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Quantitative analysis of unreacted hemihydrate in set dental stone by adiabatic calorimetry

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The unreacted hemihydrate in set dental stone was estimated quantitatively by means of specific heat measurements. With decreases in the water-to-powder ratio (W/P), increases were observed in the amount of unreacted hemihydrate in the set mass. These increases were marked in set stone with a W/P ratio less than 0.25. Furthermore, the amount of unreacted hemihydrate was higher in the interior of the dental stone than in the set surface. It is very difficult to attain a complete reaction, even with higher W/P ratios such as 0.8 in the dental mixing procedure.

1. Introduction

Set dental plaster and stone consist mainly of calcium sulphate dihydrate as a reaction product and calcium sulphate hemihydrate as an unreacted material. In the powder–liquid mixing method generally utilized with dental materials, the hydration reaction never goes to completion. Therefore, it is very important to estimate the amount of unreacted material in set gypsum, because the surface roughness [1] and strength [2] in the set mass are influenced by the residual hemihydrate.

Lautenschlager *et al.* [3] determined actual amounts of gypsum products at various times during setting by X-ray diffraction (XRD). However, the focus of their study was not the unreacted materials in the set mass. Mori and Yamane [4] first performed quantitative analysis of the unreacted hemihydrate in set plaster and stone with each standard water-to-powder (W/P) ratio by XRD. However, questions remain concerning precision because the grinding during the preparation of XRD samples leads to dehydration by mechanochemistry [5]. The aim of the present study was to quantitatively analyse the unreacted hemihydrate in set stone at various W/P ratios by means of specific heat measurements to obtain more accurate data.

2. Experimental procedures

Dental stone (New Plastone 230911, GC Corp., Tokyo, Japan) and reagent grade gypsum (calcium sulphate, G25448A, Kishida Chem. Co. Ltd, Osaka, Japan) were used in the present study. By XRD, small amounts of dihydrate and hemihydrate impurities were detected in the dental stone and gypsum, respectively, and X-ray integrated intensity ratios of hemihydrate 100 to dihydrate 020 were 36.3 and 0.006, respectively. The manufacturer's recommended W/P ratio is 0.24. 50 g of powder stone was mixed for 60 s at W/P ratios of 0.215, 0.22, 0.23. 0.24, 0.25, 0.26, 0.3, 0.35, 0.4, 0.5, 0.6, 0.7 and 0.8 with a vacuum mixer (VM-112, J. Morita Corp., Osaka, Japan) operated at a rotational speed of 365 rpm under reduced pressure. The slurry was poured into two sets of sample holders with a disc shape 30 mm diameter and 2 mm thick. Specific heat measurements were made on the set materials over a period of 48 h at a temperature of about 25 °C and a relative humidity of 50–60% after mixing. Storage conditions of the specimens were thought to be suitable, because when set stones with W/P ratios of 0.22 and 0.3 were left under the above conditions, we observed constant weight loss at 24 h after mixing. Heat was measured in air at 0.1 mV intervals in a CA thermocouple with an adiabatic scanning calorimeter (SH-2000, Shinkuriko Ltd. Co., Yokohama, Japan) using 0.3 W of electrical power.

To confirm the presence of unreacted hemihydrate, one set of samples was used for XRD at 50 kV and 150 mA (RAD-rA, Rigaku Corp., Tokyo, Japan) and another set for scanning electron microscopy (SEM) at 20 kV (S-520, Hitachi Co., Tokyo, Japan). Both experiments were performed on the set mass and on the fracture surface to estimate differences. In the XRD study in particular, the integrated intensity ratio of each reflection line of the hemihydrate and the dihydrate were measured.

3. Results and discussion

3.1. Confirmation of the unreacted hemihydrate

Fig. 1 shows the XRD profile of set stone mixed at a W/P ratio of 0.24 where *d* and *h* denote dihydrate and hemihydrate, respectively. It was obvious that a considerable amount of unreacted hemihydrate was

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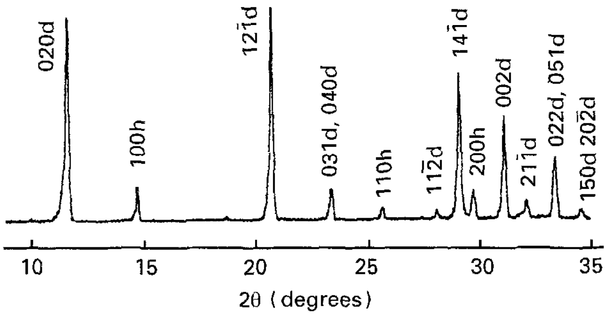

Figure 1 X-ray diffraction line profile in the set stone mixed with a W/P ratio of 0.24. d and h denote dihydrate and hemihydrate, respectively.

present in the set mass. The existence of unreacted hemihydrate was detected for all W/P ratios investigated, suggesting that complete hydration could never be achieved with mechanical mixing as used in the present experiment.

Fig. 2 shows SEM images of the set mass and fracture surfaces in set samples with W/P ratios of 0.8 and 0.22. The specimen with the higher W/P ratio (0.8) showed well-grown needle-like dihydrate structures (Fig. 2a and b), while the lower W/P ratio specimen (0.22) showed poor dihydrate growth (Fig. 2c and d). It is noteworthy that both set stones showed better dihydrate crystal growth on the set mass than on the fracture surface. Fig. 2c and d suggest the presence of unreacted hemihydrate, because no needle-like crystal characteristic of dihydrate were observed and only irregular surface structures were seen. Direct evidence to support this was obtained by XRD. Fig. 3 shows variations of the X-ray integrated intensity ratio I_h/I_d between reflection lines of hemihydrate 100 and dihydrate 020 with W/P ratio on the surface and the interior of the set stone. Several samples were

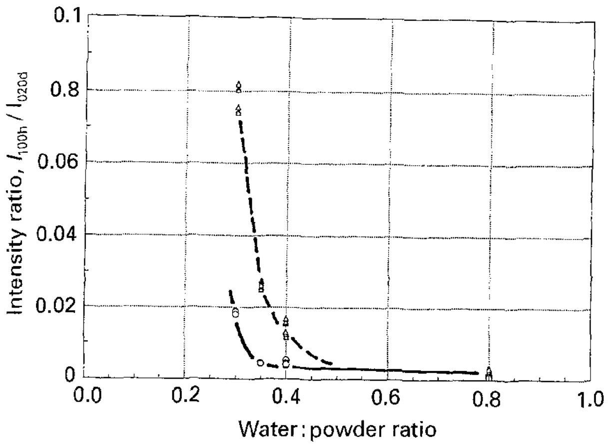

Figure 3 Variation of X-ray integrated intensity ratio between reflection lines of hemihydrate 100 and dihydrate 020 with W/P ratio on the set surface (○) and the interior (△).

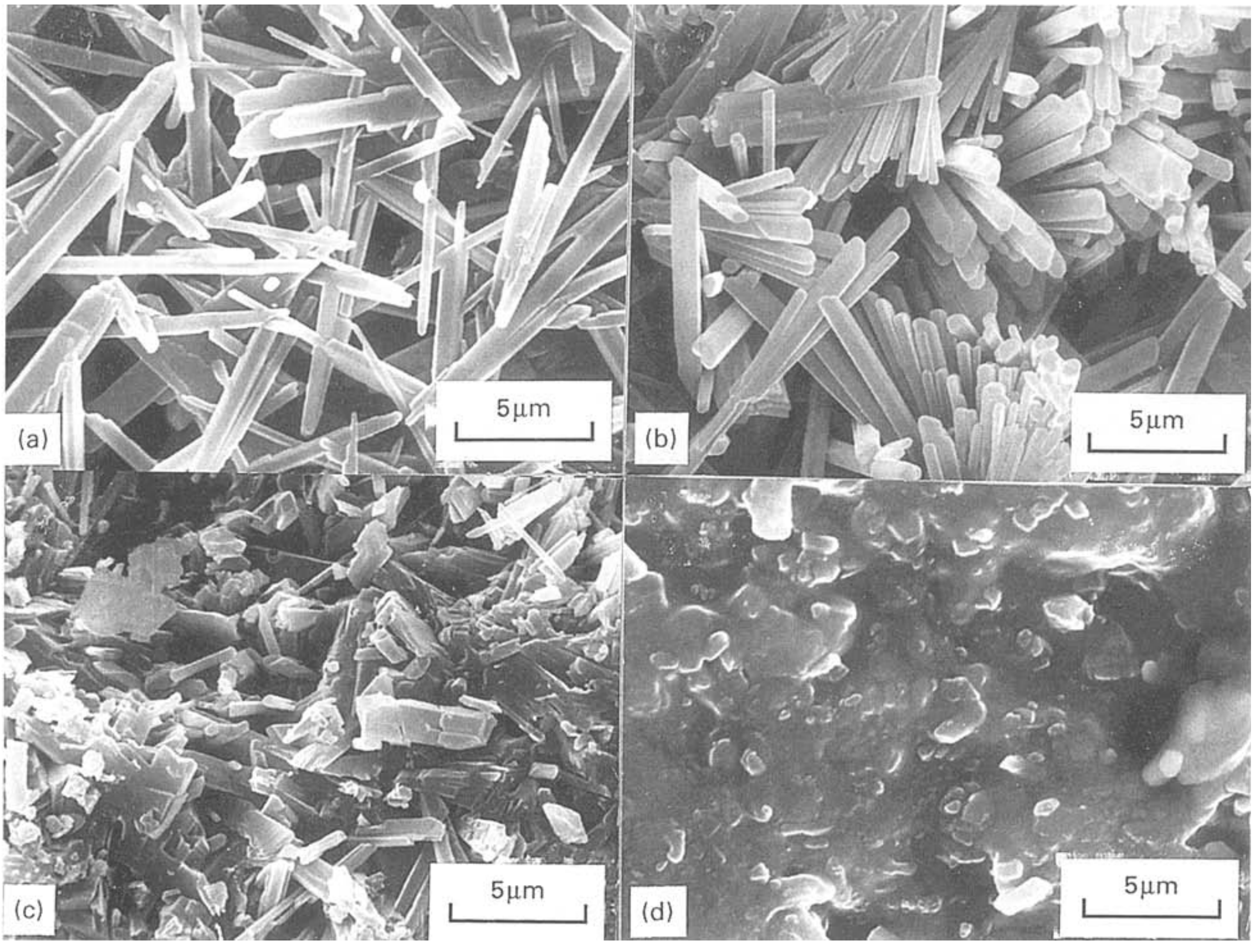

Figure 2 SEM images of (a) the set surface, (b) the fracture surface of a specimen mixed with W/P ratio of 0.8, and of (c) the set surface, (d) the fracture surface of a specimen with W/P ratio of 0.22.

prepared to confirm that the measurements were reproducible, and average values are shown in the figure. The standard deviation increases with decreasing W/P ratio, and the maximum 0.003 in the inner part of the set stone with a W/P ratio of 0.3. The amount of unreacted hemihydrate was obviously higher in the interior than on the surface. When the slurry is poured into a vessel to set, water collects near the surface. As a result, the surface shows good dihydrate crystal growth because much more water is present, while the reverse is true of the interior. Therefore, if quantitative analysis of unreacted hemihydrate in set stone is performed only on the set surface by XRD, a considerable degree of error is bound to occur. To overcome the heterogeneity, Mori and Yamane [4] used crushed powder samples for XRD analysis. However, some questions remain regarding the orientation of the crystals. There are no data concerning the quantity of unreacted hemihydrate at high W/P ratios as they only measured dental stones with a standard W/P ratio. Further quantitative analyses are expected to provide more precise data.

3.2. Specific heat measurements

Fig. 4 shows specific heat curves in stone powder and reagent grade gypsum, which correspond to hemihydrate and dihydrate, respectively. One or two endothermic peaks can be seen in this figure. Similar data have been reported previously by differential thermal analysis. According to Matsuya *et al.* [5, 6], the dehydration of the gypsum occurs in two steps; $CaSO_4 \cdot 2H_2O \xrightarrow{(a)} CaSO_4 \cdot \frac{1}{2}H_2O \xrightarrow{(b)} CaSO_4$, while that of stone powder proceeds in only one step; $CaSO_4 \cdot \frac{1}{2}H_2O \xrightarrow{(b)} CaSO_4$. We can estimate the mass of dihydrate or hemihydrate from the quantity of endothermic heat for each reaction. If a specimen consists of dihydrate and hemihydrate, the second peak (b) is expected to increase and the first peak (a) to decrease compared with the sample containing only dihydrate. Fig. 4 shows a specific heat curve obtained from a mixture of 50% dihydrate and 50% hemihydrate. As might be expected, the first peak (a) was markedly decreased in comparison with that of the dihydrate-only sample (△). In this case, the amount of dihydrate can be estimated from the quantity of heat of the first peak. Details of the analysis are given in the Appendix.

As mentioned above, the set stone consisted of dihydrate and hemihydrate. Fig. 5 shows specific heat curves of set stone samples with W/P ratios of 0.22, 0.24 and 0.6. As the W/P ratio decreased, the heat of the second peak increased relative to that of the first peak. This suggests that the amount of unreacted hemihydrate increases in the set mass. The dehydration of set stone with a lower W/P ratio such as 0.22 seems to occur in three steps with an additional peak on the lower temperature side of the first peak. As can be seen in Figs 4 and 5, the heat of the endothermic reaction in the first peak was considerably greater than that in the second. It usually took two or three hours at the first peak for a temperature elevation of 0.1 mV in the CA thermocouple (about 2.5 °C).

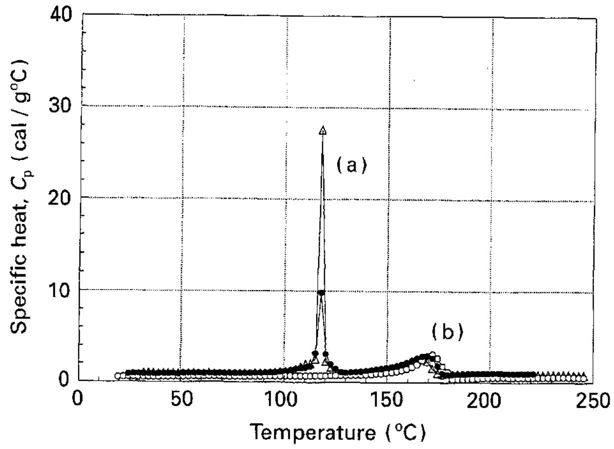

Figure 4 Specific heat curves of hemihydrate (○), dihydrate (△), or 1:1 mixture (●) samples.

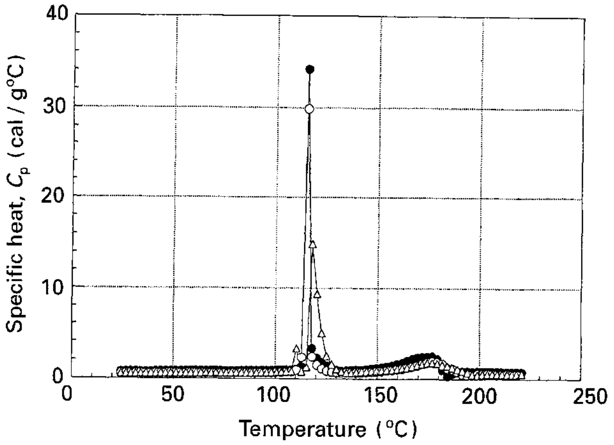

Figure 5 Specific heat curves of set stone mixed with a W/P ratio of 0.22 (△), 0.24 (○) or 0.6 (●).

Therefore, we detected no temperature rise under a constant electric power supply but rather a temperature drop at the first peak. We observed a maximum temperature drop of 4.2 °C, depending on the amount of sample, and differences were observed in the behaviour of samples with regard to this temperature drop and rise depending on the W/P ratio. During dehydration of set stone with higher W/P ratios, the temperature decreased very slowly with a subsequent increase, again very slowly, after levelling out briefly. On the other hand, in samples with lower W/P ratios, the temperature drop and subsequent increase were produced quickly, resulting in an additional peak. The first large peak was attained very slowly. Generally, increases in W/P ratio in dental stone result in increases in porosity of the set stone [4, 7]. As decreasing the W/P ratio results in a more rigid mass, this presumably makes escape of free water during dehydration very difficult, especially at the central part of the set stone. Therefore, hydration in the vicinity of the surface will produce the observed additional peak, and the first large peak will be produced by dehydration in the central parts of the set stone very slowly because of this hindrance to the escape of free water. Water vapour generated from gypsum is expected to

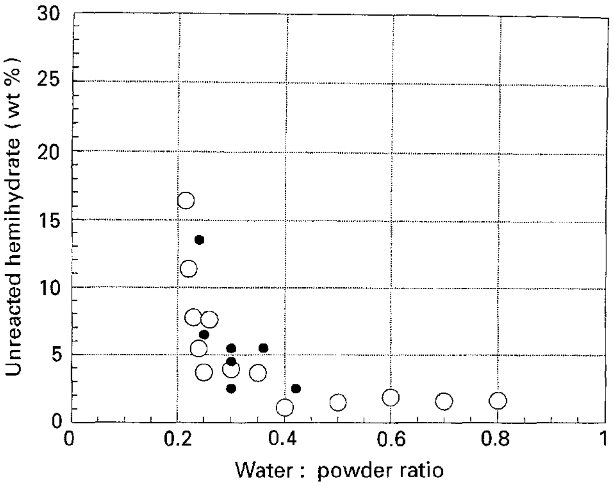

Figure 6 Variation of unreacted hemihydrate in set stone with W/P ratio estimated by specific heat measurements in the present study (○) and by XRD (●) by Mori and Yamane [4].

accumulate around the dehydrated product as reported previously by Miyazaki [8]. We showed two-step dehydration in a powder sample of crushed set stone with a low W/P ratio of 0.21 [9]. This was attributable to the bulk of this lower W/P ratio specimen and is not inherent. The data analysed are shown in Fig. 6. A high W/P ratio (0.4–0.8) produced set stone with a small amount of unreacted hemihydrate, while a low W/P ratio below 0.25 caused marked increases in the amount of unreacted hemihydrate. The results reported by Mori and Yamane [4] are also shown in Fig. 6 for comparison, the tendency being for these data points to be in agreement with those of the present study. The levels of unreacted hemihydrate estimated in the present study, however, also showed some deviations. It is very difficult to accomplish perfect adiabatic control in specific heat measurements, especially when the reaction heat is very high. Therefore, some thermal leakage cannot be avoided, thus producing a degree of error. The level of unreacted hemihydrate increased abruptly in set stone with a W/P ratio less than about 0.25, with the maximum amount of unreacted hemihydrate reaching about 16.5 wt %. This suggests that the use of a W/P ratio lower than the standard causes difficulty in the mixing of powder and water. When dental stone is mixed at a W/P ratio that is too low, the strength and durability of the set mass decreases. With respect to the results of the present study, W/P ratios of less than 0.24 (below which unreacted hemihydrate markedly increased in the set stone) should be avoided. Complementary studies of mechanical properties would have given some indication of the sensitivity of the mechanical properties to small changes ratios at these low W/P ratios, and such studies are currently in progress in our laboratory.

Appendix

Assuming that a set stone contains the dihydrate ($CaSO_4 \cdot 2H_2O$) x(g) and the hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) y(g), the sample weight, W is given by;

$$W = x + y \tag{1}$$

Total endothermic heat, $T_{(\mathrm{cal})}$, as determined by adiabatic specific heat measurement can be expressed by the following equation;

$$T = xM_2 + \left(x \times \frac{V_{0.5}}{V_2}\right) \times M_{0.5} + yM_{0.5} \tag{2}$$

The first and second terms on the right-hand side of Equation 2 correspond to the heat given by hemihydrate formation from dihydrate and anhydrate generation from hemihydrate in $CaSO_4 \cdot 2H_2O$ of the set stone, respectively. The third term corresponds to the heat of anhydrate formation from hemihydrate in $CaSO_4 \cdot \frac{1}{2}H_2O$ of the set stone which was present before heating. M_2 and $M_{0.5}$ are the endothermic heats per gram (cal/g) which corresponds to the reaction heat from pure dihydrate to hemihydrate and from pure hemihydrate to anhydrite, respectively. In practice, the constants M_2 and $M_{0.5}$ can be determined from measurements in pure dihydrate and pure hemihydrate. In the present study, the averages of five measurements each were adopted as the value of M_2 and $M_{0.5}$. V_2 and $V_{0.5}$ represent the molecular volume of dihydrate and hemihydrate, respectively. Therefore, only x and y are unknown in Equations 1 and 2.

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