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Author(s): Gibbons, G J; Williams, R; Purnell, P; Farahi, E

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# 3D Printing of Cement Composites

*Dr Gregory J Gibbons, Reuben Williams, Dr Phil Purnell, Elham Farahi*

## **Addresses for Correspondence:**

Dr Gregory J Gibbons:

Address: IARC, WMG, School of Engineering, University of Warwick, COVENTRY, CV4 7AL, UK.

Phone: +44 (0) 24 7652 2524

Fax: +44 (0) 24 7657 5365

E-Mail: g.j.gibbons@warwick.ac.uk

Mr Reuben Williams:

Address: late of School of Engineering, University of Warwick, COVENTRY, CV4 7AL, UK.

Dr Phil Purnell:

Address: 205, School of Civil Engineering, University of Leeds, LEEDS, LS2 9JT, UK

Phone: +44 (0) 113 3430370

Fax: +44 (0) 113 3432265

E-Mail: p.purnell@leeds.ac.uk

Elham Farahi:

Address: Senior Consultant, AMEC Nuclear Waste Technology Services,  
The Renaissance Centre, 601 Faraday Street, Birchwood Park, Birchwood,  
Warrington, WA3 6GN

Phone: +44 (0)1925 675489

Fax: +44 (0)1925 675551

## **Abstract:**

The aims of this study were to investigate the feasibility of generating 3D structures directly in rapid-hardening Portland cement (RHPC) using 3D Printing (3DP) technology. 3DP is a Additive Layer Manufacturing (ALM) process that generates parts directly from CAD in a layer-wise manner. 3D structures were successfully printed using a polyvinylalcohol: RHPC ratio of 3:97 w/w, with print resolutions of better than 1mm. The test components demonstrated the manufacture of features, including off-axis holes, overhangs / undercuts etc that would not be manufacturable using simple mould tools. Samples hardened by 1 day post-build immersion in water at RT offered Modulus of Rupture (MOR) values of up to  $0.8\pm 0.1$ MPa, and, after 26 days immersion in water at RT, offered MOR values of  $2.2\pm 0.2$ MPa, similar to bassanite-based materials more typically used in 3DP (1-3 MPa). Post-curing by water immersion restructured the structure, removing the layering typical of ALM processes, and infilling porosity.

## **Keywords:**

3D Printing; Additive Layer Manufacturing; Rapid Manufacturing; rapid-hardening Portland cement; Flexural strength

## **1. Introduction**

The increasing need for custom-made, short run components in many branches of industry - from military to aerospace to biomedical – is driving the emergence of Additive Layer Manufacturing (ALM) technologies, which involve direct production of functional 3D components from CAD drawings without the intervening production of moulds, forms, dies, mandrels or other tooling. Subtractive technologies – from whittling wood to CNC milling machines – have been used for centuries but are in general energy, capital and material intensive and often limited in their ability to form intricate structures, with product design being dictated by the manufacturing process. Thus a more sustainable additive approach has been the focus of modern systems, at all scales from sub-micron up to metre-size.

A wide range of ALM systems for metals and polymers exist, e.g. laser sintering and stereolithography, but these do not suit macro-scale ceramic components. 3D Printing (3DP) technologies, however, are often based on ceramics. Layers of powdered material – usually modified bassanite, gypsum or related material i.e. plaster of Paris (poP) – are sequentially deposited, onto which water-based binders are sprayed using ink-jet printer technology. Materials other than bassanite have been investigated, including engineering ceramics, e.g. zirconia and alumina, for parts <sup>1</sup>, investment casting shells <sup>2</sup>, and ceramic composites <sup>3</sup>. Recently, attention has turned to bioceramics, e.g. hydroxyapatite <sup>4, 5</sup>, where the control over structure and porosity provided by 3DP is exploited to manufacture customised bone implants offering tailored and more optimal geometry and internal structure.

The system is widely used for rapid prototyping but is generally unsuitable for producing functional parts since the as-printed ceramic has poor strength and water resistance, and considerable post-processing (e.g. polymer impregnation or high temperature sintering) is required to obtain functional properties. The high-temperature post-process required to either sinter the ceramic particles *in situ* or to remove a polymer binder, makes it impossible to use 3DP bioceramic (e.g. hydroxyapatite) scaffolds to deliver heat sensitive bioactive molecules such as growth factors or certain drugs. Furthermore, HA also resorbs very slowly following implantation and traditional sintered HA implants are also very brittle, so there is a significant risk of mechanical failure.

Hydraulic cements would have many advantages over poP-based 3DP precursors:

- A wide range of cement chemistries is available (e.g. low-cost calcium silicates and aluminates, or calcium phosphates for bio-medical applications).
- The cement would react with water to form strong insoluble ceramic hydrates, so no further processing would necessarily be required (other than possible water curing).
- The mechanical properties of the ceramic could be customised simply by adjusting e.g. cement/filler types or water/cement ratios.
- The functional properties of the ceramic can also be adjusted. Changing the water delivery rate would adjust the sub-micron porosity distribution in the hydrated ceramic; active fillers such as drugs or catalysts could easily be included via the powder feedstock or multiple liquid reactants.
- Most cements are orders of magnitude cheaper than current 3DP ceramic precursors.

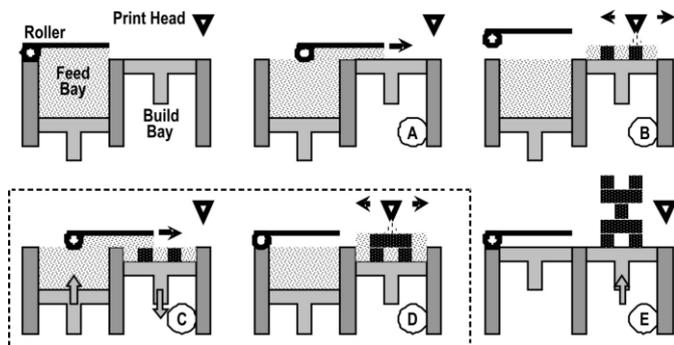
3DP offers the potential to deliver multiple materials to each layer. Currently, multi-head 3DP systems are only concerned with aesthetic function i.e. production of multi-coloured prototypes. A more intelligent use of multi-head delivery systems would be to produce tailored functional/structural composite components by sending different components to each channel of the print head. While one channel would carry the hydration medium, another might carry bioactive moieties (e.g. controlled drug release, growth factors); another might carry a reinforcing polymer; still another might carry a solution designed to modify the affinity of the active surfaces of the designed porosity for a certain molecule (e.g. tailored catalysts). Combined with the tuneable micro- and nano-porosity afforded by cements, this would allow complete control over the functional and structural morphology of components from the nano- to millimetre scales.

An example of an immediate application for using cement technology in ALM is custom hard tissue implants. In order to address this, a number of researchers have tried to incorporate macroporosity into HA structures<sup>6</sup>. Bone grows into the pore structure, adding toughness to the implant, and eventually the HA implant material becomes completely integrated into the new bone structure. These ‘scaffolds’ can be made by a variety of approaches (e.g. the use of porogens, dip casting of polyurethane foams), including ALM<sup>4</sup>. Using ‘cold-setting’ calcium phosphate cements in a 3DP system would make it possible not just to include such bioactives, but to place them into precisely defined locations within the structure to guide tissue formation. This process has only recently been reported<sup>7</sup> and consequently there is enormous scope to refine and exploit this technology. Other applications can be envisaged from any situation where a combination of bespoke geometry, precisely defined material properties and tailored porosity from macro-to nano-scale are required: catalyst substrates, high-performance filters, specialist adsorbents and so on. Simple enhancement (both in terms of performance and cost) of existing RP systems is also a valuable application.

In this paper, we present the results of a preliminary ‘proof-of-concept’ study, using a modified commercial 3DP set-up and a rapid-hardening Portland cement (RHPC) to 3DP ceramic components directly from CAD models. We also report some mechanical and microstructural properties. To our knowledge, this is the first published article to do so.

## 2. Materials and Methods

A Z402 (Z Corporation, USA) mono 3DP machine was used. A schematic of the process is given in Fig.1.

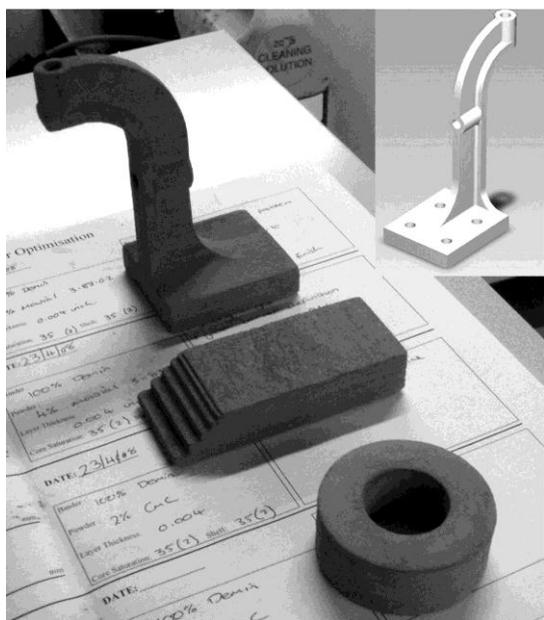


**Fig. 1:** Schematic of 3D-printing process. **A:** the roller deposits a layer of powder on the build platform. **B:** ‘ink jet’ print head sprays liquid reactant onto powder layer, controlled by CAD software. **C & D:** build platform lowers by 1 layer thickness, next layer deposited and reactant printed; repeat as necessary. **E:** after all layers are printed, build platform ejects and unreacted powder is removed to excavate finished component.

robustness of the green (uncured) printed forms.

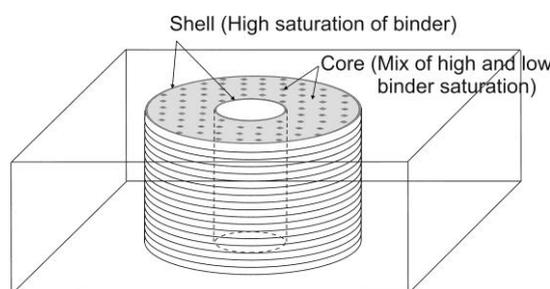
The process prints large cross-sectional layers as an outline ‘shell’ and a cross-hatched ‘core’: the ‘saturation’ (i.e. delivery rate of liquid reactant) of the core and shell can be adjusted slightly (core saturation – CS and shell saturation - SS) (Fig. 2.). Various ratios of RHPC : organic modifier (between 90:10 to 99:1) were employed with each CS/SS ratio. A layer thickness of 0.102 mm was used throughout. Four curing regimes were used:

12h, 24hrs or 26 days in water at room temperature, or 1 day in water at 80°C. Samples were



**Fig. 3:** Demonstration 3D-printed parts. Large bracket is 125 mm high. Inset: CAD model of bracket.

The powder was a standard RHPC chosen as (of the cements available) its particle size distribution most closely matched that of the proprietary bassanite-based 3D printing powder (evaluated using laser diffraction particle sizing – Mastersizer 2000, Malvern Instruments Ltd). The liquid reactant employed was demineralised water. Small quantities (<5% w/w) of organic modifiers (carboxymethylcellulose, PVA, glycerol) were added to powder and/or liquid reactants to help optimise the resolution and

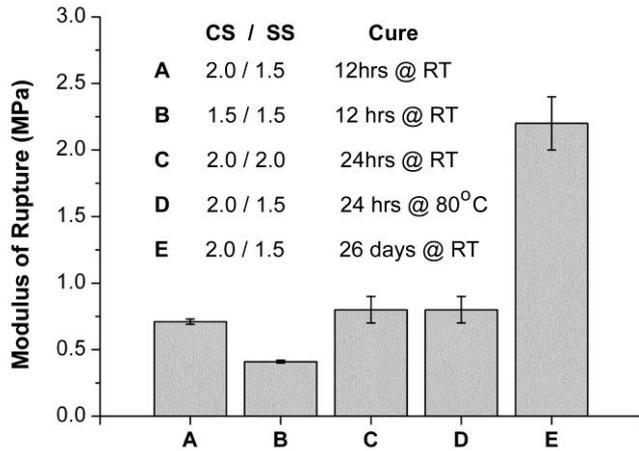


**Fig. 2:** The core and shell printing approach used by the ZCorp 3D Printer.

mechanically tested in 4-point flexure (Testometric micro 100kN with 10kN custom adapter), using a cross-head speed of 0.5 mm/min, major/minor spans of 75/45 mm, and samples having nominally 21x21 mm section. A simple modulus of rupture (MOR) was reported with no shear correction. The MOR was calculated from 5 replicates for each condition. Structural analysis used SEM of fracture surfaces and optical microscopy of sawn surfaces. Further details are available on request.

### 3. Results and Discussion

Preliminary results suggested that the best green forms (sufficient green strength to be handled and best resolution) were obtained by using 97:3 w/w RHPC:PVA (Mowiol 3-83, Synthomer Ltd, UK) as the powder and demineralised water as the liquid. Some typical

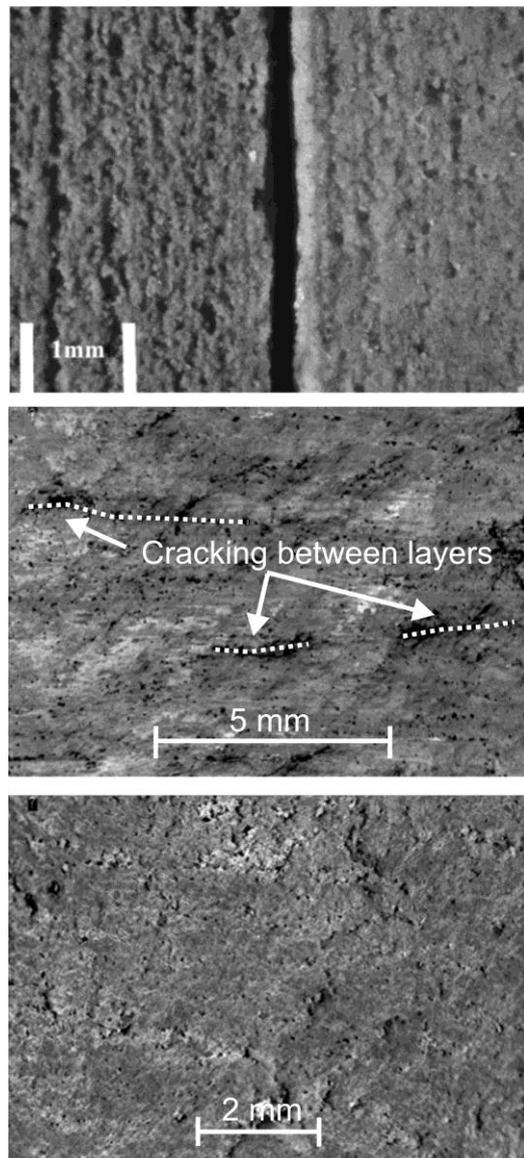


**Fig. 4:** Flexural strength vs. build parameters and curing regime.

(with a statistical significance) by 40% owing to poor consolidation of the green form during printing. Increasing the shell saturation by 25% gave no statistically significant increase in MOR over samples manufactured using a lower shell saturation (C c.f. A). Curing for 1 day at 80°C (ostensibly thermodynamically equivalent to ~50 days at room temperature assuming an activation energy of  $\sim 40 \text{ kJ mol}^{-1}$ <sup>8</sup> for cement hydration) gave only a marginal increase in strength (D c.f. A), while curing for 26 days at room temperature increased mean strength by a factor of  $3.1 \pm 0.4$ , from  $0.71 \pm 0.02 \text{ MPa}$  to  $2.2 \pm 0.2 \text{ MPa}$  (E c.f. A), and is statistically significant. High temperature curing of a cement typically produces a calcium sulphate hemihydrate gel, with slightly lower density and thus, with other conditions being equal, a slightly lower strength. However, the degree of hydration in the 3DP samples at 24hrs will be minimal since the water : cement ratio (w/c) is low and we are initially air curing, so the purpose of the high temperature cure is ensure that a high degree of hydration has taken place in a short time, rather than to give strength per se. We would have expected the strength of the hot cured and 26 day cured samples to be similar, but the observed difference is large (c.f. D and E of Fig. 4). Clearly the curing mechanisms involved in these components are different from those in normal cement paste hydration. Surprisingly, the strength of 26 days cured samples was comparable to that of similarly cured compression moulded cement composite samples<sup>9</sup> despite the relatively low density (pre-cured  $960 \text{ kg m}^{-3}$ , post-cured  $1300 \text{ kg m}^{-3}$  cf.

‘complex’ parts are shown in Fig. 3. Resolutions of  $< 1 \text{ mm}$  were achieved in these preliminary experiments. The process can produce parts with features (internal cavities, off-axis holes, overhangs/undercuts etc) that cannot be directly created using simple moulds.

Fig.4 shows the results of flexural testing of rectangular prisms. The errors given are  $\pm \sigma / \sqrt{n}$  ( $n$ =number of samples). Reducing the core saturation by 25% (A cf. B) reduced the strength of the parts



**Figure 5:** Structure of printed parts characterised in Figure 3. Top: optical micrograph of sawn surface (left = A, right = F). Middle: SEM of fracture surface, A. Bottom, SEM of fracture surface, F.

1800 kg m<sup>-3</sup> in pressed composites and 1300 kg/m<sup>-3</sup> for typical 3DP poP parts). The w/c ratio for samples with core saturation of 2.0 is estimated (from build parameters) as 0.2. w/c has an effect on cement strength, with too low a value resulting in incomplete chemical conversion, and too high a level resulting in excess porosity. The value for 3DP is low compared to the theoretical w/c of 0.38 for complete chemical conversion. This may suggest why the post-cured samples see improved strength.

The structure of the printed parts is shown in Fig. 5. In the young parts the layered structure and significant porosity in the 10-100 µm range can be seen clearly. Although the top image of Fig. 5 is from a rough sawn sample, it clearly shows the layered structure and porosity. More careful sample preparation would be necessary to fully characterise the young structure. The path of the fracture surface is heavily influenced by the layer structure, with cracking observed both between (layer delamination) and across layers. In the cured parts, layering is less distinct, porosity has been reduced (but not eliminated) and the fracture surface path is less influenced by the layers (fracture is more normal to layers, with no evidence of interlayer delamination).

#### 4. Conclusions

It has been demonstrated that complex components can be manufactured using cement-based 3DP. Components have comparable mechanical properties to those of typical poP-based 3DP components (1-3 MPa<sup>10, 11</sup> prior to any post-processing e.g. infiltration with polymers), despite being low density

Since they are manufactured from hydraulic cements, they are also inherently resistant to moisture unlike poP-based systems. The structure inherits a layered aspect from the printing process, which becomes less distinct as components are cured. Heat curing at 80°C is not effective as a means of rapid post processing.

With further optimisation of powder, liquid and print parameters, the resolution limit of 0.1 mm (i.e. the layer thickness) should be achievable.

3DP offers a low w/c ratio compared to a standard RHPC mix. New methods to increase the w/c ratio when 3D printing may be beneficial to the initial strength of the printed parts.

#### 5. Acknowledgements

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