

## Effects of colloidal silica suspension mixing on porosity of phosphate-bonded investments after setting and heating processes

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A numerical simulation model, which was based on the setting and heating reactions of the binder phase of phosphate-bonded investment compacts, was developed to compute the porosities of set and burnout compacts. Densities and concentrations of microsilica particles in dilute suspension were measured and input into the simulation model. Validity of the model was confirmed by experimental results, that is, colloidal silica suspensions were prepared using different silica concentrations and mixed with investment powders. Porosities of these set and burnout compacts were experimentally measured. Effects of these factors on the porosity of compacts were examined using the developed simulation model: liquid/powder (L/P) ratio, concentration of microsilica particles in colloidal silica suspension, and ratio of binder component ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) in investment powder. It was concluded that numerical simulation is a viable tool for dental materials research.

**Keywords:** Phosphate-bonded investment, Porosity, Colloidal silica, Refractory, Density

### INTRODUCTION

Numerical simulations of physico-chemical phenomena make it possible for materials science to go from experience-based to science-based. They permit descriptions and forms of material processes which are otherwise impossible to achieve experimentally. While providing the pragmatic benefits of saving time and money, numerical simulations meet the functional criteria of providing good qualitative and quantitative insights. With this slew of advantages, numerical simulations are naturally gaining a strong foothold in the engineering field and well poised to gain wide acceptance in materials science.

In our previous studies, transient thermal stress in gypsum-bonded investments<sup>1,2)</sup> and porosity of gypsum- and phosphate-bonded investments after setting and heating processes<sup>3,4)</sup> were determined using the numerical simulation method and confirmed with experimental results. These simulations were not only rapid and convenient in providing accurate numerical estimates but also provided new and useful insights into the influences of investment powder composition and dental casting procedure in preventing thermal fractures in high-temperature furnaces.

Gypsum-bonded investments are commonly used for the casting of gold alloys. These investment materials produce an expansion which adequately compensates for the shrinkage/contraction of gold alloy during solidification, thus producing castings that meet stringent dimensional requirements. Phosphate-bonded investments, on the other hand, are primarily designed for alloys used to produce copings or frameworks for metal-ceramic prostheses. They are also the universal investment material for base metal alloys (such as Co-Cr and Ni-Cr) and press-die ceramics. In the fabrication

of cast dental restorations, some patterns require the setting expansion to be adjusted. To this end, investments are mixed with a specially prepared colloidal silica suspension, of which its concentration can be adjusted to effect significant changes in setting expansion<sup>5)</sup>. The accuracy of cast dental restorations also depends on the permeability, dimensional accuracy, and strength of the investment mold. Studies have shown that the porosity parameter affects these critical mold properties<sup>6-8)</sup>.

In this study, the effects of different silica concentrations in colloidal silica suspension, which was used as a mixing liquid for phosphate-bonded investment powders, on the porosity of set and burnout compacts was investigated. Investigations were carried out using a numerical simulation model based on theoretical reaction and mass change which occurred during setting and heating processes. Numerical simulation results were then confirmed by experimental measurements.

### MATERIALS AND METHODS

#### *Phosphate-bonded dental investments*

Four commercial phosphate-bonded dental investments were used in this study: two conventional investments *versus* two rapid-heating investments. The two conventional investments used were Velvety (Shofu, Kyoto, Japan; code A) and Ceravest G (GC, Tokyo, Japan; code C). The rapid-heating investments used were Velvety Superquick (Shofu, Kyoto, Japan; code B) and Ceravest Quick (GC, Tokyo, Japan; code D). Investments A and B used the same mixing liquid as recommended by their manufacturers.

#### *Experimental measurements*

To confirm the validity of numerical simulation results, dilute suspensions of different silica concentrations

as well as set and burnout compacts were prepared. All experimental measurements were carried out at room temperature, and the experimental results to be compared against the calculated results.

### 1. Mixing liquid

Densities of as-received liquid and that diluted with distilled water were measured from a weight-to-volume ratio. Each time a 0.1-mL droplet of as-received or diluted liquid was added to dish, the weight would be measured using a microbalance (AUW220D, Shimadzu, Kyoto, Japan). This step continued until the volume of liquid reached 1.0 mL. pH of as-received liquid was measured using a pH meter (F-52, Horiba, Kyoto, Japan).

To measure the density of silica solute in as-received liquid, the as-received liquid was kept in a desiccator with silica gel for 7 days. Dried powder obtained was silicon dioxide gel with adsorbed water. Dehydrated powder was obtained by heating silicon dioxide to 200°C and then cooled in ambient air. Density of heated/dehydrated powder was obtained after measuring the volume and weight of dry and heated/dehydrated powders using a gas pycnometer (AccuPyc 1330, Shimadzu, Kyoto, Japan) and the microbalance respectively.

### 2. Mixing and setting of investment casting slurries

As-received investment powders were mixed with as-received liquid or diluted liquid at liquid-powder (L/P) ratios recommended by their manufacturers. Mixed slurry was poured into a polyethylene mold of 8 mm outer diameter, 6 mm inner diameter, and 10 mm height. The top and bottom surfaces of the mold were each clamped with a glass plate for 30 min. After which, the mold was removed and the slurry mixture was left to set in ambient air. Outer dimensions of each set sample were measured using a digital caliper.

To prepare dry set samples which were hardened samples with extremely low excess water content, set samples were kept in a desiccator with silica gel for 1 day. For burnout samples, they were left to set for 180 min in ambient air after mixing with liquid, heated at a rate of 5°C/min up to 800°C, and then cooled to room temperature.

For set and burnout compacts, their individual density  $\rho$  was calculated from its weight and outer dimensions. Solid density  $\rho_s$  of each type of compact was calculated from its weight and volume measured using the gas pycnometer. Porosity  $P$  of each type of compact was computed from its density  $\rho$  and solid density  $\rho_s$  as follows:

$$P = 1 - \rho / \rho_s \quad (1)$$

#### Numerical simulation model

1. Concentration of microsilica particles in mixing liquid  
Assuming that each as-received liquid was a mixture of distilled water and amorphous silica particles, its density  $\rho$  and volume  $V$  are presented as follows:

$$\rho_L V_L = \rho_S V_S + \rho_W V_W \quad (2)$$

$$V_L = V_S + V_W \quad (3)$$

Here, as-received liquid, silica and water in suspension are represented by subscripts  $L$ ,  $S$ , and  $W$  respectively. The following equation was then derived:

$$\frac{V_S}{V_L} = \frac{\rho_L - \rho_W}{\rho_S - \rho_W} \quad (4)$$

Mixing ratio of as-received liquid to water at 1:k is presented as follows:

$$V_L : V_T = 1 : k \quad (5)$$

Here, added distilled water is represented by subscript  $T$ .

Resulting liquid after dilution (subscript  $G$ ) is presented as follows:

$$\rho_G V_G = \rho_L V_L + \rho_W V_T = (\rho_L + k\rho_W) V_L \quad (6)$$

$$V_G = V_L + V_T \quad (7)$$

Thus, the following equation was derived:

$$\frac{V_L}{V_G} = \frac{\rho_G}{\rho_L + k\rho_W} \quad (8)$$

The liquid/powder (L/P) mixing ratio,  $m$ , is the ratio of mixing liquid volume  $V_G$  mL to weight of as-received powder  $W_0$  g. Thus,  $V_G$  could be calculated from the following equation:

$$V_G = m W_0 \quad (9)$$

Concentration of silica in dilute suspension is thus given as follows:

$$\frac{W_S}{W_G} = \frac{\rho_L - \rho_W}{\rho_S - \rho_W} \cdot \frac{\rho_S}{\rho_L + k\rho_W} \quad (10)$$

Volume of reacted water  $V_R$  which dissipated during the setting reaction and that of excess water  $V_E$  in the mixed slurry, which were already derived in a previous study<sup>4</sup>, are given as follows:

$$V_R = \frac{5M_W}{M_A} \cdot \frac{\rho_A}{\rho_W} V_A \quad (11)$$

$$V_E = V_G - V_R \quad (12)$$

where  $M$  is the molecular weight of each component and subscript  $A$  represents  $\text{NH}_4\text{H}_2\text{PO}_4$  in as-received powder.

### 2. Porosities of set and burnout compacts

Equations to calculate the porosity and density of compact which had been mixed with water were already shown in a previous study<sup>4</sup>. These values were calculated from the volume and mass data of investment powder

components (binder (P) and refractory (X)), water content in mixed slurry (G), reaction product  $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$  (D), and burnout product  $\text{Mg}_2\text{P}_2\text{O}_7$  (F). After volume  $V_S$  of colloidal silica in mixing liquid was input into the equations derived in the previous study<sup>4</sup>, the following equations were derived:

$$P_1 = 1 - \frac{V_D + V_X + V_S}{(V_P + V_X + V_G)(1 + 3\alpha)} \quad (13)$$

$$P_2 = 1 - \frac{V_F + V_X + V_S}{(V_P + V_X + V_G)(1 + 3\alpha)} \quad (14)$$

Where, subscript 1 and 2 represent dry set compact (wherein excess water from set compact was removed) and burnout compact respectively. The term  $\alpha$  is the linear setting expansion.

## RESULTS

### Densities and concentrations of microsilica particles

Densities of silica particles in dried powders (kept in desiccator) and heated powders (by dehydration) are shown in Table 1. Densities of dried powders were low compared to heated powders because the former had adsorbed water *i.e.*, hydroxyl groups. The estimated densities in heated powders were almost the same as that of amorphous silica<sup>9</sup>.

Experimentally measured results of the densities of silica particles in dilute solutions well agreed with the calculated results using densities of as-received liquids. Substituting the solid density of silica particles,  $\rho_s$ , into Eq. (10), the concentration of silica particles in each dilute

Table 1 Densities of silica particles in as-received mixing liquids ( $\text{g}/\text{cm}^3$ )

As-received liquid	Dried powder (SD)	Heated powder (SD)
A and B	1.98 (0.04)	2.24 (0.02)
C	1.91 (0.02)	2.22 (0.01)
D	1.77 (0.01)	2.16 (0.03)

Table 2 Concentrations of silica particles in mixing liquids (mass%)

Investment	pH	Ratio of dilution (as-received liquid : distilled water)				
		1:2	1:1	2:1	4:1	1:0
A and B	9.1	16.2	23.2	29.7	34.5	41.2
C	3.7	11.7	16.9	21.9	25.7	31.0
D	9.8	10.1	14.8	19.2	22.5	27.3

solution was computed and shown in Table 2 alongside the pH values of as-received liquids. Concentrations of silica particles in commercial colloidal silica liquids commonly range from 20% to 40%<sup>10</sup>—within which was the range of silica concentrations of as-received liquids used in this study.

### Porosities of set and burnout compacts

For compacts which were prepared using dilute suspensions mixed with distilled water according to manufacturers' instructions, their measured porosities are shown in Figs. 1 and 2. Density of mixing liquid is taken as abscissa. Solid and dashed lines represent

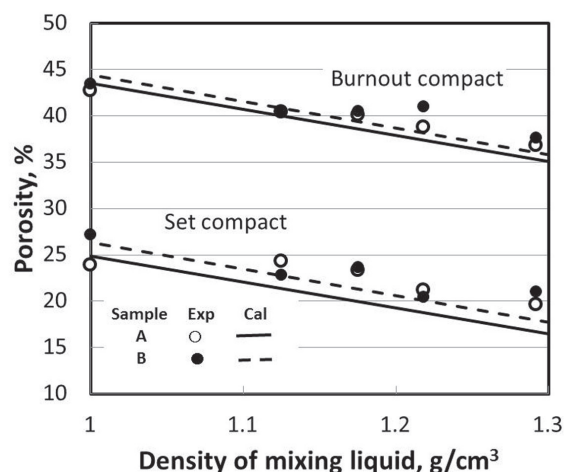


Fig. 1 Porosities of set and burnout compacts of investments A and B which were mixed with different concentrations of colloidal silica suspension as recommended by manufacturer.

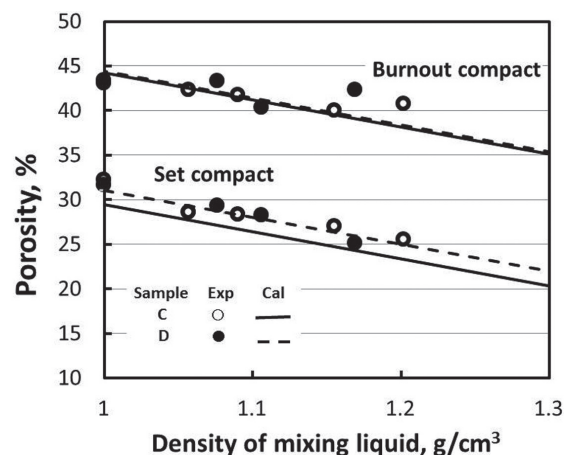


Fig. 2 Porosities of set and burnout compacts of investments C and D which were mixed with different concentrations of colloidal silica suspension as recommended by manufacturer.

theoretical results computed using Eqs. (13) and (14). Experimentally measured porosities were higher than calculated results using the simulation procedure.

The porosity of phosphate-bonded investments is generally lower than that of gypsum-bonded investments<sup>3,4</sup>. For this reason, special additives are added to commercial phosphate-bonded investment powders to increase their permeability during casting. As for the solvents of as-received mixing liquids, they are typically not distilled water. They contain special ions such as sodium which may affect the setting reaction. Consequently, the densities of microsilica particles in as-received liquids are not chemically stable in the setting and heating processes, which then affect the porosities of set and burnout compacts. An investment mixed with as-received liquid typically shows higher setting expansion than that mixed with water. Therefore,  $\alpha$  in Eqs. (13) and (14) is high compare to the input data in this study, and input with a higher value to arrive at a more accurate porosity estimate.

Taking into consideration the factors which affect the setting and heating processes of phosphate-bonded investments and using a higher linear setting expansion in Eqs. (13) and (14), the computed results for both set and burnout compacts agreed well with the experimental results. Differences in porosity between the computed and experimental results for set and burnout compacts were 0.3–2.5% and 0.6–1.2% respectively. Therefore, the numerical simulation model used in this study was reliable in estimating the porosities of set and burnout compacts of phosphate-bonded investments.

Set compacts of rapid-heating investments had higher porosity than the conventional investments. This was because the density of quartz (2.651 g/cm<sup>3</sup>) is higher than that of cristobalite (2.352 g/cm<sup>3</sup>). From this rapid-heating investments had a higher volume of liquid added during mixing under the same L/P ratio for both type of investments. For burnout compacts, rapid-heating and conventional investments had almost the same porosity. This meant that permeability would not be affected during casting of dental alloys<sup>6–8</sup>.

## DISCUSSION

Estimating the porosities of set and burnout compacts by numerical simulation helps to predict the permeability and strength of mold during investment casting. These useful data could even be leveraged to design and develop a new investment material. More importantly, the validity of a numerical simulation model in estimating the porosities of set and burnout compacts could be confirmed by comparing against experimental results.

In this study, the densities and porosities of set and burnout compacts were estimated by entering these data into a numerical simulation model: composition of investment powder (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, MgO, and refractory components such as cristobalite and quartz), L/P ratio, and concentration of silica particles in colloidal silica suspension. Results obtained in this study were then used to investigate the effects of these factors on the

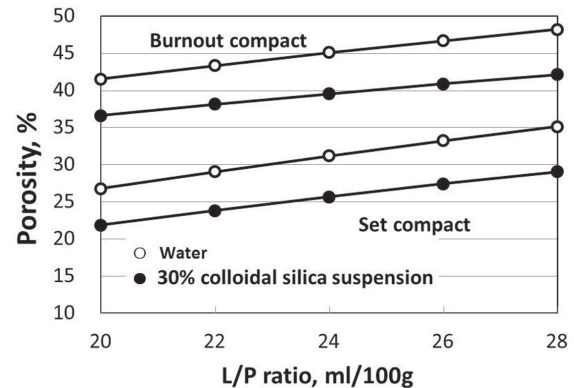


Fig. 3 Simulated results for the porosities of set and burnout compacts which were mixed with a range of L/P ratios.

Computed results for mixing investment powder with water or 30% colloidal silica suspension are depicted.

porosity of set and burnout compacts of phosphate-bonded investments: L/P ratio of mixing liquid, silica concentration in mixing liquid, and ratio of ammonium dihydrogen phosphate (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) in investment powder.

### Effects of L/P ratio and silica concentration of mixing liquid on porosity of compacts

Figure 3 shows the computed results for the porosities of set and burnout compacts *versus* the L/P ratio of mixing liquid. The mixing liquid used was water or 30% colloidal silica suspension. To ensure slurry was at the desired consistency, the selected L/P ratio ranged between 20 and 28 mL/100 g. For the investment powder, the blending ratio (mass%) of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, MgO, quartz, and cristobalite was assumed to be 1:1:1:7. Linear setting expansion was assumed to be 1.86%. Results showed that L/P ratio was a significant factor in determining the porosity of set and burnout compacts. Simulation also revealed that compacts prepared with water as a mixing liquid had higher porosities than mixing with colloidal silica suspension.

Volume of mixed slurry which was poured into a mold was the sum of the volumes of investment powder and mixing liquid. When water was used as the mixing liquid, water content increased with increase in L/P ratio. As water which dissipated during the setting reaction remained unchanged irrespective of L/P ratio, excess water ( $W_E$ ) concomitantly increased with increase in L/P ratio. Therefore, water increment in poured slurry was due to gain in excess water volume. As the volume of binder phase after setting reaction was also not affected by L/P ratio, the volume of excess water in set compact increased with increase in L/P ratio, which then caused more pores to be formed in the compact after the setting process. As a result, porosity increased with increase in L/P ratio.

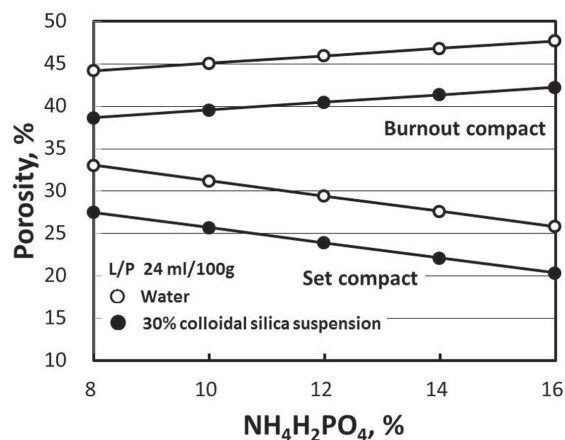


Fig. 4 Simulated results for the porosities of set and burnout compacts according to different contents of  $\text{NH}_4\text{H}_2\text{PO}_4$  in investment powder.

Computed results for mixing investment powder with water or 30% colloidal silica suspension are depicted.

Colloidal silica suspension consisted of microsilica particles and water. When colloidal silica suspension was used as the mixing liquid, water content in the suspension was lower at the same L/P ratio as compared to water being used as the mixing liquid. As water, which dissipated during the setting reaction remained unchanged irrespective of L/P ratio, excess water ( $W_E$ ) concomitantly decreased for the same L/P ratio. As a result, porosity of set compact decreased due to decrease in volume of excess water. Besides, microsilica particles in the suspension remained in the set compact after the setting reaction. Therefore, porosity decreased because of the content of silica particles. If the microsilica particles did not react with other components during the heating process, the porosity of burnout compact also decreased because of the preceding lower porosity of set compact.

#### Effect of binder component ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) on porosity of compacts

Figure 4 shows the computed results for the effect of binder phase on the porosity of set and burnout compacts. Blending ratio (mass%) of MgO, quartz, and cristobalite in the investment powder was assumed to be 1:1:7. Content of  $\text{NH}_4\text{H}_2\text{PO}_4$  ranged between 8% and 16%, while L/P ratio was fixed at 24 mL/100 g. Results showed that the ratio of  $\text{NH}_4\text{H}_2\text{PO}_4$  in investment powder was a significant factor in determining of the porosity of set and burnout compacts.

Density of investment powder decreased with an increase in the ratio of  $\text{NH}_4\text{H}_2\text{PO}_4$ . This was because the density of  $\text{NH}_4\text{H}_2\text{PO}_4$  ( $\rho=1.803 \text{ g/cm}^3$ ) was lower than the other components of the investment powder. When under the same L/P ratio (*i.e.*, 24 mL/100 g), the volume of mixing liquid decreased and the volume of water which dissipated during the setting reaction

( $V_R$ ) increased. Therefore, excess water ( $W_E$ ) in set compact decreased, resulting in lower porosity of the set compact.

Amount of MgO which reacted with  $\text{NH}_4\text{H}_2\text{PO}_4$  to form the binder phase increased with increase of  $\text{NH}_4\text{H}_2\text{PO}_4$  content, consequently reducing the mass of MgO as a refractory component. Volume of  $\text{Mg}_2\text{P}_2\text{O}_7$ , which was formed after the heating process, increased with an increase in binder phase. Density of  $\text{Mg}_2\text{P}_2\text{O}_7$  ( $\rho=2.60 \text{ g/cm}^3$ ) was higher than that of  $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$  ( $\rho=1.71 \text{ g/cm}^3$ ). As result, the volume of burnout compact was reduced under an unchanged apparent volume, causing the porosity to increase.

## CONCLUSION

The effects of different concentrations of silica particles in colloidal silica suspension on the porosity of set and burnout compacts of phosphate-bonded investments were experimentally and theoretically determined. Validity of the theoretically computed simulation results was confirmed using the experimental results. The numerical simulation model developed in this study was used to investigate the effects of these factors on the porosity of investment compacts: L/P ratio, silica concentration in mixing liquid, and ratio of  $\text{NH}_4\text{H}_2\text{PO}_4$  in investment powder. It was concluded that numerical simulation is a viable tool to be used in the dental field for research on investment casting.

## APPENDIX

Subscripts for liquid	Representation
W	Water in as-received suspension
L	As-received liquid
S	Silica in as-received liquid
T	Distilled water added to suspension
G	Liquid after dilution
R	Water dissipated during setting reaction
E	Excess water
Subscripts for powder/solid phase	Representation
0	As-received powder
A	$\text{NH}_4\text{H}_2\text{PO}_4$
B	MgO
D	$\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$
F	$\text{Mg}_2\text{P}_2\text{O}_7$
P	Binder
X	Refractory

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