**Modified 3D printed powder to Cement-based material and mechanical properties of cement scaffold used in 3D printing**

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**Abstract:**

Additive manufacturing is a common technique used to produce 3D printed structures. These techniques have been used as precise application geometry in different fields such as architecture and medicine, and the food, mechanics and chemical industries. However, in most cases only a limited amount of powderhas been used to fabricate scaffold (structure). In this study, a unique mix of cements (calcium aluminate cement passed through a 150 µm sieve and ordinary Portland cement) was developed for Z- Corporation’s three-dimensional printing (3DP) process. This cement mix was blended and the resulting composite powders were printed with a water-based binder using a Z-Corporation 3D printer. Moreover, some samples were added lithium carbonate to reduce the setting time for the cement mixture. The aims of the study were to firstly, find the proper cementitious powder close to the targeted powder (Z-powder); and secondly, evaluate the mechanical properties of this material. Cubic specimens of two different batches with varying saturation levels were cast and cured in various scenarios to enhance the best mechanical properties. The samples were characterised by porosity analyses, compression tests, Olympus BX61 Microscope imaging, 3D profiling Veeco (Dektak) and the Scanning Electronic Microscope (SEM). The maximum compressive strength of the cubic specimens for cementitious 3DP was 8.26 MPa at the saturation level of 170% for both the shell and core. The minimum porosity obtained was 49.28% at the saturation level of 170% and 340% for the shell and the core, respectively.

**Keywords:**

3D printing; Calcium Aluminate Cement; Ordinary Portland Cement; Lithium Carbonate; Compressive strength; Porosity; 3D profilometer, and SEM.

**Introduction:**

Currently, rapid prototype technology is being developed for different purposes, in particular, three-dimensional printing (3DP) has been employed in food preparation, medicine/healthcare and various industry applications ([Castaneda et al. 2015](#_ENREF_3); [Wegrzyn et al. 2012](#_ENREF_25)). It is suggested that this technology could completely change a range of production methods ([Lipson & Kurman 2013](#_ENREF_16)). The principal advantage of rapid prototype technologies is that we can directly construct parts in one step from the CAD data ([Vaezi & Chua 2011](#_ENREF_24)). The use of 3D printing could reduce 35-60% of the overall costs of concrete construction due to the removal of formwork ([Lloret et al. 2015](#_ENREF_17)).

[Tay et al. (2016](#_ENREF_22)) addressed three main applications of additive manufacturing in the construction industry. Both the concrete printing (extrusion) and D-shape (powder-based) are used as off-site printing and contour-crafting is used for the purposes of in-situ printing applications. The following papers focus on concrete printing (extrusion) ([Gosselin et al. 2016](#_ENREF_7); [Le, Austin, Lim, Buswell, Gibb, et al. 2012](#_ENREF_11); [Le, Austin, Lim, Buswell, Law, et al. 2012](#_ENREF_12); [Lim et al. 2012](#_ENREF_13); [Lim et al. 2011](#_ENREF_14); [Lin et al. 2015](#_ENREF_15); [Lloret et al. 2015](#_ENREF_17)).

This paper mainly focuses on the powder-based printer (D-shape) application in which novel materials are proposed to increase the number of printability powders used in the 3DP technique. The method involves blending the cementitious powder with an additive powder, which must be compatible and able to assist in the construction of a solid part with appropriate strength to be handled following its reaction with water. From the literature, [Zhou et al. (2013](#_ENREF_28)) describe the procedure of powder-based 3D printing as a method where the print head concurrently drops binder solution on powder to build up the scaffold. For instance, after completion of the first layer, the roller returns to the feed area and spreads another layer of powder. The procedure that they use repeats the construction of the scaffold which takes approximately 40 mins to be completed. The unbounded materials remain around the printed scaffold which is solely used to temporarily support the construction. The structure is dried at 73ºC for one hour and then cleaned up by applying compressed air to clean any unbounded powder off. [Bredt et al. (2003](#_ENREF_2)) used four different types of plaster and particulate materials. In their work, the original aqueous fluid contained about 95% water and 5% humectant, glycerol. Potassium sulfate was added as an accelerator to produce modified fluid containing about 92% water, 5% glycerol and 3% potassium sulfate. This paper uses similar aqueous fluid which is commercially available as Z-binder (ZB 60 or 63). [Utela et al. (2008](#_ENREF_23)) and [Withell et al. (2011](#_ENREF_26)) used Z-Corporation's 310 printer with an HP10 cartridge, which requires a viscosity of 1.35 cps and surface tension of 45 dynes/cm. Water as the binder has a surface tension of 72 dynes/cm and it is reduced by adding Isopropyl Alcohol (IPA) in order to be used by the printer head. In the study of [Lam et al. (2002](#_ENREF_10)) distilled water is used as a binder which is mixed with blue dye to decrease the surface tension of the water until it can be worked by the 3D printer head.

[Zhou et al. (2013](#_ENREF_28)) conducted an experiment on the powder calcium sulphate hemihydrate (CaSO4.0.5H2O). This is one of the first materials which have been used in 3D powder printing. The particle size of the powder affected the thickness of the layers. In most cases, thin layers with relatively higher resolution are preferable and fine powder is the traditional choice. However, thicker layers are attainable using the largest possible particle size of the powder. This paper uses the 3D printer with layer thickness indication 0.1mm which has a greater thickness than the maximum particle size of the prepared powder. The results of [Withell et al. (2011](#_ENREF_26)) showed that layer thickness affects not only the final resolution but also the required penetration depth of the printing liquid.

 A broad range of polymers and metals can be employed in additive manufacturing, for example, laser sintering and stereolithography. However, these methods are inappropriate for cement and ceramic components; therefore, specific 3D printing has been developed for ceramic-based materials. [Lam et al. (2002](#_ENREF_10)) used a polymer powder starch mix that contains corn starch, dextran and gelatin to develop the 3D printing process. The materials used in various ratios consisted of 50% wt of corn starch (~10 μm), 30% wt of dextran (>100 μm) and 20% wt of gelatin (>100 μm). The corn starch consisted of polysaccharide and two polymers D-glucose, amylose and amylopectin. Dextran is a polysaccharide while gelatin comes naturally from the collagen of animals.

[Gibbons et al. (2010](#_ENREF_6)) achieved the best green form for material composition of 97:3 w/w Rapid hardening cement: Polyvinyl alcohol. They conducted four curing methods, these being 12 h, 24 h and 26 days in water at room temperature and 1 day in the water at 80oC. Curing for 26 days at room temperature resulted in enhancement of the strength by a factor of 3.1 ± 0.4 from 0.71 ± 0.02 MPa to 2.2 ± 0.2 MPa. It was found that 25% reduction in core saturation diminishes the flexural strength. According to [Ma et al. (2015](#_ENREF_18)), 3DP can be applied to carbon powders having a particle size ranging from 45 to 105 µm, and by using acetone-based furfuryl resin as a solution binder. The bending strength of the 3D printed specimens achieved less than 5 MPa, however, after pre-sintering it increased up to 10 MPa. [Zhou et al. (2014](#_ENREF_27)) applied 3DP to produce samples containing different powder combinations of CaP: CaSO4 and water-based binder. Their suggestion aimed to realise the effect of parameters such as binder drop penetration behaviour, powder-binder wettability, process powder bed packing and the final sample’s quality. Their results indicated that the particle size of CaP and ratio of CaP: CaSO4 are the most important factors. Furthermore, the loose powder has a higher heterogonous level and results in slow drop penetration, low wetting ratio, large drop penetration, reduced green mass and poor green strength of the 3D-printed samples. Accordingly, this study attempts to discuss in more detail the particle size that has an impact on the porosity and binder penetration in the modified powder.

This paper presents a study of cement powder used in 3DP productions and this powder has a significant influence on applications in the structural engineering field. The size distribution of material is analysed and a series of tests is performed on the mechanical properties of the materials being applied. Our knowledge of porosity depends on the particle size distribution, layer thickness, and binder/powder distribution.

**Materials and methods**

 *Material composition*

The distribution size of powder used in the 3D printer (Z-printer150, Z-Corporation, USA) was acquired using particle size laser distributor (Cilas 1190) and the results are shown in Figure 1. The Z-printer powder consists of plaster, vinyl polymer and carbohydrate. D10, D50, and D90 values, which are representative of the mean particle size for 10%, 50%, and 90% of the materials, respectively, were obtained by this method equal to 1.48, 23.07 and 70.12 µm, respectively. The specific surface area of Z-powder was 0.999 m2/gr when tested by (BELSORP-max).

The two main materials used in this study are ordinary Portland cement (OPC) (Geelong cement) and calcium aluminate cement (CAC) (CIMENT FONDU, Kerneos). Portland cement is a conventional cement type used worldwide, and it consists of calcium, silica, alumina and iron. CAC is another type of cement comprising hydraulic calcium aluminates. It is also known as “aluminous cement", "high-alumina cement" and in French, "Ciment Fondu". This type of cement is utilised in specialised applications (e.g. emergency repairs and foundation construction, a [ductile iron pipe](https://en.wikipedia.org/wiki/Ductile_iron_pipe) for waste water, concrete pipes for sewerage, the petrochemicals industry and the rehabilitation of man-accessible sewer infrastructures). Particle size distributions for 10%, 50% and 90% of OPC are 0.19, 8.93 and 38.46 µm, respectively, and for CAC they are passed through 150 μm sieves which are 3.38, 79.93 and 127.11 µm, respectively. The sieve is performed for CAC between 75 and 150 μm. The bulk particle densities for CAC and OPC are 1.23 and 0.92 gr/cm3 respectively while the specific surface area for the mixture of both kinds of cement is 1.021 m2/gr, which is tested by (BELSORP-max) as shown in Table 1. The mixed ratio contains 67.8% CAC and 32.2% OPC. For comparison purposes, 4.5% of the total mix is replaced by lithium carbonate (lithium carbonate, reagent grade, ACS) as an agent to accelerate the setting time of the cement ([Lin et al. 2015](#_ENREF_15)). It can produce rapid setting, low cost, high early strength, excellent adhesion and stability.

The CAC was sieved by 150 to 75 µm sieves and shaken for about 5 mins. Then it was blended with OPC by using a Hobart mixer; lithium carbonate was added and the mixer was operated at the rotation speed of 1450 rpm for 10 mins. Since the CAC and OPC powders have different particle size distributions (i.e. OPC is finer than CAC), these two types of cement powders were mixed to obtain one powder with a similar allocation of the target powder which is used in the Z-printer.

In this study, a mixture of CAC and OPC was implemented as the powder and Zb60 (containing humectant and water) was the binder to build 3D objects.

*Fabrication of specimens by printing*

The specimens were made using a 3D printer Z150 manufactured by Z-Corporation containing an HP11 (4810A) nozzle. The 3D printer consisted of a build bin and a feed bin. The build bin produces the 3D samples and a roller mounted together with the print head on the gantry spreads the powder to create the 3D samples layer by layer. The feed bin is filled entirely with powder. Then, the print nozzle moves and applies the binder onto the powder at certain locations to make the specimens layer by layer and this ultimately creates the sample. The container of 3D printer is filled with the mixture powder of CAC and OPC. The roller spreads a new layer on the bedded layers in the build bin in order to feed bin allows powders derived from the container. The build bin will move downward by the same thickness of one layer so that the new layer can be constructed. When the layer spreads fully out, the nozzle will release the liquid to form a new layer. These actions will be repeated till the sample is completely constructed.

*Coordinate system*

In the 3D printing process, there are three axes that printer can print the samples beside those in the directions displayed in Figure 2. [Feng et al. (2015](#_ENREF_5)) state that the X-axis is considered to be the direction of the nozzle that moves to drop the binder onto the powder. The Y-axis, perpendicular to the X and Z axes, is the vertical direction, as shown in Figure 3.

*Compressive strength*

Cubic specimens with dimensions of 20 × 20 × 20 mm3 were fabricated to measure the compressive strength and determine the pore size distribution of the 3D printed powders. Samples were prepared in three primary batches including: 1) CAC and OPC with lithium carbonate produced by the 3D printer, 2) CAC and OPC without lithium carbonate produced by the 3D printer and, 3) CAC and OPC with lithium carbonate through hand mixing (manual mixing) of concrete which is explained in Table 2. Hand mixing is a manual combination of precise components with water. In the 3D printer Z150, the maximum saturation level for the shell and core are 170% and 340%, respectively. Therefore, the saturation levels using the shell were between 75% and 170% and for the core were between 150% and 340%.

The cubic samples weretested in different ages and different curing saturations, which were perpendicular to the X-axisand parallel to the Z-axis. The samples were tested as a green part; that means the cubic sample was taken from the 3D printer directly without curing see Figure 4. Following this, samples were cured in water at room temperature for 1, 7 and 28 days. Some other samples were cured in water which contained 2% of Ca(OH)2 (calcium hydroxide).

The water/cement (W/C) ratio was determined through the binder/ powder mass ratio *(Mb/Mp)* which is available in 3D printer software according to Eq. (1) and the results are shown in Table 3;

$\frac{M\_{b}}{M\_{P}}=\frac{ρ\_{b}.V\_{b}}{ρ\_{P}.V\_{P}}$ (1),

Where *Mb* and *Mp* are the mass of binder and powder, respectively; *ρb* and *ρp* are the density of binder and powder, respectively; and *Vb*and *Vp* are the volume of binder and powder, respectively.

*Porosity test*

Porosity tests were conducted on the samples shown in Table 2 and Figure 9 according to the AS 1774.5:2014. The tests were done in vitro for cubic samples. The samples were dried in an oven (Vtech, XU 225) at 105°C for about 2 hours and left to cool down to room temperature. The samples’ weight at this stage is designated as dry weight (m1). Then, samples were inserted into a porosity and bulk density tester (XQK-03), and the air was sucked inside the tester for about 10 min. Later, water was poured into the bucket till the water covered the samples by about 5 cm, then a waiting period of 10 minutes ensued to ensure that the samples were completely saturated by water. Then, the weight of the samples in soaked water was measured on the scale (m2), followed by rolling the four side samples on the damp cloth measured as a (m3). From this the apparent porosity of cubic samples was calculated using equation (2):

$Pa=\frac{m3-m1}{m3-m2}x100$ (2),

The obtained Scanning Electronic Microscope (SEM) images were analysed by Image J software and then compared with the porosity test conducted in the laboratory depicted in Table 4. It was observed that some differences emerged. Analysis by Image J is not precise due to SEM focusing on a specific area in the cubic samples and therefore does not represent the whole sample. The difference in the analysis by Image J software with the test at vitro is about (3-10) %.

**Results and discussion**

There are 29 samples in this study consisting of three batches; the first two batches are created via 3D printing, the third and last batches are generated by hand or manual mixing. There are massive differences between the hand mixed and 3D printed specimens due to the way the samples are formed. The compressive strength of 3D printed samples is weaker than the hand-made mixed cementitious and they have higher porosity as well.

A previous study by [Utela et al. (2008](#_ENREF_23)) indicated that the most important property of 3DP is the shape and size of particles. The powder of 3DP can be dropped in either a wet or dry state. In the wet or dry state a particle size smaller than 5 µm can be deposited but in the dry state it is preferable that particles are larger than 20 µm. [Asadi-Eydivand et al. (2016](#_ENREF_1)) stated that ZP150 powder has a particle size distribution as D10, D50, and D90 are 0.64, 27.36 and 68.83 µm, respectively. The D10, D50 and D90 represent the range and midpoint of the particle size that is based on sieve analysis results which calculates the act for 10%, 50% and 90% of the mass. The dimensions of the printed specimen are not as accurate as those designed by SolidWorks software. The standard deviations are between (0.09) to (1.79) mm. Measurements of all samples are summarised in Table 5. Results show that most of the samples with greater than 100% saturation levels are oversized. This may be due to unbounded powder that was not completely removed during the depowdering process, or the samples had swollen due to the higher rate of water permeability penetrating the samples. Samples with 75% saturation levels (S75-C75) and (S75-C150) are of smaller size than the usual design as a consequence of not enough hydration occurring between the particles and less densification.

 The compressive strength of cubic samples is illustrated in Figure 5. Results show that by increasing the saturation level of 3DP specimens, compressive strength values increase gradually. This is very different to the results obtained by manual mixing of cement with water, which causes lower strength at high W/C ratio. All the tests were done using a Tecnotest machine (300kN, Italy). Furthermore, the cubic samples’ porosity was checked according to the Australian Standard (AS 1774.5:2014). Results show that by increasing the saturation level, total porosity decreases for 3DP specimens. [Maier et al. (2011](#_ENREF_19)) stated that capillary pores and other large holes are mainly responsible for reduction in elasticity and strength. They also found that after curing for 72 hours an intermixed crystal network developed, and this filled up the pore spaces and minimised total porosity.

As shown in Figure 5, the compressive strength increased when the saturation level increased, while the shell and core have similar saturation levels as explained in Table 2. At the same saturation level (shell and core) of (S100-C100-LW) 100% to (S170-C170-LW) 170% compressive strength incremented from 3.08 MPa to 8.26 MPa for 28 days, respectively. It is almost 37% higher than the lowest saturation level of 100%. It is linked to porosity in that when porosity increases the strength declines. Open pores affect the strength of specimens while they are being cured in water. On the other hand, there is not enough hydration and reaction between the cement particles when specimens are being printed. In addition, the CAC contains a large amount of alumina filler that leads to a demand for more water and hydration on a quicker basis ([Klaus et al. 2016](#_ENREF_9)). As a result, particles are unbound from the printed specimens. The maximum saturation level of Z150 is for the shell 170% and the core 340% (S170-C340) and this saturation level could not be increased. Hydration therefore will not increase between the cement particles. [Maier et al. (2011](#_ENREF_19)) claim that the limited amount of water released from the printer head and the process did not provide sufficient strength for the specimen. However, the 3DP samples have less strength than the hand mixed samples, as shown in Figures 5 and 6.

It is obvious from the graph (5) for different saturation levels, the optimum strength is (3.83MPa) at a saturation level of (S150-C300-LW) in 3DP samples for 28 days. This may be due to the level of porosity between particles where the saturation level is minimal. It is slightly different with other saturation levels. As shown in Figure 6, lower water ratios for hand mixed samples result in higher strength. The tests have been applied for all kinds of different saturation levels after finding the ratio of saturation levels is converted to the water/cement ratio. As illustrated in the graph (6) at saturation level S100-C200 in 3DP which is equal to W/C 0.31, the highest compressive strength can be obtained (19.05MPa). According to ([Feng et al. 2015](#_ENREF_5)) 3DP has an impact on compressive strength when printing samples in different directions. They contend that the speed of the printer in X-direction is faster than other directions. Further, the time of printing adjacent layers at the Y-direction is shorter than printing adjacent layers in the Z-direction. The level of bond between two parts of the particles is thereby higher in a shorter print time, resulting in higher strength in a continuous strip rather than the strip in between. In this study the load is parallel to the Z-direction when this load is applied, cracks pass through the interior strip (Vertical) direction, Figure (7). 3DP cubes also find the lateral sides get spalled and ruptures occur due to crushing.

Moreover, Table 2 shows that using different curing agents like calcium hydroxide Ca(OH)2, does not alter the specimens’ strength. The results for compressive strength are similar to results for samples cured in water.

Tests were done to assess the compressive strength of CAC & OPC without lithium carbonate shown in Figure 8. The same saturation levels of the shell and core of samples S75-C75-OW to S170-C170-OW respectivelyincreased the materials’ strength from 1.065 to 3.33 MPa after 28 days. It is three times higher than the minimum saturation level. On the other hand, the optimum strength at different saturation levels after 28 days curing of sample S100-C200-OW recorded the highest compressive strength (3.32MPa). It is clear that these differences are due to changes in the saturation levels of 3DP.

Figure 9 illustrates the outcome of porosity of 3D printed samples at different and similar saturation levels when using lithium carbonate and no lithium carbonate. The lowest level of porosity was recorded at the different saturation levels of samples at S170-C340-LW. Illustrated in Figure 10 is the test performed using Scanning Electronic Microscope (SEM) and it exhibits the porosity between particles of the printed cubic specimen. Plate-like large crystal growths occurred which have some other unreacted particles on the surfaceof the specimens. Moreover, it can be seen that there are deep holes and incohesive particles on SEM (left and right side of Figure 10). It is evident that hydration was not completed between the cement particles.

The 3D profiling served to detect the porosity of specimens. As shown in Figure 11, the different saturation levels of specimens with different magnifications were tested to explore the porosity and surface roughness of the samples. The test was conducted employing 3D profile Veeco (Dektak) with the following magnifications: 2.5x, 20x and 50x. The clear porosity and haphazard surface shape of the 3D-printed specimens are visible in Figure 11. The samples on the same spot were tested in the side layer (Z-direction, vertical direction in 3DP) for the green part and the cured samples in water. However, after 7 days the cured samples in water were tested by the 3D profile and it showed pit (porous holes) on their surface area. The topographical shape of height distributions changed dramatically. It shows the value of skewness (*Ssk*) after curing and most samples have positive signs, which mean many high spikes appeared on the surface. The *Ssk* parameter correlated with load bearings and porosity. According to [Petzing et al. (2010](#_ENREF_20)) the *Ssk* is zero when the height distribution has a symmetrical surface. This is validated by the centre line for symmetrical and unsymmetrical purposes. So the direction of skew is differentiated above the mean line (negative skew) or below the mean line (positive skew). Figure 11 shows that the samples released and left many particles. Therefore, pit (porous holes) clearly appeared on the surface of cured samples in water.

In general, the 3DP process is complex and many studies continue to focus on different materials formulation. According to this study, the 3D printed cubic specimens did not produce high compressive strength due to open pores between the layers and strips which were not completely filled. This led to less compressive strength. Generally, the powder consisted of; CAC passing sieve 150 µm and OPC does not achieve enough strength in 3DP specimens. One of the reasons for this may be the water (binder) of the printer is not quite enough to hydrate all particles of the material. The morphology of the particles and presence of interparticle pores could be another reason. The fine particles of cement may provide an additional reason, and according to ([Kirchberg et al. 2011](#_ENREF_8)) fine particles increase the contact angle and reduce the powder’s wettability. Moreover, the binder was also not pure water, as it included about 5~10% of polyvinyl alcohol or glycerol (humectant) or methanol (20% volume of binder). The research of [Sun et al. (2013](#_ENREF_21)) used nozzles of 30 Micron to print the layers of ink on the glass to control the ink solidification, and it used solvent materials in water (boiling point 100oC) evaporation during the printing process to induce partial solidification, while ethylene glycol (b.p. 197.3 c) and glycerol (b.p. 290 c) acted as humectants. That humectant is not suitable for use as a mixed water-based binder because it reduces the compressive strength of cementitious materials.

**Conclusion**

To sum up, an approach has been developed to use a new material instead of the Z-powder 3DP (Z-corp 150). Recently, 3DP has been used for a variety of purposes, and in this paper 3D printing was applied to civil engineering materials. The study was done on Z-Corp 150 which replaced the Z-printer powder as it has similar properties. The results indicated that with increasing saturation levels, compressive strength increased when the shell and core of samples had the same saturation level, i.e. 100% saturation level (S100-C100). The maximum saturation level of 170% recorded the highest compressive strength. While in different saturation levels of shell and core (core double times of shell), in this saturation level the optimum compressive strength is at S150-C300. Moreover, it is generally agreed that porosity has an effect on the compressive strength of cementitious materials, with more pores meaning there is less strength. In addition, cubic specimens for manual mix design (hand mix) commit different concepts. Since it is logical that by increasing the water /cement ratio the strength of cement will reduce, the reverse will be the case for the 3DP if there is not enough water to hydrate the cement and work as a dripping system. Different structures could be designed using these types of cementitious (CAC&OPC) materials and could print in different angles and directions so that the mechanical strength and amount of porosity of the printed specimen could be accurately determined.

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**Table (1)** Properties of powders for starting Z-powder and CAC & OPC materials.

**Table (2)** Numbers of 3DP cubic specimens at different saturation levels with lithium carbonate (Li2CO3).

**Table (3)** The different levels of saturation converted into water/cement ratio.

**Table (4)** Porosity with different saturation levels of CAC & OPC without Li2CO3 analysed by Image J.

**Table (5)** Measurement of 3D printed (green part) cubic specimens

**Figure 1.** Particle size distributions for Z-printer powder, OPC, CAC and combination of CAC & OPC.

Figure 2. Diagram of 3DP process (reproduced from ([Chia & Wu](#_ENREF_3))).

**Figure 3.** Directional Depiction of the 3D printing process.

**Figure 4.** Morphology surface of cubic specimens (left) (Olympus BX61 Microscope -10X) and samples of CAC, OPC with Li2CO3 prepared by 3D printing (right).

**Figure 5.** Compressive strength of 3DP cubic samples with lithium carbonate.

**Figure 6.**  Compressive strength of hand mixed cubic samples

**Figure 7.** (50\*50) mm diagonal crack inside the Z-powder specimen.

**Figure 8.** Compressive strength test of 3DP cubic specimens without lithium carbonate (Li2CO3).

**Figure 9.** Porosity of 3D printed samples

**Figure 10.**  SEM image of 3D printed samples, left (1µm) right (20µm).

**Figure 11.** 3D profiling for 3D printed samples.