Department of Civil Engineering

Optimization approach for calcined clay and slag based geopolymer mortar – an experimental investigation for 3DCP

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Summary

After water, concrete is the most used substance on the planet. Approximately three tonnes of concrete is produced per person annually *(Gagg, 2014).* Traditionally, large amounts of Ordinary Portland Cement (OPC) are needed for the production of concrete. The production of OPC is very energy intensive and therefore a major generator of carbon dioxide, which is considered to be a potent greenhouse gas. High CO_2-emissions are caused by calcination of limestone and combustion of fossil fuel during an energy intensive production process.

To reduce the CO_2-emissions caused by the concrete manufacturing, there is a growing interest in alternative and low CO_2-binders. A great example of alternative binders are alkali-activated materials (AAMs), often referred to as geopolymers. Alkali-activated materials are inorganic polymers acting as the binder agent in concrete, often containing by-products from the industry such as fly ash and blast furnace slag *(Davidovits, 1989)*. Unlike OPC, AAMs are synthesized by activation of an aluminosilicate source (fly ash, slag, metakaolin) with alkaline activators. AAMs have attracted a lot of attention in the industry because of its superior mechanical properties, excellent resistance to sulphate attack, low creep and low drying shrinkage compared to OPC.

Besides sustainability, the total cost is also a relevant factor for the construction industry. 3D-printing of concrete removes the need for formwork and enables the industry to create complex shapes as well as optimization of material use. It also provides an opportunity for an automated building process with a minimal amount of labour and material wastage. Combining the use of alkali-activated materials (AAMs) in an innovative and automated 3D-printing process may therefore offer many advantages for the construction industry.

Although fly ash and slag are relatively cheap and available at the moment, metakaolin is still a very promising feedstock material for geopolymers in the future. Slag is becoming less available because of its effective usage in the manufacturing of blending cements and concrete nowadays *(Malhotra and Mehta, 1996).* Also, due to decreasing levels of coal-fuelled power generation, availability of fly ash is becoming a problem for the Netherlands. From a long-term point of view, metakaolin is therefore becoming a very attractive alternative to fly ash and slag, especially for the Netherlands.

The goal of this research is to provide an optimization approach for metakaolin and slag based geopolymer concrete/mortar for the purpose of 3D-printing. Optimization is established by considering the fresh properties (slump and setting time) and mechanical properties (compressive and flexural strength). These properties have proven to be key in formulating appropriate mixture designs for 3D-printing, since the mixture should be flowable enough to be extruded through the hose, while ensuring high early strength for buildability and shape stability of the printed layers.

In this research, an optimalization approach is given for calcined clay and slag based AAMs for the purpose of 3D-printing. Optimization is established by considering the fresh properties (slump and setting time) and mechanical properties (compressive and flexural strength). The parameters investigated in this research are:
a) calcined clay/slag ratio; (b) modulus of the alkaline solution; (c) water/binder ratio;
(d) Na_2O/precursor ratio.

This study has shown that the water to binder ratio is the most important factor for optimizing slump and setting time values of various mixtures. To optimize the mechanical strength of calcined clay and slag based geopolymer mortars, it's most effective to change the calcined clay content. Furthermore, incorporation of more than 25% of calcined clay in the precursor leads to approximately zero 1-day and 7-day strength for almost all mixture designs within the chosen ranges. This is mainly caused by

the low reactivity of the calcined clay powder and the large delay in setting. The replacement of calcined clay by pure metakaolin results in much higher strength properties as well as faster setting. However, the workability decreases considerably with this replacement. The incorporation of metakaolin in geopolymer mortar requires a higher water demand to guarantee adequate workability for the application of 3D-printing.

Altogether, the study shows that a blended system of blast furnace slag and calcined clay has potential for further use in 3D-printing. Optimal properties are acquired for mixtures containing low calcined clay content (25%). Higher calcined clay content result in almost zero 1-day and 7-day strength and it therefore not recommended for 3D-printing.

It is therefore recommended to use calcined clay only in small quantities for 3D-printing. The chosen parameters can be adjusted in such a way that technical requirements can be satisfied, using the formulae established with fitted regression of the experimental data. Using the principle of orthogonality in the design ensured that the effect of one parameter could be estimated separately without any interaction of the other parameters. Following an orthogonal design approach therefore effectively contributed to a reduction of the number of mixture designs that needed to be evaluated (25 instead of 135). This methodology therefore shows high potential for further use in research regarding optimization of concrete and mortar.

Content

1 Introduction

Today, concrete is one of the most used materials in the world. After water, concrete is the most used substance on the planet. Approximately three tonnes of concrete are produced per person annually *(Gagg, 2014).* Traditionally, large amounts of Ordinary Portland Cement (OPC) are needed for the production of concrete. The production of OPC is very energy intensive and therefore a major generator of carbon dioxide, which is considered to be a potent greenhouse gas. High CO_2-emissions are caused by calcination of limestone and combustion of fossil fuel during an energy intensive production process. See figure 1 for the contribution of concrete to global carbon dioxide emissions.

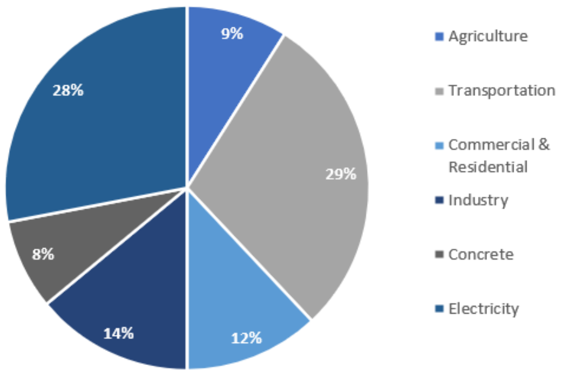

Figure 1: Carbon dioxide emissions by business sector (Warburton, 2019).

Despite the environmental issues related to the production of traditional concrete, consumption of Portland cement still has grown nearly exponentially in the last two decades, as can be seen from figure 2. The growth of the cement production has levelled off in the last couple of years, meaning that the climax point has been reached: the global cement production has stopped increasing.

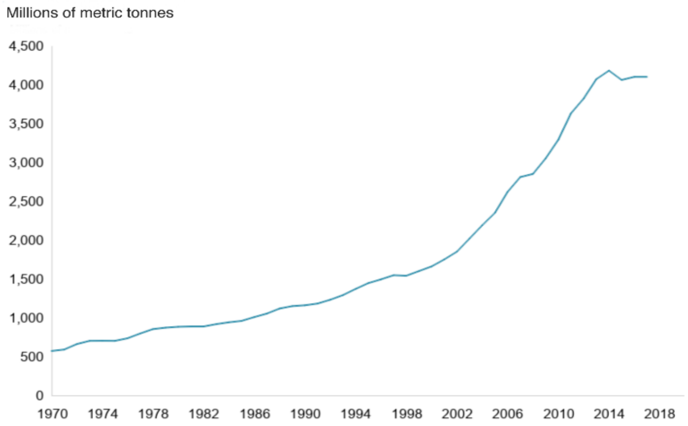

Figure 2: Global cement production. Source: USGS (2018).

The levelling of the global cement production is mainly caused by a growing interest in alternative and low CO_2-binders as an alternative to OPC. A great example of alternative binders are alkali-activated materials (AAMs), often referred to as geopolymers. Alkali-activated materials are inorganic polymers acting as the binder agent in concrete, often containing by-products from the industry such as fly ash and blast furnace slag *(Davidovits, 1989)*. Unlike OPC, AAMs are synthesized by activation of an aluminosilicate source (fly ash, slag, metakaolin) with alkaline activators.

AAMs have attracted a lot of attention in the industry because of its advanced mechanical properties and greater durability.

Besides sustainability, the total cost is also a relevant factor for the construction industry. Formwork can contribute up to 50% of the total cost of a construction. The assembly of formwork is a relatively labour intensive process and very difficult for complex geometrical shapes. 3D-printing of concrete removes the need for formwork and enables the industry to create complex shapes as well as optimization of material use. It also provides an opportunity for an automated building process with a minimal amount of labour and material wastage. Combining the use of AAMs in an innovative and automated 3D-printing process may therefore offer many advantages for the construction industry. According to *Kothman et al. (2019)* and *Bos et al. (2016)*, 3D-printing of concrete offers the following advantages in comparison to the traditional construction method of concrete:

- the ability to optimize the material distribution according to the need of application;
- freeform structure printing capability;
- printing on demand;
- the reduction of material waste.

There is already a good understanding of AAMs containing fly ash and/or blast furnace slag. However, geopolymers based on alkali activation of metakaolin are gaining popularity as well because of their excellent thermal stability, comparable mechanical properties to cement and consistent chemical compositions *(Duxson et al., 2007)*.

Although fly ash and slag are relatively cheap and available at the moment, metakaolin is still a very promising feedstock material for AAMs in the future. Slag is becoming less available because of its effective usage in the manufacturing of blending cements and concrete nowadays *(Malhotra and Mehta, 1996)*, in addition to the cost and technical challenges of supply chain *(van Deventer et al., 2012)*. Also, due to decreasing levels of coal-fuelled power generation, availability of fly ash is becoming a problem for the Netherlands. From a long term point of view, metakaolin is therefore becoming a very attractive alternative to fly ash and slag, especially for the Netherlands.

In this study, a systematic experimental approach is presented to obtain an optimum mix design for calcined clay and slag based AAMs for the application of 3D-printing. This optimization will be done by considering various fresh and mechanical properties.

This report is organized into seven chapters. In chapter 2, a state-of-the-art literature review about the use of metakaolin in AAMs is given, as well as optimum design properties (target values) for the purpose of 3D-printing. Chapter 3 presents the methodology of the research. The results will be discussed in chapter 4. Furthermore, in chapter 5 and 6, an analysis of the results, discussions and conclusions will be provided. Chapter 7 will include recommendations for further research in this field.

2 Literature review

As is mentioned in the introduction, a geopolymer binder is considered to be an effective alternative for Portland cement, since it ensures high strength properties, while lowering the energy consumption. There is already a pretty good understanding of AAMs containing fly ash and/or blast furnace slag with respect to fresh properties, mechanical properties and durability. In this chapter, the focus will be on geopolymer concrete containing metakaolin.

In this chapter, a review will be provided for AAMs containing metakaolin. The influence of metakaolin content and composition of activator solution on the fresh and mechanical properties of metakaolin based AAMs will be discussed. Finally, optimum properties for 3D-printed geopolymers will be given.

2.1 Metakaolin

2.1.1 General

As metakaolin is gaining popularity in the concrete industry, it is important to understand the characteristics and the origin of this material. Metakaolin [$Al_2O_3.2SiO_2$] is a pozzolan just like volcanic ash. It is the anhydrous calcined form of the clay mineral *kaolinite* [$Al_2Si_2O_5(OH)_4$], which is a naturally occurring (abundant) mineral in the earth's crust. Metakaolin is produced by heating clays containing kaolin within the temperature range of about 600-900 °C. The reactivity of metakaolin strongly depends on the characteristics of the raw material that is used, as it can be obtained from various sources, like tropical soils, high purity kaolin deposits, etc.

2.1.2 Metakaolin in geopolymer concrete

Metakaolin has a higher reactivity than many other pozzolanic materials and has therefore been proven to be a valuable admixture for concrete applications, e.g. OPC-concrete with metakaolin as SCM or geopolymer concrete. This high reactivity is often attributed to the relatively high specific surface area (SSA). This indicates the importance of the SSA of metakaolin in the manufacturing of high strength geopolymer.

However, metakaolin with high SSA may demand high water content for good workability, depending on its application. Metakaolin is therefore not often used for mass production of concrete, it's only used in small quantities. The high water demand is also related to its plate-like morphology *(Murray, 2000)*, see figure 3. The properties and reactivity strongly depend on the type of clay that is used and its physical and chemical composition, e.g. density, mineralogical composition, specific surface area (SSA), particle size, metakaolin content, thermal treatment history, etc.

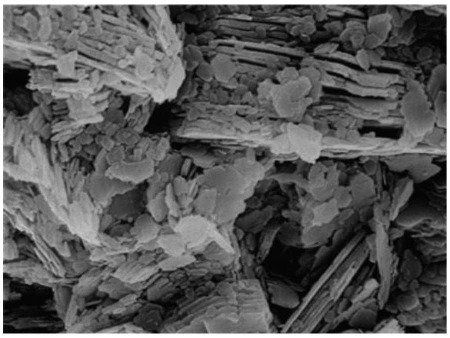

Figure 3: Morphology of kaolin particles. (Murray, 2000).

In the last couple of decades, the use of white metakaolin has been extensively studied as an aluminosilicate source for concrete. As high purity kaolin clay is used in different industries as well, there is a competing demand for this material. This competing demand for metakaolin and the intensive purification process to obtain metakaolin from kaolinite clay, both contribute to a relatively high price *(Zhou et al., 2017)*. Calcined clay is considered to be a more cost-effective alternative, as less intensive purification is needed, while the supply is much larger. Large supply is a result of enormous clay reserves due to clay waste generated by the ceramics industry and construction industry *(Lopez et al., 2009)*. The reactivity of calcined clay typically depends on the calcination process of kaolinite clay, as metakaolin is formed during heating at high temperatures. Calcined clay with increasing metakaolin content shows increasing reactivity.

It is important to limit the heating temperature during the calcination of kaolin-containing clay, since it is reported by several sources that the over-calcination of kaolinite clay reduces its reactivity. Generally, the production of metakaolin is done with carefully controlled heat treatment of kaolin at 700–800 °C for optimal properties *(Shvarzman et al., 2003)*.

The source materials in an alkali-activated material, like metakaolin (MK), ground granulated blast furnace slag (BFS) and fly ash (FA) are treated with an alkaline liquid to obtain the binder agent. Solutions containing sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) are typically used to activate the source materials through geopolymerization. Metakaolin basically provides aluminosilicate source for the geopolymerization process. Heat treated natural pozzolans like metakaolin are often used to improve the resistance of concrete to sulphate attack, to mitigate alkali-silica reactions (ASR) and are very useful for applications in which low permeability and very high strength is required.

Geopolymerization of metakaolin is achieved by a couple of steps *(Yao et al., 2009)*:

- dissolution of MK particles;
- initial polymerization of dissolved alumina and silicate species into Al-O-Si oligomers;
- further polymerization into large amorphous gels or direct crystallization of the oligomers into aluminosilicates;
- crystallization of the amorphous polymers into aluminosilicates.

The geopolymerization process of metakaolin is schematized in figure 4.

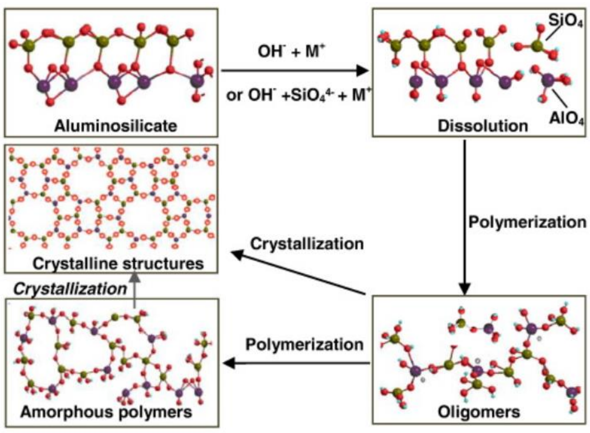

Figure 4: A model of the geopolymerization process. (Yao et al., 2009).

2.1.3 Metakaolin versus fly ash/slag

For the upcoming years, the trade perspective of fly ash (vliegas) and slag (hoogovenslak) is negative, meaning that its availability is becoming a problem for the Netherlands in the near future (figure 5). The trade perspective of calcined (gecalcineerde klei) is considered to be positive according to *Betonhuis (2021)*.

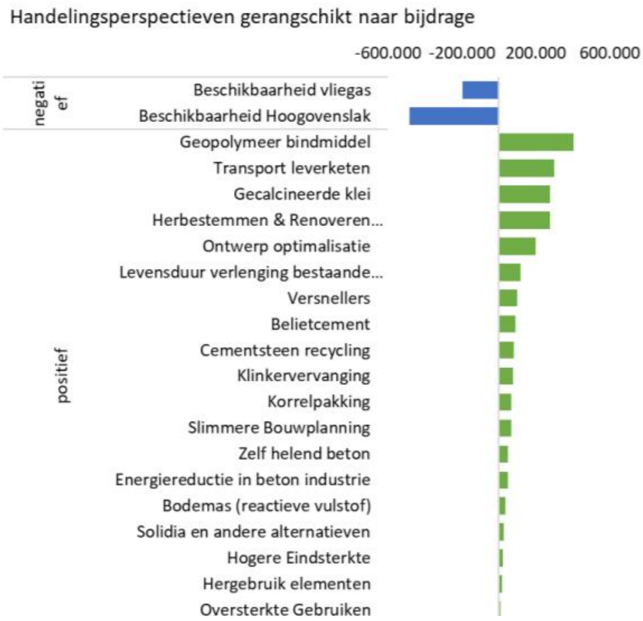

Figure 5: Trade perspective of various materials in concrete ranked according to their contribution, according to concrete manufacturer Betonhuis (2021).

The negative trade perspectives of fly ash and slag is caused by the fact that these materials are becoming less and less available in many countries because of their effective usage nowadays in the manufacturing of blending cements and concrete *(Malhotra and Mehta, 1996)*, in addition to the cost and technical challenges of supply chain *(van Deventer et al., 2012)*. As metakaolin has consistent chemical compositions, high reactivity and a positive trade perspective, it is therefore a promising feedstock material for geopolymers in the future. The consistent chemical composition of metakaolin is a result of the controlled calcination process of kaolinite.

The chemical composition of metakaolin and calcined clay has been described in the previous paragraph. Blast furnace slag is a pozzolanic by-product, formed when iron ore or iron pellets, coke and flux (limestone or dolomite) are melted together in a blast furnace. Properties of blast furnace slag strongly depend on the production process. Slag primarily consists of limestone (CaO) and silica (SiO_2). The shape of blast furnace slag particles is irregular with a glassy surface. Fly ash is also a pozzolanic by-product, formed during coal combustion. The properties of fly ash vary significantly depending on the source and composition of the burned coal. Fly ash contains high amounts of silica (SiO_2), aluminium oxide (Al_2O_3) and lime (CaO). Particles of fly ash have a spherical glassy shape.

Slag is considered to be a binder that is rich in calcium and silicon. In case of a binder containing solely slag, moderate alkaline conditions without external heating are required to activate the binder. The main product is *CASH-gel*, a reaction product that provides geopolymer concrete or mortar its mechanical strength. In case of a binder containing only metakaolin or fly ash, the binder is rich in aluminium and silicon and contains low calcium content. When fly ash and metakaolin are used as a binder in geopolymer concrete, an amorphous alkaline aluminosilicate hydrate is formed, also known as NASH-gel *(Garcia-Lodeira et al., 2015).* Because of the low calcium oxide content, aggressive working conditions are needed to activate the binder at a fast rate, such as higher alkalinity and higher curing temperatures. Furthermore, metakaolin requires the highest content of alkali activator in comparison to fly ash and/or slag based AAM *(Provis & Winnefeld, 2018).* Also, the reactivity of metakaolin is generally lower than the reactivity of slag and higher than fly ash.

Nedeljcovic et al. (2016) states that the combination of low and high calcium binders provides a more uniform development of the microstructure and therefore optimal properties. In this study, the focus will therefore be on AAMs containing slag and metakaolin or calcined clay.

2.2 Fresh properties of metakaolin based geopolymers

In the previous paragraph, the feasibility of (partially) replacing fly ash and/or blast furnace slag with metakaolin was explained. In this paragraph, the focus will be on examining the fresh properties of geopolymer mortars and concrete with metakaolin.

In a study conducted by *A. Albidah et al. (2020)*, the influence of different mix design parameters is investigated for 100% metakaolin based geopolymer concrete. Locally available raw kaolin is calcined at 750°C for 3 h to produce the MK. Alkali activators are comprised of a mixture of sodium hydroxide solution (NaOH) with a concentration of 14M and sodium silicate solution consisting of Na_2O-14.7%, SiO_2-29.4% and H_2O-55.9% by mass. Mixes are cast in four groups to investigate the effect of four parameters: sodium silicate to sodium hydroxide solids ratio (1.30-3.00), alkaline solids to MK ratio (0.21-0.41), aggregate content and water to solids ratio (0.38-0.54) on the properties of geopolymer concrete. The workability for the mixes is evaluated based on the slump test as specified by *ASTM* standards.

Mixes with low sodium silicate to sodium hydroxide (solids) ratio, 1.3 (MR=0.74) and 1.6 (MR=0.84), show almost no slump. A low sodium silicate to sodium hydroxide ratio is also related to a low modulus (SiO_2/Na_2O molar ratio) of the alkaline activator. A low modulus indicates high Na_2O content relative to the SiO_2 content, resulting in chemical reactions that occur at a faster rate due to the high Na_2O content. This explains the low slump, paired with fast setting. Increasing the sodium silicate to sodium hydroxide solids ratio to 2 (MR=0.95) and 2.5 (MR=1.07) produces more workable mixes with a slump of about 30 mm. Exceeding a certain value of the sodium silicate to sodium hydroxide ratio, 3.0 in the study (MR=1.16), results in a more cohesive mix with lower slump values of 20 mm. In general, increasing sodium silicate to NaOH solids ratios contribute to an enhanced workability as a result of the higher H_2O/Na_2O ratio. A too high sodium silicate to sodium hydroxide ratios may result in less workable mixes. However, it is important to mention that the workability of a geopolymer concrete mix highly relies on binder proportions, e.g. quantities of metakaolin, sodium hydroxide and sodium silicate. If the goal is to have a high aggregate content for example, a high sodium silicate to sodium hydroxide solids ratio can still ensure adequate workability of the mixture.

In the same study, zero slump is observed for mixes which had alkaline solids to MK ratios of 0.21, 0.25, and 0.3. An improved workability is achieved for mixes with higher alkaline solids to MK ratio (0.37 and 0.41). In general, a decrease in MK content and therefore an increase in alkaline solids to MK ratio results in a mix with higher slump and therefore higher workability.

In another study of *Huseien et al. (2018)*, the effect of metakaolin as substitution (0-15%) for ground granulated blast furnace slag (BFS) on the early strength of geopolymer mortars for potential repair applications is reported. Solution concentrations ratio of SiO_2:Na_2O are varied in the range of 1.08–1.26 to achieve appropriate geopolymerization. Various proportions of Na_2O:dry binder (7%, 8%, 9%, 11% and 13%) were used. The study shows that the setting time and the flow increase with increasing MK content.

The particle size of metakaolin is mentioned as a reason for the increase in flowability of mixtures containing increasing MK content. As MK particles are much smaller (75% of the particles smaller than *10 µm*) and less angular than slag particles, the workability increases for increasing MK content. The particle size thus plays an important role in the dissolution process and flow of the mortar. MK has a lower calcium content and higher silicate and aluminium content than slag. Higher MK content results in an increased setting time due to the lower calcium content in the mixture. Thus, the MK (as part of a binary blended binder) actively decelerates the setting time of geopolymer mortars under ambient curing conditions. For the purpose of 3D-printing, the addition of slag is only beneficial in a continuous printing process for better buildability. In case of batch mixing, a slow setting is preferred to prevent cold joints between the printed layers. For this application, low content of slag is preferred.

In the same study, the influence of the concentration of the sodium hydroxide solution on the fresh properties of the mortar is investigated as well. The flow of the mortar is found to be higher at lower Na_2O contents. One observation is that the flow was reduced from 23 to 15 cm when the molarity of the sodium hydroxide solution is increased from 10 to 18 M, as this results in a higher Na_2O content. An increase in Na_2O content (higher molarity of NaOH solution) also leads to an increase in the Na^+-content and therefore a reduction of the SiO_2:Na_2O content. This results in an increase of the released heat, a lower flow rate and lower setting time (fast setting). The lower setting time is a result of a fast rate of chemical reaction due to the high Na_2O content. Curing at high temperature can accelerate this reaction rate even further. The relation between SiO_2:Na_2O ratios and flow and setting time is given in figure 6.

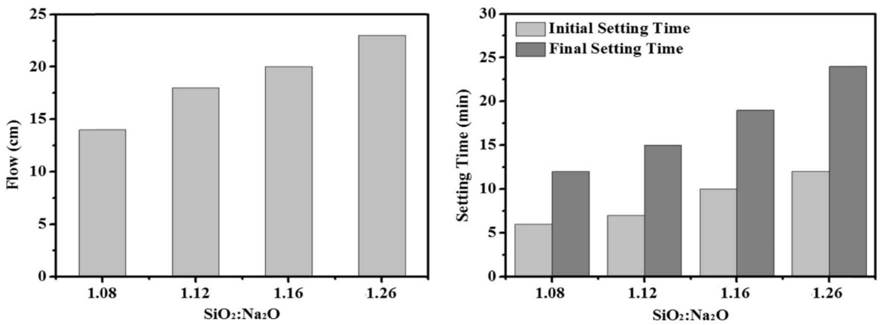

Figure 6: Impact of SiO_2:Na_2O on the flow and setting time of geopolymer mortar. (Huseien et al., 2018).

The study also mentions the influence of the alkali solids to binder ratio on the fresh properties of the mortar. The flowability increases with an increasing alkali solids to binder ratio (S:B). An increase of the alkali solution increases the water content and therefore leads to an increase of the workability as well. The setting time is also improved considerably for increasing S:B ratios. The relation between Na_2O:dry binder ratios and flow and setting time is given in figure 7.

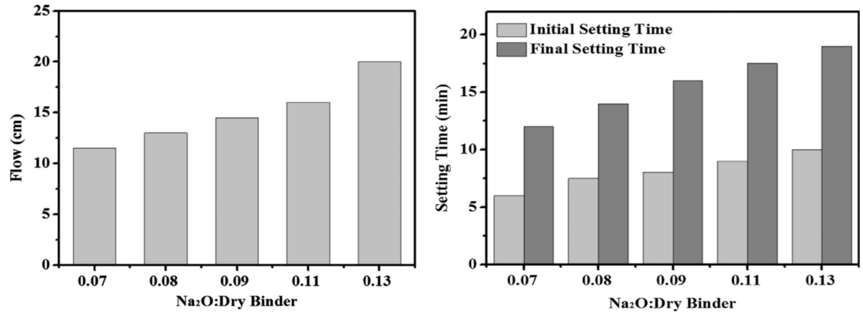

Figure 7: Impact of Na_2O:dry binder on the flow and setting time of geopolymer mortar. (Huseien et al., 2018).

Hasnaoui et al. (2019) aims to find the optimum formulation for metakaolin and slag based geopolymer mortar for varying metakaolin and slag content and different compositions of the alkali solution. The rheology, porosity, mechanical properties and susceptibility to efflorescence are investigated for 24 different mortar mix designs. The research is divided into two different phases. In the first phase, the effect of GBFS + MK/Activator (2-5) was evaluated for equal amounts of ground granulated blast furnace slag and metakaolin using two modular ratios (MR) of 1.4 and 1.6. An optimum GBFS + MK/Activator ratio is selected based on workability, mechanical strength and the stability to efflorescence. This optimum ratio is used for evaluating the effect of GBFS/MK (25/75, 50/50 and 75/25) and MR (1.0, 1.2, 1.4, 1.6, 1.8 and 2.0).

The study shows that the flow time increases for increasing ratios of GBFS + MK/Activator. This means that the workability is reduced for an increasing content of metakaolin and slag. When the GBFS + MK/Activator ratio is above 3, the modulus ratio (MR) of the alkali solution does not influence the flow time, meaning that a stiff mortar is obtained regardless of the MR. This is a result of the high water demand of slag and especially metakaolin, in comparison with the activator. For ratios of GBFS + MK/Activator under 3.0, a modular ratio of 1.4 improves the workability of the mixtures. A mixture with a GBFS + MK/Activator ratio of 3.0 is selected for the second phase, as its shows good workability (similar to Portland cement mortar) and good mechanical properties.

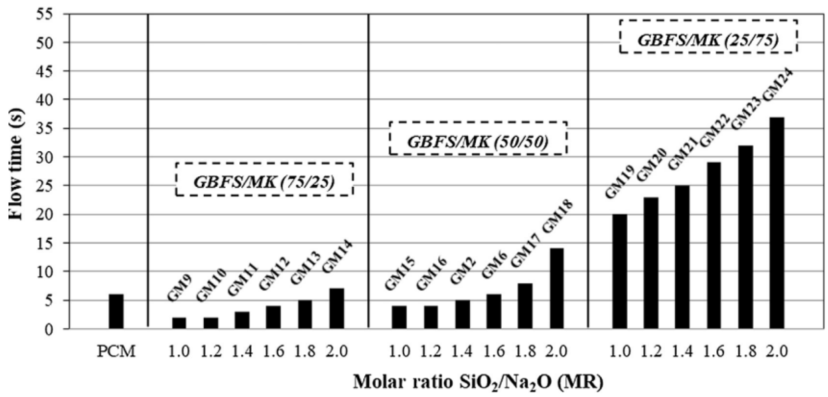

Figure 8: Flow time of Portland cement and geopolymer mortars. (Hasnaoui et al., 2019).

An overview of the flow times for the various mixtures is provided in figure 8. The flow time increases significantly with increasing content of metakaolin, while higher incorporation ratio of GBFS enhances the workability. This increase in flow time can be assigned to the high fineness and therefore high specific surface area (SSA) of MK powder. The plastic viscosity of geopolymer mortars are found to increase as well with increasing content of MK, due to an increasing specific surface area (due to high fineness of MK). An increase in MR also leads to an increase in flow time (lower workability), due to the high silica content in the alkali solution which contributes to a rise in solution viscosity. This contributes as well to a higher flow time (figure 8).

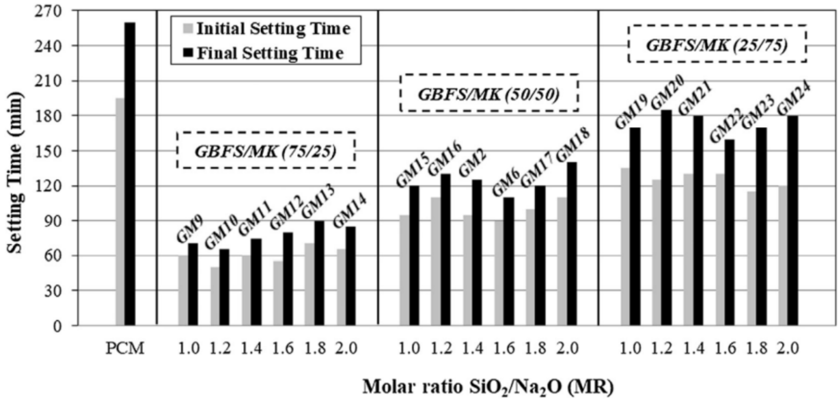

Figure 9: Initial and final setting time of Portland cement and geopolymer mortars. (Hasnaoui et al., 2019).

The influence of the GBFS/MK ratio and MR on the setting is reported as well in this study. Higher content of GBFS results in a low initial and final setting time. This accelerated setting time is caused by the high calcium content (CaO) in GBFS. No clear correlation is found between the modulus and the setting time of the different geopolymer mixtures (figure 9).

In a study by *Alanazi et al. (2017)*, the influence of the modulus of the alkaline solution and slag content on a metakaolin-based geopolymer is investigated by focusing on the early strength and durability of the geopolymer pastes. Moduli in the range of 0.8-1.80 are investigated. The study shows that the maximum compressive strength for a metakaolin based (100%) geopolymer mortar is obtained for a modulus of 1.0. Silica and alumina dissolved at a high rate for this modulus, therefore accelerating the geopolymerization process. Exceeding this modulus will result in impedance of the geopolymerization process. *Škvára et al. (2006)* states that sodium plays an important role in the geopolymerization process, as sodium ions have a charge balancing function. An excess in sodium ions prevents the precipitation phase from contacting the precursor and alkaline activator and therefore hinders the structural formation, leading to lower strength. This study also shows that partially replacing the metakaolin with slag (30%) results in a mixture with a higher workability but not necessarily higher early compressive strength. Possible reasons for this effect will be discussed in paragraph 2.3.

2.2.1 Summary

The addition of metakaolin as a replacement for slag to geopolymer concrete generally decreases the workability and decelerates the setting time of a geopolymer mortar due to the lower calcium content of metakaolin. This effect typically depends on physical and chemical properties of metakaolin. An increase in concentration of the sodium hydroxide solution results in a faster reaction rate and therefore lower workability and shorter setting time. An increasing concentration of the sodium hydroxide solution contributes to a higher Na_2O-content and therefore a lower modulus (molar ratio SiO_2/Na_2O) of the alkaline solution. A low modulus is related to less slump, less flowability and low setting time (fast setting). It is recommended to ensure low moduli of the alkaline solutions in the range of 1-1.20 to obtain zero slump. However, using lower moduli than 1.00 might result in significant strength loss of the mortars. Furthermore, mixtures with a high alkali solids to binder ratio generally show an increase in workability and deceleration of the setting (higher setting time) as a result of the increased water content.

See table 1 for an overview of the literature regarding the fresh properties of MK based geopolymer concrete and/or mortar.

Table 1: Overview literature on fresh properties of metakaolin based geopolymer concrete/mortar.

MK (%)	***GGBFS (%)***	***FA (%)***	**M_s** ***SiO_2:Na_2O***	**NS/NH solids ratio**	**Na_2O/ binder**	**Water/ binder ratio**	**Concentr-ation**	**Curing method**	**Fresh properties**
100%	0%	0%	0.74-1.16	1.30-3.00	0.06-0.11	0.38-0.54	NH: 14M	Ambient curing	Mixes with low NS/NH solids ratio (1.3, 1.6) showed almost no slump. Increasing the NS/NH ratio to 2 and 2.5 produced more workable mixes (slump=30 mm). Exceeding a certain limit of the NS/NH ratio (3.0) resulted in a more cohesive mix with lower slump values of 20 mm. (Albidah et al., 2020)
0-15%	85-100%	0%	1.08–1.26	3.0	0.07-0.135	-	NH: 10, 14, 16, 18 M	Ambient curing	The study showed that the setting time and the flow increased, while the density decreased with increasing MK content. Another observation was that the flow was reduced from 23 to 15 cm when the molarity of the sodium hydroxide solution was increased from 10 to 18 M, as this resulted in a higher Na_2O content. The flow ability increased with an increasing alkali solids to binder ratio (S:B). The setting time was also improved considerably for increasing S:B ratios. (Huseien et al, 2018).
25-75%	25-75%	0%	1.0-2.0	2.2-85.6	0.06-0.14	0.50	-	Ambient curing	A study by *Hasnaoui et al. (2019)* reports optimum fresh properties (workability and setting time) for mixtures with a GBFS + MK/Activator ratio of 3.0. Higher metakaolin content results in a higher flow and setting time and therefore less good fresh properties in comparison with Portland cement mortars. An increase in molar ratio SiO_2/Na_2O leads to an increase in flow time (lower workability) for all mixtures. No clear correlation is found for the molar ratio and the setting time of the mixtures.
70-100%	0-30%	0%	0.80-1.80	2.8-10.6	0.10-0.19	0.45-0.59	-	Ambient curing	In a study by Alanazi et al. (2017), the effect of modifying the modulus of the alkaline solution and the effect of slag content on metakaolin based geopolymer is investigated by focussing on the early strength and durability of the geopolymer pastes. The study showed that the maximum compressive strength for a metakaolin based (100%) geopolymer mortar was obtained for a modulus of 1.0. This study also showed that partially replacing the metakaolin with slag (30%) resulted in a mixture with a higher workability but not necessarily higher compressive strength.

2.3 Mechanical properties of metakaolin based geopolymers

According to *Padmakar et al. (2017)*, maximum strength is obtained for geopolymer concrete containing only metakaolin (100%) as pozzolanic material in the binder. In this study, the compressive strength, tensile splitting strength and flexural strength are determined after 7, 14 and 28 days for various proportions of metakaolin and ground granulated blast furnace slag in geopolymer concrete. This is done under ambient curing and using a sodium hydroxide solution with a concentration of 10M.

According to the study of *Albidah et al. (2020)* with only metakaolin (100%) as pozzolanic material, the highest 28 day-compressive strength is achieved for mixes with sodium silicate to sodium hydroxide mass ratios within the range of 1.3-2. The high amount of reactive silica contributes to higher density of Si-O-Si bonds. However, increasing the ratio to 2.5-3.0 results in a strength drop of approximately 10-20 MPa. This observation is assigned to the excess silica content, which impedes the geopolymerization process. This shows that there is optimum dosage of the alkali activator, which also applies to the fresh properties of geopolymer concrete for this specifically selected combination of parameters. This is in line with the findings of *Morsy et al. (2014)*. In the study of *Morsy et al. (2014)*, the changing parameter is the sodium silicate to sodium hydroxide solids ratio (0.50-2.50) for a fly ash based polymer mortar. *Morsy et al.* observes a maximum compressive strength for a ratio of 1.0. As the ratio increases, the strength decreases. An increase of this ratio results in an increase of the sodium and silica concentration. Excessive sodium silicate hinders structure formation and therefore led to lower strength of the geopolymer.

The early strength development of the metakaolin based geopolymers in this study indicates a fast geopolymerization due to the availability of soluble silicate species and therefore an improved dissolution of silica and alumina in metakaolin. The type of solution that is used for the activation of the binder agent is essential in explaining the strength development. When using a solution with soluble silicate (sodium silicate), reactions occur at a higher rate than when hydroxides (sodium hydroxide) are used. In case of a soluble silicate as an activator for the binder agent, reaction steps overlap, meaning that dissolution, accumulation of reaction products, and polycondensation of the structures occur simultaneously. Strength development is therefore very fast, resulting in a high early age strength *(Palomo et al., 1999).*

The study by *A. Albidah et al. (2020)* also shows a positive trend of increase in the 28-day compressive strength of geopolymer concrete when the alkaline solids to MK ratio is increased from 0.21 to 0.37 (decreasing MK content). For higher ratios than 0.37, a strength drop is observed, which is attributed to the excessive silica content which contributes to the impedance of the geopolymerization.

The study conducted by *Huseien et al. (2018)* shows the effect of metakaolin as substitution (0-15%) for ground granulated blast furnace slag (BFS) on the early strength of geopolymer mortars. The compressive strength of samples with MK showed lower early strength in all cases (5, 10, 15% replacement). For all substitution ratios, the 28-day compressive strength is higher compared to the reference mixes containing 100% slag. This indicates a delayed geopolymerization process of mixtures containing MK. The higher 28-day strength is a result of the higher Al_2O_3 and SiO_2 content in metakaolin in comparison to blast furnace slag, which improves geopolymerization due to the additional production of NASH and CASH-gel.

An increase in molarity of the sodium hydroxide solution consequently results in an increase of the Na_2O content and thus a reduction of the SiO_2:Na_2O ratio. The compressive strength increased with increasing SiO_2:Na_2O ratios, as an increase of this ratio enhances the degree of dissolution of silica and alumina and accelerates the hydrolysis, while impeding the polycondensation. The highest strength was observed for a molarity of 14 M. This is considered to be the optimum concentration for the NaOH solution. For higher molarities, the dissolution of calcium is inhibited, resulting in less hydration products and a lower rate of hydration. It was also reported that an excess in hydroxide ions (OH^-) caused the aluminosilicate gel to precipitate at an early age, resulting in lower strength.

Huseien et al. (2018) also discusses the effect of alkali solids to binder ratio on strength. A high early age and 28-day strength for a low Na_2O:binder ratio (8%) are reported. An excess in water, thus higher water to binder ratios, basically reduces the geopolymerization rate (the amount of CASH and NASH gel) and therefore results in poor microstructure and lower strength.

In the study of *Srinivas et al. (2020)*, no optimum is observed for various concentrations of the sodium hydroxide solution. Solutions with a concentration of 8M, 11M and 15M are used for metakaolin (30%) and fly ash based (70%) geopolymer concrete, with the goal of determining the mixture with maximum compressive strength. Strength increases for increasing concentration of the sodium hydroxide solution and maximum strength is obtained for a concentration of 15M, for oven curing as well as for ambient curing conditions. According to the observations, workability increases as well for increasing concentrations of the sodium hydroxide solution. Maximum strength is obtained for oven curing, as this activates the geopolymerization process at an early age, contributing to high early age strength.

Hasnaoui et al. (2019) aims to find the optimum formulation for metakaolin and slag based geopolymer mortar for varying metakaolin and slag content and different compositions of the alkali solution. The effect of GBFS + MK/Activator is evaluated for equal amounts of ground granulated blast furnace slag and metakaolin using two modular ratios (MR) of 1.4 and 1.6.

A significant decrease of strength is observed for increasing GBFS + MK/Activator ratios. An increase of this ratio results in a reduction of the high reactive amorphous silicate content in the binder leading to the weakening of the geopolymer matrix. For ratios smaller than 3.0, higher mechanical properties are obtained in comparison to Portland cement mortar. A molar ratio of 1.6 results in better mechanical properties for all cases when compared to a molar ratio of 1.4. An optimum GBFS + MK/Activator ratio was selected based on workability, mechanical strength and the stability to efflorescence.

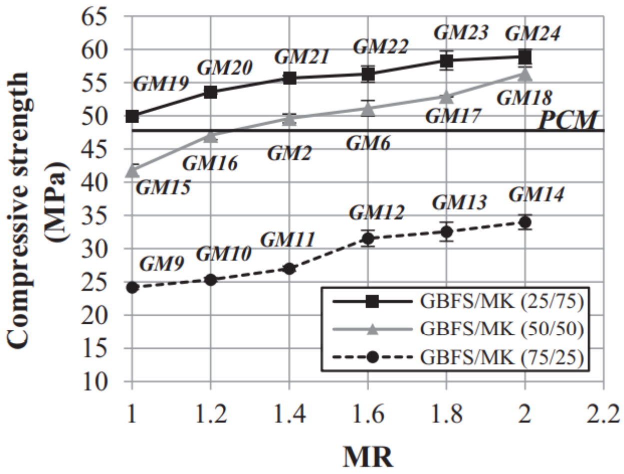

Figure 10: Compressive strength of GMs at 28 days as a function of molar ratio. (Hasnaoui et al., 2019).

Based on the abovementioned optimum ratio, the effect of GBFS/MK (25/75, 50/50 and 75/25) and MR (1.0, 1.2, 1.4, 1.6, 1.8 and 2.0) are inspected. Geopolymer mortars with low metakaolin and high slag content show the lowest 28-day compressive strength (see figure 10), which is in accordance with the study by *Huseien et al. (2018)*. This effect is a result of the high CaO content in the slag, which has a negative influence on the geopolymerization process. Higher metakaolin contents generally contribute to better 28-day compressive strength. MK provides a source of amorphous Al_2O_3 and SiO_2, which contributes positively to the geopolymerization process and therefore the mechanical properties. This effect can also be explained by the high reactivity of MK due to its large fineness and high SSA. However, an excess in MK can negatively influence the strength properties. Therefore, the impact of MK on the strength properties was less significant for high incorporation ratios, as can be seen in figure 10.

The study shows improvement in mechanical properties for higher molar ratios of SiO_2/Na_2O. An increase of this molar ratio results in an increase of the Si/Al ratio, which contributes positively to the formation of Si-O-Si bonds. These bonds are stronger than those of Si-O-Al and Al-O-Al and therefore, an increase of strength properties is observed from the results.

Davidovits (2013) reports that a good geopolymer binder consists of 55 to 70% by weight of raw materials (MK + GBFS) and 25 to 35% of alkaline solution. *Davidovits (2013)* therefore recommends a ratio GBFS+MK/Activator solids ranging from 3.1 and 5.6. Furthermore, a molar ratio SiO_2/Na_2O of the alkaline solution in the range of 1.45-1.95 is recommended for user-friendly conditions. An increase in GBFS+MK/Activator solids ratio results in lower workability (low slump) and a reduction in strength.

According to *Burciaga-Díaz et al. (2010)*, for higher replacement ratios of blast furnace slag by metakaolin, a higher amount of Na_2O is needed to obtain the highest maximum strength. A higher amount of Na_2O means a lower modulus (SiO_2/Na_2O molar ratio) of the alkaline solution. It can therefore be concluded that for higher replacement ratios of slag, an alkaline solution with a lower modulus is needed. The mean compressive strength of 1, 28, 90 and 360 days is taken. *Hasnaoui et al. (2019)* reports increasing 28-day compressive strength for increasing moduli of the alkaline solution, independently of the metakaolin content.

Furthermore, *Burciaga-Díaz et al. (2010)* recommends a modulus in the range of 1–1.5 to promote an adequate activation of binders of BFS and MK and their binary mixes. 10% of Na_2O/dry binder was reported to be a good amount for adequate activation of a binary BFS and MK binder.

Alanazi et al. (2017) shows that the best mechanical performance is achieved for a modulus of 1.0, for a metakaolin based geopolymer mortar. In this study, the influence of the modulus is studied by varying the modulus in the range of 0.8-1.8. Highest early strength for a metakaolin based mortar is achieved for a modulus of 1.0, independent of the number of curing days. A modulus of 1.2 showed very similar strength properties (figure 11). *Alanazi et al. (2017)* shows that high SiO_2/Na_2O ratios do not necessarily lead to better strength properties.

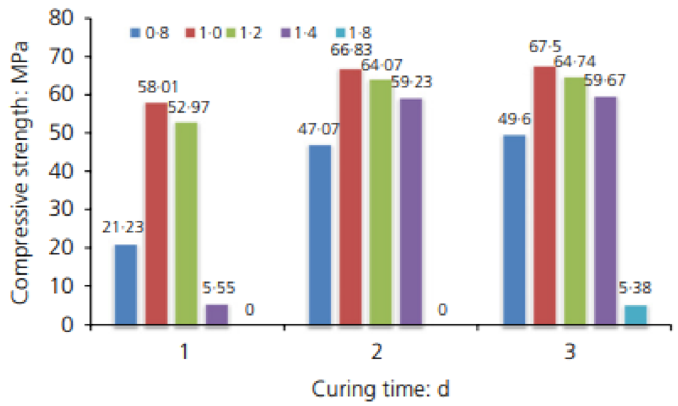

Figure 11: Average compressive strength of geopolymer mortar with different ratios of silicon dioxide/sodium oxide (0.8, 1.0, 1.2, 1.4 and 1.8) at curing ages of 1, 2 and 3 days. Alanazi et al. (2017).

2.3.1 Summary

Increasing metakaolin content generally results in enhanced strength properties after 28 days, due to the increased silicate and aluminium content, hence a higher polymerization rate. An increased silicate and aluminium content is related to a higher density of Si-O-Si bonds, which tend to be stronger than Si-O-Al and Al-O-Al bonds. The early age strength is lower for increasing metakaolin content in geopolymer concrete.

Strength development strongly depends on the composition and concentration of the alkali activator. A higher modulus of the alkali activator results in better mechanical properties. However, higher moduli are also related to higher slump and slow setting.
For a metakaolin based geopolymer, a modulus in the range of 1.0-1.2 is typically recommended for high early strength properties and to control the slump and setting time.

An overview of the literature regarding the mechanical properties of MK based geopolymer concrete and/or mortar is provided in table 2.

Table 2: Overview literature of the mechanical properties of metakaolin based geopolymer concrete/mortar.

MK (%)	***GGBFS (%)***	***FA (%)***	**M_s** ***$SiO_2:Na_2O$***	**NS/NH solids ratio**	**Na_2O/ binder**	**Water/ binder**	**Concentr -ation**	**Curing method**	**Mechanical properties**
100%	0%	0%	0.74-1.16	1.30-3.00	0.06-0.11	0.38-0.54	NaOH: 14M	Ambient curing	According to the study of *Albidah et al. (2020)* with only metakaolin as pozzolanic material, the highest 28 day-compressive strength was achieved for mixes containing NS/NH ratios of 1.3-2. However, increasing the ratio to 2.5-3.0 resulted in a strength drop of approximately 10-20 MPa. The study also showed a positive trend of increase in the 28-day compressive strength when the alkaline solids to MK ratio is increased from 0.21 to 0.37. For higher ratios, a strength drop is observed.
50-100%	0-50%	0%	-	-	-	-	NaOH: 10M	Ambient curing	The geopolymer concrete specimens are cast and tested for different types of strengths for 3, 7, and 28 days. Mechanical strength properties increased with increasing metakaolin content, irrespective of curing period. *(Padmakar et al., 2017).*
0-15%	85-100%	0%	1.08–1.26	3.0	0.07-0.135	-	NH: 10, 14, 16, 18 M	Ambient curing	The compressive strength of samples with MK showed lower early strength in all cases (5, 10, 15% replacement). However, the 28 day-strength was in all cases higher for the MK substituted samples than was the case for samples prepared without any MK. The compressive strength increased with increasing SiO_2:Na_2O ratios and is at an optimum for a molarity of 14M. A high early age and 28 day strength is reported for a low Na_2O:binder ratio (8%). *(Huseien et al, 2018).*
0%	0%	100 %	-	0.5-2.5	-	-	NH: 10M	Oven curing +ambient curing	In the study of *Morsy et al. (2014)*, the changing parameter was the sodium silicate to sodium hydroxide solids ratio (0.50-2.50) for a fly ash based polymer mortar. They observed a maximum compressive strength for a ratio of 1.0. As the ratio increases, the strength decreases.
70%	0%	30%	1.12-1.37	2.5	0.09-0.11	0.39-0.41	NH: 8M, 11M and 15M	Oven curing + ambient curing	Solutions with a concentration of 8M, 11M and 15M are used for metakaolin (30%) and fly ash based (70%) geopolymer concrete, with the goal of determining the mixture with maximum compressive strength. Strength increases for increasing concentration of the sodium hydroxide solution and maximum strength is obtained for a concentration of 15M. According to the observations, workability increases as well for increasing concentrations of the sodium hydroxide solution. Maximum strength is obtained for oven curing. *(Srinivas et al., 2020).*
25-75%	25-75%	0%	1.0-2.0	2.2-85.6	0.06-0.14	0.50	-	Ambient curing	A study by *Hasnaoui et al. (2019)* reports optimum mechanical properties for mixtures with a GBFS + MK/Activator ratio of 3.0. A significant decrease of strength is observed for increasing GBFS + MK/Activator ratios. For ratios smaller than 3.0, higher mechanical properties are obtained in comparison to Portland cement mortar. Increasing MK content and increasing MR result in better mechanical properties.
0-100%	0-100%	0%	0-2.0	-	0.05-0.15	-	-	Ambient curing	According to *Burciaga-Díaz et al. (2010)*, for higher replacement ratios of blast furnace slag by metakaolin, a higher amount of Na_2O and therefore a lower modulus is needed to obtain the highest maximum strength. For higher replacement ratios of slag, an alkaline solution with a lower modulus is needed. Burciaga-Díaz et al. (2010) recommends a modulus in the range of 1–1.5 to promote an adequate activation of binders of BFS and MK and their binary mixes. 10% of Na_2O/dry binder was reported to be a good amount for adequate activation of a binary BFS and MK binder.
70-100%	0-30%	0%	0.80-1.80	2.8-10.6	0.10-0.19	0.45-0.59	-	Ambient curing	In a study by Alanazi et al. (2017), the effect of modifying the modulus of the alkaline solution and the effect of slag content on metakaolin based geopolymer is investigated by focussing on the early strength and durability of the geopolymer pastes. The study showed that the maximum compressive strength for a metakaolin based (100%) geopolymer mortar was obtained for a modulus of 1.0. This study also showed that partially replacing the metakaolin with slag (30%) resulted in a mixture with a higher workability but not necessarily higher compressive strength.

2.4 Shrinkage behaviour of metakaolin based geopolymers

One of the biggest problems related to 3D-printing of concrete is shrinkage. Due to the larger exposed surface area of 3D-printed concrete structures, more drying shrinkage occurs as a result of evaporation of free water in the cement matrix. Shrinkage will not be investigated during this experiment, but the influence of precursors will be discussed to ensure that all relevant aspects are considered for the mixture designs.

In case of Portland cement, five mechanisms regarding shrinkage can be distinguished:

i. *Plastic shrinkage* induced by water loss caused by evaporation;
ii. *Thermal shrinkage* due to exothermic reactions during the hydration process;
iii. *Chemical shrinkage* due to hydration. This shrinkage occurs because the volume of the reaction products is smaller than the volume of the reactants, which results in shrinkage.
iv. *Drying shrinkage* that is caused by an imbalance of the internal humidity of the material and the humidity of the environment. This imbalance results in a desiccation mechanism and a contraction of the matrix.
v. *Autogenous shrinkage* as a result of self-desiccation.

Geopolymer mortars do not necessarily exhibit the same shrinkage mechanisms as cement mortar.

In the study of *Li et al. (2019)*, the chemical shrinkage of metakaolin based geopolymers is studied. In this research, the results show three stages of chemical deformations for a metakaolin based geopolymers: chemical shrinkage in the first stage, chemical expansion afterward and chemical shrinkage again in the final stage. Metakaolin based geopolymers show a different mechanism than OPC-based binders, which only show monotonic chemical shrinkage.

Kuenzel et al., (2014) and *Rihai et al., (2020)* substitute metakaolin with sand in metakaolin based geopolymers. They conclude that reducing the amount of geopolymer (metakaolin) effectively decreases shrinkage. Replacing metakaolin with sand results in a stiffer and stronger matrix, therefore reducing shrinkage.

Archez et al. (2021) investigates the influence of precursors, like metakaolin, alkaline solution and different additives, on autogenous shrinkage of metakaolin based geopolymers. This study shows that an increase in alkalinity of the alkaline activator contributes to a significant reduction in shrinkage. The influence of the type of metakaolin was negligible in this study, as two types of metakaolin were used (M1 with Si/Al = 1.17, D_{50} = 10 µm and M2 with Si/Al = 1.46, D_{50} = 20 µm).

In the study of *Li et al. (2017)*, the autogenous deformation of metakaolin based geopolymers (MKG pastes), synthesized from different types of metakaolin and activators during a period of 7 days, is determined. In early age, the geopolymer made from MK1 with a mean particle size of 38 µm shows higher autogenous shrinkage than is the case for geopolymer made from MK2, with a mean particle size of 69.23 µm. This suggests that choosing a metakaolin powder with higher particle size contributes to less autogenous shrinkage. In later age, the deformation behaviour is mainly determined by the silica content in the activator. The NaOH concentration is fixed at 9.3 M. The SiO_2/Na_2O molar ratio varies at 0, 0.33 and 0.66. In a later stage, the autogenous deformation behaviour of metakaolin based geopolymers is mainly determined by the SiO_2 content of the alkali activator. The deformation behaviour of geopolymers is very complex. For mixtures containing MK1, a high SiO_2/Na_2O is related to less autogenous shrinkage. For mixtures containing MK2, a different trend line is observed. A low SiO_2/Na_2O ratio (0) results in autogenous shrinkage, while a high SiO_2/Na_2O ratio (0.33-0.66) results in autogenous expansion. This indicates complex deformation behaviour of geopolymer binders, depending on both the raw materials and chemical composition of the activator.

In a study by *Li et al. (2021)*, the influence of metakaolin on shrinkage behaviour of alkali-activated slag-fly ash paste is investigated. The addition of metakaolin in the binder significantly reduces the chemical and autogenous shrinkage as a result of a decrease in the alkalinity of the pore solution, reduced drop in internal humidity as well as an increase in porosity of the paste. In geopolymerization of metakaolin, more Na^+ and OH^- from the pore solution is consumed, resulting in a drop in alkalinity of the pore solutions. Moreover, the strength decreases for increasing metakaolin content. It's important to note that the modulus of the alkaline solution (0.76) is kept at a constant value throughout the experiment. Mixtures with a higher metakaolin content demand a higher Na_2O content for proper activation of this raw material, and therefore show lower ultimate strength for the same modulus as for pastes only containing fly ash and slag.

Shrinkage behaviour will not be within the scope of this study.

2.5 Optimum properties of 3D-printed concrete and characterization methods

Determining the rheological properties of mortars has proven to be crucial for successful 3D-concrete printing. The paste should be flowable enough to be pumped through the hose and to fuse with other layers, while maintaining sufficient early age strength properties for proper buildability. The paste must therefore quickly recover its yield stress after extrusion to ensure buildability. To ensure continuous flow, printing material requires a long setting time.

In this paragraph, fresh and mechanical properties for successful 3D-printing of concrete will be discussed, as well as some characterization methods based on European standards.

2.5.1 Flowability

Determining the slump and flow of fresh mixtures is field-friendly and standardized across Europe through the Eurocode.

According to *Tay et al. (2018)*, mixtures with a slump value between 4-8 mm and spread diameter between 150-190 mm showed optimal printing quality and buildability for their specific 3D-set up. The slump value was determined by using the *Hägermann cone*.

Ma et al. (2019) found optimal printing quality and buildability for slump values in the range of 32-88 mm and spread diameter in the range of 174-210 mm. The slump value was determined with the *mini-slump cone* for mortar. These differences in optimal slump value and spread diameter are probably caused by differences in the setup of the 3D-printer and used slump cone in the slump test.

The European standard **NEN-EN 12350-2** is used to describe concrete with a relatively low flowability by the drop in height when the cone is removed. This standard is not suitable for very flowable concrete mixtures. A mixture with almost no slump is ideal for 3D-printing applications, as it ensures that the filament keeps its shape when extruded.

2.5.2 Initial and final setting time

In order to ensure proper bonding between layers after 3D printing, time interval between layers should be smaller than initial setting time. The goal is to prevent setting of one layer, before the other layer is deposited on top. Therefore, the initial setting time should not be too short and the final set must not be too late. Initial setting time indicates the time from which the fresh mortar starts to lose its plasticity. After the final set, there is no plasticity of the mortar left.

The initial and final setting is generally determined by using a Vicat-needle or a penetrometer. This is an important parameter for 3D-printed concrete, as this indicates the strength and stiffness development over time. The initial setting time is therefore an important parameter for 3D-printing of concrete. For 3D-printing in the lab at small scales, there is often not a lot of time between printing layers. However, for 3D-printing in practice (large scale), the printing period may be up to 3-4h for one building component (Perrot et al., 2016). To prevent weak, cold joints, the setting time should therefore be higher than 3-4h for large-scaled structures. For small scaled structures in the lab, a much smaller setting time will suffice. Since blast furnace slag and metakaolin are generally highly reactive materials, setting times are expected to be short. Deceleration is needed by coming up with proper mix designs (modular ratio, activator/solids ratio, w/b ratio).

To determine the setting time, the Vicat test is used, according to European standards. In this Vicat test, the penetration force is kept at a constant value and the penetration depth is used as an indication of the stiffness of the mortars. Two forces form the mortar are exerted on the needle: compressive and shear forces. With these forces, the static yield stress can be determined.

In case of a penetrometer, a different mechanism is used to determine the initial and final setting time of the mortar. The tip of the device is driven into the mortar at a constant speed. The required force is then measured and recorded at different ages of the mortar until the final set of the paste. With this test, a broader range of static yield stress can be recorded.

In both cases, the resistance of the mortar to penetration is determined at regular time intervals. Penetration depth and elapsed time are recorded during this process.

The European standard **NEN-EN 196-3** or American standard **ASTM C191** are used for determination of the setting time.

2.5.3 Plastic viscosity and yield stress

Other important parameters for description of the rheology of mortars are the plastic viscosity and yield stress. To ensure good pumpability and flow of the mortar, it is necessary to maintain a low yield stress and viscosity. A low yield stress means that little stress is required to make the material flowable, hence making the mixture perfect for extrusion of cementitious materials. However, when the yield stress and viscosity are too low, the material will not be able to hold its shape when extruded. The concrete mixture must therefore be thixotropic in nature. Ideally, the mixture must show low viscosity during flow and a high yield stress at rest. These properties should therefore be optimized.

Typically, 3D-printed cementitious materials show an increase in static yield stress with time. It's necessary to study the development of static yield stress up to 30 minutes starting from the time of mixing to ensure that the evolution of the static yield stress and viscosity is fast enough for good buildability and stability of the layers. It is expected that mixtures with higher slag content will show faster yield stress evolution, due to the higher reactivity of blast furnace slag compared to metakaolin. Higher slag content will therefore result in an acceleration of the hardening process. The composition of the alkaline activator (modulus) is the factor with the largest influence on the viscosity of a defined mixture. The higher the modulus of the alkaline solution, the higher the apparent viscosity *(Favier et al., 2014)* (see figure 12).

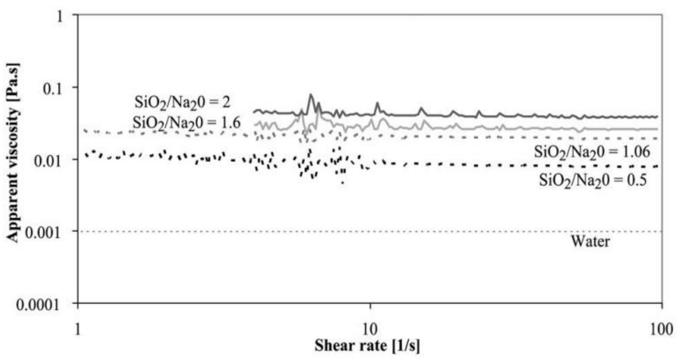

Figure 12: Viscosity as a function of shear rate at 20°C for different SiO_2/ Na_2O silicate solutions (H_2O/Na_2O = 16). (Favier et al., 2014).

The Danish Technological Institute has demonstrated that mixtures containing CEM I and fly ash with a plastic viscosity and yield stress in the ranges of **38.7 ± 4.5 Pa.s and 0.59 ± 0.08 kPa** respectively were suitable for pumping and extrusion. For mixtures containing CEM I and limestone filler, other values for the plastic viscosity and yield stress were recommended: **21.1 ± 2.4 Pa.s** and **0.27 ± 0.03** kPa respectively *(Thrane et al., 2009).* No recommendation is provided for metakaolin based geopolymer.

Le et al. (2012) recommends values for the yield stress in the range of **0.3-0.9 kPa** to prevent blockage during pumping and filament failure during extrusion. These values are in accordance with the findings of the Danish Technological Institute and will therefore be used as the target value.

Rheological behaviour of the mortars can be studied with a *rheometer*. With this device, the shear stress (τ) is measured under an imposed shear rate ($\dot{\gamma}$). A pre-shearing step (τ_0) is often performed to homogenize the mortar. In this way, an identical initial condition is ensured for each formulation (see equations (1) and (2)).

$$\tau = \tau_0 + K\dot{\gamma} \quad \text{(eq. 1)}$$
$$\tau = \mu\dot{\gamma} \quad \text{(eq. 2)}$$

With:
τ_0 = initial yield stress [Pa]
K = plastic viscosity [Pa.s]
$\dot{\gamma}$ = shear rate [s^{-1}]
μ = viscosity [Pa.s]

In the American standard **ASTM C1749-17a**, more information about this procedure is provided. Determining the yield stress and viscosity will not be within the scope of this study.

2.5.4 Compressive strength

For 3D-printed concrete, early age strength development is of significant importance. It ensures that yield stress evolution of the bottom layers is sufficiently good before other layers are printed upon these bottom layers. This is necessary for good buildability of the mortar layers, so that no failure occurs between printing layers. It's therefore recommended to ensure a high early compressive strength.

It is expected that mixes containing higher slag content will show higher early strength development. Mixes with high metakaolin content will show high 28-day strength and lower early strength.

2.5.5 Durability

Durability is not within the scope of this study and will therefore not be monitored during the experiment. However, optimum design parameters regarding durability will be discussed for a complete overview.

One of the biggest durability problems related to 3D-printing of concrete is shrinkage, which can induce cracking. Due to the large exposed surface area of 3D-printed concrete structures, more drying and plastic shrinkage occur as a result of evaporation of free water in the matrix. The increase in cracking directly results in a decrease of the durability and therefore loss of service time.

Effective solutions for mitigating the effect of shrinkage would be including fibres to reduce the amount of cracks, admixtures that reduce or compensate shrinkage or simply controlling the mix design in such a way that shrinkage is minimized.

As mentioned in the literature review, the increase in alkalinity of the alkaline activator directly reduces the autogenous shrinkage of metakaolin based geopolymers (*Archez et al., 2021)*. The mean particle size of metakaolin also has some influence on shrinkage behaviour. Using metakaolin with a smaller particle size increases the early age autogenous shrinkage. Long term shrinkage behaviour is mainly influenced by the type of activator and its silica content.

The influence of the modulus of alkali activator on shrinkage behaviour is very complex and does not necessarily follow a specific trendline *(Li et al., 2017)*. The trendline depends on other factors as well, like the mean particle size and composition of the metakaolin powder. The addition of increasing content of metakaolin to a slag based binder effectively reduces the shrinkage behaviour of the geopolymer paste *(Li et al., 2021)*.

2.5.6 Overview

In table 4, an overview of relevant specifications according to the Eurocode (EC) is provided.

Table 3: Specifications according to European standards (EC).

Properties	***Specifications***	***Age at test [days]***
Slump	NEN-EN 206	Fresh
Initial and final setting time	NEN-EN 196-3	Fresh
Compressive strength	NEN 196-1	1, 7, 28

2.6 Conclusion from literature review

From the reviewed literature can be concluded that a couple of variables show large influence on fresh and mechanical properties of geopolymer concrete:

- calcined clay/slag ratio;
- modulus alkaline solution;
- water/binder ratio;
- Na_2O/dry precursor mass ratio.

The addition of metakaolin as a replacement for slag to geopolymer concrete generally decreases the workability and shortens the setting time of a geopolymer mortar due to the lower calcium content of metakaolin. However, this effect depends on physical and chemical properties of metakaolin as well as the composition of the alkaline activator. Increasing metakaolin content generally results in enhanced strength properties after 28 days, due to the increased silicate and aluminium content, hence a higher polymerization rate. The early age strength is lower for increasing metakaolin content in geopolymer concrete.

Strength development strongly depends on the composition and concentration of the alkali activator. A higher value for the modulus of the alkali activator results in better mechanical properties. However, higher moduli are also related to higher slump and slower setting.
For a metakaolin based geopolymer, a modulus in the range of 1.0-1.2 is typically recommended for high early strength properties and to control the amount of slump and setting time. Using lower moduli than 1.00 might result in significant strength loss of the mortars. Low workability, which is ideal for the purpose of 3D-printing, is often achieved for low moduli of the alkaline solution. High moduli are related to high workability and very slow setting and not practical for 3D-printing applications.

Literature often reports low water/binder ratios for the purpose of 3D-printing, to ensure high (early) strength properties and low slump and flowability. In literature, water to binder ratios between 0.30-0.50 are reported. Furthermore, the Na_2O to dry binder ratio influences the fresh and hardened properties of geopolymer mortar considerably. A higher ratio will lead to larger flow (higher workability) and slower setting.

3 Materials and methods

In this chapter, the chemical composition of the used materials will be presented. Furthermore, the experimental approach and the test matrix for the mixture designs will be presented.

3.1 Materials

3.1.1 Calcined clay and metakaolin

As mentioned in the literature review, white (pure) metakaolin powder is often related to a very high reactivity and therefore high strength development due to its very high fineness and SSA. However, due to temporary unavailability of this material, low grade calcined clay will be used.

The chemical composition and reactivity of calcined clay is provided in table 5 and 6.

Table 4: Chemical compositions of calcined clay powder. Source: Argeco, France.

Oxide weight (%)	SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	TiO_2	ZrO_2	Other
CC	55.1	38.4	0.6	2.6	0.2	1.1	0.1	1.9

Table 5: Reactive content of the low-grade calcined clay powder.

Components	Reactive content (wt %)	Reactive SiO_2 (wt %)	Reactive Al_2O_3 (wt %)	Other reactive phases (wt %)
CC	48.8	12.3	32.0	4.5

The chemical composition of metakaolin is provided in table 7.

Table 6: Chemical compositions of metakaolin powder.

Oxide weight (%)	SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	TiO_2	ZrO_2	Other
MK	50.7	46.8	0.01	0.3	0.05	1.7	0.01	0.4

3.1.2 Ground granulated blast furnace slag

The ground granulated blast furnace slag (BFS) is provided by Ecocem. The chemical composition is provided in table 8.

Table 7: Chemical composition of BFS according to Ecocem.

Oxide weight (%)	SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	TiO_2	MgO	SO^3	Cl^-	S^{2-}	Na_2O
GBFS	37.3	10.7	43.0	0.2	0.35	0.7	6.5	0.1	0.01	0.8	0.23

3.1.3 Fine aggregate (FA)

Standardized sand according to EN 196-1 will be used for the geopolymer mortar to avoid any secondary effect that the sand may have on the binder by the impurities that natural sand might contain.

3.1.4 Activator solution

A sodium silicate solution (SS) with a molar ratio (MR) of SiO_2/Na_2O = 3.33 will be used. Its composition by weight is as follows:

Na_2O - 8.25%
SiO_2 - 27.50%
H_2O - 64.25%

Sodium hydroxide (NaOH), with a purity of > 98%, is first dissolved in regular tap water and then mixed with sodium silicate solution (SS) to achieve the desired modulus for the alkaline activator. The solution is then allowed to cool for at least 24 h before sample preparation.

3.2 Methodology

The experimental approach can be schematized as presented in figure 13. For this experimental investigation, the focus will be on 4 parameters: calcined clay/slag ratio, modulus of alkaline solution, water to binder ratio and the Na_2O to precursor mass ratio.

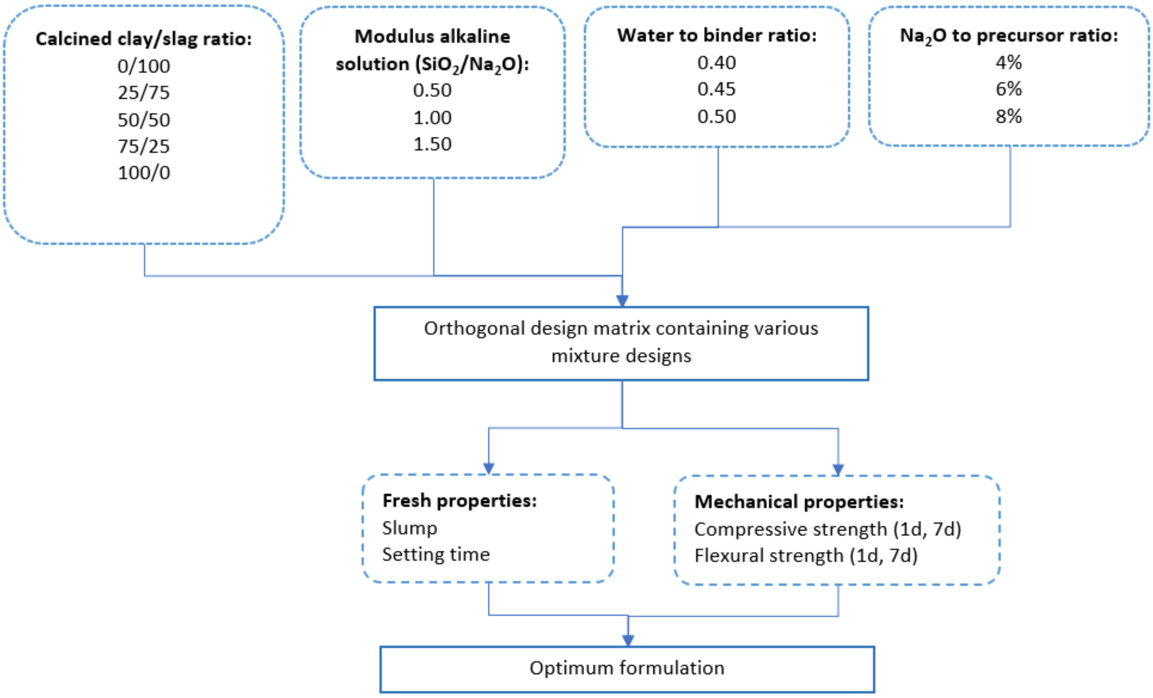

Figure 13: Experimental approach.

For the mentioned four process parameters, 5x3x3x3=135 combinations can be produced to account for all variables. Naturally, it is not feasible to evaluate all combinations. Therefore, the orthogonal design method provides a solution. A reduced number of mix designs needs to be evaluated, while every variable is taken into account. Other properties can be derived from these reduced number of experiments by using fitted regression. This method combines the accuracy of experimental design with the ability to produce rapid results by testing multiple components at once. The orthogonal experimental design is generated in *IBM SPSS*.

Properties (y) can be derived by using the following general formula:

$$\boldsymbol{y} = \boldsymbol{\beta_0} + \boldsymbol{\beta_1} * \boldsymbol{x_1} + \boldsymbol{\beta_2} * \boldsymbol{x_2} + \boldsymbol{\beta_3} * \boldsymbol{x_3} + \boldsymbol{\beta_4} * \boldsymbol{x_4} + \boldsymbol{\epsilon} \qquad \textit{(eq. 3)}$$

The values for **β** are estimated by fitted regression, **X** contains the values of the process parameters for each experiment and $\boldsymbol{\epsilon}$ contains the model's error.

$$\boldsymbol{\beta} = \left(\boldsymbol{X^T} \cdot \boldsymbol{X}\right)^{-1} \cdot \boldsymbol{X^T} \cdot \boldsymbol{y} \qquad \textit{(eq. 4)}$$

$$\boldsymbol{\beta} = \begin{bmatrix} \boldsymbol{\beta_0} \\ \boldsymbol{\beta_1} \\ \boldsymbol{\beta_2} \\ \boldsymbol{\beta_3} \\ \boldsymbol{\beta_4} \end{bmatrix}, \quad \boldsymbol{X} = \begin{bmatrix} \boldsymbol{x_1} \\ \boldsymbol{x_2} \\ \boldsymbol{x_3} \\ \boldsymbol{x_4} \end{bmatrix}$$

x_1 = calcined clay content in [%]
x_2 = modulus alkaline solution [-]
x_3 = water/binder ratio [-]
x_4 = Na_2O/precursor mass ratio [-]

Formulae will be produced for properties like compressive strength, flexural strength, slump and setting time. For each property, an unique formula needs to be produced with fitted regression. This experimental research will therefore yield multiple formulae. Through these formulae, values for parameters can be determined to obtain the specified target values. Note that not every mixture will be successfully cast in case of bad consistency. In case of such a failed mixture, the strength, slump and setting time will be set at zero for the purpose of obtaining the empirical formulae. Based on the formulae, an optimum formulation can be selected that is appropriate for 3D-printing.

Relevant specifications
An overview of relevant specifications regarding test methods of fresh and mechanical properties is provided in table 4.

Test matrix
An initially dry mix, fine aggregate, an alkaline solution containing sodium hydroxide and sodium silicate and pozzolanic material (calcined clay + BFS) are combined for the geopolymer mortar. Bong et al. (2019) assumed a binder to sand ratio of **2:3** for a geopolymer mortar used in a 3D-printing application. This ratio will be assumed as well in this study. The water from the W/B ratio consists of additional water W_{add} and water in the sodium silicate solution (SS).

Cast samples with dimensions of 40 x 40 x 160 mm^3 will be prepared and tested. Fresh mixtures will be filled into the mould and compacted. The cast samples will be stored under a plastic film until testing.

An overview of the experimental series, including the test matrix, is provided in table 9 and 10.

Table 8: Orthogonal test matrix for the experimental series.

MIX ID	CC content [%]	MR	W/B	Na_2O/precursor
1-CC25	25	0.5	0.4	6
2-CC75	75	0.5	0.45	4
3-CC100	100	0.5	0.5	4
4-CC25	25	1	0.5	4
5-CC50	50	0.5	0.4	4
6-CC0	0	0.5	0.4	4
7-CC25	25	1	0.45	6
8-CC75	75	0.5	0.45	6
9-CC50	50	1	0.4	8
10-CC75	75	1	0.4	4
11-CC100	100	0.5	0.45	8
12-CC50	50	1.5	0.45	4
13-CC100	100	1.5	0.4	6
14-CC100	100	1	0.4	4
15-CC0	0	1	0.45	4
16-CC0	0	1.5	0.4	6
17-CC25	25	1.5	0.45	4
18-CC25	25	0.5	0.4	8
19-CC0	0	0.5	0.5	6
20-CC75	75	1.5	0.5	8
21-CC50	50	0.5	0.45	6
22-CC50	50	1	0.5	6
23-CC100	100	1	0.45	6
24-CC0	0	1	0.45	8
25-CC75	75	1	0.4	6

Table 9: Test matrix for the experimental investigation

MIX ID	CC [kg/m³]	GGBS [kg/m³]	SAND [kg/m³]	SS [kg/m³]	NaOH (solids) [kg/m³]	W_{add} [kg/m³]	SS/NaOH solids ratio [-]
1-CC25	120.8	362.3	800	18.3	32.0	180.5	0.57
2-CC75	374.1	124.7	800	12.6	22.0	217.4	0.57
3-CC100	498.8	0.0	800	12.6	22.0	244.1	0.57
4-CC25	122.7	368.0	800	24.7	18.0	222.2	1.38
5-CC50	249.4	249.4	800	12.6	22.0	190.7	0.57
6-CC0	0	498.8	800	12.6	22.0	190.7	0.57
7-CC25	117.9	353.8	800	35.7	25.9	175.9	1.38
8-CC75	362.3	120.8	800	18.3	32.0	207.2	0.57
9-CC50	227.1	227.1	800	45.8	33.3	131.0	1.38
10-CC75	368	122.7	800	24.7	18.0	168.9	1.38
11-CC100	468.4	0.0	800	23.6	41.3	197.6	0.57
12-CC50	241.4	241.4	800	36.5	14.1	174.4	2.60
13-CC100	460.9	0.0	800	52.3	20.1	119.4	2.60
14-CC100	490.6	0.0	800	24.7	18.0	168.9	1.38
15-CC0	0	490.6	800	24.7	18.0	195.5	1.38
16-CC0	0	460.9	800	52.3	20.1	119.4	2.60
17-CC25	120.7	362.1	800	36.5	14.1	174.4	2.60
18-CC25	117.1	351.3	800	23.6	41.3	170.9	0.57
19-CC0	0	483.1	800	18.3	32.0	233.8	0.57
20-CC75	330.7	110.2	800	66.7	25.7	146.8	2.60
21-CC50	241.5	241.5	800	18.3	32.0	207.2	0.57
22-CC50	235.9	235.9	800	35.7	25.9	202.6	1.38
23-CC100	471.8	0.0	800	35.7	25.9	175.9	1.38
24-CC0	0	454.3	800	45.8	33.3	157.7	1.38
25-CC75	353.8	117.9	800	35.7	25.9	149.2	1.38

4 Results

As mentioned in the previous chapter, 25 mixture designs are generated to establish the relationship between the parameters (metakaolin/slag ratio, MR, w/b, Na_2O/precursor mass ratio) and fresh and mechanical properties such as slump, setting time, compressive and flexural strength through an orthogonal design approach.

The corresponding formulas are found with fitted linear regression, meaning that a linear relationship is assumed between the various process parameters. The experimental results are presented in tables 11-14.

4.1 Slump

4.1.1 Data

Table 10: Results for slump.

MIX ID	Slump [cm]
1-CC25	0.5
2-CC75	1.5
3-CC100	1
4-CC25	4.5
5-CC50	1.5
6-CC0	0.3
7-CC25	2
8-CC75	2
9-CC50	0
10-CC75	0
11-CC100	1
12-CC50	0.8
13-CC100	0
14-CC100	0
15-CC0	3.5
16-CC0	0
17-CC25	1.5
18-CC25	0
19-CC0	5.5
20-CC75	1.8
21-CC50	2.5
22-CC50	4
23-CC100	0
24-CC0	0
25-CC75	0

4.1.2 Formula

The fitted formula for slump is as follows:

$$s = -9.67 - 0.01 * x_1 - 0.70 * x_2 + 30.40 * x_3 - 0.18 * x_4 \quad \textit{(eq. 5)}$$

s = slump in [cm]

x_1 = calcined clay content in [%]

x_2 = modulus alkaline solution [-]
x_3 = water/binder ratio [-]
x_4 = Na_2O/precursor mass ratio [-]

Running a conjoint analysis for this dataset in IBM SPSS resulted in the aforementioned formula and the following importance for each process parameter on the value for slump:

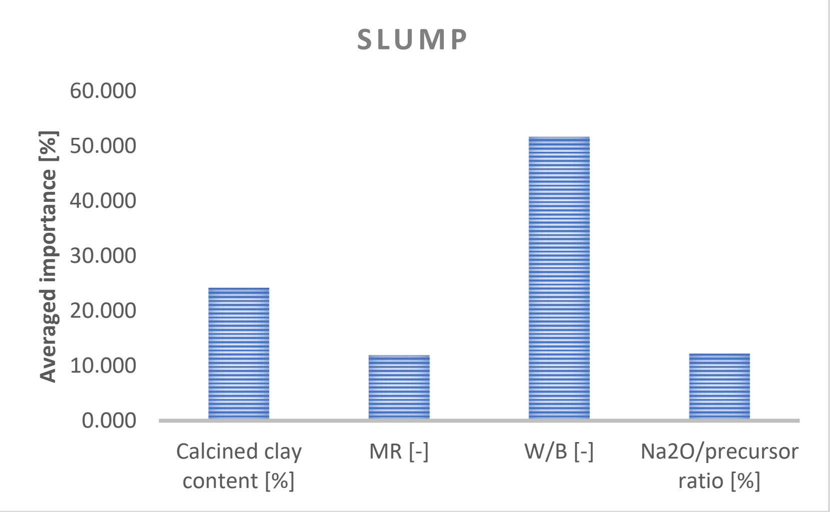

Figure 14: Averaged importance for slump.

4.2 Setting time

4.2.1 Data

The minus sign in table 12 indicates a long setting time that could not be recorded, as it is unpractical to keep the Vicat apparatus running for longer than a day. For mixtures that showed immediate setting and therefore failure during casting, a setting time of zero minutes was recorded.

Table 11: Results for the initial and final setting time.

MIX ID	Initial setting time [min]	Final setting time [min]
1-CC25	149	229
2-CC75	460	-
3-CC100	411	-
4-CC25	840	-
5-CC50	669	724
6-CC0	76	256
7-CC25	392	502
8-CC750	457	-
9-CC50	0	0
10-CC75	0	0
11-CC100	217	282
12-CC50	276	496
13-CC100	0	0
14-CC100	0	0
15-CC0	118	143
16-CC0	0	0

17-CC25	357	-
18-CC25	119	119
19-CC0	119	144
20-CC75	195	250
21-CC50	993	-
22-CC50	719	1074
23-CC100	0	0
24-CC0	67	257
25-CC75	0	0

4.2.2 Formula

The fitted formula for the initial setting time is as follows:

$$t_{initial} = -906.33 - 0.20 * x_1 - 216.46 * x_2 + 3711.14 * x_3 - 45.79 * x_4 \quad \textit{(eq. 6)}$$

$t_{initial}$ = initial setting time in [min]
x_1 = calcined clay content in [%]
x_2 = modulus alkaline solution [-]
x_3 = water/binder ratio [-]
x_4 = Na_2O/precursor mass ratio [-]

The final setting time will not be evaluated, since the data set is not complete due to extremely delayed setting of some mixtures.

The conjoint analysis resulted in the following importance for each process parameter on the value for the initial setting time:

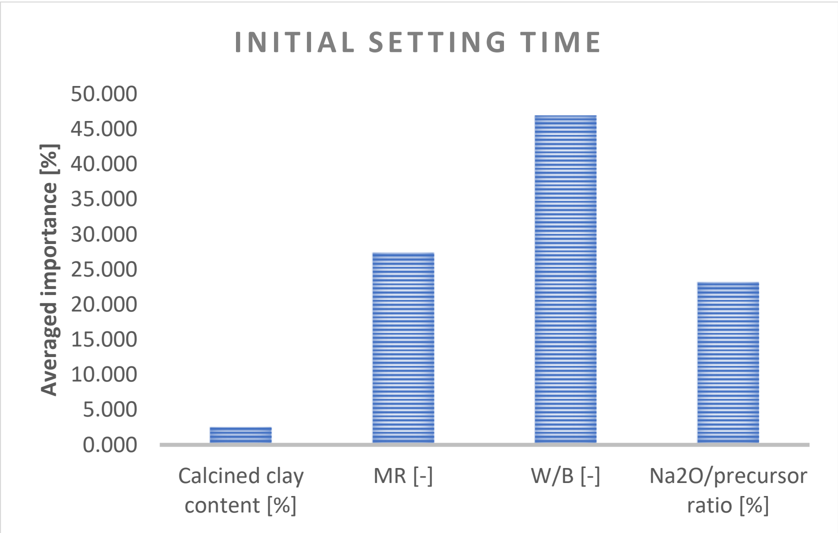

Figure 15: Averaged importance for the initial setting time.

4.3 Flexural strength

4.3.1 Data

Table 12: Results for the 1-day and 7-day flexural strength.

MIX ID	1 day flexural strength [MPa]	7 day flexural strength [MPa]
1-CC25	1.80	9.54
2-CC75	0	0
3-CC100	0	0
4-CC25	0	0
5-CC50	0	0
6-CC0	4.99	6.37
7-CC25	0	0
8-CC75	0	0
9-CC50	0	0
10-CC75	0	0
11-CC100	0	0
12-CC50	0	0
13-CC100	0	0
14-CC100	0	0
15-CC0	3.93	6.59
16-CC0	0	0
17-CC25	0	0
18-CC25	2.69	8.37
19-CC0	1.84	4.41
20-CC75	0	0
21-CC50	0	0
22-CC50	0	0
23-CC100	0	0
24-CC0	8.82	11.30
25-CC75	0	0

4.3.2 Formula

The fitted formula for the 1-day flexural strength is as follows:

$$\sigma_{fs,1d} = 3.84 - 0.03 * x_1 - 0.93 * x_2 - 4.04 * x_3 + 0.26 * x_4 \quad \textit{(eq. 7)}$$

The formula for the 7-day flexural strength is as follows:

$$\sigma_{fs,7d} = 10.79 - 0.06 * x_1 - 2.77 * x_2 - 15.08 * x_3 + 0.57 * x_4 \quad \textit{(eq. 8)}$$

$\sigma_{fs,1d}$ = 1-day flexural strength in [MPa]
$\sigma_{fs,7d}$ = 7-day flexural strength in [MPa]
x_1 = calcined clay content in [%]
x_2 = modulus alkaline solution [-]
x_3 = water/binder ratio [-]
x_4 = Na_2O/precursor mass ratio [-]

Running a conjoint analysis for this dataset resulted in the aforementioned formula and the following importance for each process parameter on the value for the flexural strength:

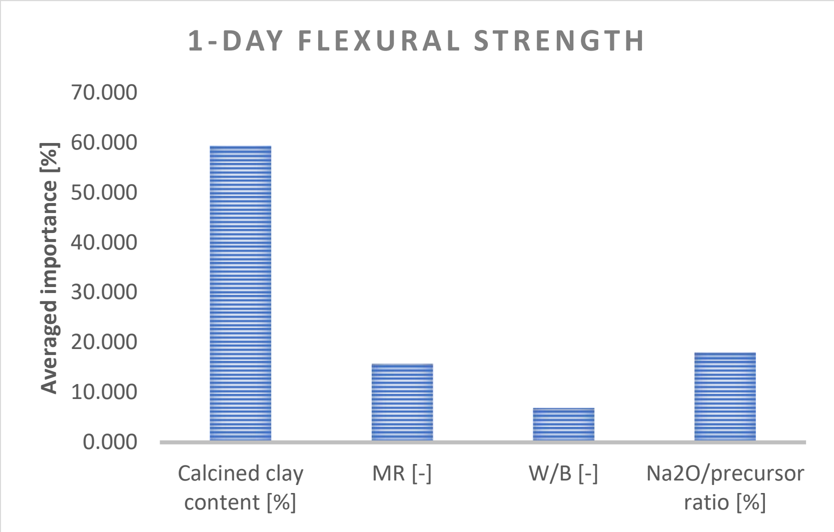

Figure 16: Averaged importance for the 1-day flexural strength.

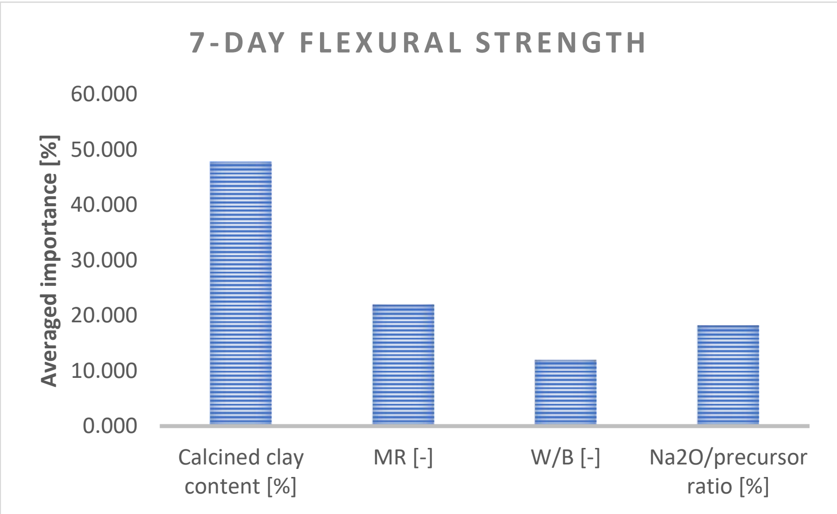

Figure 17: Averaged importance for the 7-day flexural strength.

4.4 Compressive strength

4.4.1 Data

Table 13: Results for the 1-day and 7-day compressive strength.

MIX ID	1-day compressive strength [MPa]	7-day compressive strength [MPa]
1-CC25	4.51	42.96
2-CC75	0	0
3-CC100	0	0
4-CC25	0	0
5-CC50	0	0
6-CC0	7.77	17.30
7-CC25	0	0
8-CC75	0	0
9-CC50	0	0
10-CC75	0	0
11-CC100	0	0
12-CC50	0	0
13-CC100	0	0
14-CC100	0	0
15-CC0	7.29	17.58
16-CC0	0	0
17-CC25	0	0
18-CC25	6.98	39.28
19-CC0	2.71	6.85
20-CC75	0	0.79
21-CC50	0	0
22-CC50	0	0
23-CC100	0	0
24-CC0	19.96	31.75
25-CC75	0	0

4.4.2 Formula

The fitted formula for the 1-day compressive strength is as follows:

$$\sigma_{cs,1d} = 6.88 - 0.07 * x_1 - 1.73 * x_2 - 9.58 * x_3 + 0.78 * x_4 \quad \textit{(eq. 9)}$$

The formula for the 7-day compressive strength is as follows:

$$\sigma_{cs,7d} = 49.39 - 0.18 * x_1 - 10.61 * x_2 - 86.57 * x_3 + 2.44 * x_4 \quad \textit{(eq. 10)}$$

$\sigma_{cs,1d}$ = 1-day compressive strength in [MPa]
$\sigma_{cs,7d}$ = 7-day compressive strength in [MPa]
x_1 = calcined clay content in [%]
x_2 = modulus alkaline solution [-]
x_3 = water/binder ratio [-]
x_4 = Na_2O/precursor mass ratio [-]

Running a conjoint analysis for this dataset resulted in the aforementioned formula and the following importance for each process parameter on the value for the compressive strength:

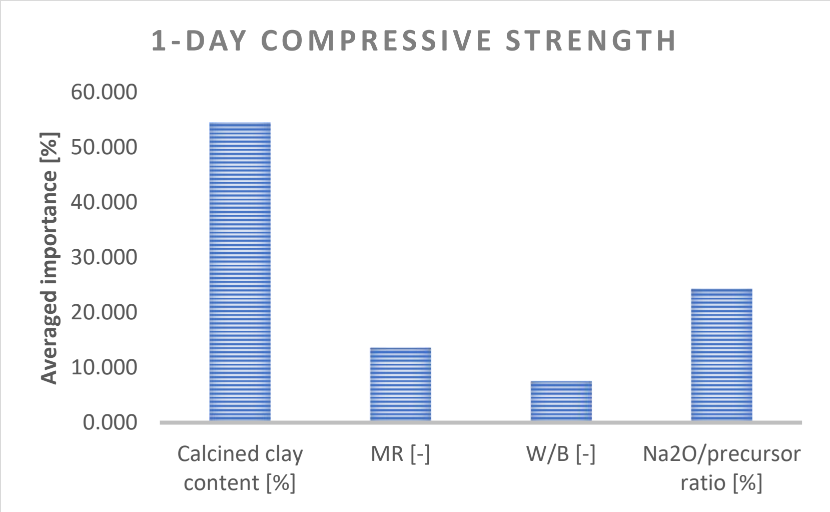

Figure 18: Averaged importance for the 1-day compressive strength.

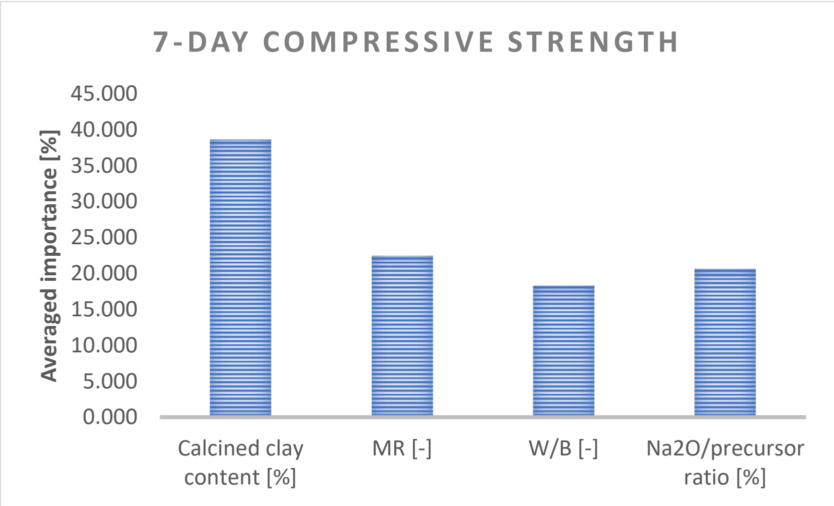

Figure 19: Averaged importance for the 7-day compressive strength.

4.5 Replacement of calcined clay with metakaolin

Using pure metakaolin instead of calcined clay with only 50% metakaolin in weight might lead to totally different results for this experimental investigation. Therefore, some promising mixtures are selected based on the previous experimental results to investigate the effect of replacement of calcined clay by pure metakaolin. Promising mixtures are mixtures 1, 11 and 20.

Based on the data provided by tables 11-14, mixture 1 shows the highest potential for further use in 3D-printing. This mixture shows almost zero slump, adequate early 1-day and 7-day strength. The initial setting time of 249 minutes and the final setting time of 229 minutes (see table 11) are reasonable for the application of 3D-printing.

Mixture 11 containing 100% of calcined clay in the precursor shows excellent setting time and slump, but zero flexural and compressive strength. Same applies for mixture 20. These mixtures are therefore selected to see whether replacement of calcined clay by pure metakaolin results in higher strength.

4.5.1 General observations

All tested mixtures containing metakaolin were too dry for a potential application in 3D-printing, compared to the reference mixes that contained calcined clay. Workability decreased considerably with the replacement of calcined clay by metakaolin. Mixtures 11 and 20 were a failure due to bad workability, meaning that they were not cast and further considered for this research. Mixture 1 was also not workable enough, but could still be cast when properly compacted. The results are provided in tables 15-19.

4.5.2 Slump

Table 14: Results for slump. MK denotes mixtures containing metakaolin, CC denotes mixtures containing calcined clay (reference).

MIX ID	Slump [cm] MK	Slump [cm] CC
Mix 1	0	0.5
Mix 11	0	1
Mix 20	0	1.8

4.5.3 Flexural strength

Table 15: Results for the 1-day flexural strength. MK denotes mixtures containing metakaolin, CC denotes mixtures containing calcined clay (reference).

MIX ID	1-day flexural strength [MPa] MK	1-day flexural strength [MPa] CC
Mix 1	9.37	1.80
Mix 11	-	0
Mix 20	-	0

Table 16: Results for the 7-day flexural strength. MK denotes mixtures containing metakaolin, CC denotes mixtures containing calcined clay (reference).

MIX ID	7-day flexural strength [MPa] MK	7-day flexural strength [MPa] CC
Mix 1	9.81	9.54
Mix 11	-	0
Mix 20	-	0

4.5.4 Compressive strength

Table 17: Results for the 1-day compressive strength. MK denotes mixtures containing metakaolin, CC denotes mixtures containing calcined clay (reference).

MIX ID	1-day compressive strength [MPa] MK	1-day compressive strength [MPa] CC
Mix 1	29.91	4.51
Mix 11	-	0
Mix 20	-	0

Table 18: Results for the 7-day compressive strength. MK denotes mixtures containing metakaolin, CC denotes mixtures containing calcined clay (reference).

MIX ID	7-day compressive strength [MPa] MK	7-day compressive strength [MPa] CC
Mix 1	37.79	42.96
Mix 11	-	0
Mix 20	-	0.79

5 Analysis and discussion

In this chapter, an analysis of the results will be provided as well as discussion of the results.

5.1 Slump

The results show that changing the water to binder ratio has the greatest influence on the value for the slump. Thus, in order to optimize the value for slump for the purpose of 3D-printing, it would be most effective to change the water to binder ratio (see figure 14). From equation 5 can be concluded that slump increases for increasing water to binder ratio and decreases for increasing calcined clay content, modulus of the alkaline solution and sodium oxide to precursor ratio.

Huseien et al. (2018) found lower workability, i.e. lower slump, for increasing sodium oxide (Na_2O) content in the binder. *Hasnaoui et al. (2019)* found increased flow time, i.e. lower slump, for higher metakaolin content and higher moduli of the alkaline activator. The results are therefore in accordance with the studies by *Huseien et al.* and *Hasnaoui et al.*

5.2 Setting time

Similar to the slump values of the various mixtures, changing the water to binder ratio is the most effective way of optimizing the (initial) setting time. Second to the water/binder ratio, the modulus of the alkaline activator is an important factor for optimizing the setting time (see figure 15). From equation 6 follows that the setting time increases for increasing water to binder ratios, and decreases for increasing calcined clay content, moduli of the alkaline solution and sodium oxide to precursor mass ratio.

Huseien et al. (2018) states as well that the setting is accelerated, i.e. reduced setting time, for increasing sodium oxide (Na_2O) content in the binder. *Hasnaoui et al. (2019)* found an increasing setting time for higher metakaolin content and did not find a clear correlation between the modulus of the alkaline solution and setting time. Note that the range of moduli investigated is much larger in the study by *Hasnaoui et al.*

5.3 Flexural strength

For the 1-day and 7-day flexural strength, the calcined clay content has the greatest influence on the flexural strength of the calcined clay and slag based geopolymer mortar. Exceeding a certain calcined clay content of 25% results in zero 1-day and 7-day flexural strength for the chosen ranges of the modulus ratio, the water to binder ratio and the Na_2O/precursor ratio (see figures 16 and 17).

Ultimately, this means that changing the calcined clay content is the way to go for optimization of the flexural strength of the various mixture designs. From equations 7 and 8 can be concluded that the 1-day and 7-day flexural strength increases for increasing sodium oxide to precursor mass ratio, while the strength is reduced for increasing calcined clay content, moduli and water to binder ratio.

5.4 Compressive strength

Similar to the 1-day and 7-day flexural strength of the various mixture designs, the calcined clay content has the greatest influence on the compressive strength. Exceeding a certain calcined clay content of 25% results in zero 1-day and 7-day compressive strength for the chosen ranges of the modulus, the water to binder ratio and the Na_2O/precursor ratio (see figures 18 and 19).

Therefore, changing the calcined clay content is the most effective way for an optimization of the compressive strength of the various mixture designs. Furthermore, it can be concluded from formulas 9 and 10 that the 1-day and 7-day compressive strength increases for increasing sodium oxide to precursor mass ratio, while the strength is reduced for increasing calcined clay content, moduli and water to binder ratio.

Albidah et al. (2020) found increasing 28-day compressive strength for mixes with increasing sodium silicate to sodium hydroxide solids ratio, i.e. increasing moduli of the alkaline solution. Exceeding a certain modulus results in a strength drop. This optimum value for the modulus cannot be deduced from the formulas, as linear regression is used to approximate the results. *Huseien et al. (2018)* found low early strength for mixtures containing high metakaolin content, as a result of the delayed geopolymerization of MK. This is in accordance with the results, as the flexural strength (1 d and 7 d) decreases for increasing calcined clay content.

5.5 Replacement of calcined clay by metakaolin

The replacement of calcined clay by pure metakaolin results in a considerable decrease in workability and setting time. Furthermore, mixture 1 showed a high increase in flexural and compressive strength compared to the reference mix. These observations can easily be explained by the higher reactivity of metakaolin in comparison to calcined clay.

As discussed in chapter 2, this high reactivity is often attributed to the high purity of metakaolin in comparison to calcined clay. The high specific surface area (SSA) of the metakaolin particles in combination with its plate-like morphology explain the high water demand. In order to guarantee good workability for an application in 3D-printing, more water is needed, e.g. a higher water to binder ratio in comparison to the reference mixes. Note that this may result in lower strength and higher porosity. To account for these effects, the alkali activator must be adjusted accordingly, e.g. higher Na_2O to precursor ratio and/or lower MR.

5.6 Mixtures for 3D-printing

Based on the data provided by tables 11-14, mixture 1 (CC/BFS=25/75, MR=0.5, w/b=0.40, Na_2O/precursor=6%) shows the highest potential for further use in 3D-printing. This mixture shows almost zero slump, adequate early 1-day strength and 7-day strength. The initial setting time of 249 minutes (≈2.5 hours) and the final setting time of 229 minutes (≈3.8 hours) (see table 12) seem reasonable for the application of 3D-printing. Further finetuning of this mixture can be established by using the formulas obtained from fitted regression of the data provided in chapter 4 (see equations 5-10).

Another observation is that incorporation of more than 25% of calcined clay in the precursor leads to almost zero 1-day and 7-day strength. It is therefore recommended to prevent the use of more than 25% of calcined clay in weight of the precursor in geopolymer mortars for the purpose of 3D-printing.

6 Conclusions

In this research, an optimalization approach is given for calcined clay and slag based AAMs for the purpose of 3D-printing. Optimization is established by considering the fresh properties (slump and setting time) and mechanical properties (compressive and flexural strength). The parameters investigated in this research are the calcined clay/slag ratio [0/100 - 100/0], modulus of the alkaline solution [0.5 - 1.50], water/binder ratio [0.40 - 0.50] and the Na_2O/precursor ratio [4% - 8%].

The main results can be summarized as follows:

i. The water to binder ratio has the greatest influence on the value for the slump and the initial setting time for a calcined clay and blast furnace slag based geopolymer mortar. Increasing the water to binder ratio will contribute to higher slump and longer setting time.
ii. The calcined clay content in the precursor is the most important factor for changing the 1-day and 7-day flexural and compressive strength.
iii. For increasing values of the Na_2O to precursor mass ratio, the early age strength, i.e. the 1-day and 7-day compressive and flexural strength, is increased.
iv. Incorporation of more than 25% of calcined clay in the precursor leads to approximately zero 1-day and 7-day strength for almost all mixture designs within the chosen ranges. This is caused by the low reactivity of calcined clay powder and the large delay in setting.
v. Mixture 1 (CC/BFS=25/75, MR=0.5, w/b=0.40, Na_2O/precursor=6%) shows the highest potential for further use in 3D-printing. This mixture shows almost zero slump, adequate early 1-day strength and 7-day strength. The initial setting time of 249 minutes (≈2.5 hours) and the final setting time of 229 minutes (≈3.8 hours), see table 10, seem reasonable for the application of 3D-printing.
vi. The replacement of calcined clay by pure metakaolin results in much higher strength properties as well as faster setting. However, the workability decreases considerably with these replacements. The incorporation of metakaolin in geopolymer mortar requires a higher water demand to guarantee adequate workability for the application of 3D-printing.

The present study shows the potential of a blended system of blast furnace slag and calcined clay for further use in 3D-printing. Optimal properties are acquired for mixtures containing low calcined clay content in the precursor (25%). It is recommended to use calcined clay only in small quantities for 3D-printing. The chosen parameters can be adjusted in such a way that technical requirements can be satisfied, by playing with the formulas found with fitted regression of the experimental data (equations 5-10). Note that these formulas are only useful for the mentioned ranges, parameters out of these ranges will not be covered. Assuming an orthogonal design approach effectively contributed to a reduction of the number of mixture designs that needed to be evaluated (25 instead of 135) for preventing interdependency between the various parameters. This methodology therefore shows high potential for further use in research regarding optimization of concrete/mortar properties.

7 Recommendations

As this research provides a methodology for estimating properties such as slump, setting time and strength for calcined clay and slag based AAMs through orthogonal design, it is recommended to continue this research by replacing calcined clay with pure metakaolin and to extend the chosen ranges for the process parameters for more comprehensive results. For the incorporation of metakaolin in AAM, it is strongly recommended to use higher water to binder ratios to account for the higher water demand. A higher water to binder ratio may contribute to lower strength. To resolve this issue, the alkaline solution must contain a higher Na_2O content. As regards the parameters, this means lower moduli of the alkaline solution and/or higher Na_2O to precursor ratios of the binder. The reactivity of low grade calcined clay containing only 50% in weight of metakaolin is far too low to obtain a concrete mixture design with adequate properties within the first 7 days of testing. It is therefore recommended to either use calcined clay only in small quantities or use calcined clay with a higher metakaolin content (high grade calcined clay).

Furthermore, not all relevant properties for assessing concrete/mortar quality are taken into account for this experimental investigation. Properties like flowability, rheological behaviour, 28-day strength, shrinkage and durability are neglected for this research to simplify the experimental procedure. It is recommended to extend this research so that more properties can be investigated.

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