



2<sup>nd</sup> INTERNATIONAL CONFERENCE ON  
**INNOVATION IN LOW-CARBON  
CEMENT & CONCRETE TECHNOLOGY**  
LONDON 8 - 10 JULY 2024

# CONFERENCE PROCEEDINGS



**Editors:** Yun Bai, Yanfei Yue, Raman Mangabhai, Jun Ren, Shi Shi



Conference proceedings of the 2<sup>nd</sup> International Conference on  
Innovation in Low-Carbon Cement & Concrete Technology

Held at

University College London, Gower Street, London  
8 - 10 July 2024

Edited by

**Yun Bai**  
**Yanfei Yue**  
**Raman Mangabhai**  
**Jun Ren**  
**Shi Shi**

## Table of content

<i>Preface</i>	i
<i>Organising committee</i>	ii
<i>Scientific committee</i>	iii
<i>Organisers</i>	iv
<i>Sponsors</i>	vi
<i>Keynote speakers</i>	xviii

### Keynote lecture

The Invention and Nature of Joseph Aspdin's Patent Portland Cement <i>Ian Richardson</i>	2
History of Hydration, from Le Chatelier to Low Carbon <i>Karen Scrivener</i>	3
A History of Calcareous Cements: Precursors to Portland Cement, 1756-1824 <i>Edwin Trout</i>	4
Centurial Evolution of Chinese Cement Industry <i>Tongbo Sui</i>	8
Green and Low-carbon Construction Materials <i>Changwen Miao</i>	9
Sustainable cements: an urgent need <i>Angel Palomo</i>	10
New Admixtures for Low-Carbon "Green" Binders <i>Johann Plank</i>	11
Development of Low Carbon Construction Materials through Innovative Recycling of Waste Materials <i>Chi Sun Poon</i>	14
Materials for Aerial Additive Manufacturing <i>Richard Ball</i>	18
Standardization of Low Carbon Calcined Clay Cements: the UK Experience <i>Colum McCague</i>	24

### Oral Presentation — Hydration (Session A1)

Hydration Characteristics and Phase Transitions of Solid Waste in Low-Carbon Cementitious Material <i>Y. S. Zhao, C. Liu, J. H. Tang, Z. L. Hu, J. M. Gao, and J. P. Liu</i>	26
Research on the Early Cement Hydration Process in the Presence of Dispersed nano Calcium Silicate Hydrated (CSH) Seeds <i>W. Li, Y. B. Fan, Y. L. Shi, and R. J. Wang</i>	31
Effect of Ca/Si and Al/S Content on Hydration Behavior of Red Mud-gypsum Based Cementitious Materials <i>N. Chang, H. Li, W. H. Liu, D. W. Zhang, W. K. Zheng, and X. Z. Wu</i>	35
Thermodynamic Data and Phase Equilibria of AFm Phases and Hydrotalcites Containing Chloride, Bromide, and Iodine Ions <i>M. Collin, D. P. Prentice, D. Geddes, J. L. Provis, K. Ellison, M. Balonis, D. Simonetti, and G. N. Sant</i>	40
The Influence of Municipal Solid Waste Incineration Bottom Ash on Portland Cement Hydration and Binder Properties <i>J. Malaiškienė, V. Antonovič, R. Boris, and R. Stonys</i>	44
Comprehensive Study The Macroscopic Properties, Hydration-Carbonation Process and Micropore Structure of Natural Hydraulic Lime-based Materials Prepared with Metakaolin as Mineral Admixtures <i>D. J. Zhang, S. P. Cui, and Y. L. Wang</i>	48

### Oral Presentation — Novel cementitious materials (Session B1)

Understanding the Behaviour of Magnesium Potassium Phosphate Cements Under Alkaline Environment <i>C. Cau, D. Coumes, L. Diaz, Caselles, G. Poras, A. Rousselet, A. Mesbah, and V. Montouillout</i>	52
--	----

## Materials for aerial additive manufacturing

Richard J Ball<sup>1,2\*</sup>, Barrie Dams<sup>1,2</sup>, Binling Chen<sup>1,3</sup>, Paul Shepherd<sup>1,4</sup>

<sup>1</sup> Department of Architecture and Civil Engineering, University of Bath, Bath, BA2 7AY

<sup>2</sup> Centre for Integrated Materials, Processes & Structures (IMPS)

<sup>3</sup> School of Mechanical Engineering, Beijing Institute of Technology, Beijing 100081, China

<sup>4</sup> Centre for Digital, Manufacturing & Design (dMaDe)

\* [Email: r.j.ball@bath.ac.uk](mailto:r.j.ball@bath.ac.uk)

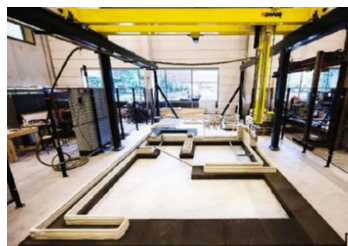
### ABSTRACT

Additive manufacturing, better known as ‘3D printing’ is being increasingly investigated as a method of constructing buildings. Typically, deposition platforms involve large ground-based gantries or robotic arms. Aerial Additive manufacturing is the world’s first project to demonstrate the feasibility of multiple self-powered untethered drones extruding material in flight to construct multiple layers. Use of drones requires the miniaturisation of the additive manufacturing deposition process and the use of lightweight cementitious material. Material in the fresh state needs to exhibit pseudoplastic (shear thinning) behaviour. This involves the material possessing a reduced viscosity while under stress in the deposition system, which then increases by orders of magnitude once deposited thereby minimising deformation due to self-weight and the weight of subsequently deposited layers. Cellulose and xanthan gum were used as rheology modifying admixtures to promote pseudoplastic behaviour, with fly ash and smooth-particle sand used to aid workability. The addition of fibres can improve the flexural and compressive strengths and improve buildability but may decrease the workability of the mix. The addition of tungsten disulphide inorganic fullerene nanoparticles was demonstrated to improve mechanical properties and the impact resistance of 3D printed material. Aerial additive manufacturing could enable work in elevated or challenging site conditions and promote architectural freedom in design.

**Keywords:** Aerial additive manufacturing, cementitious materials, pseudoplastic behaviour.

### 1 INTRODUCTION TO ADDITIVE MANUFACTURING

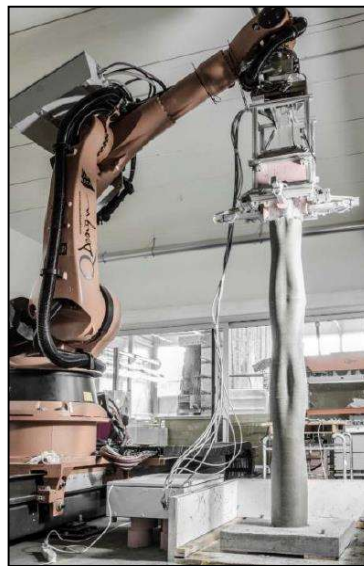
Additive manufacturing methods in the construction industry typically employ deposition methods which are ground based. These can utilise robot arms or gantries capable of moving a printing nozzle through a defined path which deposits material in layers to form the desired structure. Compared to traditional construction techniques there are several advantages including reduced wastage as material is only being used where it is needed. This can then lead to a reduction in labour costs, increased productivity, and improved health and safety with less risk of accidents on site. An additional advantage is the ability to rapidly manufacture bespoke designs without the additional costs associated with expensive moulds or of shuttering. However, there are some important disadvantages of additive manufacturing such as difficulties associated with deployment on construction sites due to the large size and weight of printing equipment, and constraints in the geometrical volume within which printing can occur which is illustrated in the ground based technologies presented in fig. 1.



(a) 3DCP, TU Eindhoven [1]



(b) Multiple mobile robots, Nanyang [2]



(c) Smart dynamic casting, ETH Zurich [3]

Fig. 1. Examples of ground based 3D printing technologies including a gantry based system, robot arms and dynamic casting technology using a robot arm manipulator.

## 2 AERIAL ADDITIVE MANUFACTURING

Aerial additive manufacturing is a new transformative approach to the autonomous construction of buildings and structures using unmanned aerial vehicles to deposit materials [4–6]. The process was developed during the EPSRC funded project ‘Aerial Additive Building Manufacturing: Distributed Unmanned Aerial Systems for in-situ manufacturing of the built environment’. The method enables the use of multiple aerial robots enabling an autonomous printing process where each robot’s printing task is optimised through swarm intelligence for collaborative robot-to-robot operations, dynamic task sharing/allocation, adaptive response to context and dynamic environment content involving functions such as collision avoidance. An illustration of how this technology may be deployed on a construction site in the future is illustrated in fig. 2(a) and a photograph of an aerial robot printing is presented in fig. 2(b).

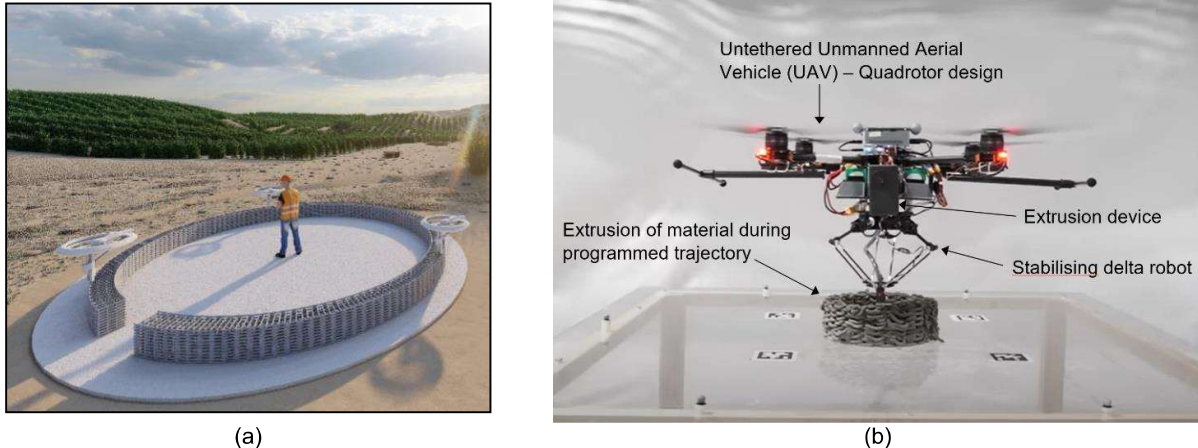


Fig. 2. Aerial additive manufacturing. (a) Image adapted from the Aerial Additive Manufacturing Project, 2023 (Yusuf Kaya). [7] (b) Photograph of aerial platform performing printing operation [8].

## 3 CARRYABILITY, WORKABILITY, BUILDABILITY AND STRENGTH

The material requirements for aerial additive manufacturing processes differ greatly to those for ground-based printing operations. Ground based printers can be connected to a mains power supply, enable material to be pumped from a large reservoir on site, and employ heavy duty wear resistant metal components in the extruder assembly where weight is of minor concern. In comparison, the power to an untethered aerial robot must be supplied from a battery with finite capacity, and lightweight printing material and miniaturised extruder components translate to reduced energy requirements and longer flight times. These factors require very specific rheological properties for aerial additive manufacturing compared to its ground based counterparts, in addition to incorporating lower density mixes. There are four key factors which define the aerial additive manufacturing performance and quality of the printed components, namely; ‘carryability’, ‘workability’, ‘buildability’ and ‘opentime’, which are described in fig. 3. Workability is defined by the ease at which material can flow through the deposition device, tube and nozzle prior to being deposited onto the substrate. Buildability can be defined as the ability of extruded material to resist deformation under self-weight, or the weight of subsequently printed layers. When specifying a material for printing there is often a trade-off between workability and buildability which can be addressed by a mix design which exhibits non-Newtonian shear thinning behaviour. Such materials have a low viscosity when subjected to high shear rates which then increases dramatically once the material is at rest. Carryability relates to the attributes of the mix which are influenced by the characteristics of the aerial robot and deposition device. The fourth parameter is ‘open time’ which defines the time during which the material remains in a printable state prior to setting. This must be sufficiently long to allow mixing, loading, printing and then cleaning of the deposition device. Once these stages have been completed rapid hardening is advantageous to ensure stability of the printed structure.



Fig. 3. Four main factors - ‘carryability’, ‘workability’, ‘buildability’ and ‘open-time’ proposed by the authors that must be optimized to enable AAM.



## 4 CEMENTITIOUS MATERIAL MIX DESIGNS AND PROPERTIES

### 4.1 Binders, aggregates and admixtures

Fig. 4. summarises the key information relating to four mix designs evaluated for their rheological and mechanical properties to reveal relative performance during aerial additive printing operations. As described previously, buildability and workability are important parameters which must be engineered appropriately to create a printable mix design. The constituents used in the mix design and the concentration to which they are used will determine the material properties. When designing a mix for aerial additive manufacturing a combination of CEM1, pulverised fuel ash, henc (hydroxyethyl methyl cellulose), and Xanthan gum provide a base mix that can be adjusted by varying the mix proportions and through including additional components. Materials such as silica flour, silica fume, angular sand and egg albumen contribute to a buildable mix which provides stability once printed and prevents sagging and deformation under load. The small particle size of silica flour and silica fume can occupy the spaces between cement particles helping to densify the mix and prevent movement. Rough edges of angular sand particles will lock together in a wet mix increasing the stress required to initiate flow and providing stability until setting. High surface area and reactivity of silica fume can also enhance the long term strength by reacting with cement clinker under the high pH conditions to produce additional C-S-H (calcium silicate hydrate) phases. However, these constituents proved to be unsuitable for aerial additive manufacturing; to print a component successfully, additional components such as smooth sand, foam and plasticisers are often necessary to enable sufficient workability of the mix so that it can be transferred successfully from the extrusion device, through a tube and nozzle. Smooth sand particles have a low coefficient of friction and promote flow, whilst liquid components may act as surfactants imparting a similar effect. These can influence the water-to-binder ratio required having a large influence on rheology. Parts b and c of the figure show how subtle differences in the mix design influence the shear thinning behaviour. At rest the viscosity ranges between  $10^6$  and  $10^7$  Pa.s, however, as the shear rate is increased from  $10^{-4}$  to  $10^2$  s<sup>-1</sup>, a drop in viscosity of several orders of magnitude to between  $10$  and  $10^2$  Pa.s is observed. Part d of the figure presents some of the key material parameters which summarise the properties including, phase angle  $\delta$  ( $^\circ$ ), complex modulus  $G^*$ , 28-day compressive strength  $f_{28c}$ , 28-day flexural strength  $f_{28f}$  (all MPa) and the force required to process the material through the deposition device and tubing (N), the N value shown on the figure being the true value divided by a factor of 10. Typical material properties were a cured compressive strength of 25 MPa, a complex modulus of 4-9 MPa within a two-hour open time, a yield stress of 1.1 KPa and material densities of approximately 1650 kg/m<sup>3</sup>. Material extrusion during autonomous flight was demonstrated with a printed 28-layer object [9].

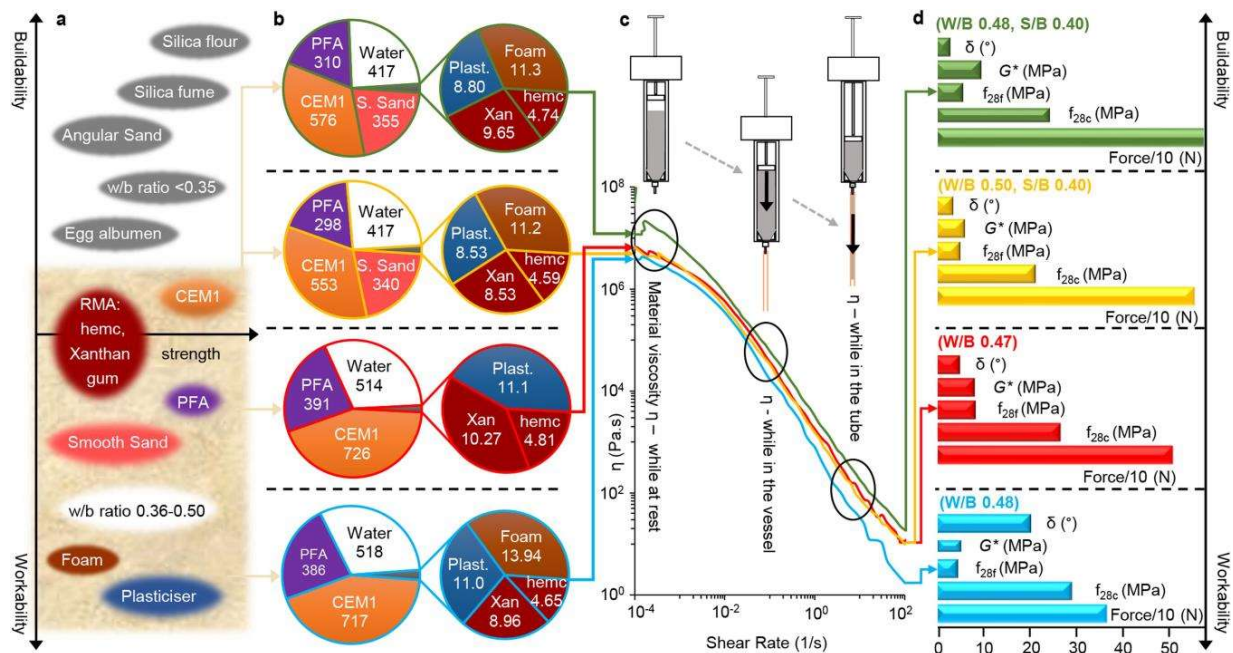


Fig. 4. Cementitious mixes evaluated for their performance for aerial additive manufacturing. [8]

### 4.2 Fibres

The addition of fibres to cementitious mixes provides additional strength leading to enhanced performance particularly under flexural loading [10]. Although this can bring benefits relating to the buildability of the material once it has been deposited, the presence of fibres can decrease the workability. The high aspect ratio of fibres results in even a small concentration having a dramatic effect on the rheological properties of the mix. Fibres can be prone to aggregation leading to non-uniform dispersion and increased frictional forces within the extrusion device, tubes and nozzle. Key fibre properties include the fibre length, diameter, stiffness and surface characteristics (friction/wettability/roughness). Synthetic PVA, aramid and kevlar fibres along with natural fibres from the banana plant were investigated to evaluate their contributions to the workability, buildability, and mechanical strength. Light and electron microscopy images showing the different morphologies of the fibres are shown in fig. 5. The addition of fibres to a cementitious matrix augmented by synthetic hydrocolloids results in compressive and flexural strength increases and transforms the method of failure from brittle to ductile. Increases in compressive strength at 28 days from  $\sim 18$  MPa to  $\sim 25$  MPa and flexural strength increases from  $\sim 3.5$  MPa to  $\sim 5$  MPa were observed between mix

designs with no fibres and the highest strength mix with fibres. Results suggest PVA and kevlar fibres are suitable for a composite cementitious material with optimised rheology specifically designed for aerial additive manufacturing.

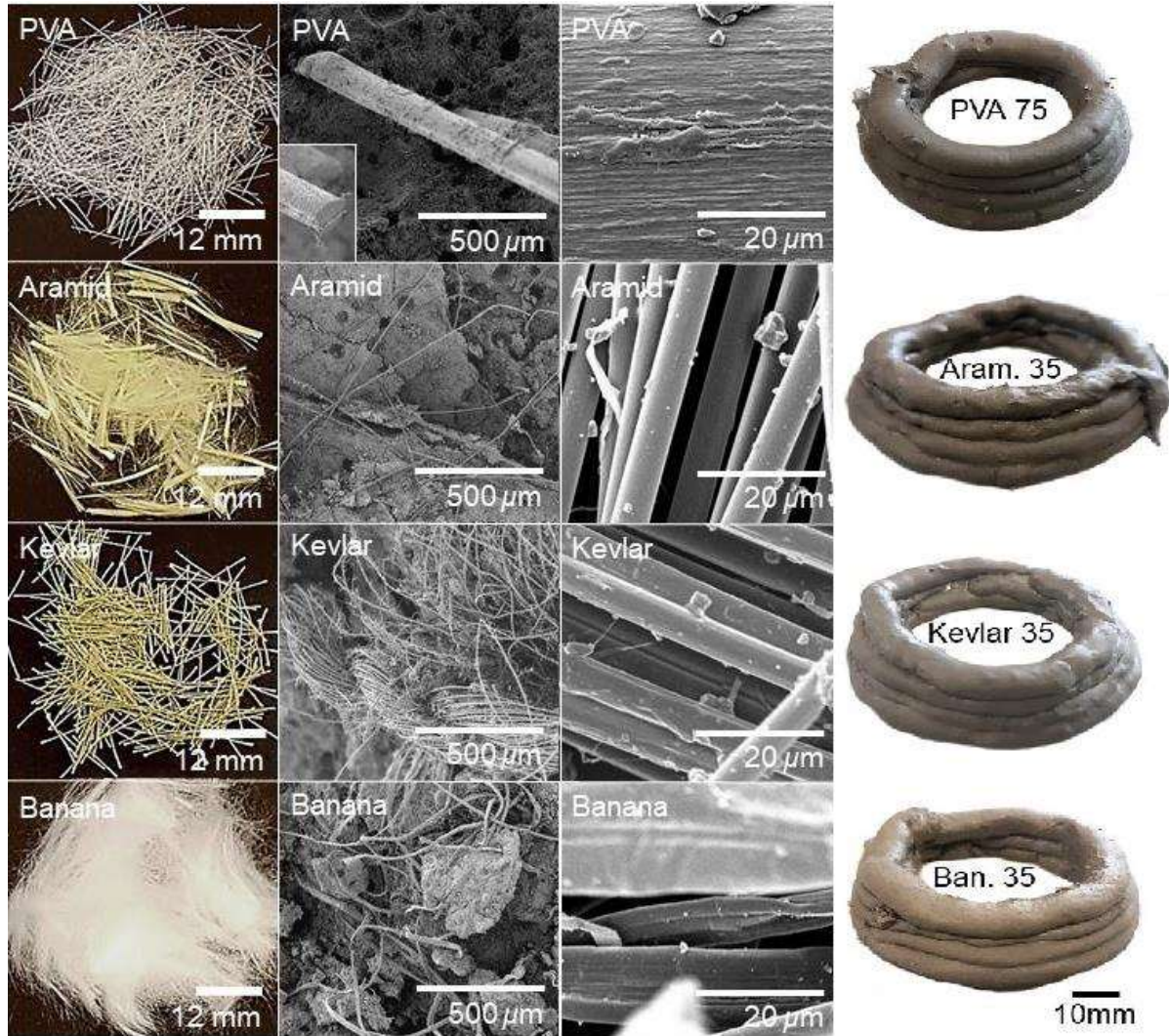


Fig. 5.. Macro (left) and SEM (centre) micro images, printed material (right). Top to bottom: PVA, Aramid, kevlar and Banana. Fibre images are 43x magnification (within matrices, centre) and 1000x (right). Adapted from [10].

### 3.3 Addition of WS<sub>2</sub> nanoparticles for improved shock-absorbing properties

The addition of nanomaterials to cementitious mix designs has been proven to improve a range of properties in civil engineering applications. Different nanoparticles can enhance mechanical properties, sustainability and multifunctionality. Examples include carbon nanotubes [11], graphene oxide [12], and nano-TiO<sub>2</sub>. There is little research in the field of cement-based composites incorporating WS<sub>2</sub> nanoparticles with a fullerene cage structure. The unique structure of these particles enables them to provide superior shock absorbing properties. WS<sub>2</sub> naturally forms sheets comprising of a layer of tungsten atoms sandwiched between two layers of sulphur atoms. These sheets then stack upon each other in weakly bonded layers. WS<sub>2</sub> with the novel inorganic fullerene structures are manufactured using well-established methods based on the sulfidation of tungsten oxide [13]. Under these conditions, the sheets adopt a curved shape forming a series of concentric shells similar to an onion [14]. Under dynamic load this unique structure can deform without breaking, while absorbing dissipating energy effectively [15,16]. When incorporated into a cementitious composite the alkaline environment promotes a reaction between the surface layers in the WS<sub>2</sub> and cement phases. A theory proposed by Chen et. al. suggests that Ca<sup>2+</sup> and OH<sup>-</sup> ions in the pore water solution disrupt the interlayer bonding causing a peeling effect and exposing a greater proportion of the sheet edges. The sulphur atoms are oxidised to sulphate releasing tungsten ions which react with calcium ions and oxygen forming calcium tungstate (CaWO<sub>4</sub>). This forms an interfacial layer between the cement matrix and WS<sub>2</sub> nanoparticles. WS<sub>2</sub> nanoparticles were incorporated into a specially designed cementitious mix for 3D printing which was then used to manufacture a series of test specimens to evaluate the mechanical properties.



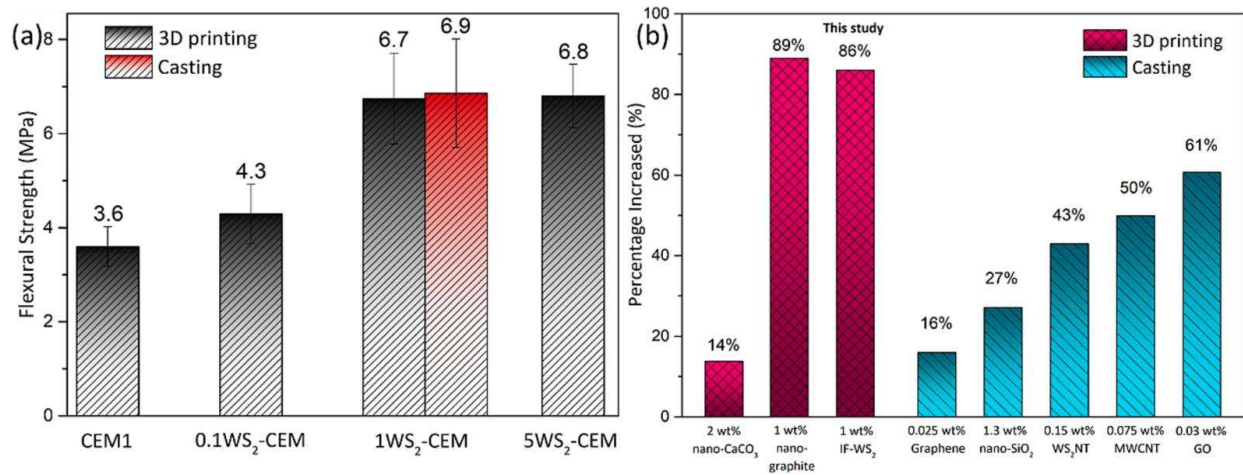


Fig. 6. (a) Flexural strength obtained from 3-point bending tests for each group of components at day-28 with a standard deviation of 0.4 MPa, 0.6 MPa, 0.9 MPa, and 0.7 MPa for 3D printed CEM1, 0.1WS<sub>2</sub>-CEM, 1WS<sub>2</sub>-CEM, and 5WS<sub>2</sub>-CEM, respectively, and 1.2 MPa for casted 1WS<sub>2</sub>-CEM, (b) the comparison of flexural strength improvement between this study and literature. [17]

Fig. 6 (a) illustrates how the flexural strength of cementitious composites is increased by the addition of up to 1 weight % WS<sub>2</sub>. Interestingly there is little improvement between 1 wt % and 5 wt %, however, this was attributed to aggregation of the particles leading to poor dispersion within the matrix. No significant difference between the flexural strength of 3D printed or cast 1 wt % WS<sub>2</sub> composites was observed, indicating that the rheological modifiers added to produce a mix capable of being 3D printed did not have a detrimental effect on the performance. Fig 6(b) is a comparison of 3D printed (using a WASP 40100 printer) and cast designs from various research projects investigating a range of nanoparticles. 3D printed nano-graphite and IF-WS<sub>2</sub> provide the highest % increase in strength.

## 4 CONCLUSIONS

This paper provided an overview of the key properties (workability, buildability, carryability, and open time) required for a cementitious material capable of being printed using an aerial additive manufacturing platform. Important differences between ground based and aerial additive manufacturing systems were described, such as mix density considerations, the microstructure of constituents and rheological properties. A range of constituents and additives were described in the context of how they can be used to modify the key properties and engineer a suitable mix. An overview of synthetic and natural fibres and how these effect properties was given. Finally, the use of inorganic fullerene tungsten disulphide nanoparticles for improving the impact resistance and mechanical properties of 3D printed material was described.

## ACKNOWLEDGEMENTS

The Aerial Additive Manufacturing project was funded by the Engineering and Physical Sciences Research Council (EPSRC) [grant number EP/N018494/1]. This study was supported by the EPSRC Centre for Decarbonisation of the Built Environment (dCarb) [grant number EP/L016869/1] and a University of Bath Research Scholarship.

## REFERENCES

- [1] F.P. Bos, Z.Y. Ahmed, R.J.M. Wolfs, T.A.M. Salet, 3D Printing Concrete with Reinforcement, in: High Tech Concr. Where Technol. Eng. Meet, Springer International Publishing, Cham, 2018: pp. 2484–2493. [https://doi.org/10.1007/978-3-319-59471-2\\_283](https://doi.org/10.1007/978-3-319-59471-2_283).
- [2] X. Zhang, M. Li, J.H. Lim, Y. Weng, Y.W.D. Tay, H. Pham, Q.C. Pham, Large-scale 3D printing by a team of mobile robots, *Autom. Constr.* 95 (2018) 98–106. <https://doi.org/10.1016/j.autcon.2018.08.004>.
- [3] T. Wangler, E. Lloret, L. Reiter, N. Hack, F. Gramazio, M. Kohler, M. Bernhard, B. Dillenburger, J. Buchli, N. Roussel, R. Flatt, Digital Concrete: Opportunities and Challenges, *RILEM Tech. Lett.* 1 (2016) 67–75. <https://doi.org/10.21809/rilemtechlett.2016.16>.
- [4] B. Dams, Y. Wu, P. Shepherd, R.J. Ball, Aerial Additive Building Manufacturing of 3D printed Cementitious Structures, in: 37th Cem. Concr. Sci. Conf. UCL, 2017.
- [5] B. Dams, L. Orr, Y.F. Kaya, B.B. Kocer, P. Shepherd, M. Kovac, R.J. Ball, Deposition dynamics and analysis of polyurethane foam structure boundaries for aerial additive manufacturing, *Virtual Phys. Prototyp.* 19 (2024). <https://doi.org/10.1080/17452759.2024.2305213>.
- [6] B. Dams, B. Chen, P. Shepherd, R.J. Ball, Development of Cementitious Mortars for Aerial Additive Manufacturing, *Appl. Sci.* 13 (2023) 641. <https://doi.org/10.3390/app13010641>.
- [7] B. Dams, B. Chen, Y.F. Kaya, L. Orr, B.B. Kocer, P. Shepherd, M. Kovac, R.J. Ball, Fresh Properties and Autonomous Deposition of Pseudoplastic Cementitious Mortars for Aerial Additive Manufacturing, *IEEE Access.* 12 (2024) 34606–34631. <https://doi.org/10.1109/ACCESS.2024.3373188>.
- [8] K. Zhang, P. Chermprayong, F. Xiao, D. Tzoumanikas, B. Dams, S. Kay, B.B. Kocer, A. Burns, L. Orr, T. Alhinai, C. Choi, D.D. Darekar, W. Li, S. Hirschmann, V. Soana, S.A. Ngah, C. Grillo, S. Sareh, A. Choubey, L. Margheri, V.M. Pawar, R.J. Ball, C. Williams, P. Shepherd, S. Leutenegger, R. Stuart-Smith, M. Kovac, Aerial additive



- manufacturing with multiple autonomous robots, *Nature*. 609 (2022) 709–717. <https://doi.org/10.1038/s41586-022-04988-4>.
- [9] K. Zhang, P. Chermprayong, F. Xiao, D. Tzoumanikas, B. Dams, S. Kay, B.B. Kocer, A. Burns, L. Orr, C. Choi, D.D. Darekar, W. Li, S. Hirschmann, V. Soana, S.A. Ngah, S. Sareh, A. Choubey, L. Margheri, V.M. Pawar, R.J. Ball, C. Williams, P. Shepherd, S. Leutenegger, R. Stuart-Smith, M. Kovac, Aerial additive manufacturing with multiple autonomous robots, *Nature*. 609 (2022) 709–717. <https://doi.org/10.1038/S41586-022-04988-4>.
- [10] R. Dams, Barrie., Amornrattanasereegul, N., Shepherd, Paul. and Ball, Cement-fibre composites for additive building manufacturing, in: P. Ball, Richard, Dams, Barrie, Ferrandiz-Mas, Veronica, Ke, Xinyuan, Paine, Kevin, Tyrer, Mark & Walker (Ed.), *Proc. IOMMM 39th Cem. Concr. Sci. Conf. Univ. Bath, University of Bath, 2019*: pp. 14–18.
- [11] S. Musso, J.M. Tulliani, G. Ferro, A. Tagliaferro, Influence of carbon nanotubes structure on the mechanical behavior of cement composites, *Compos. Sci. Technol.* 69 (2009) 1985–1990. <https://doi.org/10.1016/j.compscitech.2009.05.002>.
- [12] R. Rea, S. Ligi, M. Christian, V. Morandi, M.G. Baschetti, M.G. de Angelis, Permeability and selectivity of PPO/graphene composites as mixed matrix membranes for CO<sub>2</sub> capture and gas separation, *Polymers (Basel)*. 10 (2018). <https://doi.org/10.3390/polym10020129>.
- [13] F. Xu, N. Wang, H. Chang, Y. Xia, Y. Zhu, Continuous production of IF-WS<sub>2</sub> nanoparticles by a rotary process, *Inorganics*. 2 (2014) 313–333. <https://doi.org/10.3390/INORGANICS2020313>.
- [14] F. Xu, T.P. Almeida, H. Chang, Y. Xia, M.L. Wears, Y. Zhu, Multi-walled carbon/IF-WS<sub>2</sub> nanoparticles with improved thermal properties, *Nanoscale*. 5 (2013) 10504–10510. <https://doi.org/10.1039/C3NR03844K>.
- [15] Y.Q. Zhu, T. Sekine, Y.H. Li, M.W. Fay, Y.M. Zhao, C.H. Patrick Poa, W.X. Wang, M.J. Roe, P.D. Brown, N. Fleischer, R. Tenne, Shock-Absorbing and Failure Mechanisms of WS<sub>2</sub> and MoS<sub>2</sub> Nanoparticles with Fullerene-like Structures under Shock Wave Pressure, *J. Am. Chem. Soc.* 127 (2005) 16263–16272. <https://doi.org/10.1021/ja054715j>.
- [16] I. Kaplan-Ashiri, R. Tenne, Mechanical Properties of WS<sub>2</sub> Nanotubes, *J. Clust. Sci.* 18 (2007) 549–563. <https://doi.org/10.1007/s10876-007-0118-9>.
- [17] B. Chen, H. Tsui, B. Dams, H.M. Taha, Y. Zhu, R.J. Ball, High performance inorganic fullerene cage WS<sub>2</sub> enhanced cement, *Constr. Build. Mater.* 404 (2023) 133305. <https://doi.org/10.1016/J.CONBUILDMAT.2023.133305>.