



The effect of nanobubble water on the fresh properties of conventional concrete and 3d printing concrete

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Abstract

Micro-nanobubble- and nanobubble-infused mixing water has shown potential in improving the hardened properties of conventional concrete. However, there is no extensive reporting on the effects of pure nanobubble water on the fresh properties of traditional concrete. Good fresh properties allow for good placing and curing of concrete, affecting a concrete structure's durability. No publicly available literature exists on using micro-nanobubbles or nanobubbles in 3D concrete printing (3DCP). This study addressed the previously mentioned research gaps by carefully studying the fresh properties of both types of concrete. This study concluded that air nanobubble water slightly increases the flowability of conventional concrete. They also slightly enhance the thixotropy of 3D printing concrete.

Keywords: fresh properties, nanobubbles, 3D printing concrete, concrete

1 INTRODUCTION

Micro-nanobubble- and nanobubble-enriched water have been added to conventional concrete to alter its fresh and hardened properties. Micro-nanobubbles are gaseous bodies with a diameter size distribution of 100 μ m or smaller that are evenly distributed within a liquid medium. On the other hand, nanobubbles are gaseous bodies with a diameter of less than 1 μ m. However, in most industries where nanobubbles are applied, nanobubble diameters range between 100 nm and 200 nm [1].

There is a crucial difference between micro-nanobubble water and nanobubble water. Micro-nanobubble water is less stable than pure nanobubble water. Microbubbles with a diameter range between 1 μ m and 100 μ m are more buoyant than the smaller nanobubbles [1, 2]. As a result, microbubbles in the liquid medium gradually reduce in size before collapsing onto themselves [2]. Lower buoyancy nanobubbles, on the other hand, have longer stagnation times and move in the liquid medium in a Brownian motion [2]. Several studies have shown that temperature, pH, salt concentration in the water, and gas type all influence nanobubble stability [2-4].

Literature shows that micro-nanobubbles and nanobubbles decrease the flowability of conventional concrete, increase mechanical properties, and increase durability. This is due to nanobubbles' unique properties, which include large specific surface area, long stagnation times, long-term stability, and a high gas-liquid mass transfer rate [4-6]. In concrete, the probability of the nanobubbles colliding with cement particles is high because of the significant difference in size between the two entities. Equation 1 illustrates the collision

probability between micro-nanobubbles and cement particles where P_c is the probability of collision between a bubble and another particle, Re is the Reynolds number, D_p is the particle diameter [m], and D_b is the bubble diameter [m] [7].

$$P_{c} = \left(\frac{3}{2} + \frac{4Re^{0.72}}{15}\right) \left(\frac{D_{p}}{D_{b}}\right)^{2}$$
(1)

As a result, nanobubbles effectively disperse cement particles throughout the concrete matrix, allowing them to hydrate more easily. The hydration reaction is accelerated, resulting in decreased setting time and reduced flowability in conventional concrete [7]. Consequently, the homogeneity of the concrete mixture improves, resulting in improved mechanical and durability properties. Zeta potential measurements have also shown that nanobubbles have a negative charge, making them more effective in dispersing cement particles [2, 3, 8]. According to other researchers, the increase in hydration temperature observed using micronanobubble water in the concrete is caused by the bubble's localised collapse [9]. Some hypotheses propose that the bubbles function as nucleation points for the precipitation of calcium silicate hydrate (CSH) gel and calcium hydroxide (CH) crystals [9, 10].

Micro-nanobubbles have been used in shotcrete [10] and self-compacting concrete [11] to improve early-age strength, flowability, and durability. Arefi, Saghravani and Naeeni [12] conducted the first use of micro-nanobubble water in concrete at the University of Iran, where they observed a decrease in the workability of the concrete with micro-nanobubble water. A study by Khoshroo, Shirzadi Javid and Katebi [8] utilised air micro-nanobubbles with zeolite and chekneh pozzolan to investigate conventional concrete's fresh and hardened properties. The investigation showed a decrease in the slump of the concrete (due in part to the addition of pozzolans), a marked increase in the mechanical properties of concrete, and an increase in concrete durability.

No literature could be found on using nanobubble and micro-nanobubble water in 3D concrete printing. This significant gap in literature creates an opportunity to contribute to the global body of knowledge in this aspect of nanobubble application. In the last ten years, 3D concrete printing (3DCP) has received significant global research attention [13]. This is due to the method of construction's low labour requirement, which allows for significant cost savings. Besides significantly decreasing labour, 3D concrete printing is safer than conventional construction methods [14]. 3D printing concrete has also shown a lower carbon footprint than other construction methods [15].

Several materials, including fibres and various nanomaterials, have been used in 3DCP to change the fresh and hardened properties [16-18]. A 3D printing concrete mix begins to flow when the pressure applied to the mix during pumping exceeds the static yield stress. The dynamic yield stress needs to be maintained to keep the mix flowing. However, if the dynamic yield stress is too low, the 3D printing mix could segregate [17]. If the dynamic yield stress is too high, the concrete is difficult to pump.

Thixotropy is a key fresh property determining whether a 3D printing concrete mix is printable. Thixotropy depends on the re-flocculation of particles within the concrete matrix and the irreversible chemical reactions that bring about strength build-up after deposition. The re-flocculation rate (R_{thix}) quantifies the flocculation process or the static yield stress build-

up rate after the concrete has been deposited. Therefore, the re-flocculation time (t_{rf}) is when a 3D printing concrete mix fully regains its static yield stress after agitation. The structuration rate (A_{thix}) quantifies irreversible chemical reactions, such as hydration, which occur thousands of seconds after deposition, resulting in a yield stress increase greater than the static yield stress. However, the A_{thix} is affected by other environmental factors, making R_{thix} a better measure of the thixotropy of a 3D printing concrete mix [17].

There has not been extensive research on using pure nanobubble water in conventional concrete, and there are no publicly available studies on using nanobubbles in 3D concrete printing. This study aims to use pure nanobubble water, that is, water with bubbles smaller than 1 μ m, in conventional concrete and 3D printing concrete. The objective of the study is to investigate the effect of air nanobubble water on the fresh properties of conventional and 3D printing concrete.

2 EXPERIMENTS

2.1 Nanobubble Water Generation

An MK1 nanobubble generation machine, supplied by Fine Bubble Technologies (Pty) Ltd [19], was used to generate air nanobubbles at atmospheric pressure. The nanobubbles were generated in a 200-litre water tank for one hour. The water was collected 30 minutes after turning the machine off into 10-litre polyethene water containers and stored in a temperature-controlled room (maintained at 23 °C) for at least 24 hours. Malvern Panalytical's Nanosight NS300 was used to measure the nanobubble concentration, mean, and mode bubble diameters using nanoparticle tracking analysis [20]. At 30 minutes after generation, the average nanobubble concentration was 1.58 x 10⁸ bubbles/ml, with a mean diameter of 137.8 nm (mode 103.1 nm, standard deviation 61.5 nm). The air nanobubble water results are shown in Figure 1. These results are consistent with results obtained by N. Kalogerakis, G.C. Kalogerakis and Botha [21], who also used the same nanobubble generation machine.

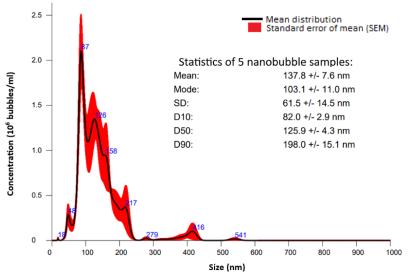


Figure 1: Nanoparticle tracking analysis results performed on 5 samples of air nanobubble water.

2.2 Mix Design and Mix Procedure

This study included two reference mixtures, one conventional concrete reference mix (REF-CONV) and a standard Stellenbosch University 3D printing concrete mix (REF-3D) [17]. One air nanobubble conventional concrete mix was used (ANBC-23). The mix contained air nanobubble water which was stored for 24 hours at 23 °C in a temperature-controlled room One 3D printing concrete mix which contained air nanobubble water stored at 23 °C for 24 hours in a temperature-controlled room was used in this experiment (ANB3DC-23). The normal tap water used in the reference mixes was also stored in the temperature-controlled room at 23 °C for 24 hours before mixing. The mix designs of the concrete mixtures are shown in Table 1. Before mixing, the dry constituents for each mix were weighed into containers, sealed, and stored in the same temperature-controlled room (at 23 °C) as their respective water types for the same amount of time (24 hours).

A CEM II/A-L 52.5 N cement from Pretoria Portland Cement (PPC) was used for all the mixes [22]. The conventional concrete mixes contained a natural pit sand, known locally as Malmesbury sand, and 13 mm Greywacke stone as coarse aggregate. The relative density (RD) of the Malmesbury sand was 2.6, the fineness modulus (FM) was 1.35, and the dust content (< μ m 75) was 2.6%. In the 3D printing concrete mixes, a mixture of Malmesbury sand and dune sand, known locally as Phillipe sand, was used. The resulting sand mixture's FM, RD, and dust content were 0.81, 2.64, and 3.2%, respectively. DuraPozz fly ash class F, CHRYSO silica fumes and CHRYSO Premia 310 superplasticiser was used in the 3D printing concrete mixes.

	Mix names			
Constituents [kg/m ³]	REF-CONV	ANBC-23	REF-3D	ANB3DC-23
Normal tap water	209	-	261	-
Air nanobubble water	-	209	-	261
Cement	348	348	579	579
Malmesbury sand	901	901	-	-
Coarse aggregate	900	900	-	-
Malmesbury & Phillipi sand mix	-	-	1169	1169
Fly ash	-	-	165	165
Silica fumes	-	-	83	83
CHRSYO Premia 310	-	-	7	7

Table 1: Conventional and 3D printing concrete mixtures.

2.3 Slump and Flow Table Test

Slump and flow table measurements were conducted just before the rheological characterisation of the conventional and 3D printing concrete mixes was performed, respectively. The slump test [23] was used to measure conventional concrete mixtures' consistency (or flowability). The flow table test [24] was used to assess the flowability of the 3D printing concrete mixes. At least three measurements of slump and flow diameter were conducted, respectively.

2.4 Rheological Characterisation and Buildability Test

An ICAR rheometer [25] was used for the rheological characterisation of the conventional and 3D printing concrete mixes. One stress growth test was used to obtain the conventional concrete mixes' initial static and dynamic yield stress. Using a series of stress growth tests as explained in a study by Kruger, Zeranka and van Zijl [17], the R_{thix}, A_{thix} and t_{rf} of the 3D printing concrete mixes were obtained. Three rheological characterisation measurements were conducted for each mix. The buildability of the 3D printing concrete mixes was evaluated to validate the effect of nanobubbles in 3D printing concrete [17]. A circular hollow column with an outer diameter of 250 mm is printed at a rate of 60 mm/s until failure. Each layer was approximately 10 mm tall and had a maximum width of 35 mm. Only one buildability test was conducted.

3 CONVENTIONAL CONCRETE RESULTS

Figure 2 shows the yield stress and slump results for the two conventional concrete mixes. The coefficient of variation (CoV) for all of the results ranged from 4% to 21%. ANBC-23 has a higher initial static and dynamic yield stress than REF-CONV by 10.7% and 4.9%, respectively. However, the yield stress results do not agree with the slightly (4.6%) higher slump result obtained for ANBC-23 compared to REF-CONV. The higher static yield stress for ANBC-23 compared to REF-CONV can be expected to translate to a lower slump. This is not the case, however, given the larger variation in slump results for ANBC-23 compared to REF-CONV as well as the still rather small variation in slump results, the slump results of these two mixes can be considered very similar. Apart from the static yield stress, the rest of the results for ANBC-23 and REF-CONV have differences of less than 5%. This shows that nanobubbles generated by the MK1 nanobubble machine do not change the fresh properties of conventional concrete significantly. The slump results shown in Figure 2 contradict the slump results in the study conducted by Arefi, Saghravani and Naeeni [12], where a significant decrease in flowability (or consistency) was observed. The difference in results can be attributed to the use of micro-nanobubble water as opposed to pure nanobubble water in this experiment, which resulted in different water properties and the subsequent effects on concrete.

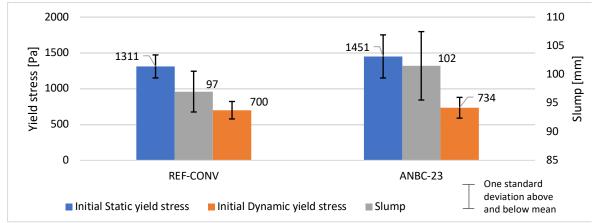


Figure 2: Slump, static and dynamic test results for REF-CONV and ANBC-23.

4 3D PRINTING CONCRETE RESULTS

Figure 3 depicts the flow diameter, static yield stress, and dynamic yield stress results for the two 3D printing concrete mixes. The coefficient of variation (CoV) for all of the results ranged from 0.2% to 20%. ANB3DC-23 has a higher initial static and dynamic yield stress compared to REF-CONV by 4.4% and 7.9%, respectively. The flow diameter results are similar with only a 1.2% decrease in the flow diameter from REF-3D to ANB3DC-23. These results mean that slightly more energy is needed to initiate and maintain the flow of ANB3DC-23. The R_{thix}, A_{thix} and t_{rf} for REF-3D and ANB3DC-23 were also comparable, as shown in Table 2. The R_{thix} of ANB3DC-23 was slightly higher than that of REF-3D. Therefore, the t_{rf} of ANB3DC-23 was shorter than that of REF-3D. The A_{thix} of ANB3DC-23 was marginally lower than that of REF-3D.

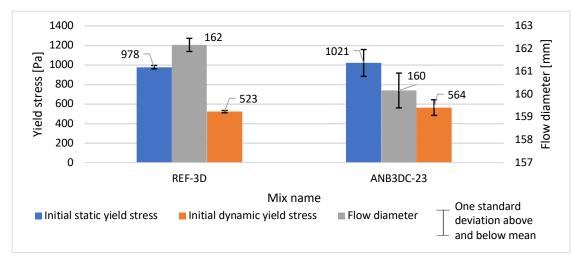


Figure 3: Flow diameter, static and dynamic yield stress results for REF-3D and ANB3DC-23.

Table 2 depicts the buildability test results. These results are comparable and correlate with the R_{thix} and A_{thix} results. The slightly higher A_{thix} result of REF-3D explains why more layers were obtained. After deposition, there was slightly faster structuration in REF-3D than in ANB3DC-23. However, as explained in the introduction several factors other than hydration influence A_{thix}; therefore, R_{thix} is a better measure of the thixotropy of a 3D printing concrete mix. From the results, it can be concluded that ANB3DC-23 is slightly more thixotropic than REF-3D.

Mix name	R _{thix} [Pa/s]	A _{thix} [Pa/s]	t _{rf} [s]	Buildability [layers]
REF-3D	2.91	0.363	156.2	21
ANB3DC-23	2.95	0.355	154.8	19

Table 2: R_{thix}, A_{thix}, t_{rf} and buildability results for the two 3D printing concrete mixes.

The results for the 3D printing concrete mixes are similar. They demonstrate that the pure nanobubble water produced by the MK1 nanobubbler does not significantly affect the fresh properties of 3D printing concrete. This means gases such as carbon dioxide could potentially be incorporated in the nanobubbles as a form of carbon capture and the gases could

participate in the hydration reaction without significantly changing the thixotropy of the 3D printing concrete mix. Because the MK1 is lightweight and compact, and requires routine maintenance every three months, transportation and maintenance costs can be kept to a minimum [19]. As long as the cost of delivering regular water to a construction site is low, the overall cost of producing nanobubble water is insignificant in comparison to other construction costs.

5 CONCLUSIONS

Air nanobubbles seem to slightly increase the flowability of conventional concrete. The air nanobubbles also increase the static and dynamic yield stress of conventional concrete. However, the change in the fresh properties of conventional concrete is not significant. Air nanobubbles slightly increase the initial static and dynamic yield stress of 3D printing concrete. Hence, the thixotropy of the 3D printing concrete is slightly enhanced. Because conventional concrete and 3D printing concrete are such different materials, the technology that works for conventional concrete may not work for 3D printing concrete. This fact also explains why the fresh properties differ when air nanobubble water is added. Hardened and durability property tests on conventional or 3D printing concrete containing air nanobubble water had not been performed at the time of writing this paper. As a result, the authors are unable to make a valid comment on the long-term properties of concrete containing nanobubble water at this time.

6 ACKNOWLEDGEMENTS

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REFERENCES

- [1] ISO 20480-1:2017, "Fine bubble technology General principles for usage and measurement of fine bubbles Part 1: Terminology," 2017.
- [2] P. Khan, W. Zhu, F. Huang, W. Gao, and N. A. Khan, "Micro-nanobubble technology and waterrelated application," *Water Sci Technol Water Supply*, vol. 20, no. 6, pp. 2021–2035, 2020, doi: 10.2166/ws.2020.121.
- [3] W. Jia, S. Ren, and B. Hu, "Effect of water chemistry on zeta potential of air bubbles," *Int J Electrochem Sci*, vol. 8, no. 4, pp. 5828–5837, 2013.
- [4] J. N. Meegoda, S. Aluthgun Hewage, and J. H. Batagoda, "Stability of nanobubbles," *Environ Eng Sci*, vol. 35, no. 11, pp. 1216–1227, 2018, doi: 10.1089/ees.2018.0203.
- [5] H. Sharma and N. Nirmalkar, "Enhanced gas-liquid mass transfer coefficient by bulk nanobubbles in water," *Mater Today Proc*, vol. 57, pp. 1838–1841, 2022, doi: 10.1016/j.matpr.2022.01.029.
- [6] J. Villadsen, J. Nielsen, and G. Lidén, "Gas–Liquid Mass Transfer," in *Bioreaction Engineering Principles*, Boston, MA: Springer US, 2011, pp. 459–496. doi: 10.1007/978-1-4419-9688-6_10.
- [7] P. Mohsen Zadeh, S. F. Saghravani, and G. Asadollahfardi, "Mechanical and durability properties of concrete containing zeolite mixed with meta-kaolin and micro-nano bubbles of water," *Structural Concrete*, vol. 20, no. 2, pp. 786–797, 2019, doi: 10.1002/suco.201800030.
- [8] M. Khoshroo, A. A. Shirzadi Javid, and A. Katebi, "Effects of micro-nano bubble water and binary mineral admixtures on the mechanical and durability properties of concrete," *Constr Build Mater*, vol. 164, pp. 371–385, 2018, doi: 10.1016/j.conbuildmat.2017.12.225.

- [9] Z. Wan, T. He, X. Ma, K. Zhang, and Y. Hu, "Research on the synergy of micro-nano bubble water and alkali-free liquid accelerator to improve the early strength and hydration rate of cement," *Journal of Building Engineering*, vol. 57, no. July, p. 104909, 2022, doi: 10.1016/j.jobe.2022.104909.
- [10] H. Liu, Z. Tian, X. Sun, J. Xiang, and X. Jiao, "Study on the multiscale properties of cement-based materials containing nano-bubble water," *Constr Build Mater*, vol. 360, no. 1, p. 129595, 2022, doi: 10.1016/j.conbuildmat.2022.129595.
- [11] B. Yahyaei, G. Asadollahfardi, and A. M. Salehi, "Study of using micro-nano bubble to improve workability and durability of self-compact concrete," *Structural Concrete*, vol. 23, no. 1, pp. 579– 592, Feb. 2022, doi: 10.1002/suco.202000208.
- [12] A. Arefi, S. F. Saghravani, and R. M. Naeeni, "Mechanical Behavior of Concrete, Made with Micro-Nano Air Bubbles," *Civil Engineering Infrastructures Journal*, vol. 49, no. 1, pp. 139–147, 2016, doi: 10.7508/ceij.2016.01.010.
- [13] A. J. Babafemi, J. T. Kolawole, M. J. Miah, S. C. Paul, and B. Panda, "A concise review on interlayer bond strength in 3D concrete printing," *Sustainability (Switzerland)*, vol. 13, no. 13, 2021, doi: 10.3390/su13137137.
- [14] M. Batikha, R. Jotangia, M. Y. Baaj, and I. Mousleh, "3D concrete printing for sustainable and economical construction: A comparative study," *Autom Constr*, vol. 134, no. November 2021, p. 104087, 2022, doi: 10.1016/j.autcon.2021.104087.
- [15] H. Alhumayani, M. Gomaa, V. Soebarto, and W. Jabi, "Environmental assessment of large-scale 3D printing in construction: A comparative study between cob and concrete," *J Clean Prod*, vol. 270, p. 122463, Oct. 2020, doi: 10.1016/j.jclepro.2020.122463.
- [16] J. Sun, F. Aslani, J. Lu, L. Wang, Y. Huang, and G. Ma, "Fibre-reinforced lightweight engineered cementitious composites for 3D concrete printing," *Ceram Int*, vol. 47, no. 19, pp. 27107–27121, 2021, doi: 10.1016/j.ceramint.2021.06.124.
- [17] J. Kruger, S. Zeranka, and G. van Zijl, "An ab initio approach for thixotropy characterisation of (nanoparticle-infused) 3D printable concrete," *Constr Build Mater*, vol. 224, pp. 372–386, Nov. 2019, doi: 10.1016/J.CONBUILDMAT.2019.07.078.
- [18] H. Yang, Y. Che, and M. Shi, "Influences of calcium carbonate nanoparticles on the workability and strength of 3D printing cementitious materials containing limestone powder," *Journal of Building Engineering*, vol. 44, no. January, p. 102976, 2021, doi: 10.1016/j.jobe.2021.102976.
- [19] Fine Bubble Technologies, "MK1 Nanobubbler Operation and Maintenance Manual," 2018. www.finebubbletechnologies.com (accessed Feb. 09, 2022).
- [20] Malvern Panalytical, "Nanosight NS300 User Guide," Worcestershire, 2019.
- [21] N. Kalogerakis, G. C. Kalogerakis, and Q. P. Botha, "Environmental applications of nanobubble technology: Field testing at industrial scale," *Canadian Journal of Chemical Engineering*, vol. 99, no. 11, pp. 2345–2354, 2021, doi: 10.1002/cjce.24211.
- [22] PPC Limited, "PPC Limited," PPC Limited, 2023. https://www.ppc.africa/ (accessed Feb. 09, 2023).
- [23] SANS 5862-1, "Concrete tests Consistence of freshly mixed concrete Slump test," SABS Standards Division, 2006.
- [24] ASTM C1437, "Standard Test Method for Flow of Hydraulic Cement Mortar: C1437-01," *Standard*, pp. 7–8, 2001.
- [25] Germann Instruments, "ICAR Rheometer," Product Specifications, 2010. https://www.germanninstruments.com/concrete-rheometer-icar-plus/ (accessed Feb. 09, 2022).