Improving the properties of dicalcium phosphate dihydrate (DCPD) powder by changing the morphology

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Dicalcium phosphate dihydrate (DCPD, CaHPO₄·2H₂O) has attracted attention as an environmental material recently because it reacts selectively with fluoride ions and transforms them into the highly stable, non-toxic material fluoroapatite [FAp, Ca₁₀(PO₄)₆F₂]. During this chemical reaction, the FAp particles retain their approximate shapes; in other words, DCPD particles act as templates for FAp particles. Our previous studies showed that the morphology of DCPD particles with tabular and petaloid shapes is controllable by use of a crystallization parameter under conditions of solution synthesis. DCPD has various applications, such as treatment of wastewater and polluted soil. Materials used for environmental purposes require not only appropriate chemical reactivity but also various powder properties to make them usable under various conditions. Thus, in this study, we compared the typical powder properties (bulk and tap densities, compressibility, Carr’s flowability index, sedimentation rate, and permeability) of the different morphologies of DCPD in terms of their suitability for environmental applications. The obtained results show that petaloid-shaped particles offer superior usability as compared to tabular-shaped particles.

Key-words : Calcium phosphate, Morphology, Flowability, Permeability

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1. Introduction

Dicalcium phosphate dihydrate (DCPD, or brushite; CaHPO₄·2H₂O) has attracted widespread attention for such applications as precursors for the main components of biomaterials¹ or toothpaste additives in the dental field.² The reactivity of DCPD with fluoride ions in aqueous solutions is useful for environmental purposes. We have revealed that DCPD has high potential for selective reactivity with fluoride ions in wastewater and polluted soil.³ Research on controlling the morphology of DCPD particles has relevance for the aforementioned purposes, because their chemical reactivity and physical properties are determined by their surface condition, size, and shape.⁴ In the case of solution synthesis, both Miller et al.⁵ and our group reported effective parameters for controlling the morphology of DCPD particles; examples include the initial pH value and concentration,⁶ coexistence ions⁷ and mixing process.⁸ Modification of these parameters makes it possible to control the morphology of DCPD particles in terms of the tabular and petaloid shapes.

DCPD reacts with fluoride ions in wastewater and polluted soil when transformed into fluoroapatite [FAp; Ca₁₀(PO₄)₆F₂], which shows higher stability and lower solubility than the environmental standard.⁹–¹¹ Unfortunately, the reaction required to form precursor on the particle surfaces is excessively time consuming. Such problems associated with formation of the precursor can be solved by induction of a nano-scaled precursor on DCPD particles as an effective pretreatment method; this enhances the chemical reactivity such that it approaches the theoretical efficiency and proceeds with low concentrations of fluoride ions.¹²,¹³ This pretreatment prepares DCPD by providing it with the appropriate qualities and the ability to perform fluoride ion immobilization more effectively than existing competing methods,¹⁴ such as methods using aluminum sulfate,¹⁵ physical adsorption with carbonized bone (bone char),¹⁶ and application of various adsorbents.¹⁷ On the other hand, no studies have investigated the powder properties of DCPD particles. We reported that the morphology is roughly maintained during the chemical conversion from DCPD to FAp,¹⁹ that is, DCPD can be used as a template for FAp. The particle morphology could therefore be used to enhance the usability of DCPD, and this could lead to applications such as improved separation of sludge.

The aim of this work is to compare various physical properties, such as the bulk and tap densities, compressi-
bility for checking powder aggregation performance, and Carr’s flowability index.19 Our research led to development of a detailed procedure for deducing indices for every flowability parameter and an explanatory summation of these indices to yield a parameter indicative of the tendency of a powder to exhibit floodable flow, sedimentation rate, and the permeability of tabular- and petaloid-shaped particles. Of particular note, the usability of petaloid-shaped DCPD particles was found to exceed that of tabular-shaped DCPD particles in terms of their coefficient of slurry, sedimentation rate, and permeability. This raises the possibility of controlling the morphology of environmental materials to reduce the cost of treating wastewater and polluted soil.

2. Experimental procedures

2.1 Preparation of the samples

We compared the following physical properties by using typical petaloid- and tabular-shaped DCPD particles. Figure 1 shows scanning electron microscope (SEM) images of the DCPD particles we used in this study. The petaloid-shaped samples A are a gelatin byproduct synthesized by adding milk of lime to a monocalcium phosphate solution under acidic conditions according to the following formula (1):20

$$\text{Ca(H}_2\text{PO}_4\text{)}_2 + \text{Ca(OH)}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}. \quad (1)$$

The petaloid-shaped sample B and tabular-shaped sample D were synthesized by mixing starting solutions of calcium hydroxide [Ca (OH)2, Wako, 96.0%] and phosphoric acid (H3O4P, Wako, 85% aq.). The starting solutions were prepared in 200 mL glass beakers; we measured the calcium hydroxide powder and phosphoric acid to adjust the initial concentration to 1.0 mol/L. We mixed two solutions by adding one to the other at a dropping rate of 1.0 ml/min with stirring by stirring blade (200 rpm).

Sample B was obtained by dropping calcium hydroxide slurry into phosphoric acid, and sample D was obtained by dropping phosphoric acid into calcium hydroxide slurry, respectively. The chemical reaction between samples B and D is formula (2):

$$\text{Ca(OH)}_2 + \text{H}_3\text{O}_4\text{P} \rightarrow \text{CaHPO}_4 \cdot 2\text{H}_2\text{O}. \quad (2)$$

Tabular-shaped sample C was the commercial chemical (Taihei Chemical Industrial Co.). These same petaloid and tabular-shaped particles can be made separately through solution synthesis.6–8

2.2 Bulk and tap density measurements

We measured the bulk and tap density according to the Japanese Industrial Standard (JIS) R1628, which is a test method for determining the bulk density of fine ceramic powder. The DCPD samples were carefully arranged according to the size of the secondary particles using a screen wire mesh with a mesh size of 1.0 mm. Thus, 80 g of each sample was weighed and poured into a 200-mL measuring cylinder while that ensuring the sample surface remained flat without the use of pressure. We measured the initial volume \(v_0\) of the sample to observe the bulk density.

We then placed the measuring cylinder on a tapping apparatus and measured the volume after every 100 tapping operations. This tap test was continued until the difference in the height after the tap operation was settled within 1.0 mm of the previous measurement. We calculated the tap density based on the final volume \(v_f\) and the compressibility \(C(\%)\) by the following formula (3):

$$C = 100 \times [(v_0 - v_f)/v_0]. \quad (3)$$

2.3 Particle size distribution measurement

We measured the particle size distribution using a laser diffraction particle size analyzer (SALD220, SHIMADZU CORPORATION). Samples weighing 10 mg were mixed with 100 mL of pure water in a measuring cylinder to produce a sample slurry. The resulting slurry was carefully poured into the sample folder and sonicated for 10 s. After this treatment, the particle size distribution was measured. Additionally, we calculated the sample uniformity \(U_l\) using the value of accumulation of 10% particle diameter \(X_{10}\) and that of accumulation of 60% particle diameter \(X_{60}\) according to the following formula (4):

$$U_l = X_{60}/X_{10}. \quad (4)$$

2.4 Angle of repose and spatula angle measurement

The angle of repose was determined by the steepest angle of descent to the horizontal plane in which the sample can be piled without slumping. The horizontal disc (diameter \(D = 60 \text{ mm}\)) was fixed, and we supplied the sample through a funnel from the top and measured the angle of repose from an eggplant corner of the slant and the horizontal disc when forming a cone-shaped accumulation. We measured the angle of repose \(\theta_i\) using the height

![Fig. 1. SEM images of DCPD powder used for analysis. The scale bar is 50 μm. A) Gelatine byproduct, petaloid-shaped DCPD. B) Solution-synthesized petaloid-shaped DCPD. C) Chemical product, tabular-shaped DCPD. D) Solution-synthesized tabular-shaped DCPD.](image-url)
from the highest point of the formed cone according to following formula (5):

\[ \theta_i = \tan^{-1}(2H/D). \]  

A spatula was fixed to a saucer, and the sample was poured onto the spatula until the spatula was completely buried by the sample. The saucer was removed without causing any vibration. We measured the height \( H \) from the highest point of the formed triangle and then removed the spatula with impact. We also measured the height \( H' \) from the highest point of the formed triangle. We used formula (5) to assess both conditions, and determined the average value as spatula angle \( \theta_i \).

2.5 Sedimentation test

We measured the sedimentation rate using JIS A0204, which is a method of testing the particle size distribution of soils. Samples of 150 g were weighed (the condition and average value were determined as spatula angle \( n \)). We used the measuring procedure described in 2.2. The samples were poured into a measuring cylinder, to which pure water was added and the quantity of slurry was adjusted to 1,000 mL. We placed a lid on the cylinder to prevent leakage of the contents and continued the shaking of the sample vessel was then submerged in the water tank. The difference in height between the socket of the upper and lower part was kept constant by allowing overflow from the upper socket. The permeability \( k_i \) was calculated by following formula (6):

\[ K_i = L \cdot Q/(h \cdot A \cdot t). \]  

\( L \): Thickness of sample layer
\( Q \): Quantity of water overflow from lower socket
\( h \): Height of gap between upper and lower socket
\( A \): Area of bottom aperture of cylindrical vessel
\( t \): Time

2.6 Permeability test

We measured the permeability by applying JIS A1218, which is a set of test methods for determining the permeability of saturated soils, using a constant head permeability test apparatus (S-164, Nishi Nihon Shikenki. K.K.). Figure 2 shows a schematic representation of the apparatus. Two screen wire meshes (mesh sizes 75 and 400 µm, respectively) were placed in cylindrical sample vessels with the meshes covering the bottom aperture. Sample powder was poured into the sample vessel and strengthened by JIS A 1210, which is a test method for compacting soil using a rammer. The procedure entailed dropping a 2.5-kg rammer from a height of 30 cm, strengthening the sample as the thickness of the sample layer was reduced to 1.5 cm. This process was repeated twice or more to compare the layer thickness dependency of the overflow water quantity. The above-mentioned two meshes were placed on the sample layer and fixed to prevent sample leakage. The sample vessel was then submerged in the water tank.

The difference in height between the socket of the upper and lower part was kept constant by allowing overflow from the upper socket. The permeability \( k_i \) was calculated by following formula (6):

\[ K_i = L \cdot Q/(h \cdot A \cdot t). \]  

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3. Results and discussion

3.1 Bulk and tap densities

Table 1 lists the bulk and tap densities of all the samples. The results show that the bulk densities are strongly dependent on the morphology. The bulk densities of the petaloid-shaped particles in samples A and B and the tabular-shaped particles in samples C and D are approximately 0.6 and 0.5 g/mL, respectively. The values of the tap densities of most of the samples are nearly the same, as shown in the table. For these morphology dependencies, the compressibility of the petaloid-shaped particles is lower than that of the tabular-shaped particles. The difference in compressibility becomes more obvious in light of the difference in Carr’s flowability index. The index scores are 14.5 for A, 17.5 for B, and 2 for C and D. When evaluating Carr’s flowability index, the extent to which this difference depends on the morphology is the largest of another experimental results, such as the uniformity, angle of repose and spatula angle.

3.2 Particle size distribution

Figure 3 shows a plot of the particle size distributions of sample A as an example. The horizontal and vertical

| No. | Bulk density/g cm\(^{-3}\) | Tap density/g mL\(^{-1}\) | Compressibility/% |
|-----|--------------------------|--------------------------|------------------|
| A   | 0.619                    | 0.845                    | 26.8             |
| B   | 0.659                    | 0.832                    | 20.9             |
| C   | 0.470                    | 0.803                    | 41.5             |
| D   | 0.498                    | 0.835                    | 40.2             |
axes represent the particle diameter and the cumulative size distribution (red) and frequency distribution (blue), respectively. These results are compiled in Table 2. The mean particle size of samples A, C, and D are comparable, whereas that of B is twice as large as the others. The uniformities exhibit almost the same values as in Carr’s flowability index chart.

### 3.3 Angle of repose and spatula angle

Figure 4 shows typical images of the angle of repose and the spatula angle (before impact). The angles of repose and spatula angles of tabular-shaped samples C and D show same values. A slight morphology dependency is found for the angles of repose of petaloid-shaped particles:

| No. | Mean particle size/μm | X₁₀ | X₆₀ | Uᵢ |
|-----|------------------------|-----|-----|-----|
| A   | 54.3                   | 14.5| 82.3| 5.68|
| B   | 97.4                   | 45.3| 121.1| 2.67|
| C   | 51.0                   | 18.5| 65.4| 3.54|
| D   | 40.0                   | 15.1| 49.1| 3.25|

Figure 4. (A) Image of pile of stacked powder on sample table (diameter D). (B) Image of powder scooped by spatula (width D).

### 3.4 Sedimentation and permeability

Figure 5 shows the results of sedimentation tests of every sample with the horizontal and vertical axes representing the time and the height of the border between the slurry and water (left) and the percentage of the height (right), respectively. These results are compiled in Table 3. In the initial part of the process, the sedimentation rate for each sample is a constant value. Sample B shows the largest value in this experiment, a result referencing the results for mean particle size shown in Table 2. Even though sample C and D are different in terms of their mean particle sizes, the same sedimentation rate is obtained. Because the petaloid- and tabular-shaped particles have different aspect ratios, the former follows Stokes’ law but the latter deviates from it. Tabular-shaped particles exhibit inferior sedimentation compared to petaloid-shaped particles. The implication of this concerns temporal cost when separating the sludge and water after waste-

| No. | Sedimentation rate /mL s⁻¹ | Bulk density after sedimentation /g mL⁻¹ |
|-----|-----------------------------|----------------------------------------|
| A   | 1.04                        | 0.600                                  |
| B   | 1.70                        | 0.618                                  |
| C   | 0.836                       | 0.495                                  |
| D   | 0.836                       | 0.496                                  |

Those of A and B are 47.5 and 36.1°, respectively, while that of the tabular-shaped particles is 43.5°. In the chart of Carr’s flowability index, the corresponding values are 12 and 19.5 for A and B, respectively, and 16 for the tabular-shaped particles. The spatula angle of the petaloid-shaped particles is 36.0° and that of the tabular-shaped particles is 34.8°, whereas their Carr’s flowability indices have the same value of 21.
water treatment. Additionally, the bulk densities obtained after the sedimentation test are in good agreement with the results in Table 1. The moisture content of the separated sludge after treatment depends strongly on the morphology; this result shows the petaloid morphology to be more appropriate than the tabular morphology in terms of sludge transportation costs.

Figure 6 compares the permeability test results for the different morphologies. We compare samples A and C, because of their similar mean particle size. In the figure, the horizontal and vertical axes represent the inverse of the sample thickness and the current velocity, respectively. The permeability $k_t$ is derived by transformation of formula (6) as the inclination. The permeability of sample A is $2.22 \times 10^{-6}$ m/s and that of sample C is $2.03 \times 10^{-6}$ m/s. The permeability of the petaloid sample is approximately 10% higher than that of the tabular sample. The permeability is generally low as both samples contain a considerable amount of silty clay.

### 3.5 Comprehensive evaluation

According to the experimental results obtained for tap density, the porosity of the deposited powders of sample A and C is comparable. The reason for the advantage in terms of permeability cannot be explained on the basis of the comparable mean particle size and porosity. Figure 7 presents a model to explain this advantage from the viewpoint of the difference in powder filling properties. Since the shape of petaloid particles is approximately spherical, they are able to aggregate without tapping. They experience a slight increase in density after the rammer press operation. Petaloid particles are in point contact with each other, and the percolation-shaped particles consequently connect continuously through the whole sample. Tabular-shaped samples, on the other hand, show an irregular orientation in the absence of tapping. Their increase in density is larger than that for the petaloid samples after the rammer press operation. Tabular-shaped particles have facet contact with each other, and collections of these particles are therefore interspersed with voids and characterized by a thin flow lines. These results suggest that the difference in the spatial distribution surrounding the voids is the cause of the difference in permeability.

Table 4 provides the value of the Carr’s flowability index for each sample. The total points for tabular samples A and B are 70.5 and 81, respectively, and that of each of the petaloid samples is 62. These results indicate that the tabular morphology can be categorized as a good condition for transportation, whereas the petaloid morphology can be categorized as an ordinary condition requiring addi-

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**Table 4.** Carr’s flowability index (angle of repose, spatula angle, uniformity, compressibility and their sum). Left values in the table are experimental results and right values are scores in Carr’s flowability index.

| No. | Angle of repose (°) | Spatula angle (°) | Uniformity (−) | Compressibility (%) | Total index |
|-----|---------------------|-------------------|----------------|---------------------|-------------|
| A   | 47.5                | 36.0              | 5.68           | 26.8                | 70          |
| B   | 36.1                | 34.8              | 2.67           | 20.9                | 81          |
| C   | 43.5                | 34.8              | 3.54           | 42                  | 62          |
| D   | 43.5                | 34.8              | 3.25           | 40                  | 62          |
tional equipment such as a vibration machine (and hence additional cost) to prevent the formation of a bridge at the hopper.

4. Conclusions

We compared some of the physical properties of petaloid- and tabular-shaped DCPD particles. The bulk density of petaloid particles was lower than that of tabular particles; this characteristic was also observed after the sedimentation test. The moisture content of the slurry depended on these results: the separation efficiency exhibited by solid and liquid petaloid-shaped powder exceeded that of tabular powder. In the case of permeability, the petaloid morphology is slightly more effective than the tabular morphology. Carr’s flowability index was also compared, and the total points show strong morphology dependency.

The usability of DCPD powder depended on the shape of its constituent particles, with the petaloid-shaped particles showing better performance compared to the tabular-shaped particles. This performance would also apply to FAp sludge after environmental treatment by DCPD.

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