The Effect Of Viscosity Modifier Agent On The Early Age Strength Of The Limestone And Calcined Clay-Based Sustainable And 3D Printable Cementitious Material

Chen, Yu; Yalçinkaya, Çağlar; Copuroglu, Oguzhan; Schlangen, E.

Publication date
2019

Document Version
Final published version

Published in
Proceedings of the 10th International Concrete Congress

Citation (APA)
Chen, Y., Yalçinkaya, Ç., Copuroglu, O., & Schlangen, E. (2019). The Effect Of Viscosity Modifier Agent On The Early Age Strength Of The Limestone And Calcined Clay-Based Sustainable And 3D Printable Cementitious Material. In *Proceedings of the 10th International Concrete Congress* (pp. 242-250)

The Effect Of Viscosity Modifier Agent On The Early Age Strength Of The Limestone And Calcined Clay-Based Sustainable And 3D Printable Cementitious Material

Yu Chen[1], Çağlar Yalçınkaya[1,2], Oğuzhan Çopuroğlu[1], Erik Schlangen[1]
[1] Delft University of Technology, Faculty of Civil Engineering and Geosciences, Section Materials & Environment, 2628 CN, Delft, the Netherlands
[2] Dokuz Eylül University, Department of Civil Engineering, 35160, İzmir, Turkey
*Phone: (+31) 644015749
*E-mail: Y.Chen-6@tudelft.nl

ABSTRACT

Recently, our group attempted to develop the ternary blended (Portland cement, calcined clay and limestone) cementitious material for 3D concrete printing (3DCP). Due to the elimination of formwork during the layer-by-layer casting process, the printed material should have favorable elastic properties and green strength at the fresh state. A small amount of Hydroxypropyl methylcellulose (HPMC) based viscosity modifier agent (VMA) is used in the printable mixture to enhance the printing shape stability during the printing process. However, adding VMA may delay the hydration of cement-based materials and affect the strength development at an early age. It is necessary to determine how the VMA additions affect the early age strength development of a 3D printable cementitious material. In this paper, three mix designs with different amounts of VMA were selected to perform the uniaxial compression test at different early ages (30 min, 1, 2, 3, 4, 6h). The setting time and compressive strength tests at 1, 7 and 28 days of those mix designs were also measured. Besides, the heat flow of different mix designs was recorded by using the isothermal calorimeter. Finally, it has been found that: (1) adding VMA could contribute to increase the green strength within the first 2h after mixing water and weaken the strength development from 2h to 6h; (2) the VMA additions mainly delayed the initial set and small effects on the final set; (3) about 50% of compressive strength at 1, 7 and 28 days were reduced for the specimens with VMA. (4) the more amounts of VMA was used in the mixture, the more retarding effects on cement hydration.

Keywords: 3D concrete printing, early age strength, limestone and calcined clay, sustainable, viscosity modifier agent.

Introduction

3D concrete printing (3DCP) is used to describe as the large-scale and cement-based additive manufacturing method. 3DCP has been under development by more than 30 of research groups during the past 10 years. Over half of the published papers are based on an extrusion-based printing technique (Buswell et al., 2018). The mix designs of binders for extrusion-based 3DCP are constituted by 70-80% of ordinary Portland cement (OPC) and a small amount of supplementary cementitious materials (SCMs), like fly ash, silica fume and slag (Panda, Unluer and Tan, 2018). The aggregate content of printable concrete is much less than conventional concrete which is also one reason of high quantity of Portland cement in the mix design. Thus, constructing 1 m3 of concrete by 3DCP may consume more amounts of OPC (Chen, Veer and Copuroglu, n.d.). Reducing the content of OPC by involving a higher volume of SCMs is one way to make 3DC sustainable. However, the limitations of using common SCMs (including fly ash, silica fume and slag) in extrusion-based 3DCP for a long-term application have been demonstrated by Chen et al. (2018). The major problem is that the uneven geographical distribution of fly ash and a shortage of silica fume and slag worldwide. Utilizing limestone and calcined clay as an alternative way for developing 3D printable concrete was also proposed. The advantages and sustainability of limestone calcined clay cement have been exploring by Scrivener et al. (2018) However, to our knowledge, few researchers are working on developing limestone and calcined clay based-cementitious material for 3DCP at present.

Eliminating formworks in 3DCP bring many advantages, for example reducing costs, labor works and wastes. However, many challenges and difficulties for cement-based materials have arisen. The rheological requirements of 3D printable cement-based materials have been summarized by Roussel (2018). As he mentioned, after deposition of concrete layers, the material should turn into a pseudo-solid immediately to be able to keep the shape and sustain its own weight. On the other hand, with the increment of the printed structure height, the load above the bottom layers is also increasing. Perrot et al. (2016) used structural build-up to describe and model the contest between the increasing load and strength development of the first deposited layer. The load increase rate is decided by the structure build-up rate that is also understood as the printing speed on the vertical direction. Both Roussel (2018) and Perrot et al. (2016) believed that the mechanical strength of the first layer is linked to the yield stress of the cement-based material. Perrot et al. (2016) also performed a uniaxial compression test on the fresh cement-based material samples to simulate layer by layer process whereas the yield stress was measured by a rheometer in their research. In contrast to yield stress, the very early age strength or green strength may be better to represent the mechanical strength of the first layer at its fresh state. Voigt, Malonn and Shah (2006) defined the uniaxial compressive strength of fresh mortar samples as green strength of the materials. The compressive strength test of fresh mortar samples was also performed by Wolf, Bos and Salet (2018). In their case, a 3D printable mortar material with about 2h of initial setting time was casted as cylinder samples. The cylindrical samples were tested at multiple ages of 0, 15, 30, 60, 90 min. And the time zero (t=0) was recorded after mixing, demolding and placing the specimens.

In the absence of molds, it is impossible to directly use the available mix designs of the limestone calcined clay mortar from literature for 3DCP. As mentioned in the last paragraph, green strength of the bottom layers is one of the most critical factors for the layer-by-layer manufacturing process. Many methods have been tailored in the material aspect to enhance the shape stability and initial green strength of the deposited layers. Adding additives may be the most efficient way to manipulate the green strength evolution. Reiter et al. (2018) summarized two groups of additives (thickening and acceleration). The viscosity modifier agent (VMA) belongs to the group of thickening which does not impact the cement hydration directly. The function of VMA is to modify the flocculation behavior of cement-based material. In our case, a Hydroxypropyl methylcellulose (HPMC) based VMA was applied to adjust the rheological properties and shape stability of the printable mortar. However, as reported by Figueiredo, Copuroglu and Schlangen (2018), HPMC could delay the hydration of OPC and might increase the air void content of the hardened material. The retarding effects of HPMC on cement hydration at an early stage have also been observed by Ou, Ma and Jian (2012). Thus, using HPMC as VMA may affect the mechanical performance of the printed mortar or concrete at the early age. This paper aims to explore how the VMA (represent HPMC) affects the early age strength development of the printable limestone and calcined clay-based cementitious materials. Three mix designs with different amounts of VMA were selected to perform the uniaxial compression test at different rest times (30 min, 1, 2, 3, 4, 6h). Moreover, the effects of VMA on setting time and compressive strength at 1, 7, 28 days were determined by using Vicat tests and uniaxial compression tests (40 mm cube). Finally, the heat flow of different mix designs was recorded to reflect the impacts of HPMC on cement hydration.

Materials and Methods

Raw Materials and Mix Designs

In this study, the CEM I 52.5R Portland cement (OPC) was used. The average particle size (D50) of cement was 17.9 µm. A calcined clay (CC) which contains about 40% of metakaolin was produced from France (D50=69.35 µm). The limestone filler (LF) has the particle size distribution ranging from 0.15 to 63.81 µm. Besides, the sand with the maximum grain size of 2 mm was used as aggregate. A polycarboxylate ether based superplasticizer (SP) and an HPMC based VMA were used to adjust the rheological and thixotropic properties of printable mixtures. The primary function of VMA is to enhance the initial shape stability of the extruded mortar.

Table 1. Mix designs by the mass ratio (The binder: OPC+CC+LF=1).

Type	OPC	CC	LF	Sand	Water	SP	VMA
B45[1]-4VMA	0.55	0.30	0.15	1.5	0.3	0.02	0.0048
B45-2VMA	0.55	0.30	0.15	1.5	0.3	0.02	0.0024
B45-Ref	0.55	0.30	0.15	1.5	0.3	0.02	0

Using the combination of limestone and calcined clay can reduce more content of OPC. According to the findings from Antoni et al. (2012), limestone to calcined clay ratio of 1:2 showed the best results in the compressive strength test. The material properties of the LC3-50 system (LC3 : 50% of clinker, 30% of calcined clay, 15% of LF and 5% of gypsum in the binder) has been demonstrated by Antoni et al. (2012), Avet et al. (2016) and Scrivener et al. (2018). In this case, the binders were designed as 55% of OPC (gypsum: 3%), 30% of CC and 15% of LF. Based on our previous extruding tests, binder to sand ratio was selected as 1:1.5 and the proper water to binder ratio was 0.3 by weight. Additionally, 2% (content of binder mass) of PCE was used to adjust the workability of the fresh matrix. As shown in Table 1, the main parameter of different mix designs is the VMA content. B45-4VMA and B45-2VMA were designed for 3D printing (see Figure 1), whereas B45-ref was used as a reference.

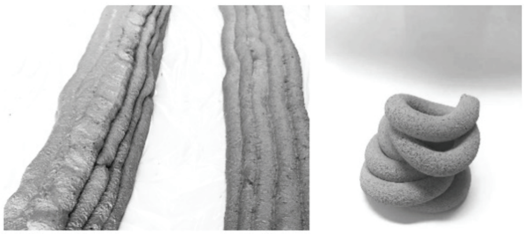

Figure 1. Photographs of extruded samples.

Green Strength

The green strength test was conducted according to the study of Voigt, Malonn and Shah (2006) and Wolfs, Bos and Salet (2018). Samples were prepared as a cylinder with the diameter of 33.5 mm and the height of 67.5 mm to perform the uniaxial compressive strength test. For preparing samples, each batch strictly followed the mixing procedures in Table 2. Initially, the plastic cylinder molds were lubricated by the silicon spray to facilitate demolding. After filling into molds, the specimens were compacted immediately to reduce air bubbles. In this study, time zero was defined as the time of adding the blended solution (water and superplasticizer). For large scale printing works, the printing time might be extended from 2h to 4h or even more depending on the specific scenario. Thus, each mix design was tested at the age of 30 min, 1, 2, 3, 4, 6h and repeated three times. The specimen was carefully demolded before conducting the uniaxial compression test. An Instron machine with the 10 kN load cell was used to conduct the test. A double-layer plastic film was attached on the top and bottom of the sample to reduce the friction between the sample with loading and base plates. The PTFE-spray has been painted in between of two layers before used. The loading rate was set to 12 mm/min and the maximum displacement was 20 mm. Therefore, it took only 2 min for processing each test. Samples remained the homogenous status during the test. The load and compressive force were directly measured and recorded by the system. The vertical and lateral deformation for each sample was also recorded by a high-resolution camera per second. The images were post-processed by using ImageJ software. The area of the cross-section for each sample was real-time calculated. The samples were casted and tested at the same room temperature with 20±2°C and relative humidity (RH) 45%.

Table 2. Mixing procedures for preparing samples.

Time (min:s)	Steps followed
-4:00	Homogenizing dry components
0:00	Adding the blended solution (water and superplasticizer), mixing with the low speed
4:00	Pause, scraping the walls
4:30	Mixing with the high speed
6:00	Stop, start to fill molds

Setting Time and Compressive Strength at 1, 7 and 28 Days

According to the norm of NEN-EN 196-3 (2016), the setting time of all mix designs was determined by an automatic Vicat apparatus at the same indoor environment (20±2°C, 55% RH). For each mix design, 40 mm cube specimens were casted for determining compressive strength at 1, 7 and 28 days in accordance with the specifications of NEN-EN 196-1 (2016). All specimens were casted at the same room conditions and immediately cured in the moisture room (20±1°C, above 99% RH). A compressive strength test machine was used with 2.4 kN/s of load rate in this test.

Isothermal Calorimetry

The heat flow of reactions was measured by the isothermal calorimeter (TAM Air) over 7 days at 20 °C. All the binder ingredients and solutions were prepared and stored at the same temperature as the test for about 24h. For each mix design, dry components were mixed with the blended solution (water and superplasticizer) manually for 5 min., and taking 6g of the fresh mixture into the glass ampoule. Then the sample was moved into the test cell of calorimeter immediately. A reference vessel which was filled by fine sand with the same specific heat capacity of the tested sample was also put into the parallel cell. During the test, a heat value was recorded every 20s.

Results and Discussion

Green Strength

Up to 30% of vertical strain (about 20 mm of displacement) was reached by the uniaxial compressive strength test on fresh cylindrical samples. Due to the lack of VMA addition in B45-Ref, the cylindrical samples at 30 min and 1h immediately slumped (see Figure 2), while others achieved the desired shape stability (Figure 3). The results of B45-Ref are only valid from 2h to 6h. In the early age of 30 min to 6h, the mechanical performance of B45-4VMA and B45-2VMA are illustrated in Figure 4. For B45-4VMA and B45-2VMA, the specimens with old ages show higher peak force. Initially, the load increases nearly linearly during the increment of vertical displacement for each sample. The samples with older age (t=3, 4 and 6h) could get a peak after the initial increasing path and the load decreases with increasing displacement afterward whereas the younger age samples (t=30 min, 1 and 2h) shows rising force with increasing vertical deformations. According to Wolfs, Bos and Salet (2018), the specimens with younger ages fail by bugling instead of forming a distinct failure plane. Cause the stiffness of cylinder samples is quite low at younger ages. As shown in Figure 3 and 4, the specimens show increasing brittleness with the time passing. However, the specimens of B45-Ref have higher peak force from 2h to 6h than that of B45-4VMA and B45-2VMA.

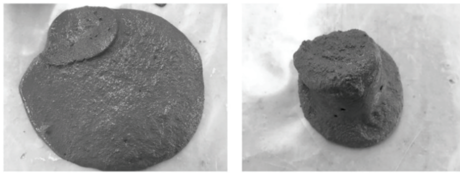

Figure 2. A demolded sample of B45-Ref at the age of 30 min (left); A demolded sample of B45-Ref at the age of 1 h (right).

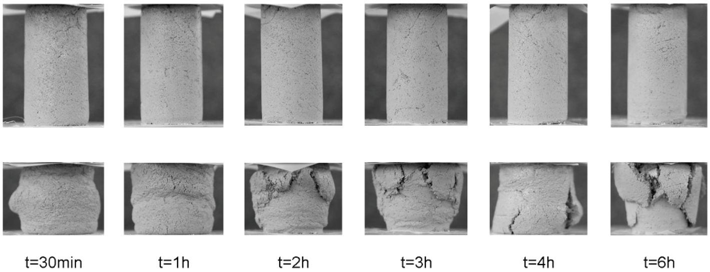

Figure 3. Photographs of B45-4VMA samples at different ages (first row); Photographs of damaged B45-4VMA samples at different ages (second row).

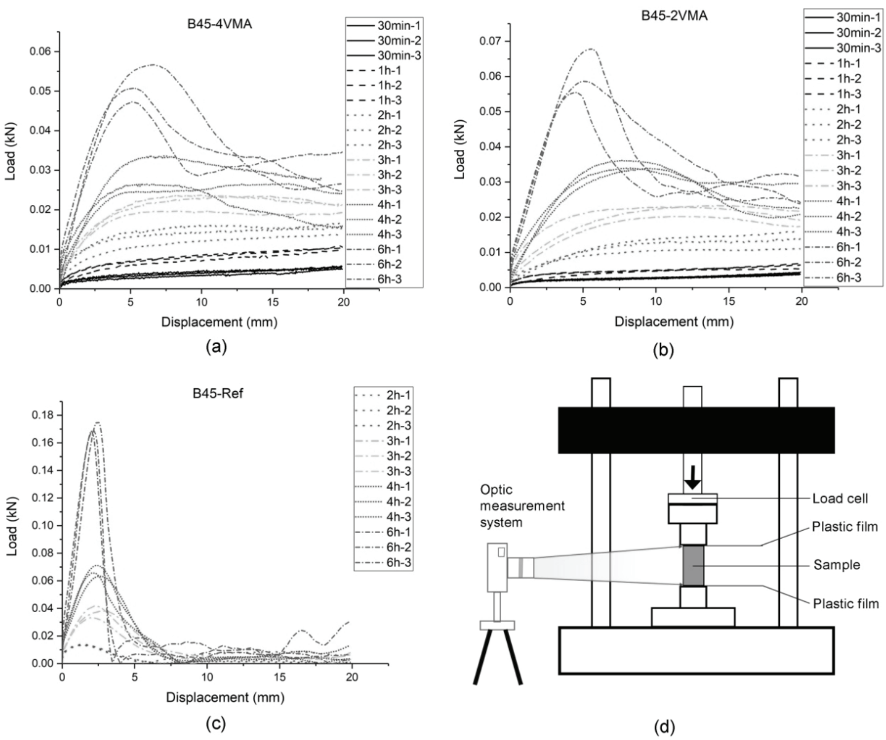

Figure 4. (a) Load and displacement curve of B45-4VMA; (b) Load and displacement curve of B45-2VMA; (c) Load and displacement curve of B45-Ref; (d) Schematic of uniaxial compression test.

Based on the recording of cross-section areas by the optic measurement system, the load-displacement results could be transferred as stress-strain curves. As recommended by Wolfs, Bos and Salet (2018), up to 25% of the strain was collected. All curves reach ultimate strength before 25% of strain in our case (see Figure 5). The peak stress in the stress-strain curve is measured as the green strength of the mix design at that age. The self-weight of specimens is not taken into consideration in this test. The green strength development of each mix design is demonstrated in Figure 5 (d). The specimens of B45-4VMA have a little bit of higher green strength within the initial 2h to compare with B45-2VMA. After 2h, B45-2VMA shows a higher growth rate of green strength and exceeds B45-4VMA after 3h. B45-Ref had the highest growth rate and green strength during the time between 2h and 6h. Thus, in this test, adding VMA could contribute to the very early age strength (within 2h), but affect the green strength development afterward. This result also confirms that VMA benefits to shape stability of printed concrete layers. Increasing the VMA amount from 0.24% to 0.48% of binder mass could enhance minimal green strength at the initial 2h whereas it will slightly decrease the growth rate of early age strength within the first 6h.

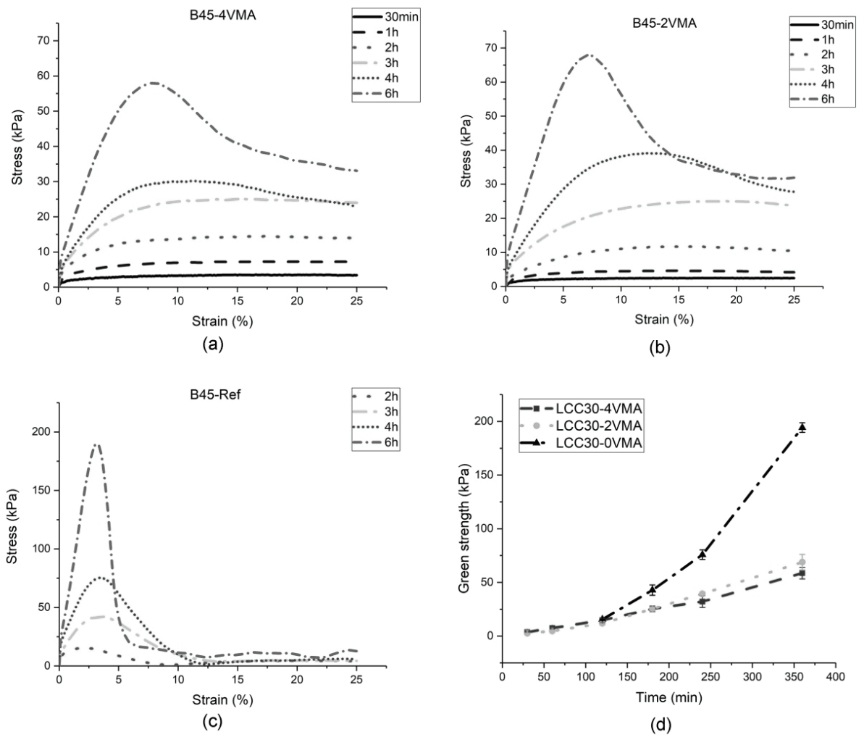

Figure 5. (a) Average stress and strain curve of B45-4VMA; (b) Average stress and strain curve of B45-2VMA; (c) Average stress and strain curve of B45-Ref; (d) Comparison of green strength between mix designs at different ages.

Setting Time and Compressive Strength at 1, 7 and 28 Days

The setting time results of different mix designs from the automatic Vicat test are displayed in Table 3. The initial and final setting times of B45-4VMA and B45-2VMA are quite close. The time gaps between their initial and final set are short. In comparison with B45-Ref, the samples with VMA (B45-4VMA and B45-2VMA) show more than 70 min delay of the initial setting time whereas 10 to 20 min delay for the final set. Thus, in this case, adding VMA prolongs the initial setting time and has a small impact on the final set. The results do not illustrate significant effects of changing VMA contents on the setting time. However, it was observed that resistance of VMA-based mixtures against needle penetration suddenly enhanced towards setting time whereas the other mixtures exhibited a conventional needle penetration resistance, which increases by the time.

Table 3. Setting time.

Type	Initial setting time (min)	Final setting time (min)
B45-4VMA	143	163
B45-2VMA	143	152
B45-Ref	71	142

For each mix design, 6 of the samples were tested at each age. As shown in Figure 6 (a), the impact of using VMA on the compressive strength at 1, 7 and 28 days is significant. As a result of VMA addition, the compressive strength of the material decreased by 50% approximately. The specimens with a small amount of VMA (B45-2VMA) show slightly higher compressive strength than those with a high amount of VMA (B45-4VMA).

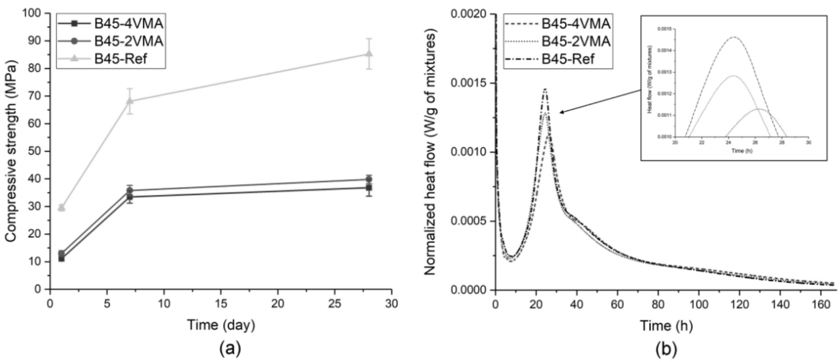

Figure 6. (a) Compressive strength of 40 mm cube casted specimens at 1, 7 and 28 days; (b) Normalized heat flow within 7 days.

Isothermal Calorimetry

The results of isothermal calorimetry tests are presented in Figure 6 (b). The hydration of cement is affected by adding VMA. In Figure 6 (b), compared with the reference sample (B45-Ref), it has been found that the height of C3S peak in both B45-2VMA and B45-4VMA is reduced. The decrease is increased by adding more amounts of VMA. The time of C3S peak is quite close between B45-2VMA and B45-Ref and about 2 h delay in B45-4VMA.

Conclusion

The obtained results of this study illustrated many effects of VMA on the very early age strength of the limestone and calcined clay based printable cementitious material. The outcomes were summarized as follow.

(1) For the first two hours (after mixing water), adding proper amounts of VMA could contribute to increasing the initial green strength, which was useful for reducing slump and retaining the shape of the extruded mortar filaments. However, the green strength was severely affected by VMA from 2h to the end of the green strength test (6h). Only small differences have been found between B45-2VMA and B45-

4VMA.
(2) In this case, using VMA could prolong the initial setting time with more than 1 hour, but less impact on the final set. The effect of VMA content on setting time was not clear according to the results.
(3) The compressive strength at 1, 7 and 28 days was severely weakened by adding VMA. More than 50% of compressive strength was reduced for the specimens with VMA.
(4) It has been confirmed that VMA could affect the hydration of cement, which reflected in delaying appear time and reducing the height of C3S peak in the normalized heat flow curve. The more VMA was added into the mixture, the more retarding effects on cement hydration.

According to the test results above, the impacts of 4VMA and 2VMA on early age strength were quite close. For the next step, it is quite essential to add at least one mix design with the higher or smaller amount of VMA addition. It is also necessary to explore the suitability of mixtures in this paper for 3D concrete printing construction. The buildability test will be conducted by using a 3D printer in the future.

Acknowledgement

Yu Chen would like to acknowledge the funding supported by the China Scholarship Council (CSC) under grant No. 201807720005. Çağlar Yalçınkaya would like to acknowledge the postdoctoral research scholarship supported by The Scientific and Technological Research Council of Turkey (TUBITAK).

References

Antoni, M., Rossen, J., Martirena, F. and Scrivener, K. (2012). Cement substitution by a combination of metakaolin and limestone. Cement and Concrete Research, 42(12), 1579-1589.

Avet, F., Snellings, R., Diaz, A. A., Haha, M. B. and Scrivener, K. (2016). Development of a new rapid, relevant and reliable (R3) test method to evaluate the pozzolanic reactivity of calcined kaolinitic clays. Cement and Concrete Research, 85, 1-11.

Buswell, R. A., de Silva, W. L., Jones, S. Z. and Dirrenberger, J. (2018). 3D printing using concrete extrusion: a roadmap for research. Cement and Concrete Research.

Chen, Y., Veer, F. and Copuroglu, O. (n.d., accepted). A Critical Review of 3D Concrete Printing as a Low CO2 Concrete Approach. Heron.

Chen, Y., Veer, F., Copuroglu, O. and Schlangen, E. (2018, September). Feasibility of Using Low CO 2 Concrete Alternatives in Extrusion-Based 3D Concrete Printing. In RILEM International Conference on Concrete and Digital Fabrication (pp. 269-276). Springer, Cham.

Figueiredo, S. C., Çopuroğlu, O. and Schlangen, E. (2018). Effect Of Viscosity Modifier Admixture On Portland Cement Hydration. In 4th Brazilian Conference on Composite Materials. Rio de Janeiro.

NEN-EN 196-3. (2016). Methods of testing cement - Part 3: Determination of setting times and soundness.

NEN-EN 196-1. (2016). Methods of testing cement - Part 1: Determination of strength.

Ou, Z. H., Ma, B. G. and Jian, S. W. (2012). Influence of cellulose ethers molecular parameters on hydration kinetics of Portland cement at early ages. Construction and Building Materials, 33, 78-83.

Panda, B., Unluer, C. and Tan, M. J. (2018). Investigation of the rheology and strength of geopolymer mixtures for extrusion-based 3D printing. Cement and Concrete Composites, 94, 307-314.

Perrot, A., Rangeard, D. and Pierre, A. (2016). Structural built-up of cement-based materials used for

3D-printing extrusion techniques. Materials and Structures, 49(4), 1213-1220.

Roussel, N. (2018). Rheological requirements for printable concretes. Cement and Concrete Research.

Reiter, L., Wangler, T., Roussel, N. and Flatt, R. J. (2018). The role of early age structural build-up in digital fabrication with concrete. Cement and Concrete Research.

Scrivener, K., Martirena, F., Bishnoi, S. and Maity, S. (2017). Calcined clay Limestone cements (LC 3). Cement and Concrete Research.

Voigt, T., Malonn, T. and Shah, S. P. (2006). Green and early age compressive strength of extruded cement mortar monitored with compression tests and ultrasonic techniques. Cement and Concrete Research, 36(5), 858-867.

Wolfs, R. J. M., Bos, F. P. and Salet, T. A. M. (2018). Early age mechanical behaviour of 3D printed concrete: Numerical modelling and experimental testing. Cement and Concrete Research, 106, 103-116.