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Sustainable 3D printed concrete with CEM III/B and volcanic ash
Reducing the amount of Portland cement in printable mortars

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Sustainable 3D printed concrete with CEM III/B and volcanic ash

Reducing the amount of Portland cement in printable mortars

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Abstract

In the concrete sector there are currently still many gains available in terms of sustainability and especially CO_2 emissions. With the size of the concrete industry and the goals set by climate agreements all over the world, these gains become increasingly important. With 3D concrete printing, a new manufacturing technique with less waste is being explored, however the materials to be printed are largely made with Portland cement as binder. This undoes a lot of the more sustainable changes made to concrete mixtures, where different types of cement have been developed to limit the amount of Portland cement produced.

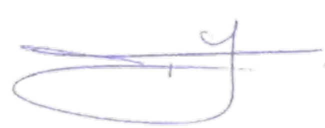
The goal of this research is to see if a sustainable mortar can be used in 3DCP. This sustainable mortar will be created by first replacing the Portland cement with cement of type CEM III/B as it has a lower embodied CO_2. This cement will then be gradually replaced by volcanic ash as a secondary binder. To reach this objective, the following research question has been formulated: 'Can a mortar, with CEM III/B and volcanic ash as its binders, be made suitable for 3D concrete printing?'

To answer this question, requirements on material properties for 3D concrete printing have been researched in literature, as well as the effects that an addition of volcanic ash has on the mixture and material properties. Mixture compositions have been developed in different stages to be used in the research.

In the first stage, non-printable mixture compositions with CEM III/B as a binder were developed based on their consistency. Then gradually the CEM III/B was replaced with up to 40 % of volcanic ash, while adjusting the mixtures based on their consistency. These mixtures with and without volcanic ash were then compared based on their strength, and the impact the replacement could have on the sustainability of the possibly printable concrete. From this a mixture with 30 % cement replacement was chosen to be used in further testing, along with two control mixtures: a commercial one, and a mixture with only CEM III/B as binder.

In the second stage, the chosen mixtures were used in print tests, and adjustments to the mixtures were made to ensure a mixture with extrudable and workable consistency. In the final stage of the research, these printable mixtures were tested and compared based on a selection of their material properties.

From the results on the material properties, it seems that for very small prints, the printable mixture with CEM III/B and 30 % volcanic ash as developed in this research is printable. For larger prints, however, it has to be concluded that the workability and open time of the current mixture is not sufficient.



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Section 1

Introduction

1.1 Problem definition

In recent years, climate change has become a huge problem. The mean global near-surface temperature during the last decade (2011-2020) was 0,95 to 1,20 °C warmer than the pre-industrial level, which makes it the warmest decade on record. European land temperatures have increased even faster over the same period, by 1,9 to 2,02 °C. Without drastic cuts in global greenhouse gas emissions, a 2 °C temperature increase will already be exceeded before 2050 [1]. CO_2 produced by human activities is the largest contributor to global warming. Other greenhouse gases due to human activity are emitted in smaller quantities. Methane, for example, is a more powerful greenhouse gas than CO_2, but has a shorter atmospheric lifetime [2].
In the built environment, concrete is used regularly as a building material. The basis of concrete consists of cement and water as a binder, aggregates and if desired other additives. While the reaction of cement and water does not produce CO_2, the manufacturing process of cement does. In 2018, the production of cement caused around 1,5 Gt of CO_2 emissions [3].
In recent years, different ways than the traditional pouring of wet concrete into a formwork have been explored in order to create concrete structures. One of these ways is the 3D printing of concrete, also known as 3DCP. This new technique offers new, more sustainable, possibilities for the use of concrete in the built environment: less concrete is used, as it is only placed where needed and no waste is created from formwork [4]. However, the concrete mixtures used in 3DCP use more cement than regular concrete mixtures [5]. This does not align with the goal of the Dutch government to reduce greenhouse gas emissions in the Netherlands by 49% by 2030 when compared to 1990 levels as part of the National Climate Agreement [6].
A big goal is to reduce the amount of cement present in concrete mixtures, and subsequently to ensure 3DCP has a smaller CO_2 footprint. The current cement used for the mortar in 3DCP at TU/e, is of type CEM I. This type of cement uses only Portland cement and no other additional constituents. Changing the cement from a CEM I to a CEM III/B could greatly reduce the amount of Portland cement needed in 3DCP, as CEM III/B cement consists of 20-34% Portland cement and 66-80% of granulated blast furnace slag as its main additional constituent [7]. The amount of cement could be even further reduced by combining the cement with a secondary binder to create the mortar.

1.2 Research objective and questions

The goal of this research is to see if a sustainable mortar can be used in 3DCP. This sustainable mortar will be created by first replacing the Portland cement with cement of type CEM III/B as it has a lower embodied CO_2. This cement will then be gradually replaced by volcanic ash as a secondary binder. To reach this objective, the following research question has been formulated:

'Can a mortar, with CEM III/B and volcanic ash as its binders, be made suitable for 3D concrete printing?'

Before this question can be answered, multiple sub-questions will need to be answered first.

1. Which requirements for material properties does a potential mortar have to meet?
2. How much CEM III/B can be replaced with volcanic ash, while still creating a mortar that meets these requirements?
3. Which additives need to be added to the mortar to make it suitable for 3D concrete printing?
4. How do the material properties of the mortar compare to a commercial concrete mixture?

1.3 Relevance

The concrete sector has been trying to lower its carbon footprint for years by reducing the amount of new Portland cement used in the building industry. This is done by increasing the production efficiency and increasing the blended content by adding materials such as blast furnace slag or fly ash [7].

Currently, the only commercial material available for 3DCP at the TU/e, uses Portland cement as a binder. This means that for this relatively new production process, the materials have become less sustainable than regular poured concrete [5]. Materials should not become less sustainable because of a new production method, so it is important to see if the knowledge on the material science of concrete can be transferred to 3DCP as well to keep concrete as sustainable as possible.

1.4 Hypothesis

The mix with CEM III/B and volcanic ash as its binders can be made suitable for 3D concrete printing. This is expected to be the case, since previous research shows that a suitable mortar can be made with up to 40 % of Portland cement replaced with volcanic ash and silica fume [8]. It is expected that a mortar of CEM III/B and volcanic ash, with proper material properties in its hardened state, can be made suitable for 3DCP by adjusting its properties in the wet state with admixtures such as accelerators and retarders to create the right consistency of the mixture during the printing process.

1.5 Approach plan

In this section, the steps needed to answer the research question and its sub-questions will be elaborated. The approach plan is divided in four parts:

1. Literature study
2. Initial experimental research on mixture composition
3. Experimental research on 3D printing
4. Further experimental research on mixture composition

The literature study will consist of research into the following topics. First typical concrete mixture designs will be investigated by finding information on their typical constituents in Section2.
For 3DCP, different material properties will be required. The second part of the literature study will focus on which characteristics a concrete mix will need in order to be printable and ways to achieve this. The results can be found in Section 3
Finally, the replacement of cement by volcanic ash will be a topic for literature study in Section 2.3. Previous research will be used to determine if there is a point where adding more volcanic ash to the mixture has an adverse effect. If such a point is found, this will be used in the experimental research as a maximum for the replacement of CEM III/B by volcanic ash.
During the initial experimental research on the mixture composition, different concrete mixtures will be tested on their consistency, tensile and compressive strength. This will be done to find a suitable mixture which is of a right consistency and sustainability to perform further printing tests with. Mixes during this part of the experimental research will include the current commercial mix used at TU/e for 3D printing as a reference, a mixture with CEM III/B as binder, and mixtures with the CEM III/B replaced by different amounts of volcanic ash. The results from these tests can be found in Section 6.1
For the experimental research on 3D printing, the reference mixture, the mixture with CEM III/B as binder and one of the mixtures with volcanic ash will be used in the experiments. The amount of volcanic ash added to the mixture in this stage will be chosen based the results of the initial experimental results. For this choice, mainly its consistency, tensile and compressive strength are taken into account. The experiments on 3D printing will consist of testing the extrusion and testing the ability of the mixtures to be stacked in layers, and if any changes to the mixture compositions will be necessary. Based on the results, as mentioned in Section **??** more superplasticizer, a retarder and an accelerant might be used in the mixtures to improve the workability during printing.
Finally, further experimental research on the mixture compositions will be performed. In this stage any relevant tests on the mixture compositions used in the experimental research on 3D printing will be performed. These tests will include new tests on tensile and compressive strength, tests on shrinkage, creep, uniaxial compression, ultrasonic waves, open time and x-ray diffraction. The experiments are described in Section 5, and the results described in Section 6.3
After these steps have been performed, the results will be presented and discussed in Section 7 before any conclusions on the main question will be drawn in Section 8. Finally suggestions on further research will be found in Section 9.

Section 2

Research into mixture design

2.1 Concrete design

In essence, concrete is made of cement, water and aggregates. Admixtures can be added to the mixture to modify certain properties of the concrete in either wet or dry state. Usually about 80 % of the weight of the concrete is made up of aggregates, while the rest is binder and admixtures. In most concrete the binder is cement, which will be activated when water is added [7].
Further information given in Section 2.1 and Section 2.2 is taken from *Materials for architects and builders*; [7].

2.1.1 Cements

Standard cement often refers to Portland cement. This is a cement made of chalk or limestone and clay and when water is added, forms a paste which sets and hardens as a result of chemical reactions between the cementitious compounds and water.
The Eurocode recognizes five main types of cement, classified by its main constituents. Besides these main constituents, many others are permitted as composites such as silica fume, fly ash and pozzolanics.

- CEM I Portland cement
- Cem II Portland-composite cement
- CEM III Blast furnace cement
- CEM IV Pozzolanic cement
- CEM V Composite cement

Besides classification by constituents, cements are also classified by its 28-day compressive strength in MPa. They are classified as either 32,5 42,5 or 52,5 MPa based on their lower characteristic strength. Cements are also classified with an ordinary (N), high (R), or low (L) early strength development which is tested via 2- or 7-day compressive strength.
A CEM I cement will be made of 100% Portland cement, while a CEM III/B will be made of 20-34% Portland cement and 66-80% granulated blast furnace slag. The granulated blast furnace slag is a cementitious by-product of the metal industry, which can be ground together in the cement mill with the Portland cement to create a blast furnace cement. Three different types of CEM III are recognized with types A, B and C which, respectively, have increasing percentages of blast furnace slag. A replacement of 50% Portland cement by blast furnace slag can reduce CO_2 emissions in the overall cement production by approximately 40%. CEM III cements will have a slower evolution of heat and development of strength over the first 28-day period, but the final strength will be comparable to that of a Portland cement.

2.1.2 Admixtures

Admixtures are materials which are added in small quantities, usually during the mixing of a mortar or concrete, in order to modify one or more of their properties or performance characteristics in the wet and/or hardened state. For this research superplasticizers, accelerators and retarders are of relevance.
Superplasticizers are used to increase workability in concrete mixtures. If increased workability is not needed, the amount of water in the concrete mix can be reduced without negatively influencing the workability. They can also produce a self levelling concrete and the effects of a superplasticizer usually last up to an hour.
Accelerators increase the reaction rate between cement and water, which increases the rate at which the concrete sets and develops its strength.
Retarders decrease the reaction rate between cement and water, causing the time between mixing and initial set to be extended. This causes the workable time of the mixture to be extended without adversely impacting the 28-day strength.

2.2 Other considerations

Concrete mixes are optimized for performance at the lowest price, where for performance usually strength and durability are most important. When determining a composition, workability of the wet concrete is taken into consideration as well as the properties in its hardened state. In standard concrete, the workability refers to the ability of the concrete to be placed within formwork, around any reinforcement and be successfully compacted to remove air pockets.
The amount of water in a concrete mix influences its workability. Low water/cement ratios mean that the cement is not fully hydrated. At high water/cement ratios the mix becomes increasingly workable, but also more porous as the water evaporates from the concrete. The increase in porosity means that the final concrete will have a lower compressive strength.
The aggregate content and size also has an influence on the workability of the mixtures. Rounded aggregates make a mixture more workable, as compared to angular aggregates with the same water/cement ratio. Large aggregates are used to minimize the water content needed while maintaining a workable mix. Excessive use of fine materials, which can pass through a 0.063 mm sieve, will increase the water requirement to maintain workability.
To determine the workability of a mixture, usually an on site slump test is performed with the use of traditional concrete, however this is not effective for very dry or wet mixes.
Also compaction of the concrete mix has an influence on the strength of the cured concrete. Compaction ensures that air voids trapped in the mixture are removed, before the concrete starts to harden.
During the curing process, concrete will shrink. The extent of the shrinkage is dependent on the types of aggregates used and how much they restrain the concrete from shrinking. Generally, smaller or lightweight aggregates result in larger shrinkage.
When concrete is placed under sustained loads, it will experience creep. The extent of the creep is largely dependent on the E-modulus of the aggregates, with a higher E-modulus having a better resistance to creep.

2.3 Volcanic ash as binder

Research into the use of volcanic ash as binder has yielded some interesting results.
Contrafatto found that volcanic ashes are suitable for a blended cement production due to their reaction with calcium hydroxide which is released during the hydration of cement [9].
Kupwade-Patil et al. found that up to 40 % of volcanic ash along with silica fume is a viable replacement for cement. They found that when more than 40 % of Portland cement is replaced with volcanic ash, a higher volume of capillary voids is present which affect the strength of the mixtures [8].
Celik et al. found that an incorporation of 15% of volcanic ash would produce concrete with similar properties as a reference mix of 100% Portland cement or to a mixture with 20% of fly ash as cement replacement. They also found that including volcanic ash in the mixture will increase the water requirement in the paste and that with an increase of volcanic ash the setting times will increase. Finally they found that any inclusion of volcanic ash will have an adverse effect on the strength development of the mortars at relatively early ages of curing. The inclusion also has an adverse effect on the ultimate compressive strength, but in proportion, the adverse effects are lower than the replacement level of the volcanic ash [10].
Kupwade-Patil et al. suggest that the optimum limit for a substitution of Portland cement and volcanic ash lies between 10 and 30 % replacement, due to the impact the volcanic ash has on the morphology and surface area of the mixture [11].
Khan and Alhozaimy found that the effects of volcanic ash on the properties of the wet concrete are insignificant in initial slump, setting times and slump loss. The compressive strength development is low when compared to Portland cement, but differences in the fineness and source of the volcanic ash did not have an influence on the compressive strength. They also found that mixes containing 15 % volcanic ash are very comparable to a mix containing 20 % fly ash, which in turn is very close to plain concrete. Finally they found that mixes containing more than 20 % volcanic ash are not able to achieve the strength of plain concrete, but can be viable when environmental benefits are of concern [12].
What can be taken from these sources is that the volcanic ash will have a negative effect on the compressive strength of the hardened material, while having little to no influence on the material in its wet state, besides increasing the water demand of the mixture. The amount of cement replaced by volcanic ash should not exceed 40 % and the ideal amount will probably be between 10 and 30 %.

Section 3

3D printing of mortars

The 3D printing of concrete can be defined as a manufacturing method which uses, additive, layer-based manufacturing techniques to create concrete elements without formwork. This lack of formwork is a large economical and ecological benefit that comes with the technique. It also means that conventional concrete mixes are not suitable for printing [5].

3.1 Mixture requirements for printing

Wolfs et al. defined four hydration stages of concrete and three stages related to the printing process [13]. For the hydration these stages are:

1. The initial hydration, which is directly after mixing when the cement first comes into contact with water
2. The dormant stage, in which the reactions of the cement are delayed. In this stage the mechanical properties of the concrete are mainly determined by thixotropic build-up which comes from interparticle forces and low rate hydration reactions.
3. The setting stage, in which the cement reactions accelerate and the materials harden.
4. The hardened stage, in which the the cement reactions decelerate.

For the printing process, the stages are:

1. Pre-deposition, where the concrete is still in the print system
2. Post-deposition/in-print, where the concrete is being printed
3. After printing, where the print process has finished

They state that the hydration and print process stages do not necessarily develop in parallel, but that the extent this depends heavily on the print material used, the print system and design of the object. Also, competing requirements may be found for the required performance in each stage.
Chen et al. further mentions that certain parameters including pump pressure, printing speed, and nozzle distance play essential roles in the printing system. Cooperation between these settings and the properties of the printable material, such as extrudability and open time, are the basis of a successful print process[5].
With all this in mind, there are four main characteristics of the cement-based materials used in 3D concrete printing, namely extrudability, workability, open time and buildability. Extrudability is also known as pumpability and refers to the ability of the material to be delivered in a continuous filament during the in-print phase. It is closely related to the workability which, in this production process, refers to the ability of the concrete to be pumped through the printer without setting, but having it set relatively fast after it has been extruded to create a filament. To aid in a suitable

workability, superplasticizers are often used to keep the water-binder ratio low, retarders are used to avoid setting of the concrete in the printer and accelerators are used to ensure the printed concrete sets quickly. The open time refers to the period in which fresh concrete can be extruded based on proper workability. Finally, the buildability refers to the shape stability of the concrete and the ability of the wet concrete to resist deformation during the fabrication process. Hereby the first layer will need to have developed enough yield strength to resist deforming due to its own weight and the weight of the layers above [5].

3.2 Considerations for mixture design.

As printable concrete is still in a developmental stage, there are no standard protocols for the composition of printable concrete yet. Although there are no protocols yet, there are however a few design considerations that are taken into consideration by many research groups. When compared to conventional concrete, 3D printed concrete requires a decreased water content to meet its demand in low slump and fast setting. A low water-binder ratio also aids in creating a concrete with high compressive strength. Superplasticizers are used to ensure a good workability in combination with the low water content, retarders make sure there is an adequate open time, and accelerators ensure that the concrete sets in a timely manner [5].

Section 4

Mixtures

4.1 Commercial mixture

Currently, the TU/e uses a commercially made mix for concrete printing. Earlier research and print tests show that this mixture is printable, which means it has a suitable consistency and properties during the printing process. After printing, however, the commercial mixtures tend to shrink a significant amount, which can lead to cracks in the newly printed objects. In this area there is room for improvement with respect to the mixture [14].
During this research, the commercial mixture will be used as a reference. It will be used to estimate the mixture consistency needed for a mixture suitable for printing, and as a guidance for the other characteristics of the mixture. Finally, the exact composition of this mixture is unknown, due to the policy of the company that produces the mixture. However, it is known that the mixture is based off a Portland cement and is of strength class C35/45 according to the packaging.

4.2 Mixture design

Before any tests can be performed on a different mixture, samples for the tests will be needed. These can only be made when a mixture with suitable consistency is prepared to be made into samples. For the mixture in this research, a main binder of CEM III/B is chosen based on the fact that it uses 20 to 34% of Portland cement and the other 66 to 80% is made of granulated blast furnace slag [7]. This has an influence on the amount of Portland cement that will have to be produced to make this mixture when compared to a mixture of 100% Portland cement.
To further limit the use of new Portland cement in this mixture, a secondary binder is introduced in the mixture. For this secondary binder, volcanic ash is chosen. This material is chosen, because of its availability. Volcanic ash can be found all over the world, as they are commonly found around volcanoes around the world. This means it will not be necessary to ship the material for long distances as this would oppose the goal to develop a sustainable cement mixture.
The first mixture composition to be developed is one with only CEM III/B as a binder, after which the cement will be replaced with different amounts of volcanic ash. Tests will then determine which amount(s) of volcanic ash are suitable replacements. Finally, during extrusion tests, the mixtures will be made suitable for printing by adding admixtures.

4.2.1 Materials used

In Table 1 an overview is given with more specific information about the materials used for the development of the mixture compositions in this research. The sand mentioned in Table 1 is used as stored in the labs, meaning at room temperature and uncontrolled humidity. During the print tests, the mixtures behaved somewhat inconsistent, despite this not being logical based on the amount of water added. To better control the moisture content in the final tests used to determine the material properties, the used sand was dried overnight in an oven at 60 °C, after which the mixtures gave more consistent results.

Table 1: Specific materials used

Material	Specifics
Cement	ENCI CEM III/B 42,5 N LH HS
Volcanic ash	Tras puzzolaan (brand: DMC) via De mortelcompagnie
Limestone powder	Specifics unknown - available from SED-lab, Vertigo, TU/e
Sand	Standard sand CEN EN 196-1
Superplasticizer	Sika viscocrete-2640 con. 35% spl
Retarder	CUGLA Cretolent F con. 25% BT
Water	Tap water

4.3 Non-printable mixture compositions

In Table 2 the final mixture compositions can be found. These mixtures were of suitable consistency to be workable for test specimen as will be described in Sections 5.2 to 5.9. In Appendix A, all non-printable mixture compositions tested during the research can be found.

In Table 2 the materials used in the mixtures can be seen in the first column. In the following column, the composition of the mixture with only CEM III/B as a binder can be found. In the final columns, the compositions for the mixtures where respectively, 10, 20, 30 and 40 % of the CEM III/B is replaced with volcanic ash can be found. The amount of limestone powder and aggregates has been kept the same in all mixtures, in order to fairly compare the mixtures on the contribution of the volcanic ash.

Table 2: Mixture compositions for non-printable mixtures

	CEM III/B	10% VA	20% VA	30% VA	40% VA
Cement (wt%)	20,29	18,27	16,23	14,20	12,18
Volcanic ash (wt%)	-	2,03	4,06	6,08	8,12
Limestone powder (wt%)	13,04	13,05	13,04	13,04	13,04
Sand (wt%)	66,66	66,66	66,66	66,67	66,66
Water/Binder (-)	0,28	0,28	0,29	0,29	0,30
Superplasticizer/Binder (-)	0,32	0,34	0,39	0,43	0,44

It can also be seen in Table 2 that the water/binder and superplastizicer/binder ratios increase as the amount of volcanic ash is increased. This is necessary to keep a workable mix, and is in line with the literature mentioned in Section 2.3 which stated that adding volcanic ash would increase the water demand of the mixture.

4.4 Printable mixtures

In Table 3 the final printable mixture compositions can be found. These mixtures were of suitable consistency to be workable as test specimen in the tests as will be described in Section 5.10. In

Appendix A, all printable mixture compositions tested during the research can be found, as well as the specific compositions used in each test mentioned in Section 5.

In Table 3 the materials used in the mixtures can be seen in the first column. In the following column, the composition of the printable mixture with only CEM III/B as a binder can be found. In the final column, the composition for the printable mixture with 30 % of the CEM III/B replaced with volcanic ash can be found. The choice for a 30 % cement replacement is further elaborated in Section 6.1.2

Table 3: Mixture compositions for printable mixtures

	CEM III/B	30% VA
Cement (wt%)	20,30	14,21
Volcanic ash (wt%)	-	6,09
Limestone powder (wt%)	13,04	13,04
Sand (wt%)	66,66	66,66
Water/Binder (-)	0,28	0,29
Superplasticizer/Binder (-)	0,32	0,46
Retarder/Binder (-)	0,16	0,22

It can also be seen in Table 3 that the water/binder ratio is very similar to the non-printable mixtures and that superplastizicer/binder ratio increases for the mixture with volcanic ash. This, and an inclusion of a retarder for both mixtures, was necessary to produce a workable and extrudable mixture.

Experimental research

This chapter describes the tests which have been performed during the research. Sections 5.2 to **??** describe the material tests performed. Section 5.9 gives an overview of which material tests have been performed on which mixtures. Finally, Section 5.10 describes the setup used for a mock print test used to determine a mixtures' suitability for 3D printing.

5.1 Mixture preparation

Before any of the tests mentioned in Sections 5.2 to 5.10 can be performed, samples will need to be prepared. Not all tests use identical samples, but the way in which the concrete mixtures are prepared is identical for all tests.

5.1.1 Commercial mixture

For the commercial mixture, the mixture is prepared by weighing a certain amount of powder from the bag, and using the instructions from the manufacturer to determine the prescribed amount of water. The water is then added to the powder while mixing at the slowest mixing speed of an electric mixer. After the water is incorporated, any dry powder still stuck to the mixing bowl is scraped off manually, after which the mixture is left to mix for 10 minutes at the second slowest mixing speed. After this the mixture is transferred to the correct mould for the corresponding test to create samples.

5.1.2 Designed compositions

The concrete mix is prepared by first weighing and combining the dry constituents. Hereby the sand is dried first for the tests where the material properties of the printable mixtures are determined, as mentioned in Section 4.2.1. The dry constituents are mixed thoroughly by hand to make sure they are evenly dispersed through the mixing bowl. Then, while mixing in an electric mixer on the slowest setting, the wet constituents are added one by one, starting with admixtures and ending with water. The mixture is then left to mix for 10 minutes at a setting which is one higher than the slowest. After this the mixture is transferred to the correct mould for the corresponding test to create samples.

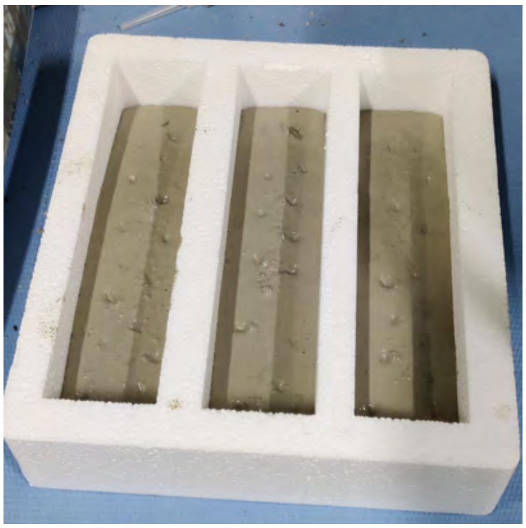
5.2 Bending tests

5.2.1 Goal of test

The goal of the bending test is to find the average ultimate bending strength of the concrete samples.

5.2.2 Methodology

For the bending tests, the prepared mixture is poured into samples of $40 \times 40 \times 160$ mm. These samples are filled halfway, after which the mixture is tamped twenty times with a rod to remove air pockets. Then the mould is filled to the top and tamped again. Finally the excess mixture is troweled off, as can be seen in Figure 1. The samples are then covered in cling film and left to dry. 24 hours after pouring the samples, the moulds are removed and the samples are left to cure in a water bath at room temperature.



(a) Samples filled halfway and tamped

(b) Filled and troweled samples

Figure 1: Filling process of concrete samples for bending tests

For these samples, tamping is chosen instead of using a shaking table, as the designed mixture has a relatively large amount of small particles and shaking would cause all the fine materials to move to the top, after which they are troweled off and removed from the sample. If the fine materials were to be removed from the samples, it would create more a more porous material which has a negative influence on the strength of the sample [15].

The samples are left to dry for 7, 14, 28 and 35 days, after which three samples are used per test moment in a test bench to determine their ultimate bending strength. The samples are tested after 35 days, to see if there is any change in bending strength after 28 days from the pozzolanic activity the volcanic ash provides.

The test setup can be seen in Figure 2 and shows two supports, 100 mm apart, with the force application at 50 N/s in the middle of these supports to create a three point bending test.

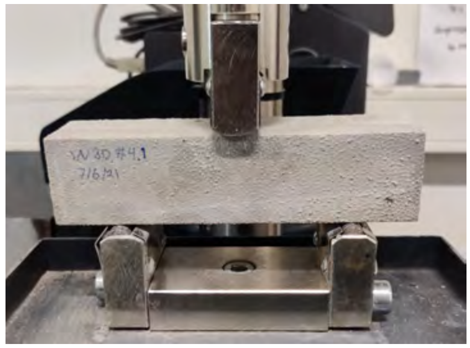


Figure 2: Set-up bending tests

From the bending test, the maximum force in kN is read by the machine, from which the ultimate bending strength in MPa is calculated via Equation 1, whereby the length, width and height of the specimen equal $100 \times 40 \times 40$ mm respectively.

$$\sigma_b = \frac{3Fl}{b \cdot h^2} \tag{1}$$

With,
σ_b = bending strength $[N/mm^2]$
F = maximum applied force $[N]$
l = length of the specimen $[mm]$
b = width of the specimen $[mm]$
h = height of the specimen $[mm]$

5.3 Compression tests

5.3.1 Goal of test

The goal of the compression test is to find the average ultimate compression strength of the concrete samples.

5.3.2 Methodology

For the compression tests, the broken halves of the bending tests are used as samples. The compression tests are performed on the same days as the bending tests.
The test setup as seen in Figure 3 shows a support of 40×40 mm on which the sample is placed, and force is applied via a surface of 40×40 mm at the top of the sample with a speed of 2400 N/s.

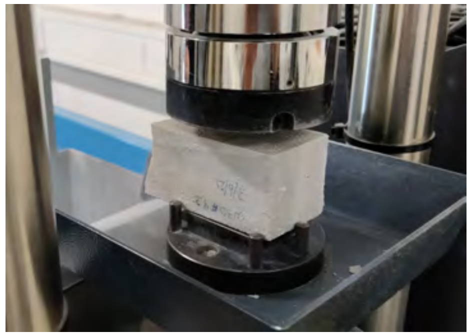


Figure 3: Set-up compression tests

From the compression test, the maximum force is read from the machine, from which the ultimate compressive strength is calculated via Equation 2, whereby the area of compression equals 40×40 mm.

$$\sigma_c = \frac{F}{A} \tag{2}$$

With,
σ_c = compressive strength $[N/mm^2]$
F = maximum applied force $[N]$
A = area of compression $[mm^2]$

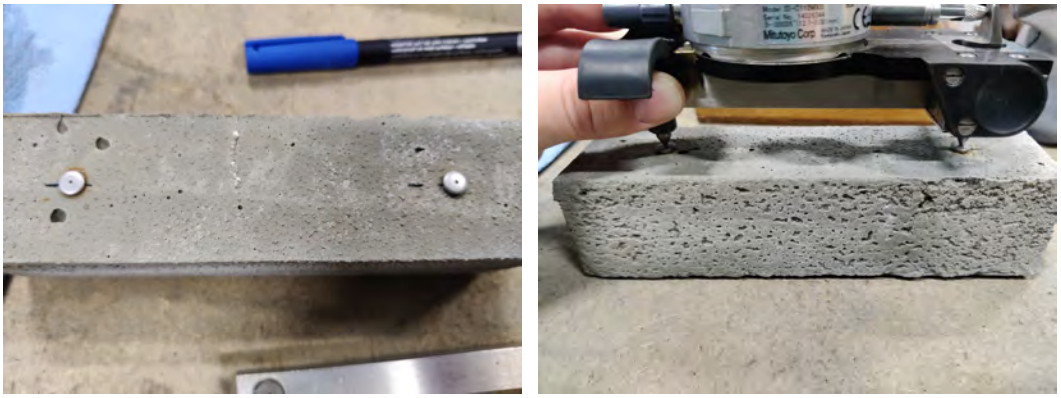
5.4 Shrinkage tests

5.4.1 Goal of test

The goal of the shrinkage test is to find the average unrestrained shrinkage of the concrete samples.

5.4.2 Methodology

For the shrinkage test, the samples are prepared in the same way as for the bending test.
The shrinkage is determined via a length measurement on the concrete samples, performed with a demountable mechanical strain gauge (DEMEC), as can be seen in Figure 4. Hereby two measuring points are glued to two opposite sides of the sample, creating two sets of two measuring points.



(a) Measurement points on sample (b) Measuring of shrinkage

Figure 4: Shrinkage tests

Since these measuring points can only be attached with glue to a sample with a solid surface, they will be attached 24 hours after pouring the samples, at which point the samples have just been demoulded. From the length measurements, the shrinkage of the concrete is calculated via Equation 3, whereby the calibration factor is 0.792, as stated by the manufacturer.

$$\varepsilon_{cs} = \frac{l_{measured}}{l_{original}} \cdot \alpha_{DEMEC} \tag{3}$$

With,
ε_{cs} = shrinkage of concrete $[-]$
$l_{measured}$ = measured distance between the measuring points $[mm]$
$l_{original}$ = original distance between the measuring points $[mm]$
α_{DEMEC} = calibration factor according to manufacturer DEMEC $[-]$

The samples for the shrinkage test will be stored vertically in a climate controlled room, which is kept at 20 °C and 20% relative humidity. Here they will stay for 28 days, during which measurements will be taken.

5.5 Creep tests

5.5.1 Goal of test

The goal of the creep test is to find the average restrained shrinkage, or creep, of the concrete samples.

5.5.2 Methodology

For the creep test, the samples are prepared in the same way as for the shrinkage test, including the attachment of the measuring points. The manner in which the creep is measured via DEMEC and calculated, is the same as in Section 5.4 and Equation 3.

The difference between the two tests lies in the conditions in which the samples are stored. Before measurements begin, the creep samples are placed under a constant load which is equal to one third of the maximum 7-day compressive strength. This constant load is applied 7 days after which the samples are produced, after which the samples will be stored in the same climate controlled room and measurements will be taken for 28 days.
The constant load is applied via a spring in a set-up as can be seen in Figure 5. Here a set up with a fixed bottom plate, and a moveable top and middle plate can be seen. The spring and sample are placed between these plates as can be seen in Figure 5. With the help of a testing bench, the spring is compressed and loaded to the desired load. Bolts are then used to make sure the top plate can no longer move upwards, keeping the spring loaded. Then the load from the testing bench is removed and the samples are stored loaded during measurements.

Figure 5: Set-up creep samples

5.6 Ultrasonic wave transmission tests

5.6.1 Goal of test

The goal of the ultrasonic wave transmission test is to find the average early age E-modulus of the concrete samples.

5.6.2 Methodology

For the ultrasonic wave transmission tests, the prepared mixture is poured into round samples in the test equipment with a diameter and height of 50 mm. These samples are filled, after which the mixture is pressed manually into the moulds, to ensure the mixture fills the mould completely around the transmitter and receiver. After this, the excess mixture is troweled off, and the samples

are covered in cling film and the test equipment is turned on for the next 24 hours.
As can be seen in Figure 6, the equipment consists of a silicone mould with four sound absorbers to avoid other influences of waves which are travelling through the mould. On two sides of the mould, a transmitter and receiver are placed [13].

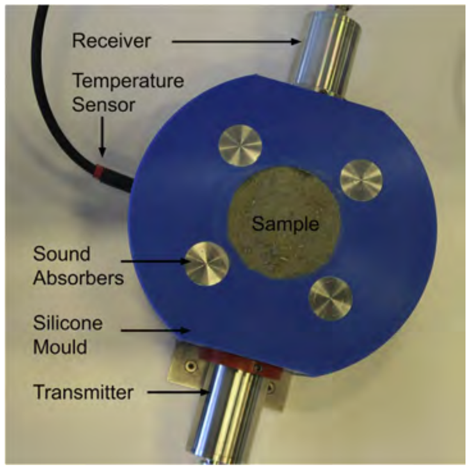


Figure 6: Set-up UWTT [13]

During the experiment, the transmitter sends an ultrasonic wave through the concrete sample each minute to the receiver which is 40 mm away. The time it takes for the ultrasonic wave to reach the receiver is measured and from this, the wave velocity is determined by the equipment. Simultaneously, the temperature of the concrete sample is measured every minute.
From the velocity measurements, the dynamic E-modulus can be calculated using the Newton-Laplace equation which can be found in Equation 4.

$$E_{dyn} = v^2 \cdot \rho \cdot k \tag{4}$$

and where k is calculated via Equation 5 with μ taken as 0,22 as per the instruction manual.

$$k = \frac{(1+\mu) \cdot (1-2\mu)}{(1-\mu)} \tag{5}$$

With,
E_{dyn} = dynamic E-modulus $[MPa]$
v = measured velocity $[m/s]$
ρ = density of the sample $[kg/cm^3]$
μ = Poisson's ratio of the sample $[-]$

5.7 Vicat tests

5.7.1 Goal of test

The goal of the vicat test is to find the initial setting time of the concrete samples.

5.7.2 Methodology

For the vicat test, the prepared mixture is poured into round samples with a diameter of 70 *mm* at the top, and 80 *mm* at the bottom. The height of the sample is 40 *mm*. Then the mould is filled to the top and the mixture pressed down manually to ensure the mould is completely filled. Finally the excess mixture is troweled off.
The sample is then placed in the test equipment as can be seen in Figure 7.

Figure 7: Set-up vicat test

During testing, the needle is lowered until it is in contact with the mixture, but not yet penetrating into the mixture. After a pause in this position to avoid initial velocity, the needle is quickly released and allowed to penetrate the mixture. After penetration has ceased, the scale at the top is read to determine the distance between the tip of the needle and the base plate. This penetration is repeated at a chosen interval in the same sample, with each new penetration no less than 10 mm from the rim or earlier tests. After each penetration, the needle is cleaned.
The time interval chosen for the mixtures differs per mixture. For the commercial mixture, based on comments from other researchers, in the first three hours, only sporadic measurements are done, after this the measurements are increased to five minute intervals. For the mixtures designed in this research, a time interval of five minutes is chosen from the start, with an adjustment to a 2,5 minute interval when the needle stops penetrating to the bottom plate rapidly.
The time interval at which the needle stops at a distance of 4 mm from the base place is recorded as the initial setting time.

5.8 Uniaxial unconfined compression tests

5.8.1 Goal of test

The goal of the uniaxial unconfined compression test is to find the stress-strain relationship of the material.

5.8.2 Methodology

For the uniaxial unconfined compression test, the prepared mixture is poured into cylindrical samples with a diameter of 70 mm and a height of 140 mm. These samples are filled first halfway, and then to the top. The mould is then hit on the sides a few times to remove any air pockets. Finally the excess mixture is troweled off.
The cylindrical moulds are made of two steel halves, which are connected together to form a cylinder. The moulds are lined with a thin sheet of baking paper on the inside to ensure the steel moulds release easily from the samples as can be seen in Figure 8.

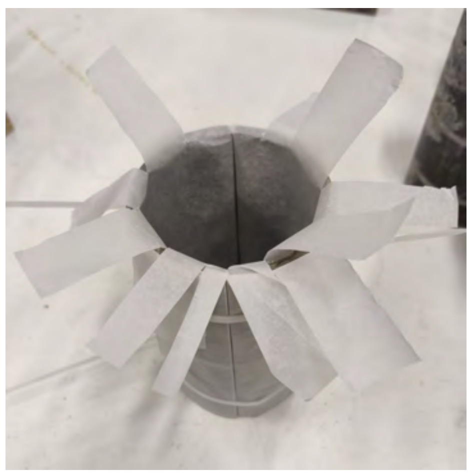


Figure 8: Set-up mould for UUCT

From one batch of mixture, four moulds are filled at the same time and left respectively for 15, 30, 60 and 90 minutes before they are used in the test.
When starting the test, the sample is transferred to an Instron testing machine which has a 5 kN load cell attached, and a cylindrical top and bottom plate with a diameter of 70 mm. The halves of the cylindrical mould, as well as the baking paper is removed from the sample, after which the displacement controlled tests are started at a rate of 30 mm/min.
During the loading of the samples, a picture is taken every 2 seconds to record the deformation of the samples. The pictures are post processed with NI vision builder to determine the exact lateral deformation.
From this, the lateral and axial deformations are related to each other and the force applied. With this data all related to each other, the stress and strain of the samples is determined via Equations

6 and 7.

$$\varepsilon = \frac{\Delta L}{L} \tag{6}$$

With,
ε = strain in the sample $[-]$
ΔL = difference in lateral length of the sample $[mm]$
L = original lateral length of the sample $[mm]$

$$\sigma = \frac{F}{A_{adj}} \cdot 1000 \tag{7}$$

With,
σ = stress in the sample $[kPa]$
F = force applied on the sample $[N]$
A_{adj} = surface of the intersection of the sample, adjusted for the axial deformations $[mm^2]$

From these results, stress-strain curves for the different samples at the different testing times will be compiled. Also the compressive stress will be compared at the different testing times, and the apparent E-modulus at 5% strain will be determined.

5.9 Tests and mixtures

Not all tests mentioned in Sections 5.2 to **??** have been performed on the commercial mix and all the mixture compositions mentioned in Tables 2 and 3. This is due to time constraints and also because not all tests are of interest to perform on mixtures which have not been designed to be used in 3DCP. Lastly, it would be wasteful to make samples for tests where the results are not yet of interest, because of changes that still have to be made to the mixture composition.

Table 4: Overview of which tests have been performed on which mixtures

	Non-printable mixtures					Printable mixtures		
Tests	CEM III/B	10% VA	20% VA	30% VA	40% VA	Com. mix	CEM III/B	30% VA
Bending	yes	yes	yes	yes	yes	yes	yes	yes
Compression	yes	yes	yes	yes	yes	yes	yes	yes
Shrinkage	-	-	-	-	-	yes	yes	yes
Creep	-	-	-	-	-	yes	yes	yes
UWTT	-	-	-	-	-	yes	yes	yes
UUCT	-	-	-	-	-	yes	yes	yes
Vicat	-	-	-	-	-	yes	yes	yes

5.10 Print tests

5.10.1 Goal of the test

The goal of the print tests is to find, via a proof of concept, if the designed mixtures are printable and which admixtures are needed to turn the non-printable mixtures into printable ones.

5.10.2 Methodology

The print tests are divided in three sets of tests. In the first set, the commercial mixture is used to find printer settings which can be used to extrude a continuous concrete filament. In the second set, the mixture with CEM III/B is tested with these same printer settings after which the mixture design is adapted to make it printable. The third set of tests is the same as the second one, but now the mixture with CEM III/B and volcanic ash as binders is used.
For all the sets of tests, a robot arm is used with an automated caulk gun, fitted with a round nozzle, as can be seen in Figure 9.

Figure 9: Set-up robot

The robot arm moves the caulk gun to a certain location at the beginning of the shape to be printed, at which point the caulk gun is filled with mixture. Hereafter the back of the caulk gun is closed, and turned on to extrude the mixture.
In quick succession the robot arm is turned on to run its designed program. This consists of a back and forth line along the bottom plate for the first run, and a program where three layers of material are stacked in the second run. The second run, where the material is stacked, is only performed if the mixture has been successfully extruded during the first run.
After the first set of tests, the printer settings as can be seen in Table 5 yield a proper print result for the commercial mixture. As mentioned before, these settings are then used for the other mixture

compositions as well. This choice was made because it would allow a comparison of the print results without other variables, besides the mixture compositions.

Table 5: Overview printer settings

	Printer settings
Diameter nozzle	15 mm
Height nozzle	15 mm
Print speed	20 mm/s
Turning speed caulk gun	2
Layer height	15 mm

For the second and third set of tests, the mixture compositions of the mixture with CEM III/B with and without volcanic ash as a binder were optimized with the print settings from Table 5. The results can be found in Section 6.2.

Results

As mentioned in Section 1.5, the experimental research is split in three sections. Due to this, the results will also be presented in these three sections. Starting with the experimental research on mixture composition where the focus is to find a mixture of suitable consistency with appropriate tensile and compressive strength. In the second section the focus will be on the results of the print tests, and the adaptations made to the mixture compositions to accommodate extrusion of the mixture. In the final section, the results on different material properties of the chosen mixture designs will be presented and discussed.

6.1 Mixture composition

To find a mixture composition with a suitable consistency, many different mixtures have been made and tried. An overview of all mixtures made and tested can be found in Appendix A. Also, final choices made based on the results from the tests on mixture composition can be found in Section 4.
In this stage of the research, first mixture compositions with only cement as binder are made and evaluated. These mixtures have not been optimized to be printable, and will be referred to as the non-printable mixtures. The mixtures tried can be found in Appendix A, Table 8. From these mixtures, one was chosen to have a suitable consistency. This mixture composition has been mentioned in Section 4.3, Table 2.
From this non-printable mixture with cement as binder, non-printable mixtures with cement and volcanic ash as a binder have been developed. Four different mixture compositions are taken into consideration with respectively 10, 20, 30 and 40 % of the cement replaced with volcanic ash. These amounts are chosen based on the literature found on addition of volcanic ash in concrete mixtures which said that a replacement of more than 40 % would be unsuitable. The exact mixture compositions can be found in Appendix A, Tables 9 to 12. The mixtures that are deemed to have a suitable consistency have also been mentioned in Section 4.3, Table 2.

6.1.1 Bending and compression tests

These five different compositions, along with the commercial mixture have been tested to determine their bending and compressive strength. The results can be seen in Figures 10 and 11. The exact strength and standard deviation values can be found in Appendix B, Table 17.
In Figure 10 the average bending strength of the samples is shown. It can be seen that the mixture without volcanic ash has the highest bending strength and as the amount of volcanic ash is increased, the bending strength decreases. The commercial mixture has a bending strength comparable to the mixture with 40 % volcanic ash.

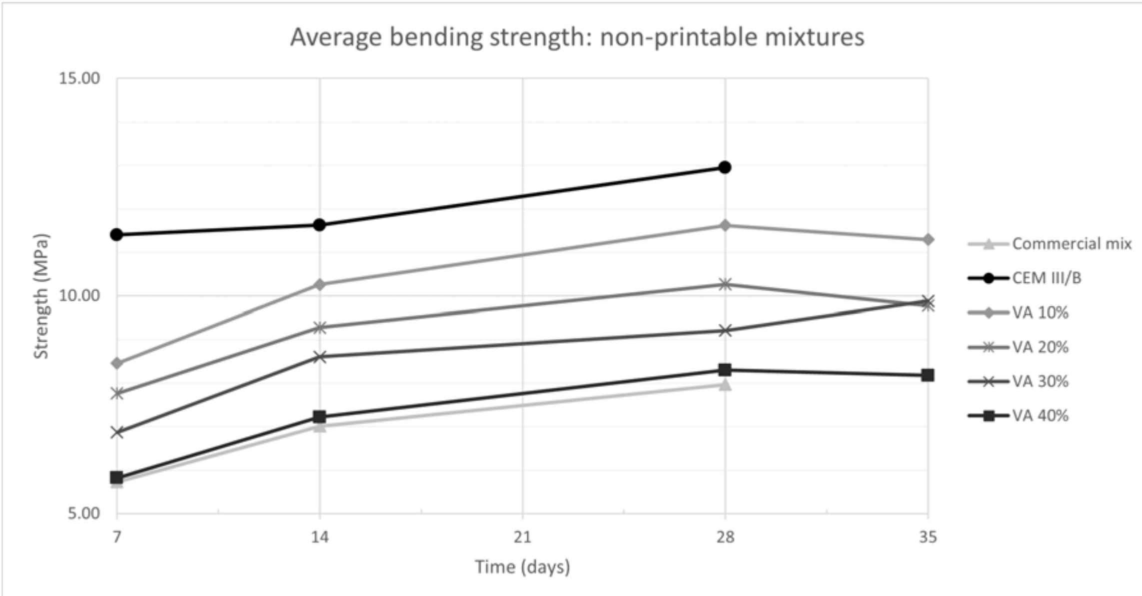


Figure 10: Results bending strength for non-printable mixtures

However, to determine which amount of volcanic ash in the mixture is a suitable candidate for further experiments in the research, the compressive strength is taken as the more determining factor. This is based of the fact that concretes are much stronger in compression than tension, and are almost never applied without reinforcement to increase the tensile strength of the material.
In Figure 11 it can be seen that as more volcanic ash is added to the mixture, the compressive strength decreases in a similar pattern as if does for the bending strength. For the commercial mixture, it is notable that the strength at 7 days is quite close to the compressive strength at 28 days, and that not a lot of strength is developed after 7 days of curing time.
For the mixtures with volcanic ash, a different pattern can be seen, where the mixtures increase in strength during the standard curing period for cement, and even afterwards. The strength development after 28 days, is possible due to the volcanic ash and the pozzolanic reactions that happen in the mixtures.
For the mixture with cement as binder, it can be seen that the compressive strength increases in the first 14 days of curing time, as is expected. However, after this the test results from the 28 day tests give a lower compressive strength than before.
There are a few possible explanations for this: first the amount of specimen used in these tests is very low, so that could influence the results negatively. Second, imperfections on the surface of the samples due to accidental damages on the polystyrene moulds could influence the strength measured in the test. Third, because of the number of samples needed, different batches of material were made to make the samples for the compression tests, so differences in preparation and outcome of mixture, such as homogeneity and porosity could also be possible explanations. And finally, it could also be a plateau in strength, possibly in combination with these explanations that caused the lower strength in the results.

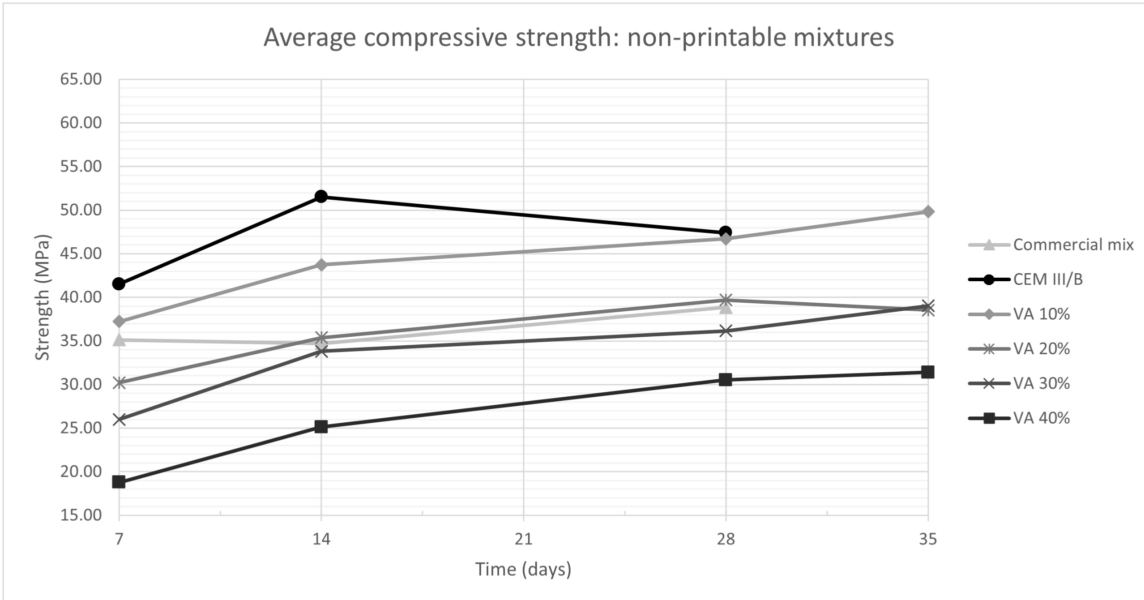


Figure 11: Results compressive strength for non-printable mixtures

The results as shown in Figure 11 are also compared to other data to see if the compressive strength is as would be expected.

For the commercial mixture, it is known that it is of class C35/45. This means that the expected compressive strength for cube samples is 45 MPa. In Figure 11, however, the 28 day compressive strength stays around 35 MPa. Further in the research, the commercial mixture has been tested in compression again. The results as shown in Figure 17, are more along the lines of 43 MPa at 28 days curing time which is closer to the expected strength based on its class.

For the mixture based on CEM III/B, the cement is of class 42,5 N, which means that at 28 days, the strength of the cement is expected to be between 42,5 MPa and 62,5 MPa [16]. The 'betonpocket 2020' gives Equation 8 to calculate the cube strength of concrete mixtures based on its age, cement strength and water/cement ratio [17].

$$f_{cube} = a \cdot N_n \frac{b}{wcf} - c \tag{8}$$

With,
f_{cube} = compressive strength $[MPa]$
a = factor $[-]$
b = factor $[-]$
c = factor $[-]$
N_n = cement strength according to norm at n days $[MPa]$
wcf = water/cement ratio $[-]$

From the 'betonpocket', a = 0,75, b = 18 and c = 30 are taken for CEM III/B cements. The water/cement ratio is taken at 0,28 as per Table 2, and the lower and upper limits of the cement strength at 28 days are taken as 42,5 and 62,5 MPa as stated by the cement class.

From Equation 8, the expected concrete strength at 28 days is then between 66,16 and 81,16 MPa. As the 28 days result of compressive strength with the non-printable mixtures as shown in Figure 17 are not very reliable, the results from the printable mixture will be taken into account as shown in Figure 17. Here the compressive strength is about 60 MPa, which is a little below the spectrum. This means that for all the mixtures, the resulting compressive strength from the experiments is slightly lower than expected. This could be due to the same reasons as mentioned earlier as an explanation for the drop in the compressive strength for the CEM III/B mixture at 28 days. Another explanation could be due to the fact that the CEM III/B mixture is not an official concrete, as is does not have large aggregates in the mixture, that Formula 8 is not completely accurate.

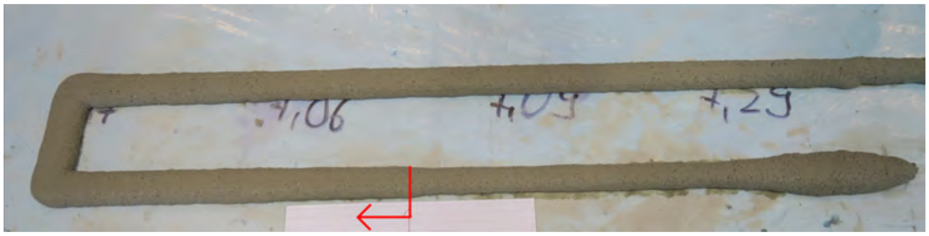
6.1.2 Choice of mixtures

After looking at the results of the bending and compressive strength in the non-printable mixtures, a choice in mixtures needs to be made for the continuation of the project. As a first mixture, the commercial mixture will be chosen. This way, the results or this research can be related to other research performed on the commercial mixture. Secondly the mixture with just cement as binder will be used as a reference mixture. By comparing the results, the influences of the volcanic ash in the mixtures can hopefully be found. Finally, one of the mixtures with volcanic ash will be used. To determine the amount of volcanic ash in the mixture, the compressive strength is taken as the leading guide along with the sustainability of the mixture.
For the sustainability, the amount of CO_2 released during the production of the mixture is taken into account. This generally means for this research that as little Portland cement as possible is wished in the mixture.
From the options explored here, replacing 40 % of the cement with volcanic ash, would be the most sustainable, but it would also mean a much lower compressive strength during a possible printing process and in the end product. Replacing 20 or 30 % would mean having a mixture that is a little less sustainable than when replacing 40 % of the cement, but also with a strength comparable to the commercial mixture. Replacing just 10 % of the cement is not a big leap towards a more sustainable mixture, but it gives quite a strong mixture, nearly comparable towards a mixture without volcanic ash after 35 days.
To be as sustainable as possible, a mixture with a high amount of volcanic ash has the preference, however the mixture with 40 % of the cement replaced gives quite a large decrease in strength. Because it is known that the commercial mixture is printable with its current strength and due to the similar strength of the mixtures with 20 and 30 % of cement replaced, the choice in this research is made to continue with a mixture that replaces 30% of the cement with volcanic ash.
From this point in the research, if unspecified, any mixture referring to a printable mixture with volcanic ash will be referring to a mixture with 30% of the cement replaced with volcanic ash.

6.2 Print tests

After choosing the mixtures to continue the research with, print tests as described in Section 5.10 are performed to adjust the mixture compositions until they can be extruded with sufficient buildability. In Appendix B.2, Table 18, all print settings that were tested on the commercial mixture can be found. The final print settings as used in the tests have been mentioned in Table 5.

In Figure 12, the result of the print settings with the commercial mixture can be seen in both a line print and stacked print. Here a continuous filament with consistent thickness can be found which is required for printing.



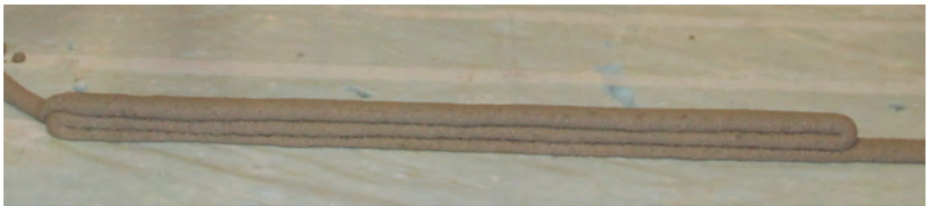
(a) Line print with settings mentioned in Table 5 used from the arrow on

(b) Layered print with settings mentioned in Table 5

Figure 12: Print tests commercial mixture

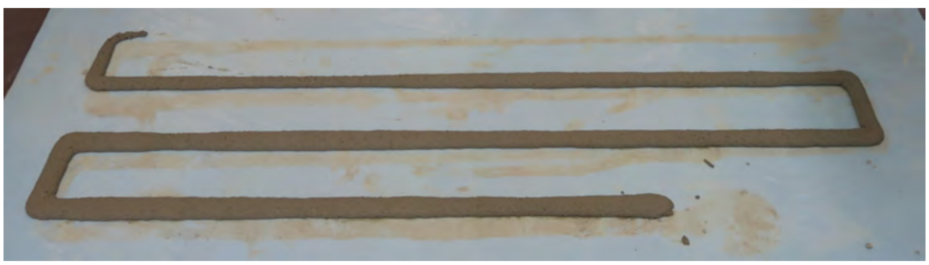
After the print settings have been determined by the prints with the commercial mixture, the developed mixtures will be tested with the robot and caulk gun on their printability. All mixture compositions that have been tested in print can be found in Appendix B.1, Tables 13 and 14.
The resulting mixtures from these tests have been mentioned in Table 3, which shows that, when compared to the non-printable mixtures, an increase of superplasticizer and the addition of a retarder are necessary to keep the mixtures workable. Without these changes, the mixtures were too stiff to be extruded through the nozzle, and the caulk gun clogged as the material was compressed inside.
After the changes to the mixtures, both a line and layered print were made for the mixtures with and without volcanic ash. The results can be found in Figures 13 and 14.

(a) Line print

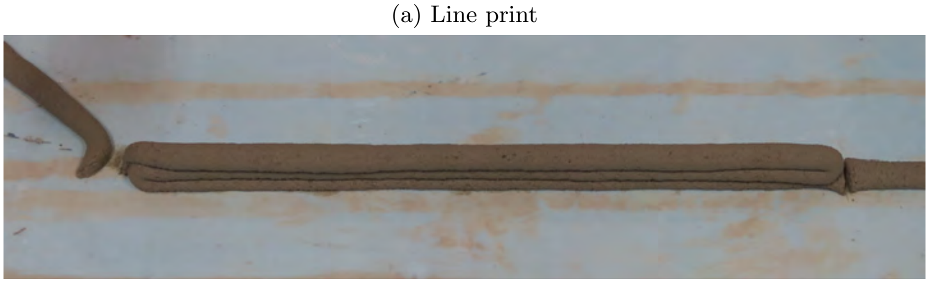


(b) Layered print

Figure 13: Print tests on mixture with just cement as binder.



(a) Line print

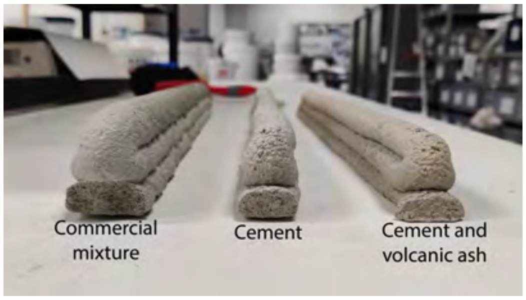


(b) Layered print

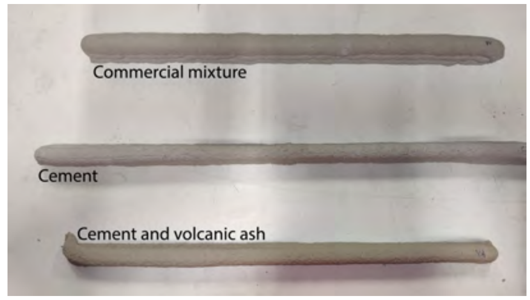
Figure 14: Print tests on mixture with cement and volcanic ash as binder.

Between the three sets of prints, there are some differences in the results of the prints. In the line prints, the most noticeable difference is the printable length. The caulk gun was completely filled for all of the tests, so the amount of material used is the same. In the print with the commercial mixture, a thicker, shorter line can be seen. The developed mixtures both behave quite similarly and give a thinner print, but also a longer line. This is because the consistency of the developed mixtures is different than the commercial one, and thus a different result can be expected.
These differences in thicknesses are also found and compared in the layered prints as can be seen in Figure 15. The commercial mixture gives a wider and higher print when compared to the mixtures

with cement. Between the mixtures with cement with and without volcanic ash, the differences that can be seen are small enough to consider them negligible. The difference in thickness should not be a huge problem in further prints of the mixtures, as differences in print settings and nozzle size could solve this, and possibly give the all prints an identical look if wished.



(a) Prints viewed from the side



(b) Prints viewed from the top

Figure 15: Comparison of the results of the layered print tests

The differences in thickness are probably caused by differences in the composition in the mixtures and the resulting differences in consistency and thickness of the wet mixtures. As the commercial mix is more liquid in consistency, it could facilitate the extrusion of a thicker filament, though the same size nozzle. As the developed mixtures are more solid when mixed, they might need more pressure or a bigger nozzle to result in the same shape.
It should also be noted that during tests, the developed mixtures dried noticeably quicker than the commercial mixture, but further tests in this research will determine the exact difference, and the differences will be discussed there in further detail.
During print tests on the developed mixtures, it became quite clear that they showed inconsistent behaviour, meaning that mixtures should have the same consistency based on the amount of all the materials added, but then developed different consistencies despite this. These inconsistencies are most likely due to a difference in water content, caused by water embodied in the sand used.
To get an even consistency in the mixtures during further tests, the mixtures prepared for the tests to determine the material properties used dried sand. This means that for the results as mentioned in Section 6.3 the sand used has been dried overnight in an oven at 60 °C.

6.3 Determining material properties

In this section of the research, the material properties of the printable mixtures will be discussed per set of tests performed as described in Section 5. The printable mixtures are the commercial mix, the mixture with cement as binder and the mixture with cement and 30 % volcanic ash as binder as mentioned in Table 3.

6.3.1 Bending and compression tests

In Figure 16 the average bending strength of the printable samples is shown. The exact bending and compressive strength and standard deviation values can be found in Appendix B, Table 19.

When compared to results of the non-printable samples shown in Figure 10, the relations between the strength of the different samples is pretty much as expected. Again the commercial mixture is weakest in bending, and the mixture with cement is strongest and the mixture with cement and volcanic ash has a strength in between the two.
When comparing the individual mixtures between printable and non printable, the developed printable mixture with cement as binder shows a lower bending strength over the entire curing process. The developed printable mixture with volcanic ash shows more early strength development, but after 35 days, the difference is negligible.
For the commercial mixture, a few noticeable differences can be seen. First the strength development after 7 days gives a value that was quite a bit higher than in the previous test. After 14 days, the strength is about the same in both tests. At 28 days, the set measured with the printable mixtures shows a dip in measurements, which is probably caused by one or a combination of the same reasons why a similar difference happened in the compressive strength as mentioned in Section 6.1.1. Here the number of samples, surface imperfections, and the fact that the samples came from different batches of mixture were named as the most probable explanations. At 35 days, the commercial mixture shows a similar strength to the 28 day samples measured with the non-printable mixtures.

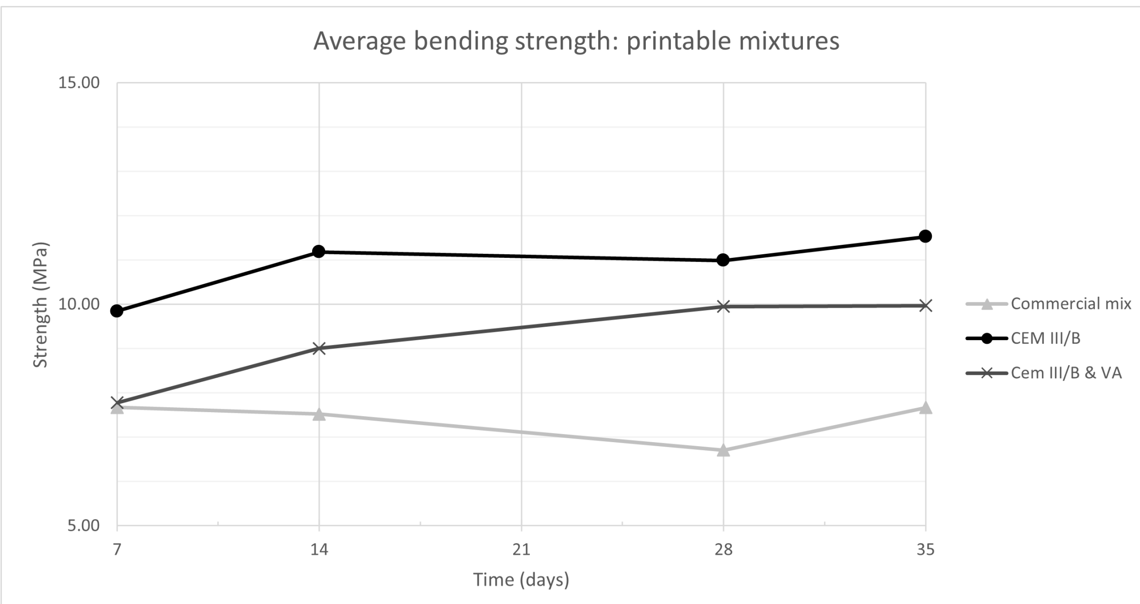


Figure 16: Results bending strength for printable mixtures

In Figure 17 the average compressive strength of the printable samples is shown. When these are compared to the non-printable samples shown in Figure 11, the way in which the compressive strengths are related is again expected based on the relation of the compressive strength of the non-printable samples.
When comparing the individual mixtures between printable and non printable, the developed printable mixture with cement as binder shows a higher compressive strength over the entire curing process. The developed printable mixture with volcanic ash shows similar 7 day strength, but a

higher strength development over the rest of the curing process.
The commercial mixture, shows a slightly higher compressive strength over the entire curing process. In this set of compressive tests, the commercial mixture and the mixture with volcanic ash also have a very similar strength at 14 days curing time. After the 14 days, the compressive strength of the printable mixture with volcanic ash does surpass the compressive strength of the commercial mixture. In the previous set of tests, the strength stayed relatively the same.
The printable mixture with volcanic ash also shows an increase of strength after 28 days, when the cement has developed its full strength, suggesting that the volcanic ash causes a further strength development after the 28 days curing time.

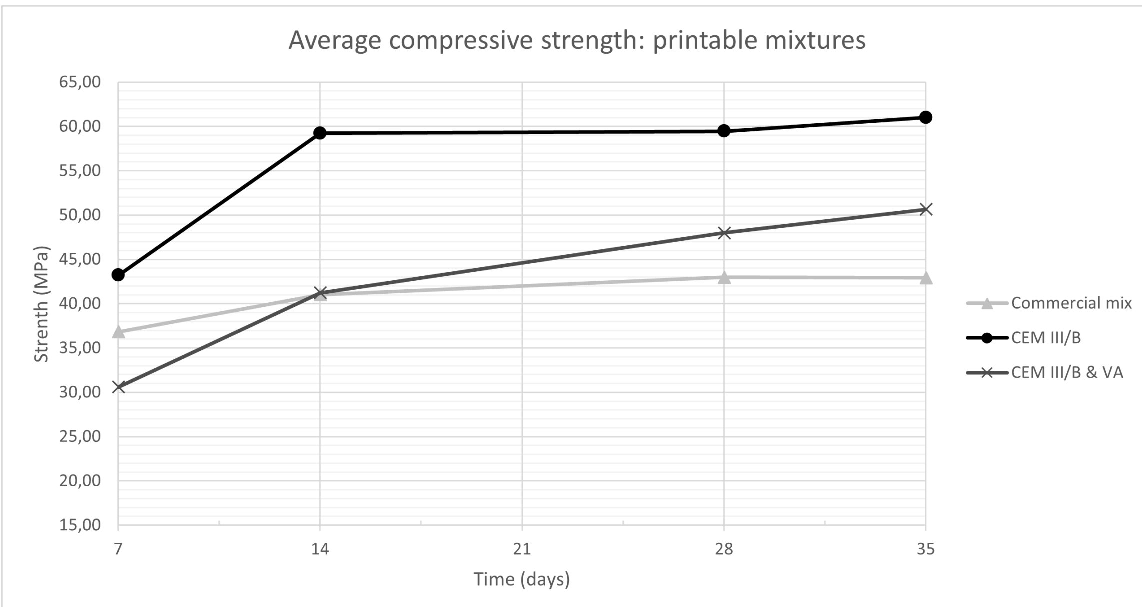


Figure 17: Results compressive strength for printable mixtures

The differences caused in the bending and compressive strength between the printable and non-printable mixtures could be caused by the changes made in mixture compositions to accommodate the print tests, or be the cause of standard deviation between the samples.

6.3.2 Shrinkage and creep tests

In Figure 18 the results from the shrinkage tests can be found. The test results show a clear distinction between the commercial mixture and the developed mixtures. The shrinkage of the developed mixtures is nearly identical and after about 6 days, the shrinkage levels off and becomes somewhat constant. The commercial mixture, however, shows an increase in shrinkage up to 28 days, and although there is less shrinkage at the end of the curing process than in the beginning, there is no clear sign of the shrinkage levelling off.
The similar initial shrinkage in all the mixtures can be explained by the water evaporating from the samples, causing the initial shrinkage.

The difference in further shrinkage could be explained by the difference in particle size in the mixtures, as for concrete, larger aggregates in a mixture result in better resistance to shrinkage [7]. The commercial mixture has a maximum particle size of 1 mm, according to the packaging, while the developed mixtures use standard sand with particle sizes up to 2 mm [18].
Also the fact that the commercial mixture seems to be wetter, might cause it to experience the effects of shrinkage due to water evaporation for a longer time in the initial stages of shrinkage. From earlier tests on the commercial mixture, it is known that it shrinks a lot, so the fact that the results of the commercial mixture are quite a lot higher, and about these values, is to be expected [19] .

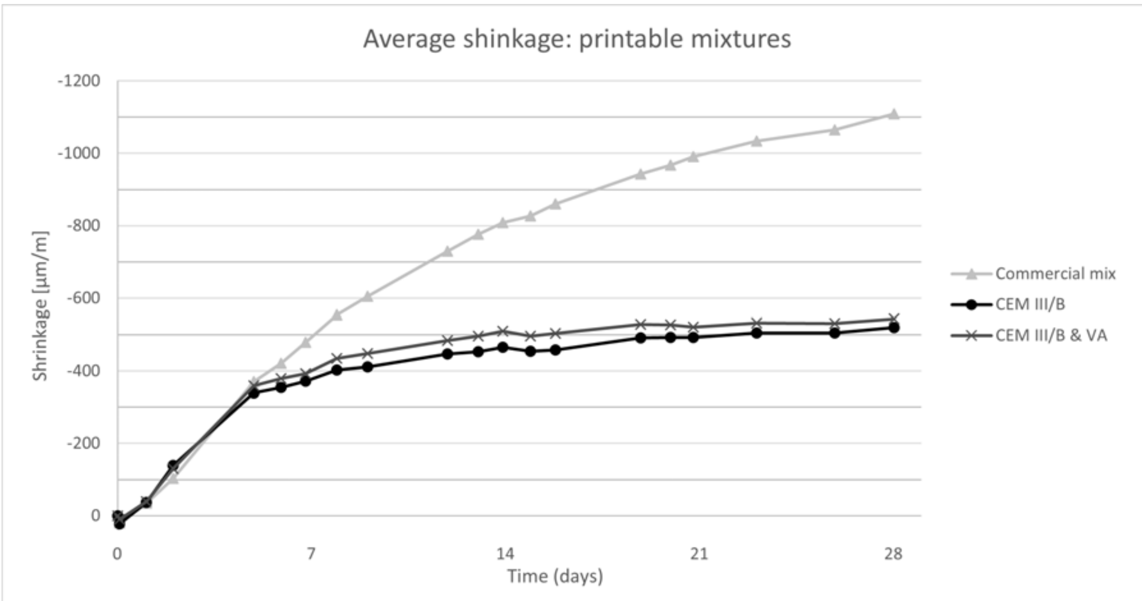


Figure 18: Results shrinkage for printable mixtures

In Figure 19 the results of the creep test can be found. As with the shrinkage tests, the commercial mixture shows a significantly larger amount of creep and no real indication of the creep stabilizing after 28 days. It should be noted that one of the samples from the commercial mix broke during loading, so the results shown are from the two remaining samples.
For the developed mixtures, the creep stabilizes around 3 to 4 days, although there is a difference in the level at which the creep stabilizes. The mixture with cement and volcanic ash shows a slightly higher level of creep, but the level is not at any point near the level of the commercial mixture.
Differences in creep for concrete are often dependent on the E-modulus of the aggregates [7]. As the developed mixtures use the same amount of sand as a sort of aggregate, it is expected that the creep developed in the samples with and without volcanic ash is similar.
The differences in the level of creep between the developed mixtures could be explained by the volcanic ash, as the addition of the volcanic ash adds more small particles to the mixture.

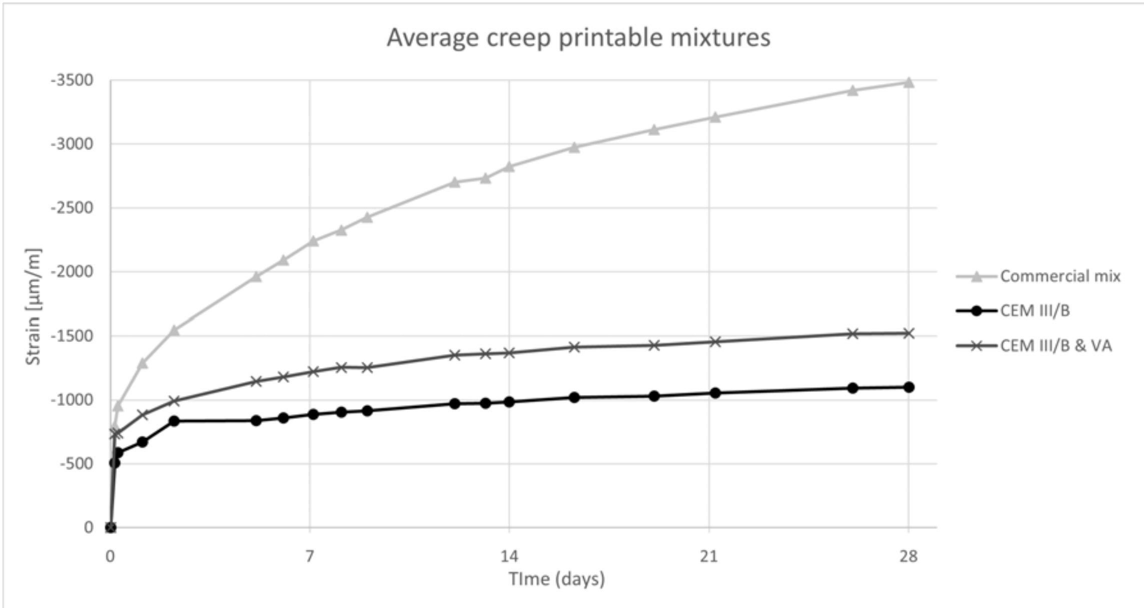


Figure 19: Results creep for printable mixtures

6.3.3 Ultrasonic wave transmission tests

In Figure 20, the results from the ultrasonic wave transmission tests can be found. The densities used to calculate the E-modulus via Formula 4, can be found in Appendix B.3.2. The results from the individual samples can also be found there.

In Figure 20, it can be seen that within the first two hours, the designed mixes with cement and cement and volcanic ash develop their E-modulus more quickly, whereas the commercial mix has a quite slow initial development.

Other research performed on the commercial mixture mentions the wave velocity in the first 120 minutes [20], [13]. If the raw data from the ultrasonic wave transmission tests are taken as they are displayed in Appendix B.3.2, Figure 29, it can be seen that the development of the commercial mixture is very similar.

In Section 6.3.4, the initial setting times from the mixtures can be found, and they show a similar pattern, where the developed mixtures have a quicker initial setting time.

For the developed mixtures, the quick initial development of the E-modulus, combined with the initial setting time, could pose a problem when printing larger objects than attempted in this research as the mixtures will not be workable for the time needed to complete the print.

To possibly delay the initial development of the E-modulus, admixtures, e.g. more retarder, might be added to the developed mixtures.

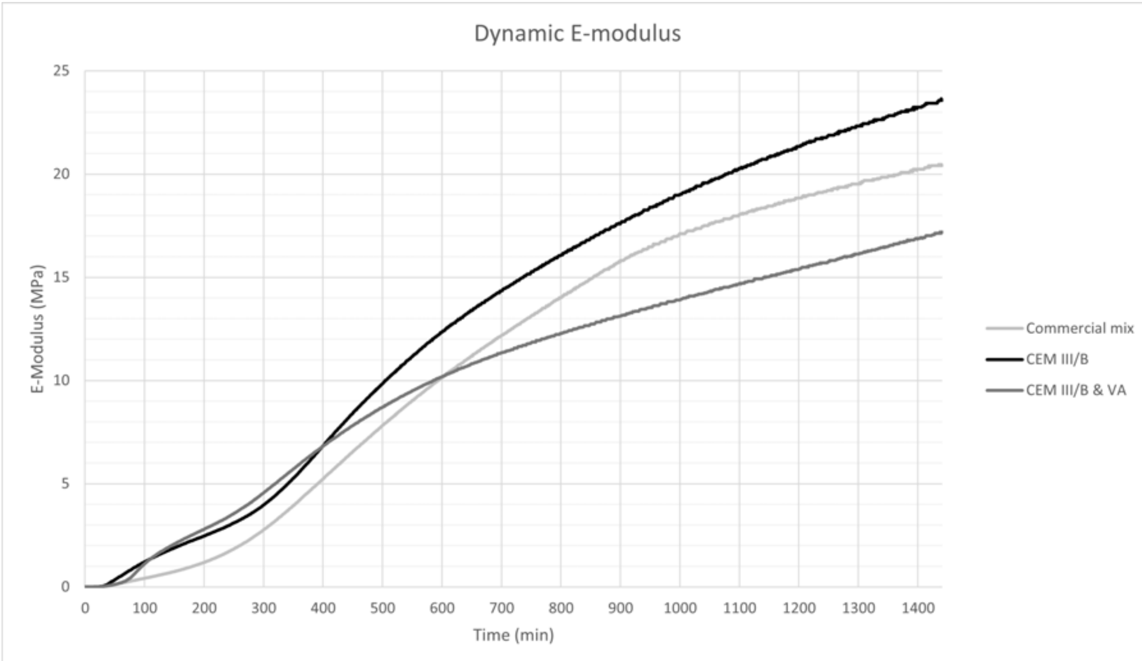


Figure 20: Results dynamic E-modulus

6.3.4 Vicat tests

In Table 6, the initial setting times as determined by the vicat tests can be found. In Appendix B.3.4, the full tables of measurements made during the vicat tests can be found.

Table 6: Initial setting times printable mixtures

Mixture	Average initial setting time
Commercial mixture	2 hours, 55 minutes
CEM III/B	1 hour, 7 minutes
CEM III/B & volcanic ash	30 minutes

There is a clear difference in initial setting times between the mixtures. The long open time from the commercial mixture is suitable for print, and quite logical after seeing the results from the ultrasonic wave transmission tests, where the E-modulus develops quite slowly in the beginning. The slow strength and setting development are probably related to the consistency of the mixture, which is quite wet.

The developed mixtures set a lot quicker. These mixtures have less liquid in them when compared to the commercial mixture, which is why they set quicker. The difference in setting times between the mixture with and without volcanic ash can be attributed to the addition of the volcanic ash. As the volcanic ash particles are very small, they have lot of surface which will attract water and cause a quicker setting time. Due to the smaller amount of free water in the mixture, the mixture with volcanic ash will also have a slower strength development, which is confirmed in Figure 20, where the initial development of the E-modulus for the mixture with volcanic ash sets on at a later time than the mixture with only cement as a binder.

6.3.5 Uniaxial unconfined compression tests

In Figures 21 to 23, the resulting stress-strain curves for the uniaxial unconfined compression tests can be found. In Appendix B.3.3, the graphs can also be found in other scales for a better readability of the individual graphs.

The results show a clear difference in development of strength and rigidity. The first differences can be seen at the 15 minute tests, where the mixtures already show a difference in strength. Here the CEM III/B mix shows a slightly quicker development of strength than the commercial mixture. The mixture with CEM III/B and volcanic ash, however shows an even larger difference in development, with a much higher strength at 15 minutes.

This trend in strength development then continues for the different mixtures, resulting in clear differences at the 90 minute tests. Here it can be clearly seen that the mixture with volcanic ash has developed the highest strength, while the commercial mixture has developed the least amount of strength.

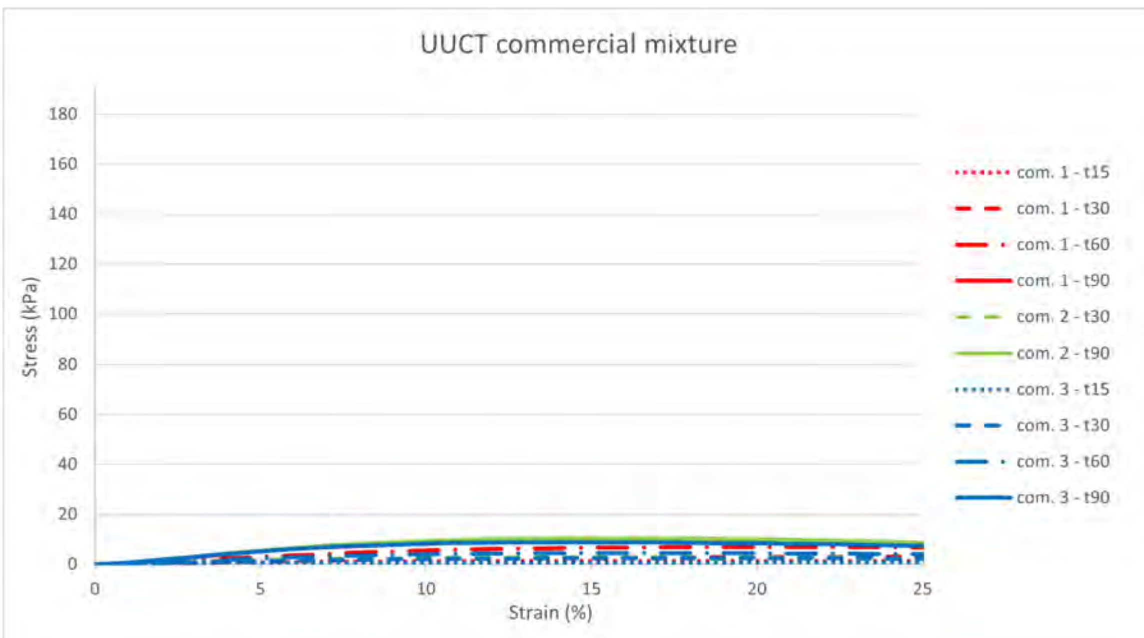


Figure 21: Stress-strain diagram for commercial mix

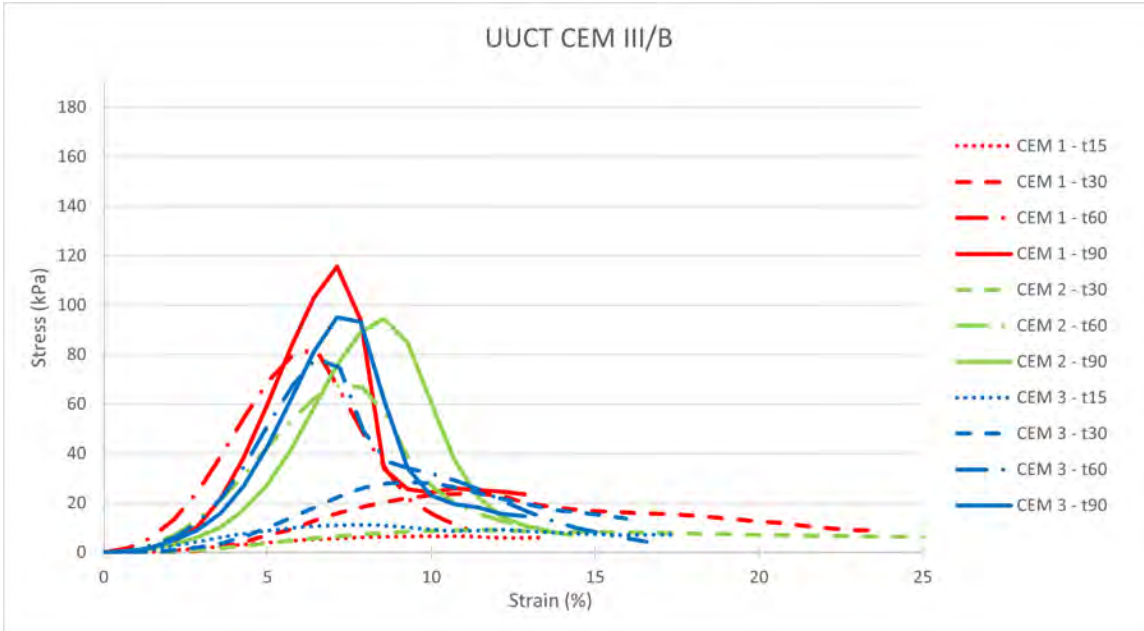


Figure 22: Stress-strain diagram for CEM III/B mix

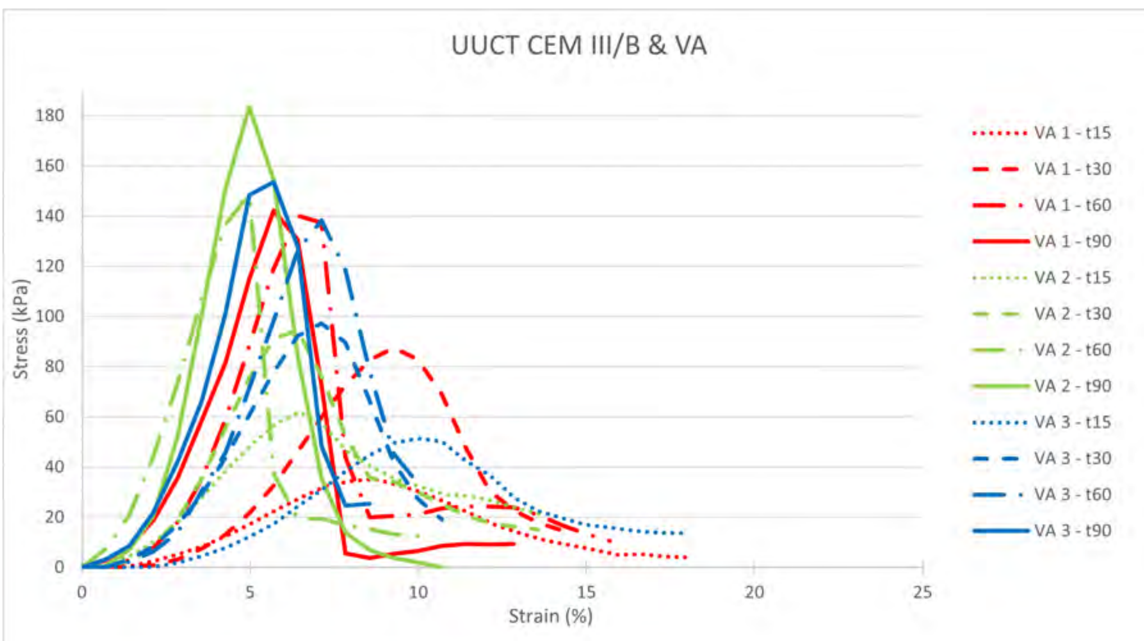


Figure 23: Stress-strain diagram for CEM III/B & volcanic ash mix

Uniaxial unconfined compression tests have been performed on the commercial mixture before [20], [13]. Here, the stress obtained at 90 minutes for the commercial mixture seems to be between 15 and 35 kPa for different tests. In comparison, the obtained values in this research are about 9 to 10

kPa. This is on the low side when comparing the test results, however the shape of the stress-strain diagram is largely similar.
The difference in results of the maximum stress in the commercial mixture lead to a question on the reliability of the uniaxial unconfined compression tests performed in this research. Also, the difference in results for the samples of the same material and time of test, suggests that there is a lot of variation in results of the tests.
The variation in results could be explained by the effect the mixing, handling and demoulding of the samples could have on the results. Between the end of mixing, and the troweling off of the samples, there is a different amount of time as the four samples can not be filled completely simultaneously. This means that some of the material might have started to set, before it was placed in the mould and this can influence the rest results as the tests seem to be quite sensitive to how and how quickly the moulds were loaded.
Also the moving of samples can influence the compaction and strength of samples. While the moving of the samples was limited in the test procedure, the samples were moved from the table where the samples were filled, to the testing machine. Here some samples might have been placed with more care than others, which might cause differences in the results.
Finally, there is also the possibility that the tests were not performed exactly the same as in the research used to compare the commercial mixture with. This is because there is no clear standardization for the uniaxial unconfined compression test, and thus execution and results of the tests can vary.
The absolute values of the tests on the commercial mixture might not be completely accurate when compared to literature, and to create a reliable data set from the performed experiments, more tests should have been performed in this research. However, the values and shape of the stress-strain diagram are similar enough to use the stress strain diagrams for comparison between the mixtures in this research. Also, the results from the uniaxial unconfined compression test are in line with results gathered from other tests in this research, so the results of this test were deemed reliable enough.
In Figure 24, the maximum stress values from the stress strain diagrams have been taken at the different testing times. In Figure 25, these maximum stresses have been transformed to an apparent E-modulus at 5 % strain.
For both these Figures, it seems that linear trends in terms of strength and E-modulus development can be fitted to the data. The fits are not very exact, especially for the mixtures with volcanic ash at 15 and 90 minutes. This might be because the initial set of the material is much quicker than for the commercial mix and the mixture with just cement as binder. This could explain the more similar strength values between the 60 and 90 minute tests for the samples with volcanic ash as well.

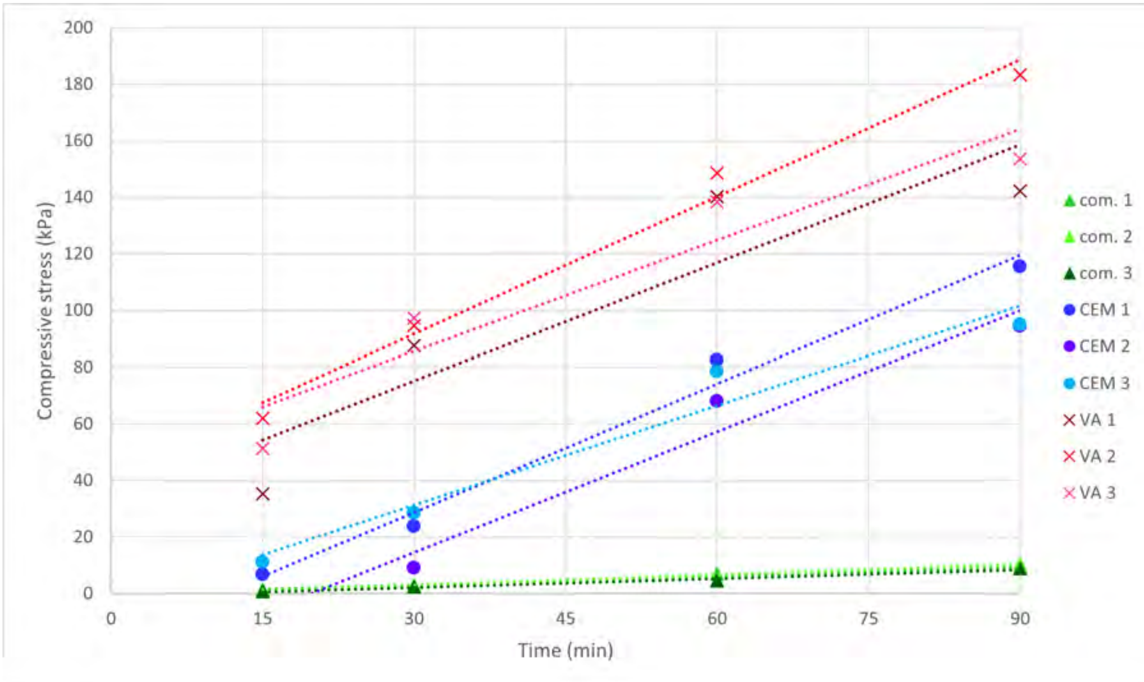


Figure 24: Trends of maximum compressive strenght

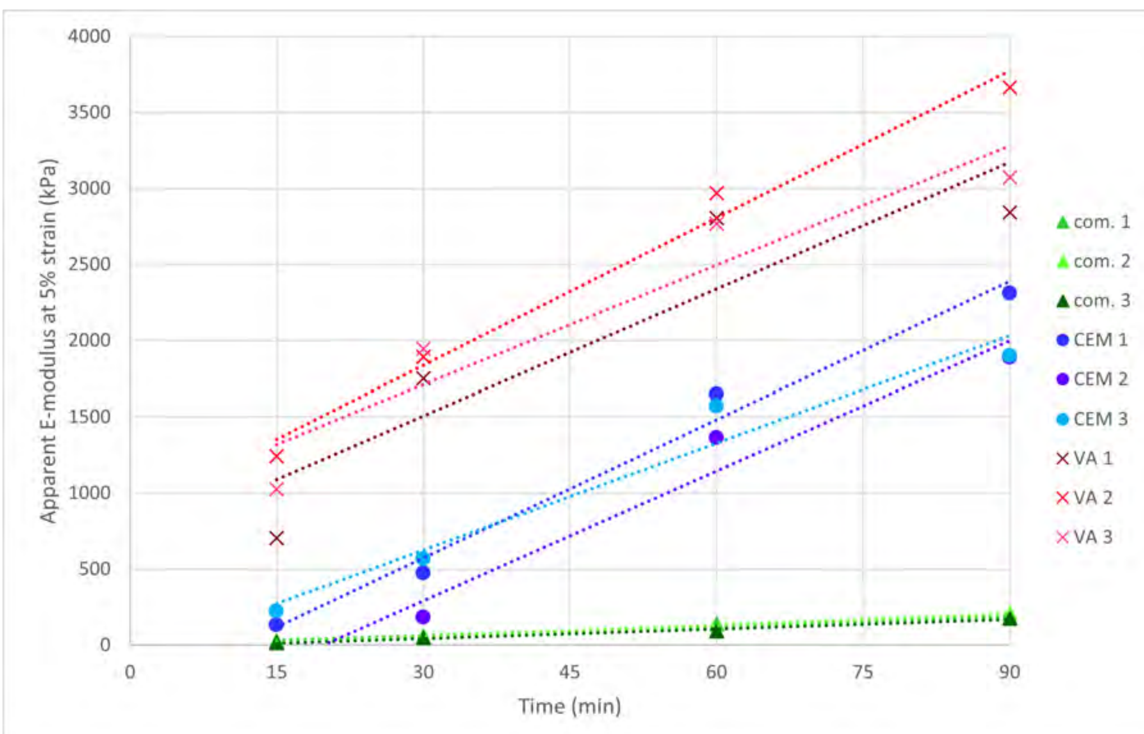


Figure 25: Apparent E-modulus at 5 % strain

6.4 Sustainability of the mixture

In this research, the main criterion used to determine the sustainability is the amount CO_2 emissions due to the product. As there is no actual CO_2 released during the making of concrete, the CO_2 emissions during the production of the cement were used to calculate an estimation of the CO_2 released during the production of the needed amounts of cement for the mixtures.
The commercial mixture is one based on CEM I, while the mixtures designed in this research are based on CEM III/B. According to cement producer ENCI the CEM III/B mix used in this research contains 20 to 34 % Portland cement [16], while their CEM I contains 95 to 100 % of Portland cement [21]. Even though the commercial mixture probably will not use this exact brand of cement, we can safely assume that all CEM I mixtures consist of the same percentages of Portland cement. The Portland cement association states that for every kilogram of Portland cement, there is about 0,9 kilograms of CO_2 produced [22]. If a simple calculation is then made for 1 kilogram of binder, meaning 1 kilogram of CEM I, 1 kilogram of CEM III/B and a mixture of 0,7 kilogram CEM III/B and 0,3 kilogram of volcanic ash, the results in Table 7 can be found.

Table 7: Estimated CO_2 emissions for 1 kilogram of binder

Binder used in mixture	Amount of cement (kg)	Percentage Portland cement	Amount of Portland cement (kg)	Amount of CO_2 (kg)
CEM I	1,00	95%	0,95	0,86
		100%	1,00	0,90
CEM III/B	1,00	20%	0,20	0,18
		34%	0,34	0,31
CEM III/B & 30% VA	0,70	20%	0,14	0,13
		34%	0,24	0,21

In these calculations, for the Portland cement, about 60% of the CO_2 emissions are from calcination, and the other 40% are from combustion during the process [22]. This means that any emissions during transport are not taken into consideration for the types of cement.
For the volcanic ash, trass is found around erupted volcanoes and then milled into a fine powder. For the production of the trass, man-made CO_2 not involved, however the mining and milling of the stone might involve man-made CO_2. As there is little information to be found about the CO_2 contributions of these actions, and as the cements are also milled after production, these contributions are neglected in this calculation.
For the cements, emissions during transport were not taken into account in the calculation. As volcanic ash is a material that can be found around the globe, and excessive transport will not be necessary for the use of volcanic ash in the mixtures, the transportation emissions will also not be taken into account for the volcanic ash.
This quick calculation only takes the cements into account. To determine which of the final mixtures is more sustainable, information about the amount of cement used in e.g. a kilogram final mixture would be needed. As the composition from the commercial mixture is unknown, this comparison

can not be made at this time.

Section 7

Discussion

7.1 Mixtures

In this research, many different mixture compositions have been tried and tested. During the development of the mixture compositions, many observations were made, which will be discussed here.

First of all, many of the mixture designs behaved quite unpredictable. Some mixtures with identical or near identical composition behaved very differently, meaning that one mixture would come together as a mixture in the mixing bowl, and another would still contain dry ingredients.

The size of the batch made, plays a large part in the unpredictability. It seemed that the standing mixtures used from the BPS laboratory were less equipped for small batches of up to 1 L, as the mixture would largely lie below the mixing paddle. Larger mixtures of 1,5 L or more would be combined better by the mixing paddle. However, for this research small batches were initially made. When these were then scaled up, the mixture would often be of the wrong consistency, and a bit more trial and error was needed to get to a workable consistency again.

During the research, after the development of the printable mixtures, the sand used for any new mixtures made was dried via oven. This was done to control the amount of water present in the mixture as this was expected to affect the workability of the mixture. The batches made with dried sand, showed more consistent results in terms of workability. It is not entirely clear if the wetness of the sand only seems to have a significant impact because of the batch size, and if with further up-scaling the effects on the workability are negligible.

For very large batches, drying all the sand in an oven is not a very practical solution to control the amount of water attached to the sand. If the wetness of the sand is of influence and will need to be controlled, a possible solution would be to determine the water content of the sand, and adjust the water added to the mixture based on that.

For this research, volcanic ash from just one supplier has been used. However, volcanic ash can be found around the world is found in many different places. Since volcanic ash is produced by volcanoes, and geological differences exist in volcanoes around the world, differences in volcanic ash from different places is guaranteed. This could influence the behaviour of the mixtures developed in this research, but has not been further investigated at this point.

7.2 Material properties

In Section 6, the results from the different tests performed in this research have been presented and the results have been discussed per test. If the results are then combined and an overview is made, it can be seen that while there are positive aspects about the developed mixtures, there is also room for improvement.

First of all, from the printing tests with the robot it becomes quite clear that with adaptations in superplasticizer and retarder to the initial mixtures developed, the developed mixtures can be extruded and stacked. However the print test is performed on a very small scale, and the mixtures can probably not be transferred to a larger scale as they are.

The biggest challenge in the current developed mixtures is the open time, which was already noticeable in the print tests. The differences in open time were then confirmed in the vicat tests, as well as the ultrasonic wave transmission tests and uniaxial unconfined compression tests. With the data combined, it shows that the initial setting and strength development of the mixture with CEM III/B and volcanic ash is the quickest. The commercial mixture has the slowest initial setting and strength development of the three printable mixtures tested.

With the mixture with volcanic ash having an open time of about 30 minutes, it is very realistic that the mixture as it has been developed in this research will not be printable on a larger scale. To facilitate this, the open time will have to be adjusted with different admixtures. Finding the effects of more retarder in the mixture could be a good start to further delay initial setting.

With these adjustments in open time, other material properties of the mixture could also be affected. For example the shrinkage could increase and the compressive strength could decrease, which might affect the suitability of the mixture negatively.

With the current open time, the bond between printed layers could also pose a problem, as the time frame to print a new layer onto the object is small. This has not been further investigated in this research though.

On the other hand, the developed mixtures also seem to have a few improvements when compared to the commercial mixture.

First the shrinkage and creep in the developed mixtures is significantly lower. This means that there is less chance of cracks developing in the printed elements due to shrinkage of the material. This is important aesthetically, but also for the strength of the printed object [23].

From the uniaxial unconfined compression tests and the ultrasonic wave transmission tests it can be seen that the E-modulus and the strength of the mixtures with CEM III/B with and without volcanic ash also develops quite quickly. This is probably positive for the buildability of the material, as it could mean that the developed mixtures can sustain their own weight as well as that of stacked layers, however print tests with more layers are needed to confirm or deny this.

When looking to the bending and compression strength of the mixtures, it can be seen that the strength of the mixture with volcanic ash develops later than the commercial mixture, but that in the end similar compressive strengths are obtained.

The quick setting and delayed compressive strength development of the mixture with volcanic ash could indicate that there is very little free water in the mixture, as it is attracted by the volcanic ash particles.

Finally there is the sustainability of the mixtures. Currently, only a very basic calculation has been made to estimate the impact that the change in cement type has on the sustainability of the mixture. From this estimate, it could be stated that the change of cement makes the mixture more sustainable, but only on the assumption that both the commercial mixture and the developed mixture have the same amount of cement in the same batch size. Since this can not be guaranteed, it is still unclear if the developed mixtures do indeed cause less CO_2 to be released.

7.3 Process

Besides the discussion on the mixture design and the results, there are also some points to discuss about the process of the research.
First the results of the Covid measures were still in effect, especially during the beginning of the research. This meant that accessibility to the lab had to be checked to ensure compliance with the maximum number of people in the lab. As the research continued and measures became less strict, the labs became more crowded again and this sometimes caused a bit more challenges with planning of equipment and the planning of the project.
Also the fact that part of the experiments were performed in the structural design lab, and part in the building physics lab meant that communication sometimes was key. Some delays in planning were caused due to miscommunication or schedules that were not properly aligned.
Last, in the final stages of the experiments on material properties, the XRD machine malfunctioned. It took a while to get it fixed, and depending on the availability of a staff member the samples might be measured in time for the final version of the report. However, earlier results from the tests could have aided in a more thorough investigation and explanation of the results.

Conclusion

In this research an answer to the question *'Can a mortar, with CEM III/B and volcanic ash as its binders, be made suitable for 3D concrete printing?'* has been researched.
To investigate different parameters of this research different sub-questions have been asked and conclusions on those will be presented first.
In Sections 2 and 3, the answer to the sub-question *Which requirements for material properties does a potential mortar have to meet?* was explored via literature study. In order to create a printable mixture, the mixture needs to satisfy four requirements: printability, workability, suitable open time, and buildability. Meeting these conditions mean that a mixture has a suitable consistency to be extruded into a filament, without setting in the printing machine. The mixture also does not set before the next layer can be printed to ensure adhesion of layers, while being set enough to sustain its own weight without deformations and the weight of the printed layers above.
In Section 2.3, the answer to sub-question *How much CEM III/B can be replaced with volcanic ash, while still creating a mortar that meets these requirements?* has been explored via literature study as well. From literature it could be concluded that the amount of cement replaced by volcanic ash should not exceed 40 % and the ideal amount will probably be between 10 and 30 %. The addition of volcanic ash will have a negative effect on the compressive strength of the hardened material, and increase the water demand of the mixture to keep it workable. In Section 6.1, the literature findings were confirmed with experimental research, where it was concluded that a 30 % replacement of volcanic ash would still create a sufficiently strong, workable and buildable material while also replacing as much cement as possible to increase the sustainability of the mixture.
During the print tests as described in Sections 5.10 and 6.2, the answer to sub-question *Which additives need to be added to the mortar to make it suitable for 3D concrete printing?* has been explored experimentally. Based on the experiments, an increase of superplasticizer and the addition of a retarder are needed to make the mixtures printable and workable.
With a set of experiments as described in Section 5 and their results as described in Section 6.3 an answer to the question *How do the material properties of the mortar compare to a commercial concrete mixture?* has been investigated. The bending and compressive strength of the developed mixture with CEM III/B and volcanic ash as binders develops a bit slower than the commercial mixture, but is quite similar in at the end of the curing period. The developed mixture exhibits a significantly smaller amount of shrinkage and creep after the initial water has evaporated from the samples. The strength and rigidity of the developed mixture in the first 90 minutes, does develop quicker than the one of the commercial mixture, which is also reflected by a quicker initial setting time. After 24 hours, the E-modulus from the developed mixture is slightly lower than the one from the commercial mixture. Lastly, from a very basic calculation, it seems that the developed mixture has a smaller CO_2 footprint in production than the commercial mixture.
The hypothesis to the question *'Can a mortar, with CEM III/B and volcanic ash as its binders, be made suitable for 3D concrete printing?'* formulated at the beginning of the research, was that the

mixture could be made printable. From the results of this research, it can be concluded that for very small prints, the printable mixture with CEM III/B and 30 % volcanic ash as developed in this research is printable. For larger prints, however, it has to be concluded that the workability and open time of the current mixture is not sufficient, however the mixture might be further adjusted with admixtures to facilitate the larger prints in future research.

Section 9

Further research

Based on the results from this research, further research on the printable mixture with 30 % volcanic ash is certainly possible and needed.

A first suggestion would be to further develop the mixture composition. The open time on the printable mixture with volcanic ash could be further investigated, and extended to a period of time which would make it suitable to perform larger scale print sessions with the material. Adding more retarder to delay the setting, as well as experimenting with a bit more water to aid in better hydration of the mixture would be a good starting point based on the results from this research. Possibly other admixtures could also be added to solve the issues with open time.

If the mixture composition is then changed, and a larger open time is obtained, the effect of the changes on the strength and shrinkage could also be of interest.

If the mixture were to be even further developed, another interesting suggestion would be to activate the volcanic ash in the mixture and create a geopolymer. This could have positive effects on the strength and possibly other characteristics of the mixture.

Another option to further develop the mixture would be to take the mixture from a printable mortar to a concrete and see, together with printer options, if larger aggregates in the mixture are a possibility. This research could then also be applied to other mixtures and could decrease the experienced shrinkage in the printed mixtures. Also if the adjustments made to the mixture to ensure the open time, cause an increase in shrinkage, this could be a possible solution to decrease the shrinkage again.

It could also be researched if the current mixture, thus with the very short open time, could be printable on larger scale. This would probably mean that the mixture would have to be mixed nearly in the printer and that a continuous mixing and printing process would need to be developed. Also the bond between the printed layers will then become of interest to research, as the printed elements will set relatively fast.

Finally, the actual sustainability of the developed mixture, as well as a proper comparison to the current commercial mixture could be executed. This would then take many more factors into account than just CO_2 emissions, such as effects of transportation, and the amount of cement in the final mixtures. Also these factors would be researched more in depth, and thus be more reliable than they are in this research.

Section 10

Word of thanks

This research would not have been possible without the help of some very important people.
First to my supervisors from the TU/e: Sandra Lucas and Theo Salet, and my supervisors from ABT: Jasper van Alphen and Luciano van Leeuwen. Thank you for the regular meetings, honest feedback on my work, tips to continue and the non project related chats.
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SECTION 11

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Mixture designs

For this research, many different mixture designs were tested and judged based on their consistency. These mixtures were tested in stages and were designed with different goals according to the stage of the project.
First, there are mixtures that were not designed to be printable, but with the goal of determining a workable mixture that was neither too dry nor too wet. These can be further subdivided into mixtures without volcanic ash and mixtures with respectively 10, 20, 30 and 40% of volcanic ash.
Secondly there are the mixtures that were designed to be printable. These mixtures can be subdivided into a mixture with and without volcanic ash.
Finally, with both the printable and non-printable mixtures there is a differentiation between the size of the batch that was made, because this had an impact on the outcome of the consistency of the mixture. Meaning that the same weight percentages of materials caused a different consistency in the mixture if a smaller or larger batch were made. For the smaller batches, about $0,25$ to 0.75 L of material was produced, while for the larger batches about $1,5$ L or more was produced.
Tables 8 to 14 give an overview of mixture compositions tested in this research, with the contents in weight percentages, a note about the batch size, and comments from observations during the mixing process. The weight percentages are calculated, and are then rounded to two decimal places. This means, especially for the smaller batches, that mixtures can seem the same per the table, but might have behaved differently in real life because of slight differences.
The mixtures will be numbered as follows:

- mixtures will be numbered with Roman numerals
- printable mixtures will be distinguished with a 'P' in front of the numeral
- Mixtures with volcanic ash will be distinguised with 'VA' behind the numeral and a number (either 10, 20, 30 or 40) representing the amount of cement replaced with volcanic ash.

This means that non printable mixtures without volcanic ash will be characterized by I, II, III, etc. Printable mixtures will become P-I etc. A printable mixture with 30% of cement replaced with volcanic ash will be denoted as P-I-VA30 etc.
In the tables the materials used in the mixture will be denoted as follows:
Cement (weight percentage) as CEM (wt%)
Volcanic ash (weight percentage) as VA (wt%)
Limestone powder (weight percentage) as LP (wt%)
Sand (weight percentage) as Sand (wt%)
Water/Binder (-) as W/B (-)
Superplasticizer/Binder (-) as SP/B (-)
Retarder/Binder (-) as R/B (-)

Table 8: Mixture design - non printable without volcanic ash

	I	II	III	IV	V	VI	VII	VIII	IX
CEM (wt%)	20,27	20,27	20,29	20,31	20,29	20,30	20,30	20,30	20,29
VA (wt%)	-	-	-	-	-	-	-	-	-
LP (wt%)	13,07	13,06	13,06	13,05	13,05	13,04	13,06	13,04	13,04
Sand (wt%)	66,65	66,65	66,64	66,64	66,66	66,65	66,65	66,66	66,66
W/B (-)	0,32	0,27	0,25	0,27	0,32	0,32	0,33	0,28	0,28
SP/B (-)	0,46	0,46	0,43	0,35	0,19	0,19	0,19	0,32	0,32
R/B (-)	-	-	-	-	-	-	-	-	-
Batch size	small	small	small	small	small	small	small	small	large
Comments	Quite liquid and seems to be bleeding	Very dry, water added during mixing, but not ideal result	Comes together after a few minutes of mixing	Very dry, water added during mixing	Water added during mixing to improve consistency	Might need a bit more water	Same as mix 6, but more water added	Increased SP to lower water, while keeping consistency, result is good	Good, used for bending and compression tests

Table 9: Mixture design - non printable with 10% volcanic ash

	I-VA10	II-VA10	III-VA10	IV-VA10	V-VA10	VI-VA10	VII-VA10	VIII-VA10	IX-VA10	X-VA10
CEM (wt%)	18,25	18,27	18,26	18,23	18,27	18,26	18,26	18,27	18,27	18,27
VA (wt%)	2,03	2,04	2,02	2,04	2,03	2,03	2,03	2,03	2,03	2,03
LP (wt%)	13,03	13,04	13,02	13,03	13,02	13,04	13,04	13,04	13,05	13,05
Sand (wt%)	66,68	66,65	66,69	66,71	66,68	66,67	66,66	66,66	66,66	66,66
W/B (-)	0,28	0,29	0,27	0,27	0,28	0,28	0,28	0,28	0,28	0,28
SP/B (-)	0,35	0,33	0,33	0,34	0,33	0,32	0,32	0,34	0,34	0,34
R/B (-)	-	-	-	-	-	-	-	-	-	-
Batch size	small	small	small	small	small	large	large	large	large	large
Comments	Very liquid and seems to be bleeding	Is hard, but at the same time more liquid than I-VA10	Pretty okay, maybe a little bleeding	Dry!	Pretty okay stay on low side of water next time	(no notes, but probably too dry)	(no notes, but probably too dry)	(no notes, but probably not okay)	Maybe a, bit liquid but approved	Also approved

Table 10: Mixture design - non printable with 20% volcanic ash

	I-VA20	II-VA20	III-VA20	IV-VA20	V-VA20	VI-V20	VII-VA20	VIII-VA20
CEM (wt%)	16,22	16,22	16,23	16,23	16,24	16,23	16,23	16,23
VA (wt%)	4,07	4,06	4,06	4,05	4,06	4,06	4,06	4,06
LP (wt%)	13,05	13,04	13,04	13,04	13,04	13,05	13,04	13,04
Sand (wt%)	66,66	66,68	66,66	66,68	66,66	66,66	66,66	66,67
W/B (-)	0,29	0,29	0,27	0,28	0,28	0,28	0,29	0,29
SP/B (-)	0,32	0,39	0,39	0,39	0,39	0,39	0,39	0,39
R/B (-)	-	-	-	-	-	-	-	-
Batch size	small	small	small	small	large	large	large	large
Comments	Too dry	Little bit on the liquid side	Pretty okay, maybe a little stiff because of small amount mixed	(no notes, probably okay, because after this larger amounts)	Too dry	(no notes, but probably too dry)	Approved	Also approved

Table 11: Mixture design - non printable with 30% volcanic ash

	I-VA30	II-VA30	III-VA30	IV-VA30	V-VA30
CEM (wt%)	14,19	14,19	14,20	14,21	14,20
VA (wt%)	6,08	6,05	6,09	6,09	6,08
LP (wt%)	13,04	13,03	13,04	13,03	13,04
Sand (wt%)	66,69	66,72	66,66	66,67	66,67
W/B (-)	0,28	0,28	0,29	0,29	0,29
SP/B (-)	0,39	0,40	0,43	0,43	0,43
R/B (-)	-	-	-	-	-
Batch size	small	small	small	large	large
Comments	Too dry	Too dry needs water	Seems promising, use to continue	Just wet enough and approved	Approved

Table 12: Mixture design - non printable with 40% volcanic ash

	I-VA40	II-VA40	III-VA40	IV-VA40	V-VA40
CEM (wt%)	12,17	12,17	12,18	12,18	12,18
VA (wt%)	8,12	8,11	8,12	8,12	8,12
LP (wt%)	13,04	13,03	13,05	13,04	13,04
Sand (wt%)	66,67	66,69	66,65	66,66	66,66
W/B (-)	0,29	0,30	0,30	0,30	0,30
SP/B (-)	0,43	0,42	0,43	0,44	0,43
R/B (-)	-	-	-	-	-
Batch size	small	small	large	large	large
Comments	Little on the dry side	Looks nice	Too dry	Pretty good and approved	Approved

After determining which mixture designs are suitable to use for printing in the larger batch size, the appropriate tests for the experimental research will need to be executed. In order to perform these tests, batches of chosen mixtures are made, and in tables 15 to 16 the configurations of the material per experiment can be found.

Table 13: Mixture design - printable without volcanic ash

	P-I	P-II	P-III	P-IV	P-V	P-VI	P-VII
CEM (wt%)	20,29	20,29	20,29	20,30	20,30	20,30	20,30
VA (wt%)	-	-	-	-	-	-	-
LP (wt%)	13,04	13,05	13,03	13,03	13,04	13,04	13,04
Sand (wt%)	66,67	66,66	66,68	66,68	66,66	66,66	66,66
W/B (-)	0,29	0,29	0,29	0,29	0,29	0,29	0,29
SP/B (-)	0,32	0,32	0,32	0,32	0,32	0,32	0,32
R/B (-)	-	-	0,16	0,16	0,16	0,16	0,16
Batch size	small	small	small	small	small	large	large
Comments	Need double size for a full kit	Unprintable	Very nice and printable	Printable as well	Suddenly very wet and not printable. Might be a mixing error	Suddenly very wet	Suddenly very wet

Table 14: Mixture design - printable with 30% volcanic ash

	P-I-VA30	P-II-VA30	P-III-VA30	P-IV-VA30	P-V-VA30	P-VI-VA30	P-VII-VA30
CEM (wt%)	14,21	14,21	14,21	14,21	14,21	14,21	14,21
VA (wt%)	6,09	6,09	6,09	6,09	6,09	6,09	6,09
LP (wt%)	13,03	13,04	13,04	13,04	13,04	13,04	13,03
Sand (wt%)	66,67	66,66	66,66	66,66	66,66	66,67	66,67
W/B (-)	0,29	0,30	0,29	0,29	0,29	0,29	0,29
SP/B (-)	0,44	0,50	0,48	0,46	0,46	0,44	0,43
R/B (-)	0,16	0,18	0,16	0,16	0,16	0,16	0,16
Batch size	small	small	small	small	small	small	small
Comments	Too dry	Too wet, runny	Also too wet	Looked good, wrong nozzle on printer, so no results	Too wet	Too wet	A little too dry

	P-VIII-VA30	P-IX-VA30	P-X-VA30	P-XI-VA30	P-XII-VA30	P-XIII-VA30	P-XIV-VA30
CEM (wt%)	14,21	14,21	14,21	14,21	14,21	14,21	14,21
VA (wt%)	6,09	6,09	6,09	6,09	6,09	6,09	6,09
LP (wt%)	13,03	13,03	13,03	13,03	13,03	13,03	13,03
Sand (wt%)	66,67	66,67	66,67	66,67	66,67	66,67	66,67
W/B (-)	0,29	0,29	0,29	0,29	0,29	0,29	0,29
SP/B (-)	0,44	0,44	0,44	0,45	0,45	0,46	0,46
R/B (-)	0,16	0,17	0,20	0,21	0,21	0,22	0,22
Batch size	small	small	small	small	small	small	large
Comments	Too dry. Looked good after 5 min. of mixing	Adjusted mixer speed to two for full mixing duration	Too dry add more retarder	Works, but might have been mixed a little too short	Mixed for full time and barely printable. Only half the mixture comes out	Printable	Suddenly quite wet

Table 15: Mixtures used in experiments - printable without volcanic ash

	P-VIII	P-IX	P-X	P-XI	P-XII	P-XIII	P-XIV
CEM (wt%)	20,30	20,30	20,30	20,30	20,30	20,30	20,30
VA (wt%)	-	-	-	-	-	-	-
LP (wt%)	13,04	13,04	13,04	13,04	13,04	13,04	13,04
Sand (wt%)	66,67	66,66	66,66	66,66	66,66	66,66	66,66
W/B (-)	0,28	0,28	0,28	0,28	0,28	0,28	0,28
SP/B (-)	0,32	0,32	0,32	0,32	0,32	0,32	0,32
R/B (-)	0,16	0,16	0,16	0,16	0,16	0,16	0,16
Batch size	large	large	large	large	large	large	large
Used in	Bending and compression tests	Bending and compression tests	Shrinkage and creep tests	Vicat and USWT tests	UUCT	UUCT	UUCT

Table 16: Mixtures used in experiments - printable with 30% volcanic ash

	P-XV-VA30	P-XVI-VA30	P-XVII-VA30	P-XVIII-VA30	P-XIX-VA30	P-XX-VA30	P-XXI-VA30
CEM (wt%)	14,21	14,21	14,21	14,21	14,21	14,21	14,21
VA (wt%)	6,09	6,09	6,09	6,09	6,09	6,09	6,09
LP (wt%)	13,04	13,04	13,04	13,03	13,04	13,04	13,04
Sand (wt%)	66,66	66,66	66,66	66,67	66,66	66,67	66,66
W/B (-)	0,29	0,28	0,28	0,28	0,29	0,29	0,29
SP/B (-)	0,46	0,46	0,46	0,46	0,46	0,46	0,46
R/B (-)	0,22	0,22	0,22	0,22	0,22	0,22	0,22
Batch size	large	large	large	large	large	large	large
Used in	Bending and compression tests	Bending and compression tests	Shrinkage and creep tests	Vicat and USWT tests	UUCT	UUCT	UUCT

Test results

B.1 Mixture composition

Table 17: Results of average bending and compressive strength of different non-printable mixtures

		Bending		Compression	
Mixture	Test age	Strength (MPa)	SD (MPa)	Strength (MPa)	SD (MPa)
Commercial mix	7 days	5,37	0,16	35,12	1,56
	14 days	7,01	0,04	34,67	1,25
	28 days	7,97	0,02	38,67	3,77
	35 days	-	-	-	-
CEM III/B	7 days	11,40	0,29	41,52	3,47
	14 days	11,62	0,58	51,50	3,47
	28 days	12,95	0,68	47,41	2,27
	35 days	-	-	-	-
10% VA	7 days	8,46	0,81	37,24	2,17
	14 days	10,26	0,08	43,73	4,32
	28 days	11,61	1,01	46,72	2,42
	35 days	11,29	0,29	49,82	3,59
20% VA	7 days	7,77	0,17	30,21	2,48
	14 days	9,28	0,11	35,38	2,74
	28 days	10,26	0,63	39,69	3,15
	35 days	9,77	0,86	38,54	2,42
30% VA	7 days	6,87	0,08	25,99	1,10
	14 days	8,61	0,07	33,82	0,89
	28 days	9,21	0,37	36,15	1,75
	35 days	9,88	0,40	39,02	2,36
40% VA	7 days	5,82	0,21	18,78	2,18
	14 days	7,22	0,27	25,11	1,94
	28 days	8,30	0,45	30,52	1,49
	35 days	8,18	0,25	31,38	2,15

B.2 Print tests

Table 18: Print settings tried with commercial mixture

	Diameter nozzle (mm)	Height nozzle (mm)	Speed (mm/s)	RPM Makita	Height of layers (mm)	Comments
Test 1	30	30	25	3	-	Nozzle too big, material is falling due to size and height of nozzle
Test 2	15	25	30	2	-	Nozzle too high, speed too fast, filament is dropped uncontrolled
Test 3	15	15	20	2	-	Nice print, used with other mixtures
Test 4	15	15	20	2	15	Nice print, used with other mixtures

B.3 Determining material properties

B.3.1 Bending and compression tests

Table 19: Results of average bending and compressive strength of different printable mixtures

		Bending		Compression	
Mixture	Test age	Strength (MPa)	SD (MPa)	Strength (MPa)	SD (MPa)
Commercial mix	7 days	7,67	0,43	38,82	1,63
	14 days	7,52	0,76	41,02	0,85
	28 days	6,71	0,41	42,97	1,58
	35 days	7,67	0,24	42,93	3,55
CEM III/B	7 days	9,84	0,33	43,20	5,20
	14 days	11,18	0,31	59,23	1,64
	28 days	10,99	0,29	59,45	2,03
	35 days	11,53	0,34	61,01	2,34
30% VA	7 days	7,78	0,14	30,59	1,36
	14 days	9,01	0,13	41,21	1,54
	28 days	9,95	0,36	47,97	2,97
	35 days	9,97	0,70	50,64	3,31

B.3.2 Ultrasonic wave transmission tests

In Figures 26 to 28 the results from the individual samples measured in the ultrasonic wave transmission tests can be found. To calculate the E-modulus the densities mentioned in Table 20 have been used for the mixtures, determined by weighing the samples made for the bending tests immediately after casting. In Figure 29, the velocity of the waves can be seen for the commercial mixtures, as used in comparison to literature.

Table 20: Average densities printable mixtures

Mixture	Average density (kg/cm^3)
Commercial mixture	$2,11 \cdot 10^{-6}$
CEM III/B	$2,22 \cdot 10^{-6}$
CEM III/B & volcanic ash	$2,20 \cdot 10^{-6}$

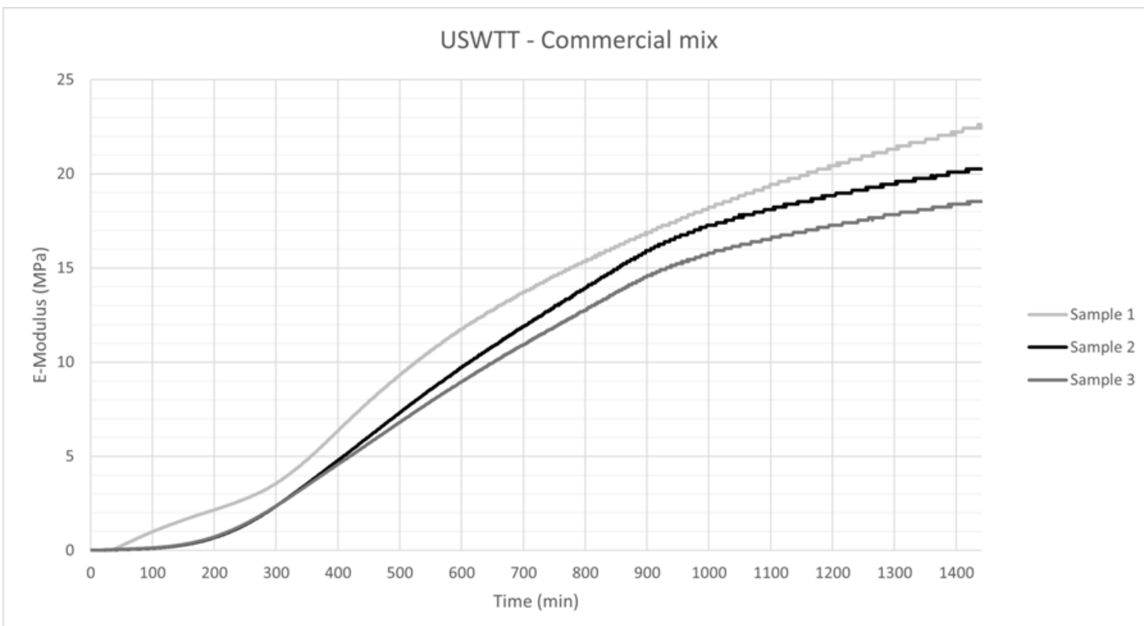

Figure 26: Results dynamic E-modulus - commercial mixture

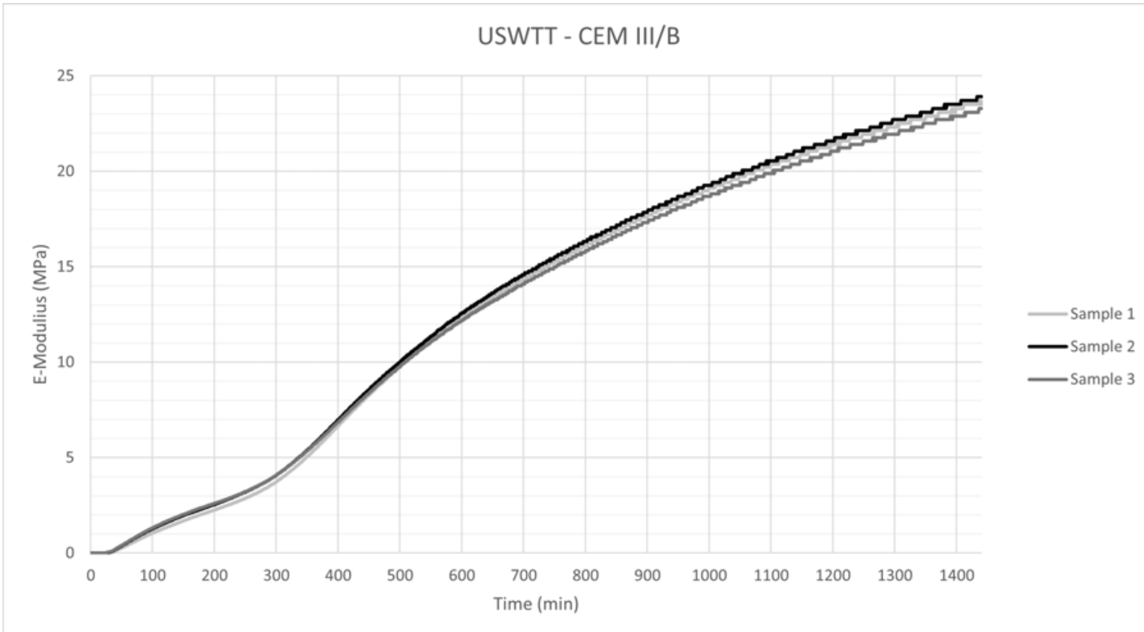

Figure 27: Results dynamic E-modulus - CEM III/B

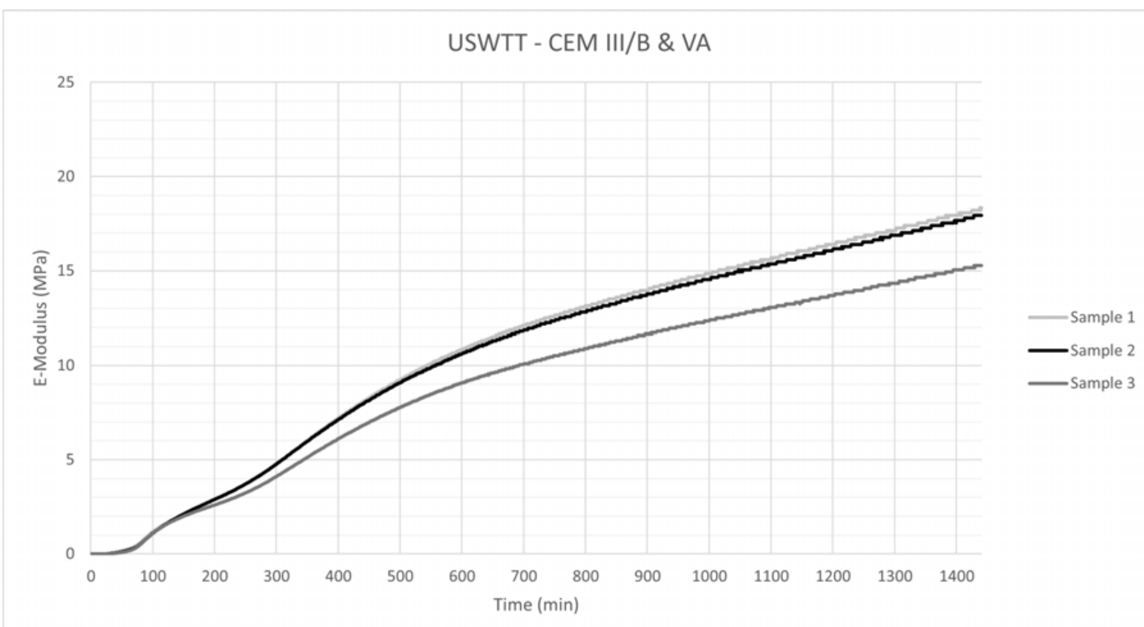

Figure 28: Results dynamic E-modulus - CEM III/B & VA

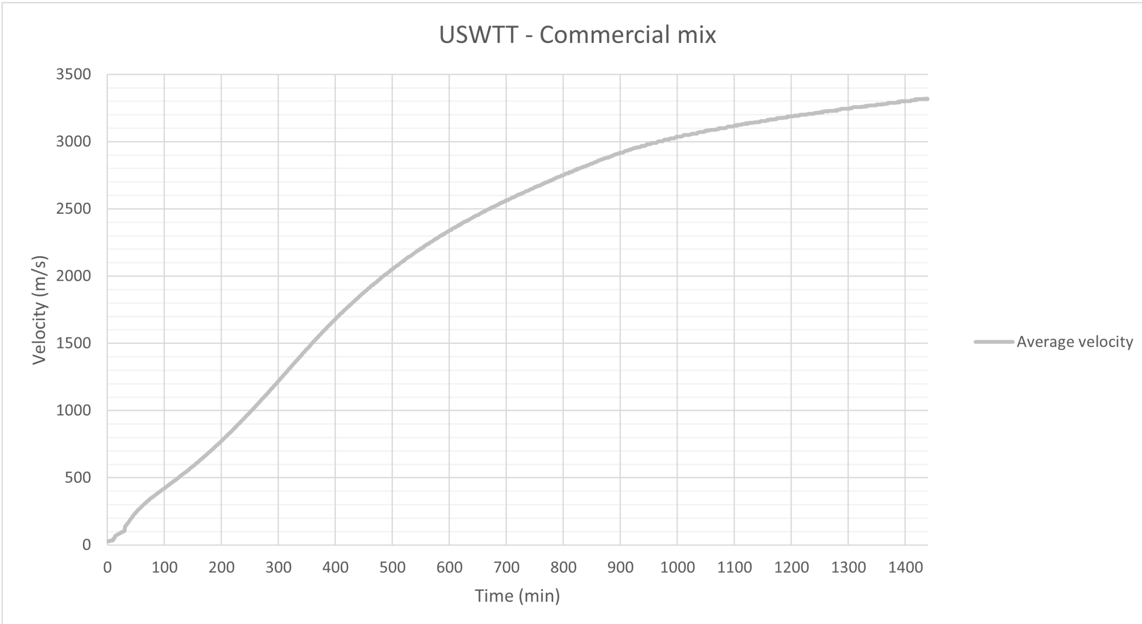

Figure 29: Wave velocity of commercial mixture

B.3.3 Uniaxial unconfined compression tests

For comparison, the scales of the graphs in Figures 21 to 23 are the same, however to improve the readability of the individual graphs, in Figures 30 to 32, the graphs have been re-scaled. Figures 30 and 31 have been re-scaled in the y-axis and Figures 31 and 32 have been re-scaled on the x-axis

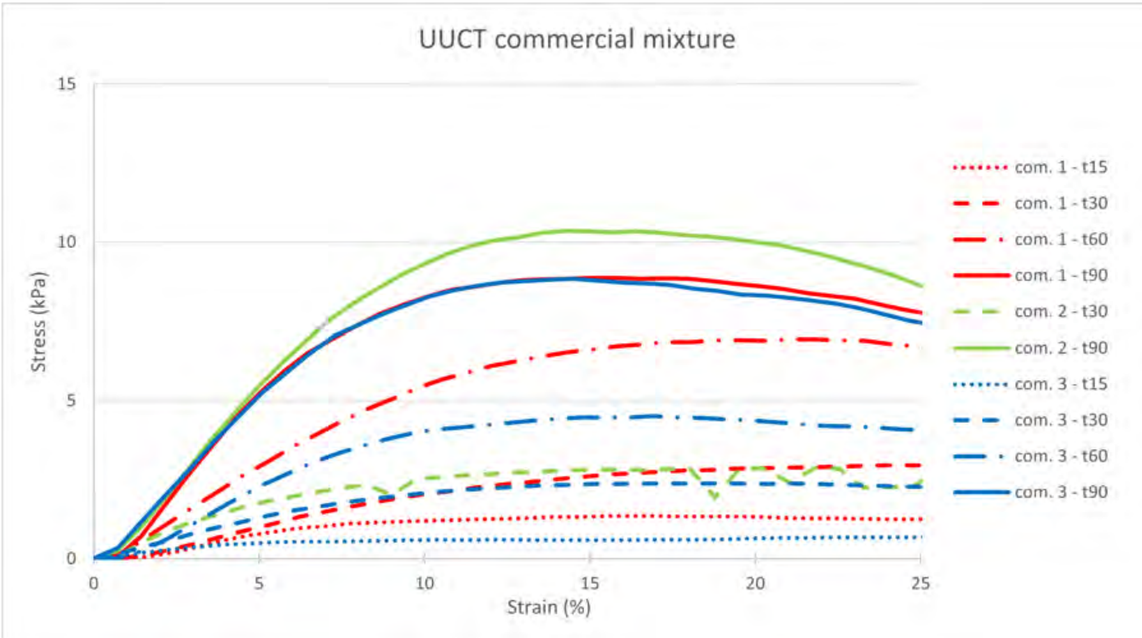

Figure 30: Re-scaled stress-strain diagram for commercial mix from uniaxial unconfined compression tests

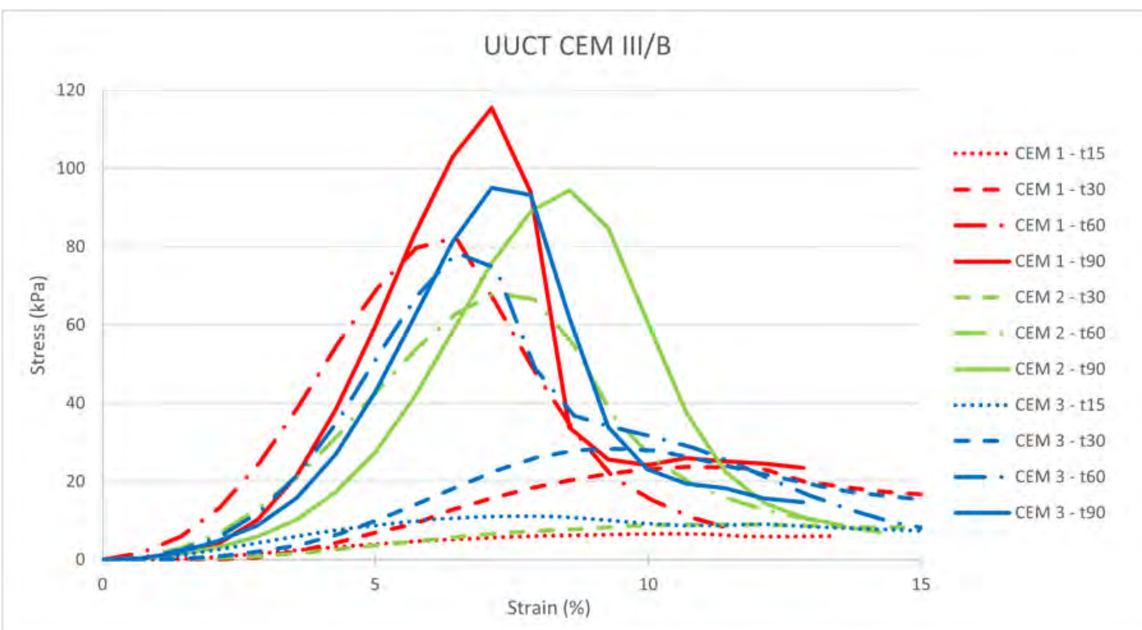

Figure 31: Re-scaled stress-strain diagram for CEM III/B mix from uniaxial unconfined compression tests

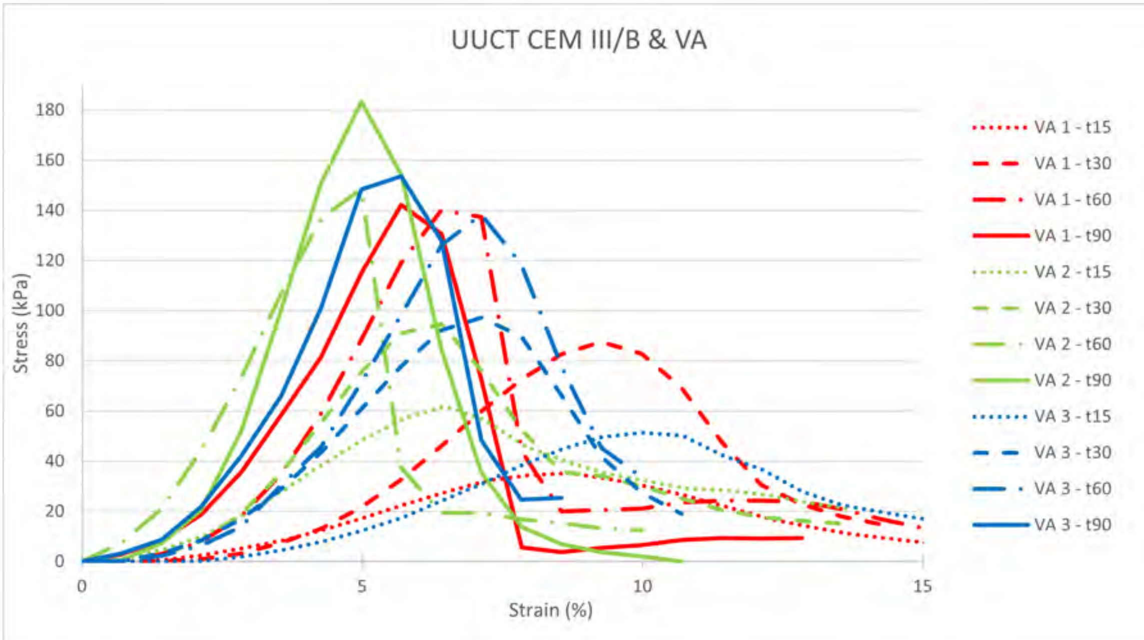

Figure 32: Re-scaled stress-strain diagram for CEM III/B & volcanic ash mix from uniaxial unconfined compression tests

B.3.4 Vicat tests

For the vicat tests, three samples of the same mixture were tested simultaneously, which means that not all samples were tested at the exact same times. This is also mentioned in the tables as sample 1 is measured 30 seconds before the mentioned time of measurement and sample 3 is measured 30 seconds after. Sample 2 is measured at the mentioned time. The measurements taken as the initial setting times for each sample can be found printed in bold and underlined in Tables 21 to 23.

Table 21: Commercial mixture vicat results measured from point of needle to bottom of sample

Time (h.min)	Sample 1 (-30 sec.) (mm)	Sample 2 (± 0 sec.) (mm)	Sample 3 (+ 30 sec.) (mm)
0.30	0	0	0
1.00	0	0	0
1.30	0	0	0
2.00	0	0	0
2.15	4	0	2
2.30	7	3	2
2.35	9	8	2
2.37,5	11	5	1
2.40	10	3	1
2.42,5	6	2	5
2.45	5	10	4
4.27,5	8	20	18
2.50	4	8	5
2.52,5	4	3	1
2.55	11	6	**13**
2.57,5	**6**	**6**	19
3.00	11	13	18

Table 22: CEM III/B vicat results measured from point of needle to bottom of sample

Time (min.)	Sample 1 (-30 sec.) (mm)	Sample 2 (± 0 sec.) (mm)	Sample 3 (+ 30 sec.) (mm)
15	0	0	0
20	0	0	1
25	0	0	1
30	1	2	0
32,5	0	1	1
35	1	1	2
37,5	0	1	1
40	0	4	0
42,5	2	1	1
45	0,5	3	1
47,5	3	3	1
50	0	1	2
52,5	1	3,5	1
55	10	40	3
57,5	3	3	3
60	2	2	3
62,5	3,5	4	4
65	2	**7**	3
67,5	**4**	40	**6**
70	31	40	4
72,5	31	4	14
75	40	40	21

Table 23: CEM III/B & VA vicat results measured from point of needle to bottom of sample

Time (min.)	Sample 1 (-30 sec.) (mm)	Sample 2 (± 0 sec.) (mm)	Sample 3 (+ 30 sec.) (mm)
10	0	0	0
15	0	0	0
20	0	0	0
25	1	1	**9**
30	1	2	30
32,5	**3**	**5**	14
35	27	26	17