

# Synthesis and Characterization of Zinc Phosphate Cement Powder and Cement-forming Liquid

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Chemical composition of cement powder influences the setting time and early compressive strength development. The setting time increases as the amounts of zinc oxide and magnesium oxide are increased. For one day compressive strength development, a cement powder with a composition 90% ZnO, 8% MgO and 2% silica resulted in the highest strength (greater than 1,090 kg/cm<sup>2</sup>). Cement-forming liquids also need to be buffered, with both aluminum and zinc ions, for a good consistency and a higher strength of the zinc phosphate cement. These liquids control the setting reactions.

**Key words :** Zinc Phosphate Cement Powder, Cement-forming Liquids, Hydration, Zinc, Silica, Magnesia, Strength, Setting time

## I. Introduction

Zinc phosphate cements, of various formulations are among the most important dental materials. They have long been used in dentistry because of their excellent manipulative and mechanical properties.<sup>1,2</sup>

The cement-forming reaction of zinc phosphate cement is based on the reaction between a base and an acid. Cement powders and cement-forming liquids react rapidly liberating much hydration heat develop very high early strength.

The zinc phosphate cements consist of about 80 to 90% cement powder, a zinc oxide and setting reaction regulator and a cement-forming liquid, normally a dilute orthophosphoric acid solution. The setting and hardening of these cements take place within 10 minutes after onset of mixing. Very high early strength, 700 kg/cm<sup>2</sup>, is developed in 24 hours. This setting reaction, which is considered an exothermic acid-base reaction, liberates extremely large quantities of reaction heat.<sup>3,4</sup>

Although reports on the properties of zinc phosphate cements have appeared in the literature,<sup>5-7</sup> comparatively little attention has been paid to explaining their setting reaction, the resulting cement structure, and the effect of varying the relative amounts of cement powder and cement-forming liquid.

In this paper, in order to explore the optimum composition the effects of chemical composition of cement powder and cement-forming liquids on physico-mechanical properties of cement paste were studied. In addition, the setting mechanisms were also discussed.

## II. Experimental

### 1. Materials

### 1.1 Cement powders

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

SiO<sub>2</sub> in the cement powder was supplied by ground crystalline quartz (commercial name, Min-U-Sil, median diameter 5 μm). Zinc phosphate cements were prepared from powders consisting of ZnO (ranging from 84 to 96 wt.%), MgO (4 to 16%) and SiO<sub>2</sub> (0 to 2%) as shown Table 1. These cements were sintered at a temperature of 1150°C for 4 or 8 hours, and ground to particle sizes ranging from 0.4 to 20 μm diameter (median diameter 6.0 μm).

### 1.2 Cement-forming phosphate liquids

Two kinds of cement liquids, buffer solutions containing aluminum and/or zinc ions, were used as cement-forming liquids. The cement-forming liquids are made from 85% orthophosphoric acid by dilution of orthophosphoric acid liquid using deionized water. Compositions of cement liquids are shown in Table 2. The buffer solutions were made by dissolving aluminum and/or zinc (ACS grade, aluminum and zinc metals) in different concentrated orthophosphoric acid solutions, thoroughly dissolving the metal ions in these acid solutions.

## 2. Experimental

### 2.1 Specimen preparation

The manipulation of zinc phosphate cement is very important for proper consistency because the setting reaction may be affected by various factors, such as temperature, cement powder to liquid ratio and mixing pro-

**Table 1.** Chemical Compositions and Sintering Conditions of Oxide Component of Synthesized Dental zinc Phosphate Cement Powders

No	Chemical composition (wt. %)			Sintering temp. (°C)	Soaking time (hr)
	ZnO	MgO	SiO <sub>2</sub>		
1	96	4	0	1,150	4
2	94	4	2	1,150	8
3	92	8	0	1,150	4
4	90	8	2	1,150	8
5	86	12	2	1,150	4
6	88	12	0	1,150	8
7	82	16	2	1,150	4
8	84	16	0	1,150	8

**Table 2.** Chemical Compositions of Dental zinc Phosphate Cement-forming Liquids (buffered) Synthesized for the Current study

No	Chemical composition (wt. %)			
	H <sub>3</sub> PO <sub>4</sub>	Al	Zn	H <sub>2</sub> O
1	55.0	3.0	8.0	34.0
2	65.0	3.0	4.0	28.0

cedure.

As a general rule (A.D.A spec. 8, 1967), the proper amount of powder should be added to the liquid slowly on a cool slab to attain the desired consistency of the cement paste. An increase in the proportion of the powder to a given amount of the liquid generally provides more desirable properties, for which reason, as much powder as possible should be used to obtain a particular consistency. The mixing procedure also influences the development of the properties of the mixture. The mixing procedure generally consists of 3 stages; initial, middle and final procedure. First a small amount of the powder is incorporated into the liquid, which liberates minimal heat, that is, dissipated. The liberated heat accelerates the setting reaction and hinders the control over the consistency being developed. Second, a large amount of the powder may be incorporated during the middle of the mixing period to saturate the liquid with the newly forming complex zinc phosphate. Finally, smaller increments of the powder are again incorporated, so that the desired ultimate consistency of the cement is not exceeded. Thus, the mixing procedure begins and ends with small increments, first to achieve slow neutralization of the liquid with the attendant control of the reaction and last to achieve a critical consistency.

### 2.2 Setting time

A plastic cylinder mold (4.8 mm high 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% R. H. Three minutes after starting the mix. A Vicat needle

(final set) 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.

### 2.3 Compressive strength

A plastic mold (12 mm high and 6 mm diameter) was placed on a flat plastic sheet and was slightly overfilled with a mixture of solid and cement-forming liquid within 3 minutes after starting the mix. A second flat plastic plate was pressed on the top of the curing cabinet held at 38°C and 90% R.H. One day after starting the mix, the compressive strength was tested.

## III. Results

### 1. Results of setting time and compressive strength measurements

Table 3 shows setting times and one day compressive strengths of 8 kinds of synthesized cement powders as a function of S/L ratio. Quartz was supplied by Min-U-Sil. ZnO, MgO and SiO<sub>2</sub> were heated at 300°C for 2 hours before being mixed together for sintering.

The cement powders which were synthesized at 1150°C sintering temperature were reacted with No. 2 buffer solution containing both aluminum and zinc ions in the diluted orthophosphoric acid solution. The results show that setting time shortens as MgO contents are increased in the cements. This trend is attributed to the characteristics of MgO, which reacts very fast with orthophosphoric acid in a few seconds. MgO did not seem to act a sintering mineralizer in this system at 1150°C.

One day compressive strengths of the cements range from 440 to 650 kg/cm<sup>2</sup> and 680 to 980 kg/cm<sup>2</sup> at S/L=2 and 3, respectively. The S/L ratio has a significant influence on the setting time and the strength of the cements. The sintering time (soaking time) is not a critical factor affecting the setting time and the strength of the cements in this study. The No.4 cement (90% ZnO+8% MgO+2% SiO<sub>2</sub>) shows the highest compressive strength

**Table 3.** Setting Time and Compressive Strength of Synthesized Cements in No.2 Buffer Solution (65% H<sub>3</sub>PO<sub>4</sub>+3.0% Al+4.0% Zn+28% H<sub>2</sub>O)

No*	Setting time (min)		1 day comp. str (kg/cm <sup>2</sup> )	
	S/L=2.0	S/L=3.0	S/L=2.0	S/L=3.0
1	26:00	2:40	445	721
2	26:00	3:00	494	841
3	13:30	4:00	654	979
4	16:00	4:00	581	1098
5	12:30	3:30	498	797
6	11:00	3:30	460	783
7	10:30	2:50	488	688
8	10:00	2:50	459	635

\*S/L: Solid/Liquid ratio in g/mL

+No is the same as that referred to Table 1.

**Table 4.** Setting Times and 1 day Compressive Strengths Measured in zinc Phosphate Cement Prepared with No.4 Cement powder and No.2 buffer Solution

S/L (g/mL)	Setting time (min)		1 day comp. strength (kg/cm <sup>2</sup> )	
	No.1	No.2	No.1	No.2
1.50	10:00	50:00	-	-
2.00	6:00	16:00	655 (23)	581 (18)
2.50	4:30	8:00	726 (25)	864 (17)
3.00	3:30	4:00	869 (25)	1,098 (17)
3.50	3:00	3:00	-	-

\*not measured. ( )=standard deviation (n=6).

at S/L=3.

Table 4 contains the setting times and 1 day compressive strengths measured in mixtures of No.4 cement and No.1 and No.2 buffer solutions containing both Al and Zn ions. No.2 buffer solution, which has a higher orthophosphoric acid concentration than No.3, gives longer setting times and a higher compressive strength.

**2. Results of pH measurements**

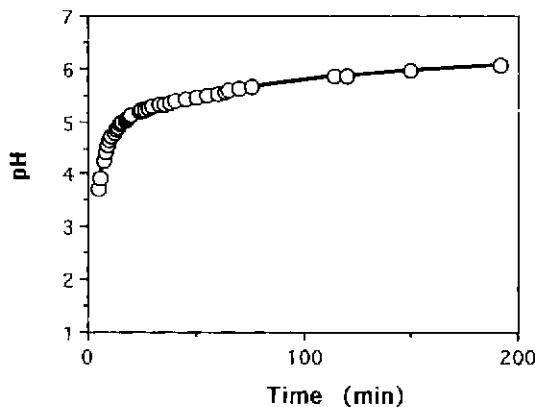
Figure 1 shows the results of pH measurements for No.4 cement (in Table 1) mixed with No.2 buffer solution (65% H<sub>3</sub>PO<sub>4</sub>+3% Al+4% Zn+28% H<sub>2</sub>O) at S/L=2.0. The dental cement shows strong acidity, pH=3.5, at the start of mixing. This pH value rapidly increases to about 5.0 within 25 minutes, and then very slowly increases to about 6 in 200 minutes.

**3. X-ray diffraction studies**

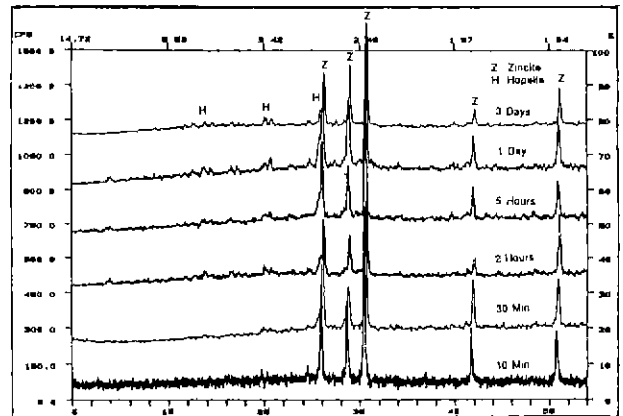
Samples were quenched by grinding in an excess of acetone after various periods of hydration. This method of stopping the phosphate cement hydration is described elsewhere.<sup>8)</sup>

Figure 2 shows the x-ray diffraction patterns of hydrated zinc phosphate cement (No.4 in Table 1) with No.2 buffer solution (Table 2) at S/L=4.0 g/mL.

Zincite (unreacted zinc oxide) decreases with in-



**Fig. 1.** pH values of the synthesized cement (No.4) in No.2 buffer solution at solid/liquid=2.0 g/mL.

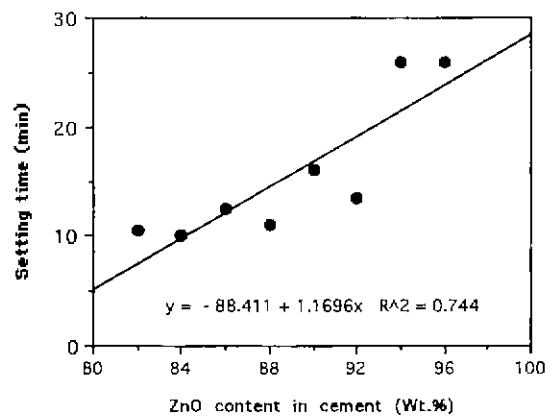


**Fig. 2.** X-ray diffraction patterns of the synthesized zinc phosphate cement (No.4) in No.2 buffer solution at S/L=4.0.

creasing hydration time. Hopeite [zinc phosphate hydrate Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O] begins to form at 30 minutes. These hydrate forms at an early hydration time, compared to specimens with pure ZnO, which do not show evidence of a crystalline hydrate up to 7 days when hydrated in No.9 buffer solution. However, in the synthesized cement, the hopeite forms as a major phase of the one day specimen. The amorphous phase appears soon after mixing cement and liquid, and then constantly increases with the length of hydration. In this cement only the hopeite and amorphous phase were detected as zinc phosphate hydrates. The unreacted zinc oxide is still a major phase at 3 days.

**IV. Discussion**

The current studies show that chemical composition influences the cement setting time and compressive strength. Figures 3 to 6 show how the percentages of zinc oxide and magnesium oxide in the powders of the zinc phosphate cement affect setting time and one day compressive strength; the powders were sintered at



**Fig. 3.** Setting times of synthesized zinc phosphate cements prepared using No.2 buffer solution as a function of zinc oxide content of the cement powder (S/L=2.0)

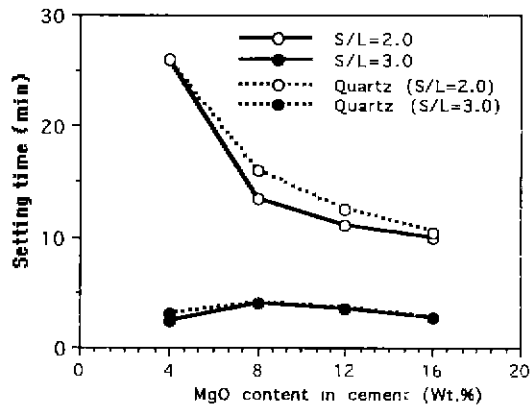


Fig. 4. Setting times of synthesized zinc phosphate cements prepared using No.2 buffer solution according to magnesium oxide and Quartz (Min-U-Sil, 2 wt.%) content of cement powder.

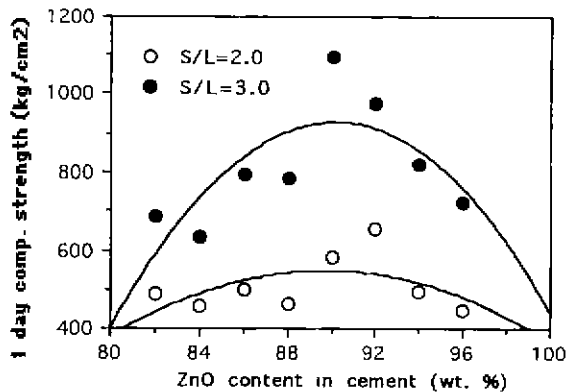


Fig. 5. One day compressive strengths of synthesized zinc phosphate cements prepared using No 2 buffer solution as a function of zinc oxide content of cement powder.

1150°C for 4 and 8 hours.

Setting time increases as the amount of zinc oxide increases at S/L=2.0 (g/mL). The effect of magnesium oxide concentration is not clear at S/L=3.0 because of the poor consistency of the paste, which is caused by rapid setting reaction. At S/L=2.0 setting time decreases as the magnesium oxide content increases. In this study, magnesium oxide does not act as a sintering aid for the zinc phosphate cement powders. Therefore, the characteristics of this oxide, which reacts with phosphoric acid solution more rapidly than zinc oxide, influence the setting reaction of the synthesized dental cement powder. The specimens containing 2% Quartz (Min-U-Sil) show that the setting time is slightly lengthened at low S/L=2.0.

For one day compressive strength, maximum strengths develop at 90% and 92% zinc oxide content for S/L=3.0 and 2.0, respectively. The effect of the magnesium oxide content on the compressive strength is significant at the low magnesium content range, less than 12%. A high content of magnesium oxide shows low strength. The maximum compressive strengths appear at 8% of magnesium oxide content for both S/L=2.0 and 3.0. The specimens

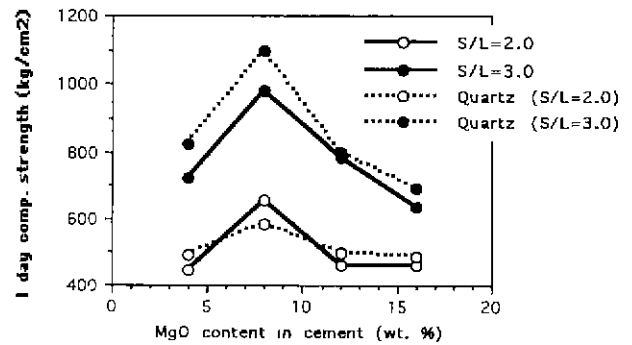


Fig. 6. One day compressive strengths of synthesized zinc phosphate cements prepared using No.2 buffer solution as a function of magnesium oxide and Quartz (Min-U-Sil, 2 wt.%) content of cement powder.

containing 2% Quartz (Min-U-Sil) show higher compressive strength than the control specimens which do not contain Quartz (Min-U-Sil). The compressive strength strongly depends on the ratio of solid to liquid. The higher ratio of solid to liquid generates higher compressive strength.

In this study, magnesium oxide acts a setting regulator for zinc oxide, Quartz (Min-U-Sil) increases the compressive strength as a filler material. Kohmura and Ida<sup>9)</sup> achieved the same results showing that inactive silica acts as a filler in the microstructure, resulting in a lengthening of the setting time and an increase in the strength of the dental cement. The optimum composition for the highest strength is 90% ZnO, 8% MgO and 2% SiO<sub>2</sub>.

For cement-forming liquids 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.

Figures 7 and 8 present effects of the water content in the buffer solution containing both aluminum and zinc ion on the setting time and one day compressive strength of the synthesized dental cement. The buffer solution with higher concentration orthophosphoric acid (lower water content) shows a longer setting time than the lower acid concentration liquid. Both buffer solutions give the same setting time at a ratio of solid to liquid greater than 3.0. The buffer solution with a high concentration of the orthophosphoric acid generates higher strength than low concentration of acid at S/L ratios greater than 2.5. Water content in the buffer solution containing both aluminum and zinc ion also influences setting time and compressive strength development as

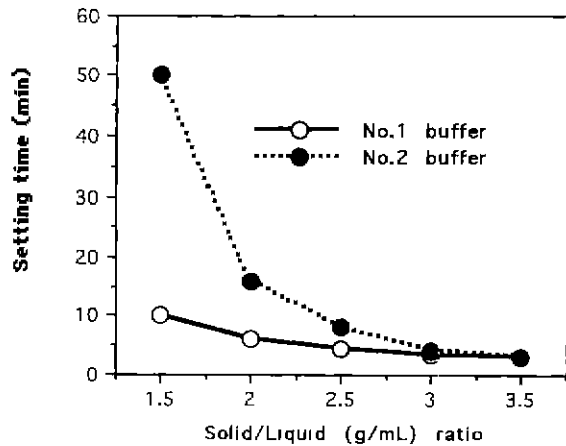


Fig. 7. Setting times measured in No.4 synthesized cement using No.1 buffer solution and No.2 buffer solution as a function of solid to liquid ratio, ranging from 1.5 to 3.5.

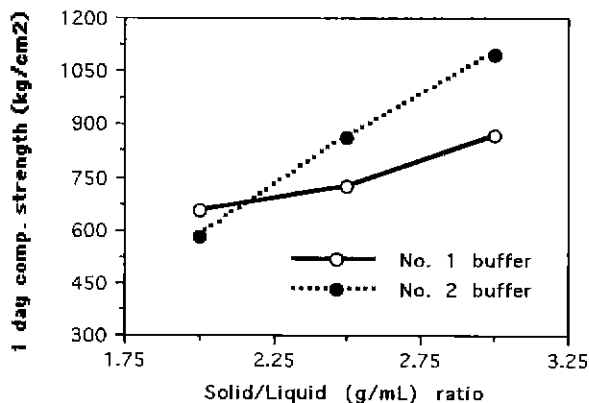


Fig. 8. One day compressive strengths measured in No.2 buffer solution as a function of solid to liquid ratio, ranging from 1.5 to 3.5.

mentioned before; insufficient water content increases setting time and increases the compressive strength development at higher S/L ratio.

## V. Summary and Conclusions

A study of the optimum composition of the cement powder shows that chemical composition influences the setting time and early compressive strength development. The setting time increases as the amounts of zinc oxide and the magnesium oxide are increased. The ground silica, which was added as a filler material, slightly lengthens the setting time. For one day compressive strength development, the cement powder with

the composition 90% ZnO, 8% MgO and 2% silica shows the best results. Magnesium oxide influences the developing strength of the cement at the low magnesium content range, less than 12%. The specimens with a high magnesium content (greater than 12%) develop low one day compressive strengths because of their very rapid setting reaction caused by the magnesium oxide. The ground silica acts as a stabilizer, an inactive filler, contributing to high strength development. The compressive strength development is strongly dependent on the S/L ratio. For most of the specimens, the higher S/L ratio gives higher compressive strength.

Cement-forming liquids also need to be buffered, with both aluminum and zinc ions, for a good consistency and a higher strength of the zinc phosphate cement. These liquids control the setting reactions for all the reactive powders, zincite, periclase and lime. High concentrations of orthophosphoric acid (low content of water) in the cement-forming liquids also generate slow setting reactions because the phosphate acid is less fully ionized in the high concentration solution.

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