated ions migrate and react with $H_2PO_4^-$, and salts precipitate. The principal reaction is the formation of an insoluble aluminum phosphate, the gel matrix. Associated side reactions are the precipitation of calcium fluoride and the formation of soluble sodium dihydrogen phosphate.

From X-ray diffraction results in this study, an amorphous zinc orthophosphate phase is formed. This matrix is not stable and crystallites of hopeite grow and form layers at the surface. Peyton and Craig (3) suggested that the surface of the alkaline powder is initially dissolved by the acid liquid. As more of the powder dissolves, the reaction products soon supersaturate the solution. Complex zinc phosphates then precipitate in a hydrated crystalline network and surround the incompletely dissolved zinc oxide particles. The amorphous phase is believed to be important for the formation of the cement and largely responsible for the strength development. Buffer solutions containing Al and Zn ions cause more amorphous phase to be formed and give high compressive strength. X-ray diffraction analysis results show that hopeite is formed in 55% concentration orthophosphoric acid liquid, and hopeite and another zinc phosphate hydrate, $Zn_2P_2O_7{\cdot}3H_2O$, are formed in 65% concentration orthophosphoric acid liquid.

Buffer solutions stabilize the pH and slow the reaction initially, so as to provide adequate workability. Although the basic cement-forming reaction is an acid-base reaction, the water content is an important factor for the setting reaction. From pH studies, buffer solutions with high concentration of orthophosphoric acid stabilize the setting reaction. Peyton and Craig (3) also mentioned that the reaction for the mixed cement may be modified by the proper dilution of the phosphoric acid with water; the presence of excess water shortens the setting time whereas an insufficient amount of water results in a prolonged setting time. The setting time and compressive strength measurement data in the present study agree well with this result.

The partial neutralization of the phosphoric acid by the aluminum and zinc ions tempers the reactivity of the resultant liquid, which is described as a buffer agent. The buffer solution stabilizes the pH and reduces the initial reaction rate, resulting in establishing a smooth, nongranular, workable cement paste during the mixing procedure. The setting time of the cement paste also may be modified by controlling the amount of water in the phosphoric acid solution. Cement-forming liquids usually contain 30 to 40% of water in the phosphoric acid solutions.

Conclusions

1. Zincite (ZnO) forms different zinc phosphate hydrates by reaction with different concentrations of orthophos phoric acid (OPA) solutions. Hopeite ($Zn_3(PO_4)_2 \cdot 4H_2O$) forms in 55 wt.% OPA solution, and hopeite and $Zn_2P_2O_7 \cdot 3H_2O$ form in 65 wt.% OPA solution.
2. MgO and CaO react rapidly with OPA solution (CaO reacts faster than MgO), and form their respective phosphate hydrates.
3. Buffer solution including both Zn and Al ions controls setting reactions for ZnO, MgO, and CaO. These reactions are slow at early reaction time, resulting in the formation of their amorphous phases form.
4. Dilution of OPA liquid and heat treatment of ZnO significantly affect the cement forming reaction.
5. The setting reactions and resultant structures are based largely on the formation of hopeite and/or zinc phosphate hydrate ($Zn_2P_2O_7 \cdot 3H_2O$) for orthophosphoric acid, and the formation of hopeite and amorphous phosphate as the essential components for developing mechanical strength for Zn and Al ion buffer solution.

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