Penetrated surface characteristics of cement - mixed sand in powder bed 3D printing

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ABSTRACT
Powder bed 3D printing is an additive manufacturing process that combines powder particles by selectively depositing a liquid activator on a powder bed. Sand molds for high-resolution casting can be realized as a high-quality green body via powder bed 3D printing. In this study, we investigated the effect of vertical penetration of aqueous droplets on the quality of the green body formed from a cement-mixed sand powder. The cement was hydrated by aqueous droplets and acted as a binder between the sand particles. The penetration ratio of the prepared powders was calculated from the penetration depth and spread diameter. Evidently, the penetration ratio and penetration resolution determined the strength and surface resolution of the green body. The results showed that an increase in the silica sand grain size led to a desirable penetration resolution with a relatively high green body strength at the same cement content. Additionally, the green body made from the sand with a particle size of 70 μm showed a relatively high green body strength and an excellent green body surface resolution even at 5% cement content, and it was determined that the green body strength and resolution depend on the penetration pattern.

1. Introduction
Powder bed 3D printing is an additive manufacturing process, which involves injecting a binder into a ceramic powder bed using a printing head, causing local solidification at the region of injection, is used in ceramic prototype manufacturing [1–3]. The desired shape, called green body, is formed by the layer-by-layer deposition of ceramic powder followed by the selective solidification of each layer.

Cement has been widely used as a binder of ceramic powder, owing to its ability to be cured quickly at room temperature, maintain dimensional accuracy to prevent deterioration of the printed parts, and because of its economic advantages. Additionally, it maintains dimensional stability even at high temperatures and facilitates the manufacture of molds for casting [4,5]. In hydraulic cement systems, an aqueous binder is injected into the powder bed containing the dried cement powder, which may cause hydrolysis-setting reactions that stabilize the printed shapes during the powder bed 3D printing. In particular, calcium aluminate cement (CAC) mixtures are promising reaction bonding systems for stabilizing the printed shape within a reasonable processing time [6,7]. CAC binders with uniform particles of submicron size can be used to fabricate casting molds for complex-shaped components with an excellent surface resolution when compared with those fabricated using general cement binders, including gypsum. Additionally, functional CAC molds can be manufactured with the required gas permeability, strength, and thermochemical properties, thus ensuring high-quality castings with an optimized design for weight reduction [8,9].

This study was performed to confirm that the quality of the actual printed green body is determined by the capillary pattern, which is inferred from the capillary pressures [10–12]. In previous studies, it was demonstrated that a higher capillary pressure at initial saturation results in a high penetration of the wetting area [13]. Modifying the capillary pressure can lead to an improved optimal saturation ratio, which can enhance the geometrical accuracy of the green bodies [12,14]. However, the aforementioned reports do not present a sufficiently clear relationship; thus, in this study, we tried to fill this gap by confirming that the quality of the actual printed green body was determined by the capillary pattern, which was, in turn, inferred from the capillary pressures. Using aqueous droplet drop testing on the powder bed, we confirmed that the quality of the printed parts was directly affected by the penetration pattern. Additionally, we attempted to predict the strength of the printed parts using the droplet penetration depth ratio alone, as reported in [12–14]. The effect of the resolution of the droplet-cured parts on the resolution of the printed parts was investigated using non-porous
sand, which was selected to control the surface porosity [14]. Further, we experimentally determined the quantitative correlation among the green body strength, binder saturation rate, and surface roughness of the droplet penetration area, using spherical silica powder with a uniform particle size distribution and by varying the CAC component ratio.

2. Experimental methods

2.1. Raw materials

Spherical fused silica powders (DIGHEN Composite Material Technology Co., Ltd.) of various particle sizes (30, 50, and 70 μm) were prepared from the cement and sand mixtures using a sieving process. Commercially available CAC (UAC 80HF2, 4 μm, UNION Corp.) with a sufficiently small average particle size of 4 μm was used to coat the surface of the sand and facilitate powder bonding in the hydraulic cement system. An aqueous activator solution (Zb63, ZCorp Co., Ltd.) was used as an activator for cement hydration.

2.2. Powder bed 3D printing

Green body samples were prepared using a powder 3D printer (Freeforms T150, SFS, Korea) with an HP 4810A 11 nozzle jet head. The powder feed space was filled with a cement-mixed powder before printing, and a roller was used to cover the build floor with the powder. The green body was drawn in CAD format and converted to the standard triangulation language (STL) format; based on the digital geometric information preset in the system, the liquid activator was dispensed from the nozzle at predetermined locations. The printer nozzle dispensed the activator solution at a level of 133% (saturation: 0.505 g/cm³), set in the system. It was printed layer-by-layer, creating new layers using the rollers until the object was complete [15–18].

Cubic specimens of dimensions 10 mm × 10 mm × 10 mm were prepared (maximum printable dimensions were 290 mm × 210 mm × 250 mm) to compare their strengths and surface resolutions. Additionally, all the cement-mixed powders had a stacking height of 300 μm [19–21].

2.3. Characterization

The sample morphologies were investigated through field emission scanning electron microscopy (SEM; Su8020, Hitachi, Japan) at an accelerating voltage range of 10–20 kV. The particle size distributions of the raw powders and sands were tested using a laser size detector (MS3000, Malvern Instruments, UK). The phase composition of the materials was analyzed by X-ray diffraction (XRD; Ultima IV, Rigaku, Japan) using Cu Kα radiation (40 kV, 40 mA) and a Jade 9 software using the International Center for Diffraction Data (2021) database. Samples were scanned at room temperature, at a start angle of 10°, an end angle of 80°, a step size of 0.02°, and a scanning speed of 2° min⁻¹. The uniaxial pressure strength was measured using a universal testing machine (MTS810, Material Test System Corp, USA) containing a cylinder with a diameter of 10 mm and a fixed speed of 0.2 mm/min. The droplet surface roughness of the 3D-printed

Figure 1. SEM images of (a) fused silica powder (sand) and (b) CACs.

Figure 2. Particle size distributions of the raw materials: CACs and fused silica powder with various particle sizes (30, 50, and 70 μm).
samples was determined using a digital microscope (DSX510, Olympus Co., Ltd.). The printed green body surface roughness of the 3D-printed samples was determined using a profilometer (SurfCorder SE3300), which is a linear variable differential-transformer-based contact-type surface resolution meter.

3. Results and discussion

3.1. Sample characterization

The fused silica particles were confirmed to be of a uniform spherical shape, as seen in the SEM images (Figure 1a), with variable size distributions. The size distributions of the particles prepared from the 30, 50, and 70 μm sieves are shown in Figure 2. A micrograph of the CAC particles is shown in Figure 1; they were confirmed to have an average particle size of 4 μm, as shown in Figure 2. This particle size is sufficiently smaller than that of the sand particles to enable bonding between the sands [5]. The cement–sand mixed powder samples were coated with CACs through a simple ball milling method, using the following fractions of dried CAC powders: 5%, 10%, 15%, and 20%. In the ball milling process, the CACs were completely dried in an oven at 200°C for 1 h. After mixing the dried CACs with sand using a general horizontal ball mill, the mixture was shaken vigorously and for a sufficiently long time to prevent clumping of the CAC components. Therefore, after the ball milling process, the cement was finally checked to ensure that no aggregates were formed, and the sample, in which the CAC components were sufficiently mixed with the sand, was used. The corresponding mixtures (using sand with an average particle size of 30 μm) were denoted as D30+ C5%, D30+ C10%, D30+ C15%, and D30+ C20%. Sands with average particle sizes of 50 and 70 μm were labeled similarly. Each sample was mixed for 12 h and sieved until the cement was sufficiently applied to the sand. Figure 2 shows the particle size distributions of the D30+ C20%, D50+ C20%, and D70+ C20% powder bed mixtures, each of which contain up to 20% CAC powder. As shown in Figure 2, even when the CAC content is maximized, the effect on the final particle size distribution is insignificant, revealing that no abnormal aggregation of the CACs occurred.

Figure 3. XRD patterns showing raw CAC contained in the cement-mixed sand, fused silica, and different crystalline hydration products contained in the green body.

Figure 4. Photograph of the 3D printing recoating system using droplets; (inset) droplets wetting the layered powder.

Figure 5. (a) Image showing the liquid droplet before contact with the powder bed surface. 3D microscopic images showing the hardened parts after a sessile drop test: (b) side view and (c) bottom view.
calcium aluminates hydrates) [22–24]. After continuing the printing process for 24 h, the peaks for the green body sample indicated crystalline hydration. Formation of hydrolysis products, calcium aluminates hydrates ($Ca_4\text{AH}_{19}$, $Ca_8\text{Al}_2\text{O}_5 \cdot 19\text{H}_2\text{O}$ and $Ca_2\text{AH}_6$, and $Ca_2\text{Al}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$) and hydrogarnet ($Ca_2\text{AH}_6$: $Ca_8\text{Al}_2\text{OH}(\text{OH})_2$), was confirmed (Figure 3). In the case of drying at room temperature, the most stable phases, $Ca_4\text{AH}_{19}$ and $Ca_2\text{AH}_6$ were finally formed after the formation of the metastable phases $Ca_4\text{AH}_{19}$ and $Ca_2\text{AH}_6$ [25]. Figure 3 shows the final formation of the $Ca_4\text{AH}_{19}$ phase. However, $CA$, $CA_2$, and $C_12\text{A}_7$ were not fully converted to $Ca_4\text{AH}_{19}$ [25–27]. It was deduced that the CAC had not sufficiently hydrated without the physical mixing of the cement into a slurry. In Figure 3, the formation of $Ca_4\text{AH}_{19}$ is more distinct than that of $Ca_4\text{AH}_{19}$ and $Ca_2\text{AH}_6$, which are metastable phases of cement. This result implies sufficient progress of hardening in the printing process. Therefore, it is possible to compare the hardness of all the samples after curing for 24 h. The peaks corresponding to fused silica in the cement-mixed sand sample are still observed in the XRD patterns of the green body samples, confirming that the fused silica in the cement mixture remained unreacted [24]. Further, no other crystalline hydration products are observed immediately after the CAC bonding reaction. Therefore, it is concluded that sand would not affect the chemical hydration of cement. Additionally, the spherical fused silica powder had a pore surface area of 0.31 m$^2$/g, leading to almost no moisture permeation [14]. Thus, we attempted to keep the physicochemical influence of sand constant during the water penetration process.

### 3.2. Powder bed recoating and sessile drop test

Powder bed recoating was performed by a 3D printing recoating system, shown in Figure 4, to determine the ability of the powder bed formation [12,14]. The system comprised of a metal frame in the XY-axis and a steel roller of diameter 30 mm, which was connected to a step motor. The axis movement and the rotation of the metal roller were controlled using a driver and speed controller, and the entire system was placed on a vibration-free rail to enable movement at a constant speed along the X-axis. A small sample volume of each powder was used, and the process was repeated five times to form a defect-free powder bed. The recoating speed of the recoating device was 270 mm/s, which was the average powder flow observed at a rotation speed of 22 rpm. Each powder was recoated to a thickness of 5 mm on a dense plastic plate to achieve the same packing density as that produced by an actual 3D printer.

The sessile drop tests of the binder droplets of fixed sizes were performed on the recoated layer, from a fixed height of 2 mm (slightly larger than the size of the droplets, such that the droplet does not come in

The aqueous activator solution that is used in a commercial powder bed 3D printer enables the hydration of cement, owing to its water content. Figure 3 shows the XRD pattern of the crystalline hydration of a printed green body sample. Before printing, the peaks of the cement-mixed sand samples matched the spectra of fused silica, CA, CA$_2$, and C$_{12}$A$_7$ (where CA represents
contact with the powder interface) using a syringe pump with a microneedle to determine the shape of the droplet after it hardens. The droplets were positioned to minimize the effect of gravity on the droplet (Figure 5a) [28]. A simple powder bed plate, as shown in Figure 4, was installed along with a precision analytical balance, below this plate, such that drops of the same mass fell at a time, to obtain 20 cured droplets for each sample.

To experimentally determine the penetration ratio of the hardened droplet in the powder samples, the wetting properties of the aqueous binder were investigated using a digital microscope, and the diameter and height of the hardened parts as well as the roughness of the surface were mapped and converted into a 3D image, as shown in Figure 5 (b). Additionally, to reduce the error range while measuring the roughness, the surface 3D image was flattened, and the threshold value was set to 0.5 mm for all the samples, as shown in Figure 5 (c). To increase the reliability of the data analysis, the surface roughness (Sa) was calculated for the entire mapped surface of 30 samples per powder, which did not lie on the partial line roughness (Ra) of the samples [29].

3.3. Green body strength and penetration ratio

Analyses of the 3D image of the cured product and the results of the sessile drop revealed the exact curing height (the penetration depth) and the degree of spread of the droplet. The penetration ratio was calculated using Equation (1). The cured product was dried in an oven at 50°C for 12 h to prevent damage to the surface because of insufficient curing. Twenty samples were prepared for each experiment, and the average penetration ratio was adopted to increase the reliability of the data.

\[
\frac{\text{Penetration depth}(h)}{\text{Spread diameter}(r)} = \text{penetration ratio} \quad (1)
\]

Compressive strength tests were performed on the 3D-printed cubic specimens to investigate the relationship between the penetration ratio of the hardened droplet and the strength of the 3D printed green body, and the corresponding results are as shown in Figure 6. Twenty samples were prepared for each experiment, and the compressive strength values were averaged to increase the reliability of the data.

The results showed that the compressive strength of the samples consistently exhibited the same trend as that of the penetration ratio of the hardened droplets. For example, in the case of the samples with a sand particle size of 30 μm, the strength of the compact increased sharply as the cement fraction increased from 10% to 15% and decreased slightly at 20% cement fraction. The same trend is observed in the compressive strengths. Notably, the samples with sand particle sizes of 50 and 70 μm exhibited completely different patterns. The samples, with a sand particle size of 70 μm, exhibited a complex pattern and did not demonstrate a clear trend; however, the green body of the D70+ C15% sample showed the highest average strength (6.1 MPa) among all the samples.

Additionally, as the particle size of the sand increased, the compressive strength of the printed body also increased, because the cement powder was more likely to be sufficiently coated on the surface of the sand and achieve cross-linkage between the sand particles [30,31].

3.4. Green body surface roughness and droplet hardening interface resolution

The Sa of the 3D-printed printed body surface was determined through 3D image rendering following a similar procedure implemented in the determination of the roughness of the droplet hardening interface, as shown in Figure 7. The printed surface was laminated in the XY-plane, while being swept by a roller during the recoating, and compacted under physical pressure.
Therefore, the surface resolutions of 20 randomly designated points in the XZ- and YZ-planes, instead of those of the XY-plane, were measured and averaged [32].

Figure 8 shows a comparison between the droplet surface roughness and the printed green body surface roughness, both of which show the same trend. The optimal surface resolution is obtained when the sand particle size is 30 µm, and the cement content is 15%. For the sands with particle sizes of 50 and 70 µm, the best surface resolution is achieved at a cement content of 10% and 5%, respectively. This is identical to the trend observed in the comparison of the penetration ratio and the strength of the printed green body. Such an identical trend is observed possibly because the droplet hardened interface results in the same resolution as the powder hardened body interfaces, created by a single droplet when the droplet is sprayed to create a wet region in the 3D printing process [33].

The quality of the green body improved as the size of the sand increased from 30 to 70 µm. Additionally, the quality of the printed green body significantly improved as the cement content decreased along the specific surface area; that is, as the size of the sand particles increased, the optimal cement content (shown in Figure 9) decreased with the decreasing surface area; The 30, 50, and 70 µm sands showed the best quality at 15%, 10%, and 5% cement content, respectively [34].

4. Conclusions

Through this study, we confirmed that the surface roughness and strength of a 3D printed green body can be predicted using the penetration pattern, via a droplet test on cement-mixed sands. Sands with particle sizes of 30 and 50 µm exhibited optimal penetration resolution and fabricated green body strength at 15 wt% and 10 wt% cement contents, respectively. Furthermore, the highest cohesive strength and best penetration resolution were achieved for the sand with a particle size of 70 µm at a 5 wt% cement content. In summary, as the size of the sand increased, the amount of cement required for optimal green body quality decreased, and the quality of the green body increased. Therefore, powders that satisfied the desired 3D printing quality could be developed by controlling the penetration pattern with the identified particle size. Consequently, modifying the cohesion strength is important for developing efficient binder-
jetting additive manufacturing processes for the optimal quality and geometrical accuracy of green bodies.

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Declarations

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