Optimization of a geopolymer mixture for a Reinforced cantilever concrete bench

Additional thesis project

Part I

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List of Symbols

NH	**Sodium hydroxide**
WG	**Waterglass [Na_2SiO_3]**
FA	**Fly-ash**
BFS	**Blast furnace slag**
RT	**Retarder**
SP	**Super plasticizer**
l/b	**liquid to binder ratio**
M	**Molarity [mol/liter]**

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Abstract

Traditional ordinary Portland cement (OPC)-based concrete consumes large quantities of natural resources for its production, which is highly energy intensive and has high CO_2 emission. Therefore, development of the geopolymer concrete based on use of industrial by-products can provide an environmentally friendly and low-carbon alternative to OPC concrete. Geopolymer concrete characterized with low permeability, high mechanical properties and excellent heat resistant has been received increasing attention in building industry.

However, there exists some challenges regarding the structural application, such as adjusting the fast setting time tailor the workability, and controlling the shrinkage of blast furnace slag based geopolymer concrete.

The main aim of this study is to design and optimize geopolymer concrete mixture for manufacturing a reinforced cantilever bench. This is accomplished by testing rheological and mechanical properties and the drying shrinkage of geopolymer concrete. The geopolymer binder was consisted of fly ash, blast furnace slag and activator. The activator was made by mixing sodium hydroxide (NaOH) and waterglass (Na_2SiO_3) solutions. The prolonged setting time of the studied mixture was achieved by using proper type and amount of chemical admixture in order to achieve enough time for casting and stable mechanical properties of the hardened concrete. The compressive strength, elastic modulus and flexural strength were evaluated.

The application of the optimized geopolymer mixture in the complex structural element such as cantilever bench has shown promising results, which encourage us to upscale geopolymer concrete for structural applications, like bridges and/or other structural elements in the building industry.

Contents

1. Literature survey

1.1 Introduction

Alkali activated materials (also called geopolymers) are an attractive alternative to the OPC-based materials. Geopolymer concrete produces less CO_2 and consumes less energy compared to OPC-based concrete [1].

The manufacture of one ton of cement produces around one ton of CO_2 as well as SO_x and NO_x and that the cement industry is considered responsible for 6% to 7% of all greenhouse gases emitted worldwide. Fifty percent of CO_2 production comes from the de-carbonation of limestone in the clinkering process and the remainder is attributed to the burning of fossil fuels. [2, 3]

It is important to mention that the mechanical properties of the geopolymer concrete depend on different factors, such as the particle size and chemical composition of raw materials, curing conditions (i.e. temperature, time and relative humidity), liquid to binder ratio (l/b), and type and concentration of the activator. The joint activation of FA and BFS has become very attractive, because it counterbalances the disadvantages that each of the raw materials exhibit when alkali activated separately. [2, 4] The blend of FA and BFS show a higher mechanical strength development compared to the strength of only alkali activated FA. The major factor is BFS ratio in the mixture, which forms C-A-S-H gel that that makes the concrete denser and thus increases the mechanical properties, like the compressive strength, flexural strength and elastic modulus. [2, 5, 6]

However, from utmost important for manufacturing is to study the shrinkage of the geopolymer concrete. Numerous studies focused on the shrinkage of alkali activated FA and Alkali activated Slag. Previous research show that relatively low shrinkage is observed in alkali activated FA and that it has good mechanical properties compared to ordinary Portland cement (OPC). [7, 8] In contrary, higher drying shrinkage has been observed in alkali-activated slag concrete than OPC concrete. [9, 10]

While most of the research on geopolymer concrete focus on micro-scale investigation, recent researchers are investigating the structural behavior of geopolymer concrete in load bearing members such as reinforced concrete beams, slabs, columns and more. [11, 12, 13]

It is very important to mention that structural properties of the concrete members is one of the most vital component in effectively introducing such concrete for buildings and other applications. Design codes for geopolymer concrete should be ascertained by performing different tests on geopolymer concrete members (reinforced and non –reinforced) in order to evaluate the possibility for convenience of structural design engineers. Based on previous research, general behavior and failure mode of reinforced geopolymer concrete members were similar with those of reinforced cement-based concrete members. This enhances the use of available codes to design structural members using geopolymer concrete mixtures. Although a number of design equations meant for geopolymer concrete structures were proposed in the past, these are still limited and still need to be further investigated. [6, 12, 13, 14, 15]

The aim of this study is to optimize the alkali-activated FA and BFS concrete mixture from the previous work for its application in a reinforced cantilever concrete bench. [14] In the previous study, the setting time of concrete was approximately 15 minutes. Due to the large cantilever bench dimensions (3 meter of length and 1.5 meter of height) it was not possible to mix and cast a large concrete volume in the formwork within 15 minutes. The challenge of this study was to provide longer final setting time for the reference mixture and to achieve required workability for casting in the bench formwork. This structural application also required specific mechanical properties of the geopolymer concrete such that it can withstand loading conditions and be stiff enough to limit deformations.

In order to regulate setting time and workability of the reference geopolymer concrete mixture, the study was first performed at the geopolymer paste level, by changing the alkaline activator composition, liquid/binder (l/b) ratio and using different types of retarders and superplasticizers. Consequently, the geopolymer concrete mixture was cast in order to test the setting time and workability of the concrete. In addition, the compressive strength, elastic modulus, flexural strength, drying shrinkage and effects of different curing duration of the optimized geopolymer concrete mixture were evaluated.

1.2 Materials

The precursors used for preparation of the geopolymer concrete mixture were FA and BFS. The chemical composition of precursors is given in Table 1. [14].The precursors were activated by mixture of two alkaline solutions, i.e., 4 molar sodium-hydroxide (4M NaOH) and sodium waterglass (Na_2SiO_3). The gravel was crushed granite with a specific gravity of 2650 kg/m^3, while the fine aggregate was natural sand with a specific gravity of 2640 kg/m^3. In order to regulate the setting time, powder admixtures were added to the mixture. The chosen admixtures for the study are the barium chloride dehydrate ($BaCl_2.2H_2O$) and CUGLA admixtures (CUGLA CRETOLENT BT (Retardant, con.25%), CUGLA MMV BT (Retardant, con.36%), CUGLA QQ (Superplasticizer, con. 35%). In order to obtain a better workability for the optimized mixture the liquid to binder ratio was 0.53, whereas for the reference mixture was 0.5. [14]

The reference and optimized mixture design are shown in the Table 2. Besides the concrete casting in the bench, the standard cube specimens and prisms for different mechanical tests and drying shrinkage tests were produced. The mixture was made by mixing first coarse and fine aggregate for 3 minutes. Then, FA, BFS, and retarder were added and mixed for 2 minutes. In the end, the alkaline activator was added and mixed for another 2 minutes. After 24 h from casting, specimens were demoulded and placed in a fog room with 20°C and 99% relative humidity and cured until testing age.

Table 1 Chemical composition of FA and BFS measured by X-ray fluorescence F [14]

Oxide	SiO_2	Al_2O_3	CaO	MgO	Fe_2O	SO_3	Na_2O	K_2O	TiO_2	P_2O	L.O.
BFS	34.3	11.53	39.1	7.81	1.42	1.6	0.23	0.58	-	-	1.15
FA	54.2	23.32	4.23	1.62	8.01	0.6	0.85	1.97	1.23	0.54	3.37

Figure 1: Geopolymer concrete materials

1.3 Methods

The first focus of the study was on paste level in order to determine the setting time and simultaneously the compressive strength of the paste specimens. The setting time of the pastes is measured under a constant temperature of (20 ± 2) °C according to [NEN-EN 196-3]. The setting time and workability tests of the fresh geopolymer concrete were assessed based on [NEN-EN 12350-2 and EN 12350-5]. Compressive strength tests of geopolymer concrete were done according to the [NEN 5988] on standard cubes with dimension of 15x15x15 cm^3. The three-point flexural bending tests were performed according to [NEN-EN 14651+A1], with the exception that the specimen size was modified to the 10×10×40 cm^3 prisms. A notch of 2.5 cm was made in the middle of the specimen and the specimen was dried for 2 hours before the three-point bending test was performed. The elastic modulus and the drying shrinkage were measured according to [NEN-EN 12390-13] and [ISO 1920-8], respectively. The specimens for elastic modulus tests and drying shrinkage tests were prisms with dimension of 10×10×40 cm^3. The specimens were cured for 1, 3, 7, and 28 days, and after each of the curing period, the specimens were moved from the curing room to the laboratory conditions at 20°C and 55% relative humidity when they were exposed to drying shrinkage test. The drying shrinkage tests consist of weight loss and length change measurements.

The specimens were sealed and cured in laboratory conditions for 24 h, then demoulded and stored in a curing chamber (99% RH, 20± 2 C) until testing.

The temperature and the conductivity of the mixture were monitored with a sensor for 10 days from the first moment of casting. The Sensor [ConSensor 2.0] is produced by ConSensor BV Rotterdam, the Netherlands. The sensor calculates the strength of curing concrete in two different ways: with the weigh maturity method and with the conductivity method. The measurement data (temperature and conductivity) are transmitted to the internet via GPRS.

2. Experimental work results of the optimized geopolymer concrete mixture

2.1 Introduction

This chapter provides the experimental work results of the optimized geopolymer concrete mixtures. To find the appropriate mixture for cantilever bench different experiments where done on geopolymer paste mixtures and concrete mixtures. To find the optimized geopolymer concrete mixture the study is divided into four phases. The first phase of the experiments was testing the setting time and workability of geopolymer concrete mixtures by using three different CUGLA admixtures.

To minimize the complicity of the research and usage of raw materials, the second phase of the research was focused on testing the setting time and compressive strength of the geopolymer pastes. The third phase was testing the setting time of the chosen paste mixtures on concrete level. For the final phase of the project an optimized mixture was chosen and tested on workability, setting time, compressive strength, flexural strength, drying shrinkage and elastic modulus.

2.2 Reference geopolymer concrete mixture

From the work of 'Kamel et al' one reference mixture of alkali-activated FA and BFS is chosen for optimization the workability and the setting time. [14] The liquid to binder ratio (l/b-ratio) of the mixture was 0.50 and the 28 days compressive strength reached 77 MPa. However the mixture lacked a long period workability and has a fast setting time of 5 minutes. The design of the reference mixture is shown in the Table 2 and the 1,7,28 and 90 days compressive strength in Figure 2. The specimens were sealed and cured in laboratory conditions for 24 hours, then demoulded and stored in a curing chamber (99% RH, 20±°C) until testing.

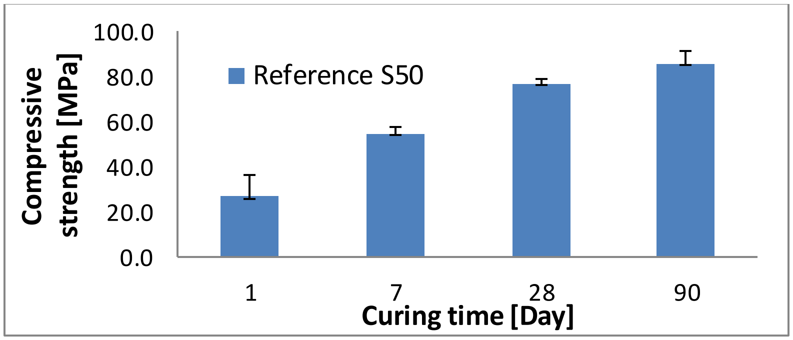

Figure 2: Reference mixture compressive strength [14]

Table 2: The reference geopolymer mixture design [14]

l/b-ratio: 0.50		Reference geopolymer concrete mixture [m^3]
Components:	**Density [g/cm^3]**	**Mass [kg]**
FA	2.44	200
BFS	2.89	200
Aggregate [0-4 mm]	2.64	789.14
Aggregate [4-8 mm]	2.65	439.81
Aggregate [8-16 mm]	2.65	524.69
Alkaline activator [NH:WG= 50:50]	1.125	200

2.3 Mixing reference mixture with CUGLA admixtures

The reference mixture (l/b-ratio 0.50) was tested with three different admixtures from CUGLA to check if they are suitable for geopolymer concrete mixtures (table 3). The difference between the mixtures was the type and amount of added admixtures. The type and concentration of admixture is shown in table 4. The mixtures are tested on slump, flow ability and setting time in an ambient temperature of 20 °C. The slump and flow ability was measured at two to three times with an interval of 3 minutes (table 4). The setting time results are shown in figure 3.

The first mixture, with 2 wt. % of binder weight CRETOLENT BT retarder, had the first 3 minutes a slump class/ flow class of S5/F2 and dropped to S3/F2 less than 9 minutes. The second mixture, 2 wt. % of binder weight CUGLA MMV BT was applied to a second mixture to compare the two CUGLA retarders. The mixture was still workable the first 6 minutes. However the third time measurement could not be completed because the mixture was stuck on the steel cone. To try increasing the workability time a third mixture was mixed with 1% of superplasticizer and 1% CUGLA MMV BT retarder. Based on the results, adding superplasticizer and retarder in the mixture does not help in reducing the stickiness of the mixture and delayed the initial setting time for 25 minutes. The final casted mixture behaved similar to the first mixture, however the initial setting time was delayed for 30 minutes compared to the first mixture.

Table 3: Components for the four mixtures

	Components	FA	BFS	Activator
	Density	**2440**	**2890**	**1255**
	Unit	**[kg/m^3]**	**[kg/m^3]**	**[kg/m^3]**
1 m^3	Mass [kg]	200	200	200
	Volume [m^3]	0.082	0.069	0.159
		Sand [0-4]	**Gravel [4-8]**	**Gravel [8-16]**
	Density	**2640**	**2640**	**2640**
	Unit	**[kg/m^3]**	**[kg/m^3]**	**[kg/m^3]**
1 m^3	Mass [kg]	793.60	442.3	527.7
	Volume [m^3]	0.30	0.17	0.20

Table 4: Workability test of geopolymer mixtures

Mixture	Admixture	l/b- ratio	Slump [cm]/ Slump class	Flow ability [cm]/ Flow class
Mixture I	CUGLA CRETOLENT BT (Retardant, con. 25%), max 2 wt. % of binder weight [*powder*]	0.5	26/S5 24/S5 14/S3	64/F6 56/F5 36.5/F2
Mixture II	CUGLA MMV BT (Retardant, con. 25%), max 2 wt. % of binder weight [*powder*]		28/S5 25/S5 -	63/F6 49/F4 -
Mixture III	CUGLA MMV BT (Retardant, con. 36%), 1 wt. % [*powder*] and 1% SP of binder weight [*liquid*]		27/S5 25/S5 -	60.5/F5 48/F3 -
Mixture IV	CUGLA MMV BT (Retardant, con. 36%), 3 wt. % [*powder*] And 1% SP of binder weight [*liquid*]		28/S5 26/S5 19/S4	66/F6 58.5/F5 41/F2

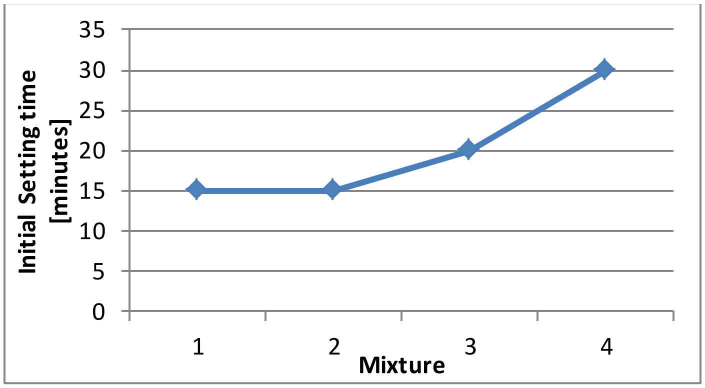

Figure 3: Initial setting time of the reference mixture with CUGLA admixtures

Conclusion: To cast a b a The CUGLA CRETOLENT BT and the CUGLA MMV BT retarders should at least prolong the setting time by 20 a 30 minutes. However the results show that the setting time of the last mixture was prolonged by 30 minutes by adding 3 wt. % retarder and 1% of superplasticizer. This amount of admixtures will affect the early age strength development of the mixture. Based on these results the admixtures are not suitable for the geopolymer concrete mixtures.

To minimize the usage of the raw materials and to have better insight in how the setting time can be prolonged and simultaneously not affect the mechanical properties of the concrete, research is going to be further made on pastes.

PHASE II

2.4 Experimental results of geopolymer paste mixtures

The next phase of the study is testing paste mixtures on setting time and compressive strength by changing the following parameters in the pastes:

- **Change of Alkaline Activator**
  i) NaOH concentration (from 4M decrease to 1.5M, 2M, 3M)
  ii) Na_2SiO_3 [WATERGLASS] quantity (50 wt. % reduction to 30 wt. %)
  iii) liquid to binder ratio [l/b]
- **Addition of barium chloride dehydrate retarder ($BaCl_2.2H_2O$)**

The compression test of the hardened paste mixtures, cured in a chamber (99% RH, 20±°C), were tested according to [NEN 5988] and [NEN 5950] on cubes with dimensions of 40*40*40 mm^3.
The different concentrations of sodium hydroxide solution are made by adding the sodium hydroxide pallets with distilled water. The four molarities of the liquid sodium hydroxide are shown in table 5.

Table 5: Molarity of liquid sodium hydroxide (NaOH)

NaOH Molarity	NaOH pallets (gram/Liter distilled water)
1.5 M	60
2 M	80
3 M	120
4 M	160

2.4.1 Effect of NaOH concentration on setting time and compressive strength

The setting time and compressive strength of four paste mixtures are tested on different concentration (molarity) of sodium hydroxide (Figure 4 and Figure 5]. All the parameters of the mixtures are kept the same. The difference is only the molarity of the liquid NaOH.

The ratio of NH: WG and the ratio of FA: BFS is kept 50:50, while the liquid to binder ratio (l/b-ratio) is kept on 0.50.

The following paste mixtures are tested:

- 1.5M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %)
- 2 M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %)
- 3 M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %)
- 4 M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %)

In all the experiments, three cubes for each paste mixture where prepared and tested to determine the 3 days average compressive strength.

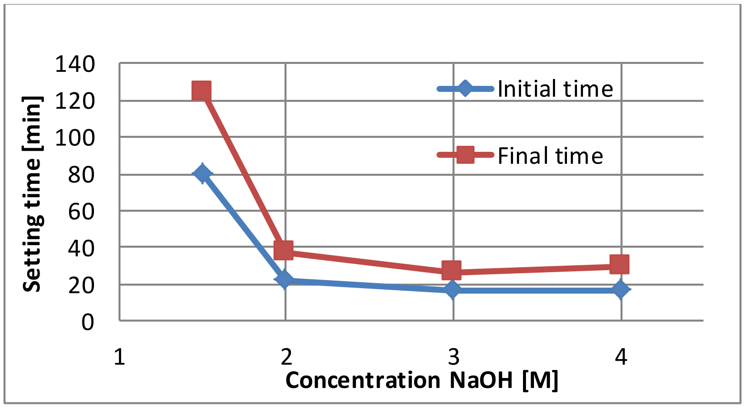

Figure 4: Initial and final setting time of different NaOH molarity

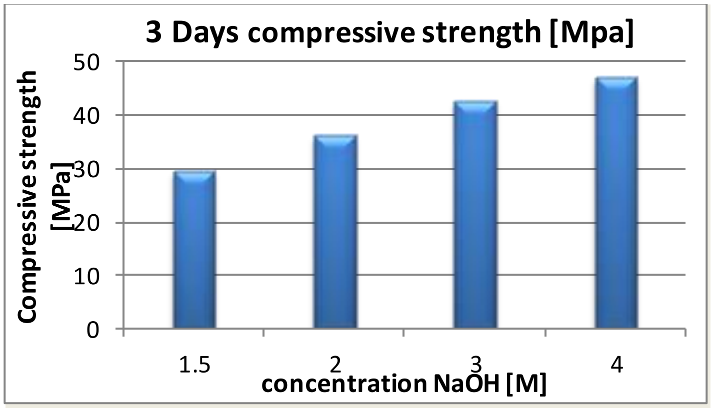

Figure 5: 3 Days compressive strength of 1.5M, 2M, 3M and 4M NaOH

Conclusion: Based on the results in Figure 4 and 5, the concentration of sodium hydroxide effects the setting time and the compressive strength of the paste mixtures. A lower NaOH concentration delays the setting time and simultaneously lowers the compressive strength. The final setting time of 3M and 4M differed only by 4 minutes and the compressive strength by 5MPa. In the next experiments 4M NaOH is going to be further studied on setting time and compressive strength.

2.4.2 Effect of 4M NH: WG ratio on setting time and compressive strength

The next part of the experiment 4M NaOH concentration is further investigated on setting time and compressive strength. For the experiment three paste mixtures were prepared with a different ratio of liquid 4M NaOH and waterglass. The ratio of FA: BFS is fixed on 50:50 and liquid to binder ratio (l/b) is 0.50. No admixtures where added to the mixtures.

The three mixtures are in the following ratios:

- Mixture I: 4 M NaOH (30 wt. %) and Na_2SiO_3 (70 wt. %)
- Mixture II: 4 M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %)
- Mixture III: 4 M NaOH (70 wt. %) and Na_2SiO_3 (30 wt. %)

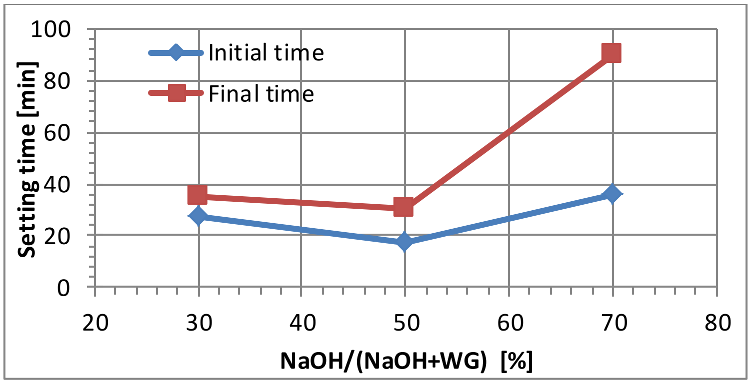

Figure 6: Setting time of different ratio 4M NaOH and waterglass [WG]

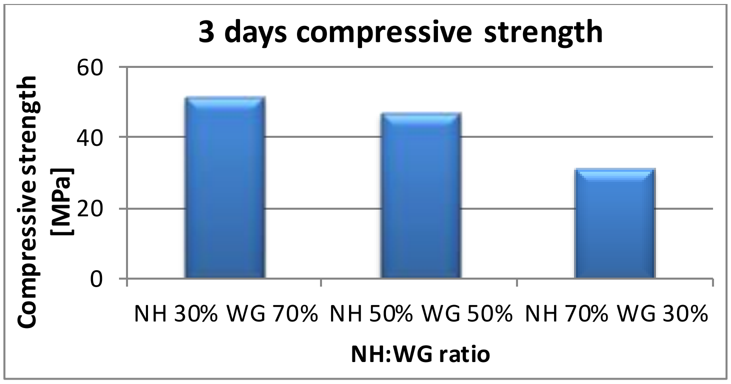

Figure 7: 3 Days compressive strength different ratio of 4M NaOH and waterglass [WG]

Conclusion: A lower waterglass ratio delays the setting time and simultaneously lowers the compressive strength (Figure 6 and Figure 7). The average 3 days compressive strength of mixture I and II was almost identical with a difference of 4.6 MPa. However the initial setting time between the two mixtures was 20 minutes.

2.4.3 Effect of (l/b) ratio on the setting time and compressive strength

The activator consisted of 4M NaOH concentration and waterglass with a ratio of 50:50. Three paste mixtures with an l/b-ratio of 0.45, 0.5 and 0.55 were casted. A higher liquid to binder ratio delays the setting time but it also lowers the compressive strength (Figure 8 and Figure 9). The liquid to binder ratio effects the setting time linearly.

- 4 M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %, l/b=0.45
- 4 M NaOH (50 wt.%) and Na_2SiO_3 (50 wt.%), l/b=0.5
- 4 M NaOH (50 wt.%) and Na_2SiO_3 (50 wt.%), l/b=0.55

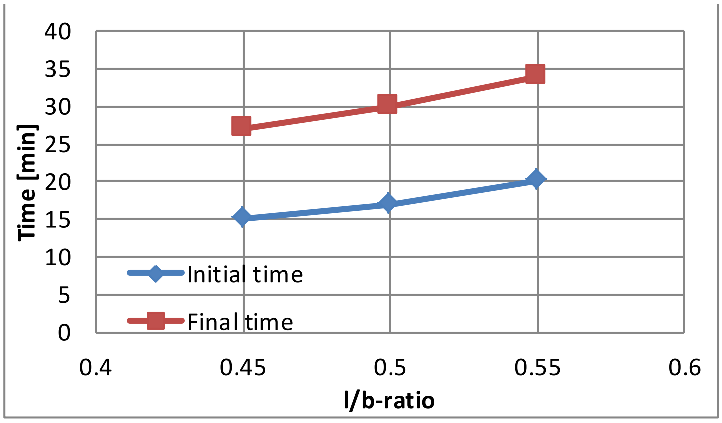

Figure 8: Effect of l/b-ratio on the setting time

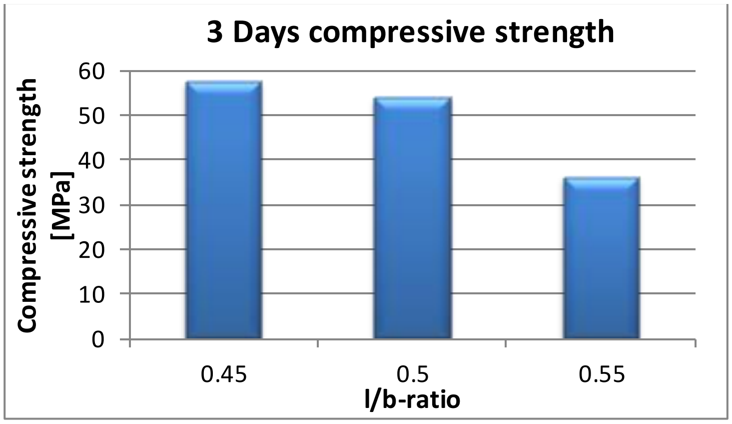

Figure 9: Effect of l/b-ratio on the compressive strength

Conclusion: The compressive strength of l/b-ratio of 0.45 and 0.55 was 21.3 MPa and the initial setting time was delayed for an extra 5 minutes. This means changing the liquid to binder ratio will not much effect the setting time of the paste mixture.

2.4.4 Effect of barium chloride dihydrate retarder on the setting time and compressive strength

To have more insight how the barium chloride dihydrate retarder can delay the setting time; four mixtures with different quantity of the retarder were casted. The percentage of added retarder was calculated by the total weight of binder (FA and BFS). The ratio of FA: BFS is fixed on 50:50 and liquid to binder ratio (l/b) is 0.50.
The four mixtures are as follows:

- 4 M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %), 0% wt. RT
- 4 M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %), 0.25% wt. RT
- 4 M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %), 0.50% wt. RT.
- 4 M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %), 0.75% wt. RT

Figure 10 and 11 shows the setting time results of the four paste mixtures. The retarder with addition up to 0.5 wt. % Retarder (of total binder weight) has the best effect on setting time delay without compromising the compressive strength. However the expected setting time of the concrete mixture is less than 50 minutes due to the present of dry aggregates.

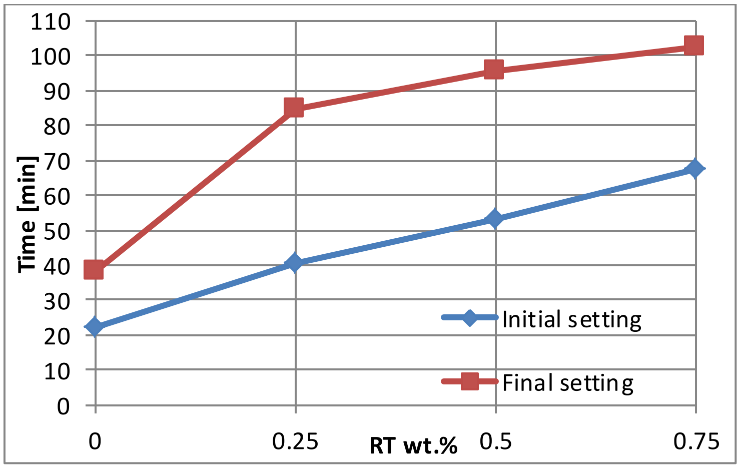

Figure 10: Setting time with difference quantities of retarder

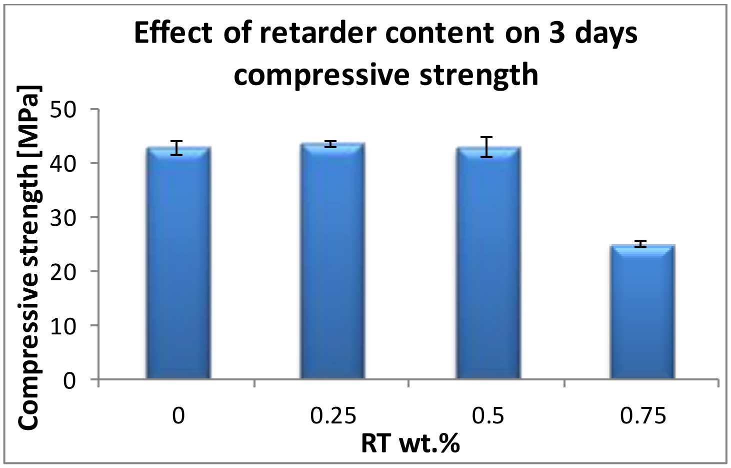

Figure 11: 3 days compressive strength of paste [4 M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %) with different quantities of retarder

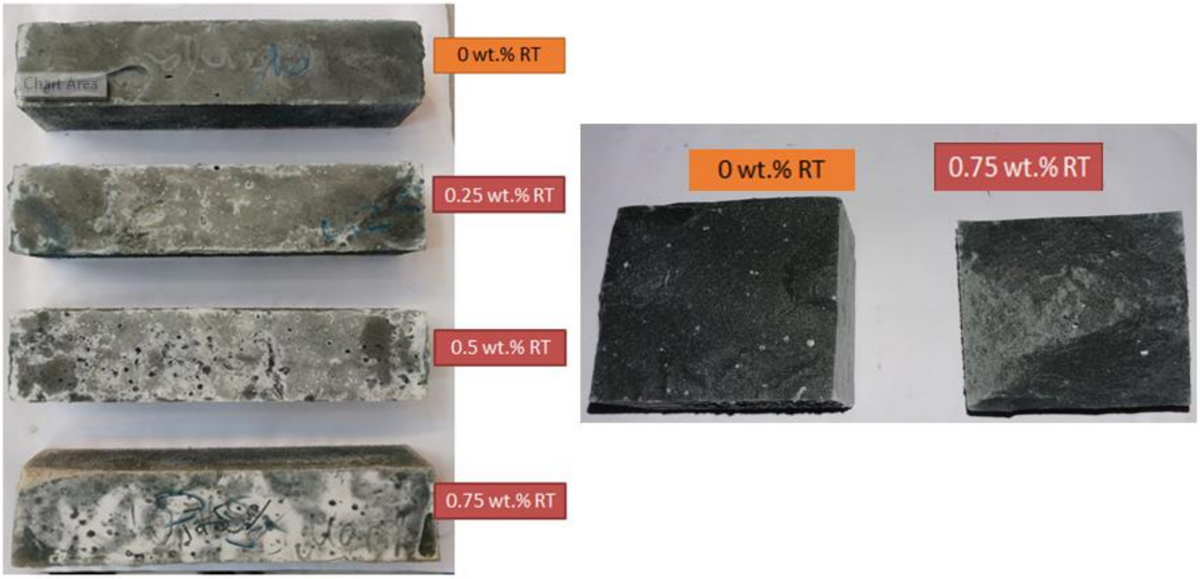

Figure 12: Reactivity of 3 days old specimens caused by the addition of barium chloride dehydrate retarder

In Figure 12 the specimen with 0.75% of binder weight of barium chloride dihydrate retarder consists of material that was not reacted compared to the reference specimen without the retarder. This indicates that the quantity of retarder in the mixture affects the hydration process, but also delays the strength development of the specimen.

The next step of the study is adding 0.5% wt. barium chloride dehydrate retarder to pastes with 1.5M and 2M NaOH concentration.

2.4.5 Effect of retarder on the setting time and compressive strength of 1.5M and 2M NaOH concentration

In all the experiments, the average of three cubes (40x40x40 mm^3) for each mixture where prepared and tested to determine the compressive strength. The mixtures consisted of 1.5M and 2M NaOH concentrations with 0.5% of total binder weight barium chlorides dihydrate retarder. The compressive strength of the pastes was tested on 3, 7 and 28 days.

- 1.5 M NaOH (50 wt.%) and Na_2SiO_3 (50 wt.%), 0.5% wt. RT
- 2.0 M NaOH (50 wt.%) and Na_2SiO_3 (50 wt.%), 0.5% wt. RT

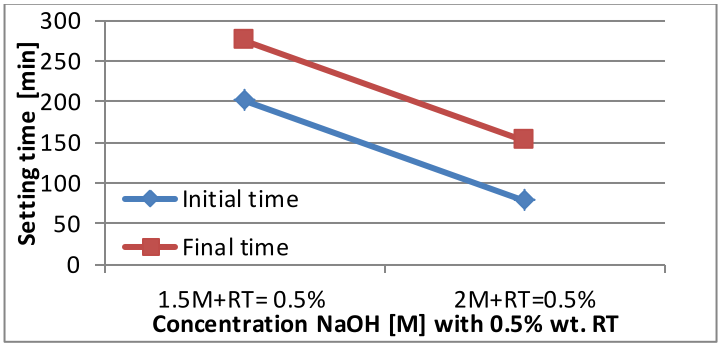

Figure 13: Setting time of 1.5M and 2.0 M NaOH with 0.5 wt. RT

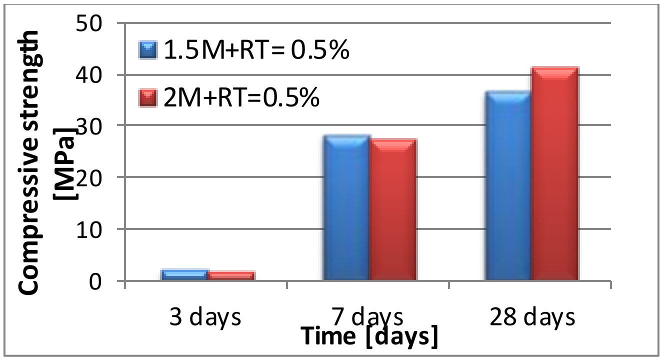

Figure 14: 3,7 and 28 days compressive strength of 1.5M and 2.0M NaOH concentration with 0.5 wt. RT

Comparing the setting time of the 1.5 and 2M in Figure 4 and Figure 13; the initial setting time is 120 minutes delayed for 1.5M NaOH with 0.5 % wt. RT and 55 minutes for 2M NaOH with 0.5 % wt. RT. In Figure 15, the compressive strength of the mixtures was compared to see how the retarder influences the strength development. The mixture with 1.5M NaOH there was a difference of 27.3 MPa and for 2M NaOH a difference of 34 MPa.

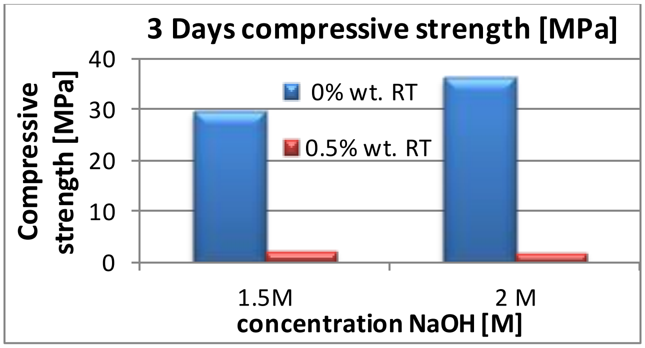

Figure 15: 3 days compressive strength of 1.5M and 2M with 0% and 0.5% wt. RT

Conclusion: The advantage of a low concentration of sodium hydroxide ensures a longer workability and flow ability time of the concrete mixtures. The disadvantage of these mixtures is a lower compressive strength and tensile strength caused by the lack of activation process of the FA and BFS to form an enough bond between the aggregates and the paste.

The same experiments will be performed at a higher concentration of sodium hydroxide [2M, 3M and 4M NaOH]and different quantity of retarder by again testing the setting time and the compressive strength.

2.4.6 Setting time and compressive strength of 2M and 3M NaOH concentration with variation of retarder quantity

The compressive strength of the pastes was tested on cubes of 40x40x40 mm^3 with the same curing conditions as the previous mixtures (99% RH, 20± 2 C).
The mixture properties are as follows:

- Mixture I: 2 M NaOH (50 wt.%) and Na_2SiO_3 (50 wt.%), 0.25% wt. RT
- Mixture II: 3 M NaOH (50 wt.%) and Na_2SiO_3 (50 wt.%), 0.25% wt. RT
- Mixture III: 3 M NaOH (50 wt.%) and Na_2SiO_3 (50 wt.%), 0.5% wt. RT

The setting time of mixture I and III in (Figure 16) was almost similar. However the average compressive strength on curing days of 3, 7 and 28 for Mixture III was much higher. Mixture II performed better in compressive strength and had a final setting time of 60 minutes. The different in strength between the 28 days compressive strength of mixture I and III is 20.4 MPa and mixture II and III is 16.7 MPa.

In Figure 18, the cube specimens with a higher concentration of NaOH showed a darker gray color. This means more hydrated binder and a better bond between the aggregates and the binder.

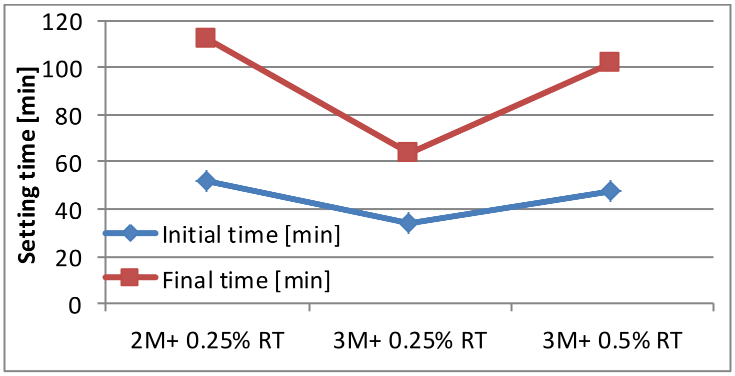

Figure 16: Setting time of 2M and 3.0 M NaOH with 0.25% wt. and 0.5% wt. Retarder

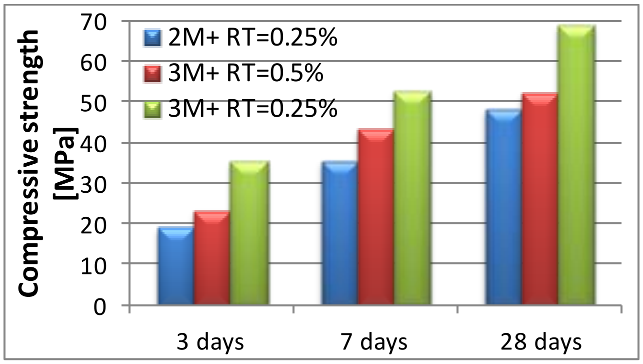

Figure 17: 3,7 and 28 days compressive strength of 2M and 3.0M NaOH concentration with 0.25% wt. and 0.5% wt. Retarder

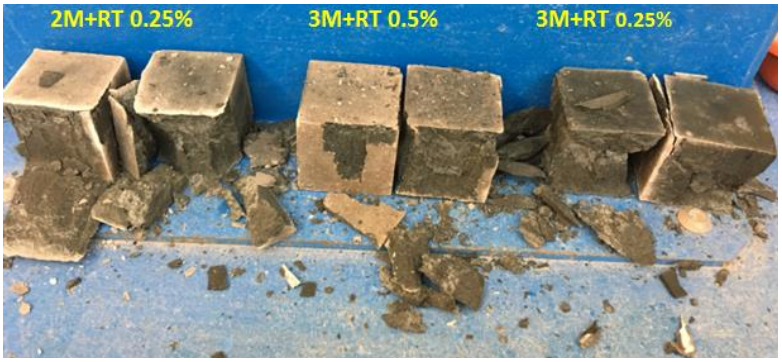

Figure 18: 28 days compressive strength tested samples with 2M NaOH -0.25% wt. RT, 3M NaOH-0.25% wt. RT and 3M NaOH-0.5% wt. RT

The total experimental results of paragraph 2.2.3.4 to 2.2.3.6 are shown in Figure 19 and Figure 20. It can be concluded that the setting time and mechanical properties of the paste mixtures depends on the ratio between NaOH and waterglass, but also on the concentration of NaOH. Barium chloride retarder improves the workability and flow ability of the mixture and simultaneously delays the hydration process the first week after mixing.
Based on the experimental results, paste mixtures with 2M +0.25% wt. RT and 3M+ 0.5% wt. RT has the best effect on setting time delay without compromising the strength. The setting time and compressive strength results of all the paste mixtures are given in Table 6. The next step of the study is performing initial setting time check on concrete mixtures.

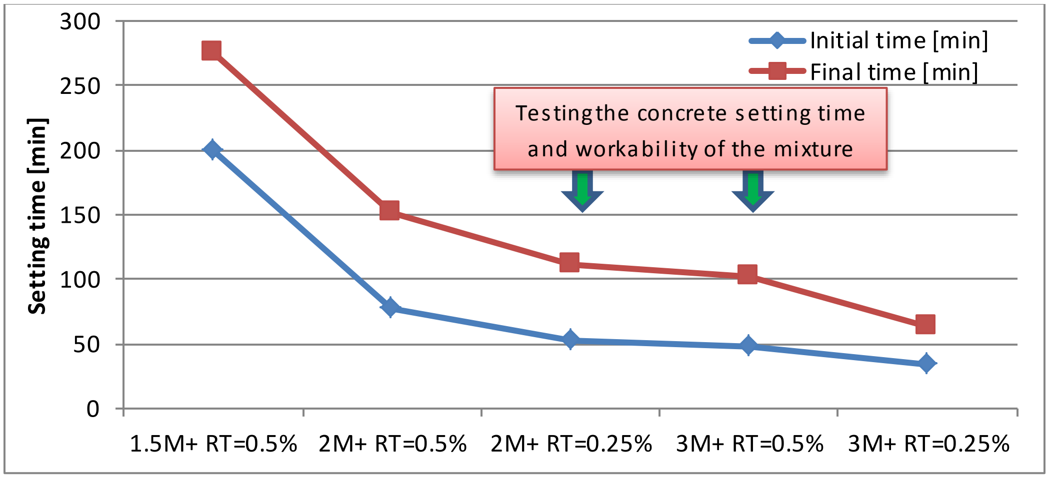

Figure 19: experimental setting time results with different concentration of NaOH and retarder

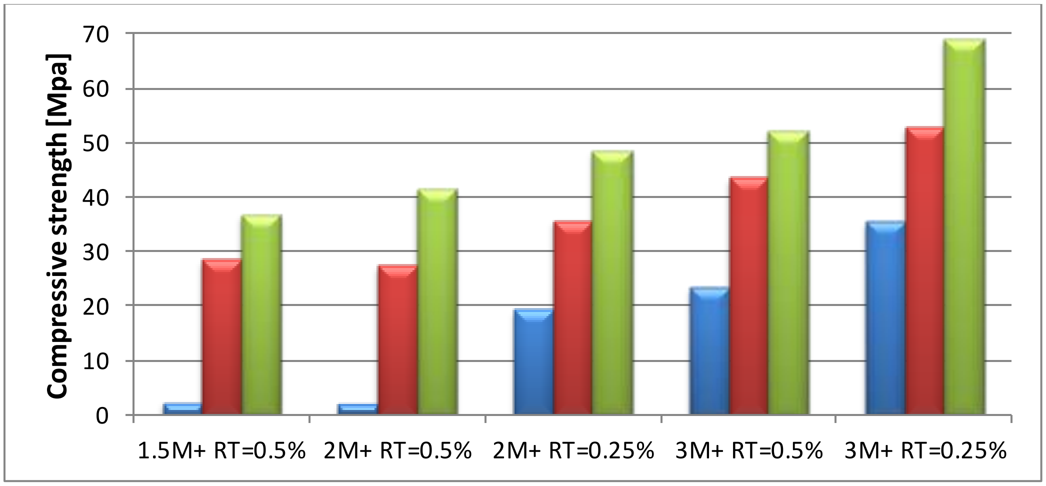

Figure 20: 3, 7 and 28 days compressive strength results with different concentration of NaOH and retarder

Table 6: Setting time and compressive strength of paste mixtures

PASTE LEVEL			Setting time [min]		Compressive strength [MPa]		
Sample ID			Initial	Final	3 days	7 days	28 days
Alkaline Activator composition change	**NaOH:WG= 50:50; FA:BFS= 50:50; (l/b)-ratio=0.50**	**1.5M** NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %)	80	124	29,5	-	-
		2 M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %)	22	37	36,1	-	-
		3 M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %)	17	26	42,8	-	-
		4 M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %)	17	30	47	-	-
	4M NaOH:WG -ratio; FA:BFS= 50:50; (l/b)-ratio=0.50	4 M NaOH (30 wt. %) and Na_2SiO_3 (70 wt. %)	27	35	51,6	-	-
		4 M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %)	17	30	47	-	-
		4 M NaOH (70 wt. %) and Na_2SiO_3 (30 wt. %)	36	90	31,2	-	-
	Change the liquid to binder ratio (l/b); FA:BFS=50:50; 4M NaOH:WG= 50:50	4 M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %)-**l/b=0.45**	15	27	57,5	-	-
		4 M NaOH (50 wt.%) and Na_2SiO_3 (50 wt.%) -**l/b=0.5**	17	30	54	-	-
		4 M NaOH (50 wt.%) and Na_2SiO_3 (50 wt.%) -**l/b=0.55**	20	34	36,1	-	-
Addition of Barium chloride dehydrate retarder [RT]	**FA:BFS= 50:50; l/b-ratio=0.50; NaOH:WG= 50:50**	1.5 M NaOH (50 wt.%) and Na_2SiO_3 (50 wt.%) + 0.5% wt. RT	200	275	2,2	28,4	36,7
		2 M NaOH (50 wt.%) and Na_2SiO_3 (50 wt.%) + 0.5% wt. RT	77	152	1,89	27,3	41,3
		2 M NaOH (50 wt.%) and Na_2SiO_3 (50 wt.%) + 0.25% wt. RT	52	112	19,2	35,7	48.5
		3 M NaOH (50 wt.%) and Na_2SiO_3 (50 wt.%) + 0.25% wt. RT	34	64	35,5	52,9	69
		3 M NaOH (50 wt.%) and Na_2SiO_3 (50 wt.%) + 0.5% wt. RT	48	102	23,3	43,4	52.2
		4 M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %) + 0% wt. RT	22	38	42,8	-	-
		4 M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %) + 0.25% wt. RT	40	84	43,5	-	-
		4 M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %) + 0.50% wt. RT	**53**	**95**	**42,8**	-	-
		4 M NaOH (50 wt. %) and Na_2SiO_3 (50 wt. %) + 0.75% wt. RT	67	102	24,9	-	-

2.5 Experimental test results of geopolymer concrete mixtures

2.5.1 Setting time of 2M and 3M NaOH concentration geopolymer concrete mixtures

Experiment 1: The first focus of the test was casting 9 liter of mixture [2M NaOH, 0.25 % wt. RT, NH: WG=50:50] in an ambient temperature of 20°C. The mixture components are provided in table 6.

The setting time of the mixture (Figure 21) could not be controlled by only additions 0.25% wt. barium chloride dehydrate retarder. The mixture initial setting time was 20 minutes. The setting time of the mixture does not provide enough time to mix and cast a large amount of the mixture in the mould.

To prolong the setting time two more mixtures of 2M NaOH are casted with different quantities of retarder, different NH: WG-ratio and an addition of CUGLA QQ (con. 35%) super plasticizer.

Based on the previous knowledge, a higher molarity provides a better mechanical strength development, but quickens the setting time. The (l/b-ratio) of the four tested mixtures was fixed on 0.50 [Table 7].

The mixtures are as follows:

- Mixture I: 2M NaOH, 0.25 % wt. RT, NH:WG=50:50, l/b-ratio 0.50
- Mixture II: 2M NaOH, 0.50 % wt. RT, 1% SP, NH:WG=75:25, l/b-ratio 0.50
- Mixture III: 2M NaOH, 0.25 % wt. RT, 1% SP, NH:WG=65:35, l/b-ratio 0.50
- Mixture IV: 3M NaOH, 0.50 % wt. RT, 1% SP, NH:WG=65:35, l/b-ratio 0.50

Table 7: Mixture components with 2M NaOH and 3M NaOH concentration

	Components	FA	BFS	Activator
	Density	2440	2890	1255
	Unit	[kg/m^3]	[kg/m^3]	[kg/m^3]
1 m^3	Mass [kg]	200	200	200
	Volume [m^3]	0.082	0.069	0.159
		Sand [0-4]	**Gravel [4-8]**	**Gravel [8-16]**
	Density	2640	2640	2640
	Unit	[kg/m^3]	[kg/m^3]	[kg/m^3]
1 m^3	Mass [kg]	793.60	442.3	527.7
	Volume [m^3]	0.30	0.17	0.20

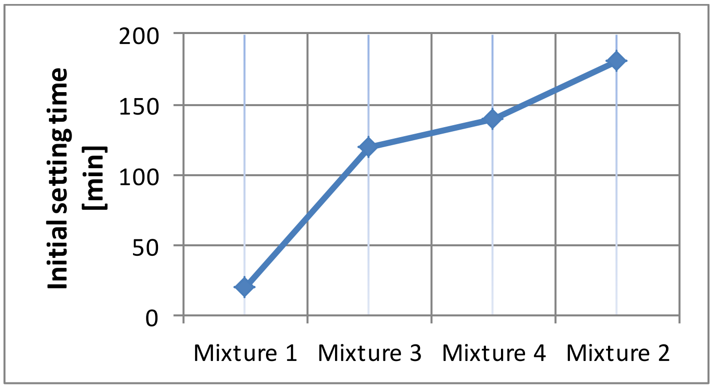

Figure 21: Initial setting time of 2M and 3M NaOH concentration geopolymer concrete mixtures


2M NaOH, 0.25%wt. RT

2M NaOH, 0.50%wt. RT, 1% SP, NH:WG=75:25

2M NaOH, 0.25%wt. RT, 1% SP, NH:WG=65:35

3M NaOH, 0.50%wt. RT, 1% SP, NH:WG=65:35

Figure 22: Workability [slump] tests

Conclusion: The fourth mixture [3M NaOH, 0.50 % wt. RT, 1% SP, NH: WG=65:35] showed a satisfactory workability (slump of 28 cm/ slump class S5) and an initial setting time of more than 120 minutes.

The next step of the study is testing more geopolymer concrete mixtures with 3M NaOH concentration and 0.5% wt. RT. This time fixing the ratio of NH: WG (50:50) and only changing the amount of CUGLA QQ (con. 35%) super plasticizer.

Experiment 2:

The two mixtures are as follows:

- 3M NaOH, 0.5%wt. RT,1%wt. SP, NaOH:WG=50:50
- 3M NaOH, 0.5%wt.RT, 2%wt. SP, NaOH:WG=50:50

Conclusion: The workability (slump class S5 to S3) of the two mixtures was satisfactory and at least 90 minutes delay of initial setting time. However, the bond between aggregate and paste did not exist. The one day aged hardened concrete crumbled under the hand pressure.

Based on these results, the effect of coupled retarder and super plasticizer has a negative effect on workability and the mechanical strength of the mixtures. In order to check the effect of both separately new mixes were prepared, this time focusing on 3M and 4M NaOH concentration. For a better workability the liquid to binder ratio (l/b-ratio) was increased from 0.5 to 0.53.

2.5.2 Workability, setting time, compressive strength and bond strength of 3M and 4M NaOH concentration geopolymer concrete mixtures

To choose a final concrete mixture for the cantilever bench, four final mixtures were casted. The ratio of sodium hydroxide and waterglass is fixed on [NH: WG=50:50] and the (l/b-ratio) on 0.53 (Table 8).

Table 8: Mixture components with 3M NaOH and 4M NaOH concentration

	Components	FA	BFS	Activator
	Density	2440	2890	1255
	Unit	[kg/m^3]	[kg/m^3]	[kg/m^3]
1 m^3	Mass [kg]	200	200	212
	Volume [m^3]	0.082	0.069	0.159
		Sand [0-4]	**Gravel [4-8]**	**Gravel [8-16]**
	Density	2640	2640	2640
	Unit	[kg/m^3]	[kg/m^3]	[kg/m^3]
1 m^3	Mass [kg]	793.60	442.3	527.7
	Volume [m^3]	0.30	0.17	0.20

The setting time, workability, 2 days compressive strength and the bond between the aggregates and paste was checked. The results are given in table 9 and Figure 23. The 2 days compression test of the hardened geopolymer concrete mixtures, cured in a chamber (99% RH, 20±°C), were tested on cubes with dimensions of 150*150*150 mm^3. The mixtures properties are as follows:

- Mixture I: 3M NaOH, 0.50%wt. RT, l/b-ratio 0.53
- Mixture II:3M NaOH, 1%wt. SP, l/b-ratio 0.53
- Mixture III: 4M NaOH, 0.5%wt. RT, l/b-ratio 0.53
- Mixture IV: 4M NaOH, 0.75%wt. RT, l/b-ratio 0.53

Table 9: Initial setting time, workability, compressive strength and bond between aggregates of four mixtures

MIXTURES **l/b=0.53, NH:WG=50:50**	**Slump [cm]/slump class**	**Bond between aggregate and the paste**	**Compressive strength of 2 days curing [MPa]**
Mixture I	22.5 /S5	bad	12.2
Mixture II	18.5/S4	bad	18.5
Mixture III	25.5/S5	better	29.1
Mixture IV	22.3/S5	better	25.9

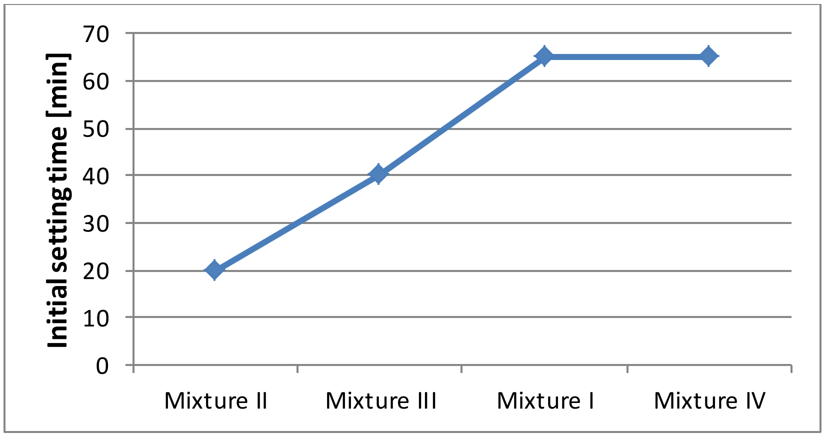

Figure 23: Initial setting time of the mixtures

The CUGLA QQ (con. 35%) super plasticizer did not show a satisfactory workability and it affected negatively the bond between aggregates and paste. However mixtures with the barium chloride dehydrate retarder prolonged the initial setting time and showed a satisfactory workability with a slump class of S5. Mixture III with 0.5% wt. retarder and mixture IV with 0.75% wt. retarder behaved similar in delaying the setting time. The third mixture did not show any segregation during the slump tests, compared to the fourth mixture, and it had the highest compressive strength value. Based on these results the third mixture (4M NaOH, 0.5%wt. RT) is going to be further tested on rheological and mechanical properties before choosing it as a final mixture for the cantilever bench.

Figure 24: Slump test of mixture III (4M NaOH, 0.5%wt. RT)

Figure 25: Segregation during the slump test of mixture IV (4M NaOH, 0.75%wt. RT)

3M NaOH, 0.50%wt. RT

3M NaOH, 1%wt. SP

4M NaOH, 0.5%wt. RT

4M NaOH, 0.75%wt. RT

Figure 26: 2 days curing compressive strength test of the four mixtures

3. Mechanical and rheological properties of the chosen geopolymer concrete mixture

From the experimental results presented in the previous paragraph, the final mixture (4M NaOH, 0.5%wt. RT) is casted in large amount and tested on setting time, workability, compressive strength, flexural strength, E-modulus test, Poisson's ratio and drying shrinkage. Components of the reference mixture of Kamel [14] and final optimized mixture of the bench are shown in Table 10.

Table 10: The reference and optimized geopolymer mixture design

l/b-ratio= 0.53		Reference geopolymer concrete mixture [14] [m^3]	Optimized geopolymer concrete mixture [m^3]
Components:	**Density [g/cm3]**	**Mass [kg]**	**Mass [kg]**
Fly ash	2.44	200	200
Blast furnace slag	2.89	200	200
Aggregate [0-4 mm]	2.64	789.14	789.14
Aggregate [4-8 mm]	2.65	439.81	439.81
Aggregate [8-16 mm]	2.65	524.69	524.69
Alkaline activator	1.125	200	212
($BaCl_2.2H_2O$) admixture	3.1	-	2 (0.5 wt.% of the binder)

3.1 Setting time and workability at the concrete level

The optimized mixture has showed a satisfactory workability with a slump class S5 (a slump of 25.5 cm) and F4 flow class (average diameter of 55 cm). The initial setting time of the concrete in ambient room conditions was 40 minutes (Figure 27).

Figure 27: Slump test of optimized concrete mixture

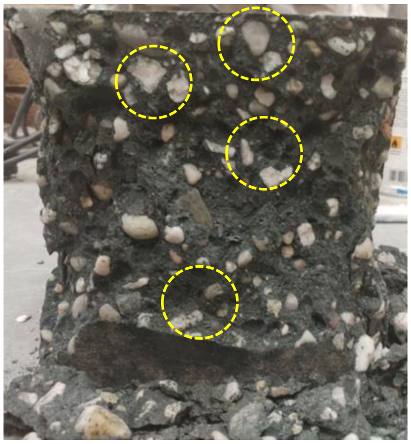

Figure 28: Dotted yellow circles indicate good bonding between matrix and aggregates in the optimized mixture

3.2 Compressive strength

The compressive strength of the reference and optimized mixtures from 1 day to 90 days is shown in the Figure 29. It can be seen that at 1 day the compressive strength for the optimized mixture was lower than for the reference mixture. The lower compressive strength is attributed to the use of the retarder. However the effect of the retarder on compressive strength is not significant at the later ages. Only a slightly lower value for the compressive strength results are found for optimized mixture. Compared to the reference concrete mixture with l/b-ratio of 0.50, the slightly lower compressive strength in optimized mixture is caused by the higher l/b-ratio (0.53) in order to obtain a better workability.

An example of the concrete cube after compressive strength test is shown in Figure 28. It is clear that the good bond between matrix and aggregates was obtained, which contributes to the development of high strength of geopolymer concrete.

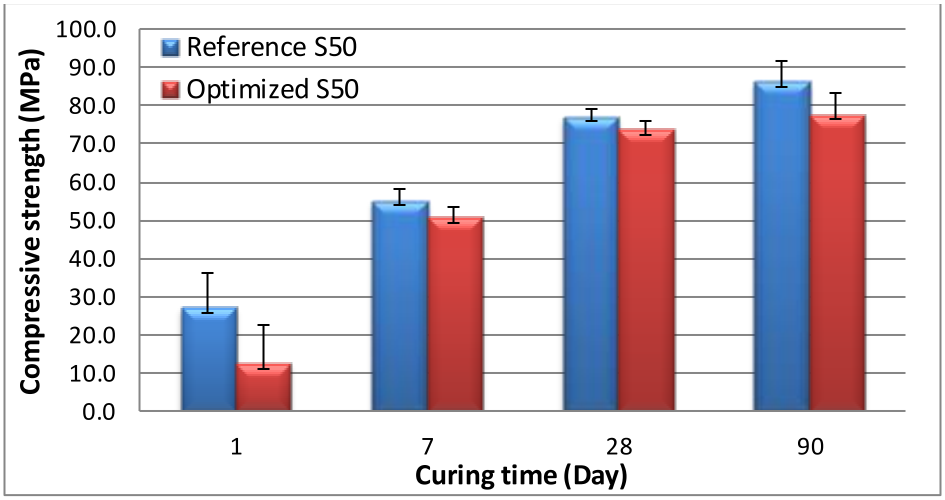

Figure 29: Compressive strength test results for reference and optimized mixture

3.3 Flexural strength

The flexural strength test setup is shown in Figure 30. The flexural strength of the mixture is 4.58 MPa at 28 days, with a standard deviation of 0.311 MPa (Figure 31).

Figure 30: Flexural strength test setup

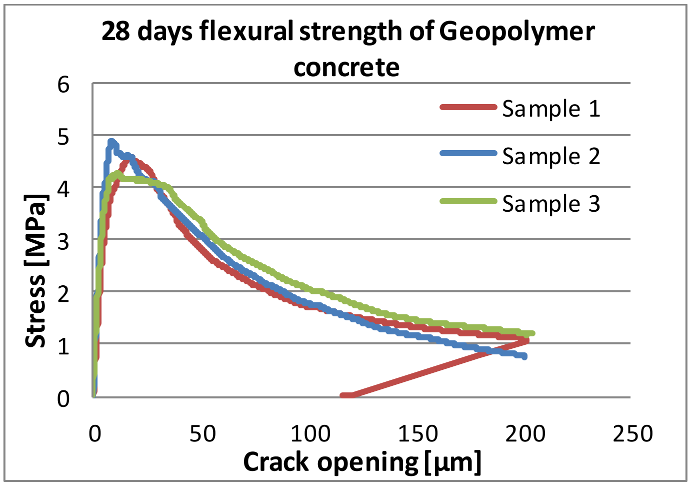

Figure 31: Flexural strength at 28 days

3.4 Elastic modulus and Poisson's ratio

The elastic modulus test set up is given in the Figure 32. The tests were done at curing age of 3, 7 and 28 days. Figure 33 shows that the elastic modulus increases over time. The elastic modulus of the optimized mixture at 28 days is 31.26 GPa. Comparing the research work of Criado, Aperador and Sobrados, the modulus of elasticity is between 30.51 and 23.56 GPa. Their research show that an increase in FA decreases of the modulus of elasticity, exhibiting a low ductility and toughness compared to 100% of slag binder. [2]

Figure 32: E-modulus test setup

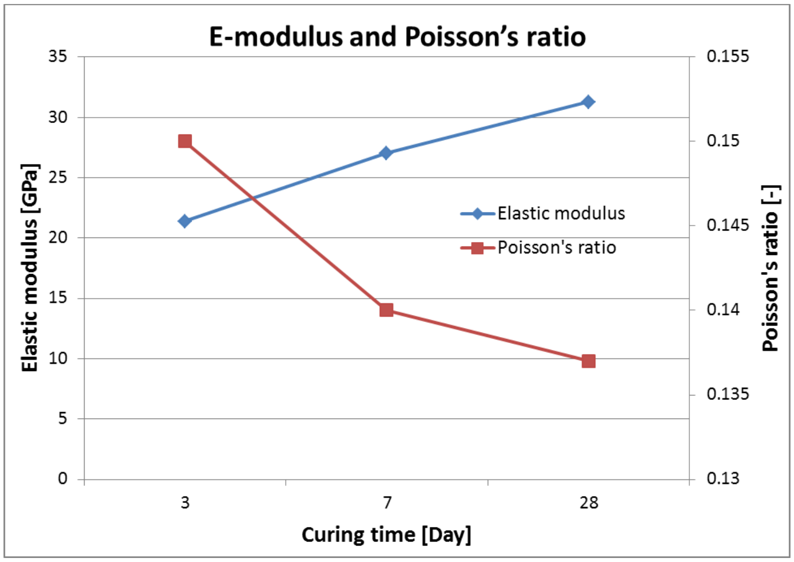

Figure 33: E-modulus and Poisson's ratio

3.5 Drying shrinkage test

After demoulding the specimens three prisms were kept unsealed in order to investigate moisture exchange with the surrounding environment, i.e. to measure drying shrinkage and weight loss. The prisms are placed in a climatized room, where the temperature (20ºC ± 2ºC) and relative humidity (50% ± 2%) are kept constant. The drying shrinkage test setup is shown in the Figure 34. The rest of the samples were placed in the fog room with 20°C and 99 % relative humidity and kept there until the curing age of 3, 7 and 28 days. Subsequently, they were exposed to the shrinkage test. The results of drying shrinkage and weight loss of optimized mixture are shown in Fig. 35- 38. It is clear that the drying shrinkage of the samples exposed to dry after 1 and 3 days curing is larger compared to 7 and 28 days cured samples. The weight loss is caused by the evaporation of free water. Comparing the drying shrinkage results shown in Figure 38 for geopolymer concrete with the results of CEM III/B concrete measured by Mors [16] the 69 days shrinkage strain of CEM III/B specimens cured for 28 days showed a factor of around 1.5 higher than that of geopolymer concrete.

This observation is also consistent with the finding reported of Sarathi Deb, Natha and Kumar Sarker. [17] Their findings show that higher slag content and a low sodium hydroxide ratio in the mixture decreases the drying shrinkage. Thus, drying shrinkage depends on the binder ratio but also on the composition and ratio of the activator.

The effect of drying shrinkage on the development of the surface cracking is shown in the Figure 39. The samples cured for 28 days prior to shrinkage testing did not exhibit cracking on the surface.

Figure 34: Drying shrinkage test setup

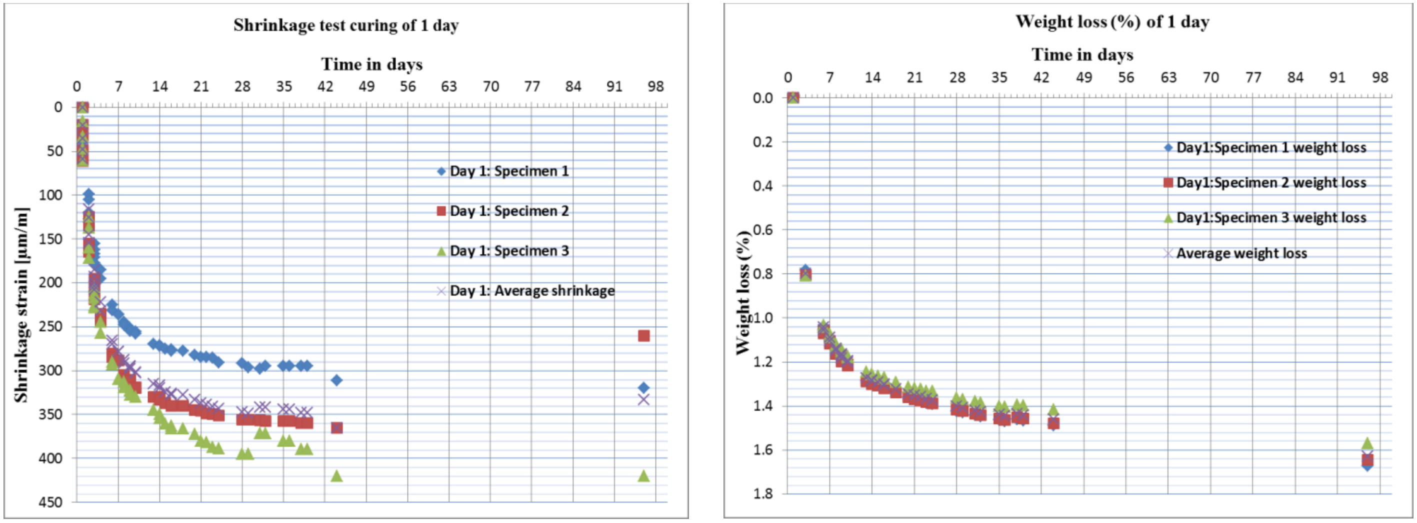

Figure 35: Drying shrinkage and weight loss for the samples exposed to drying after 1 day of curing

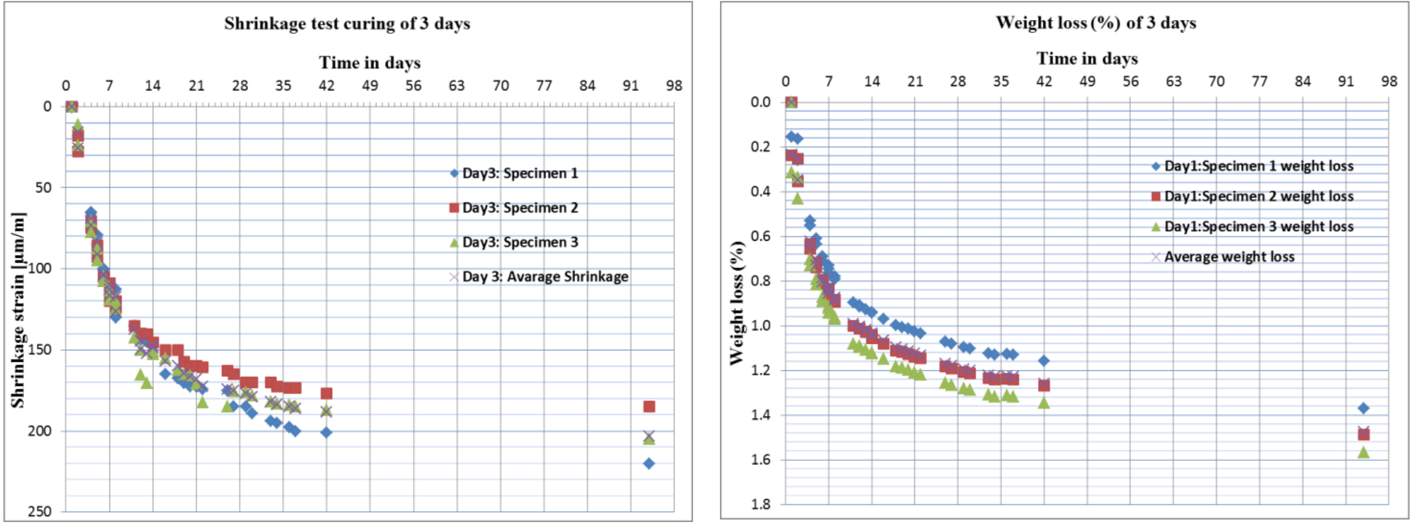

Figure 36: Drying shrinkage and weight loss for the samples exposed to drying after 3 days of curing

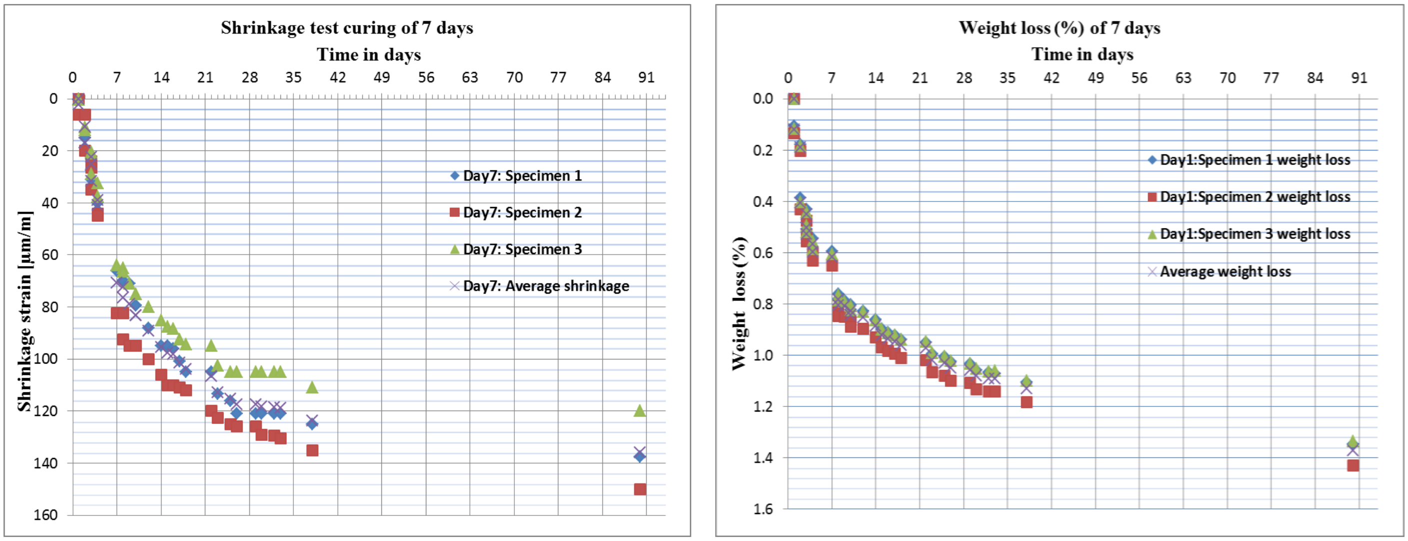

Figure 37: Drying shrinkage and weight loss for the samples exposed to drying after 7 days of curing

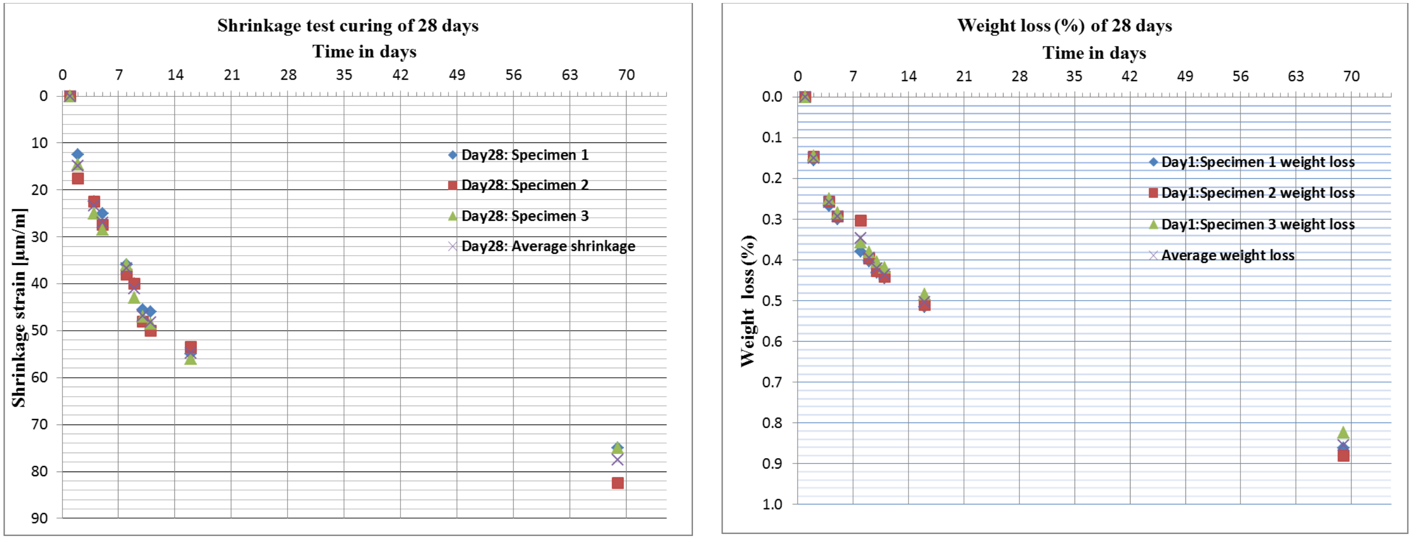

Figure 38: Drying shrinkage and weight loss for the samples exposed to drying after 28 days of curing

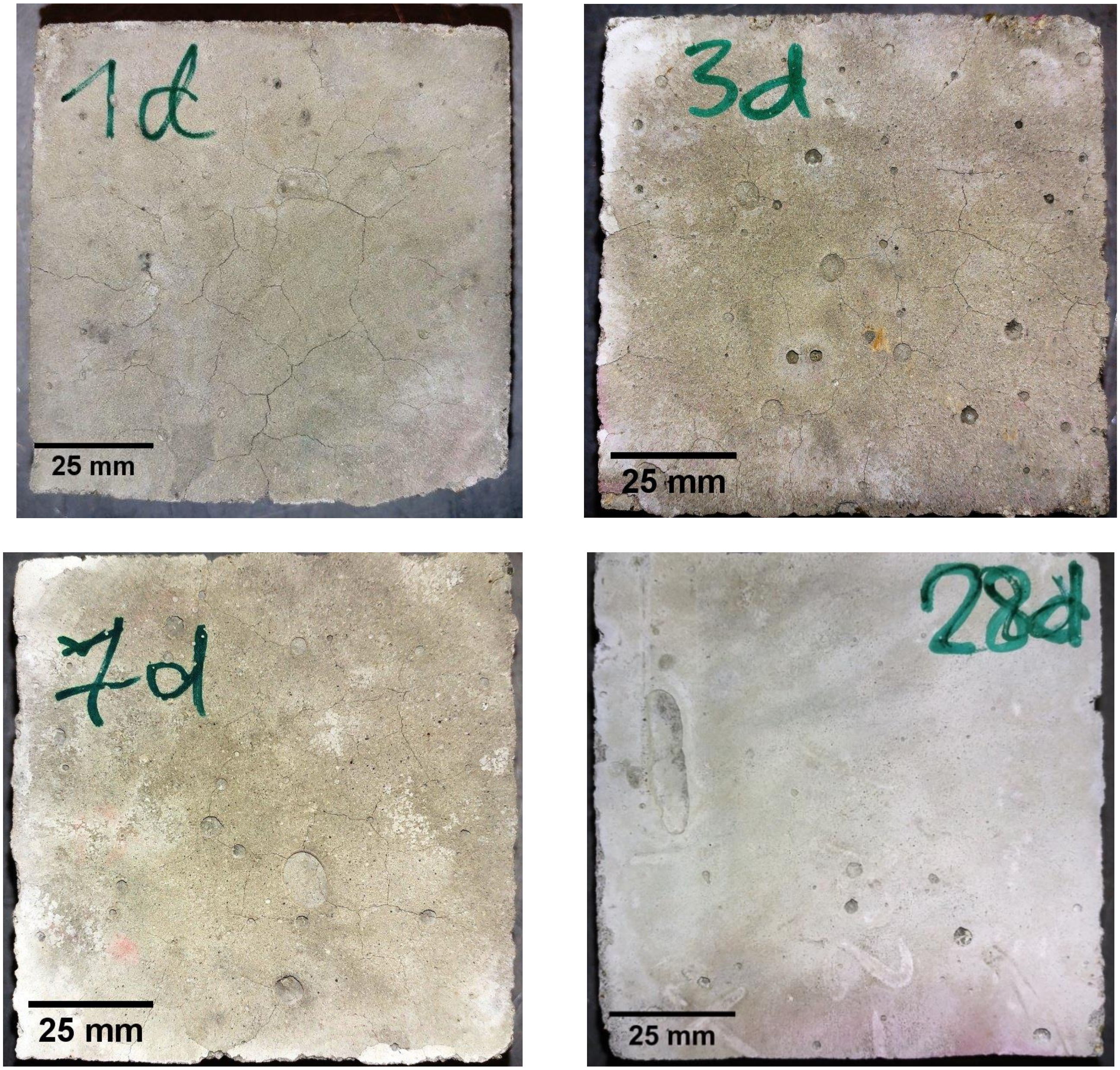

Figure 39: Development of the drying shrinkage cracks on the specimens surface cured in the fog room for 1, 3, 7, 28 days and subsequently exposed in the room with 20ºC ± 2ºC and relative humidity 50% ± 2%. The photos are made 90 days after first measurements.

3.6 Conductivity and Temperature development

The temperature and conductivity of the mixture was measured starting from time of mixing till 10 days after. The sensor results show that the highest temperature the mixture reached is 32°C after 28 hours of casting. Simultaneously, the conductivity was reduced from 10.5 Gmax/G to 4.5 Gmax/G. (Figure 40). The mixture started to reach a constant temperature (21.5° C) and conductivity 7 days after mixing. This indicates that most of the material is already hydrated.

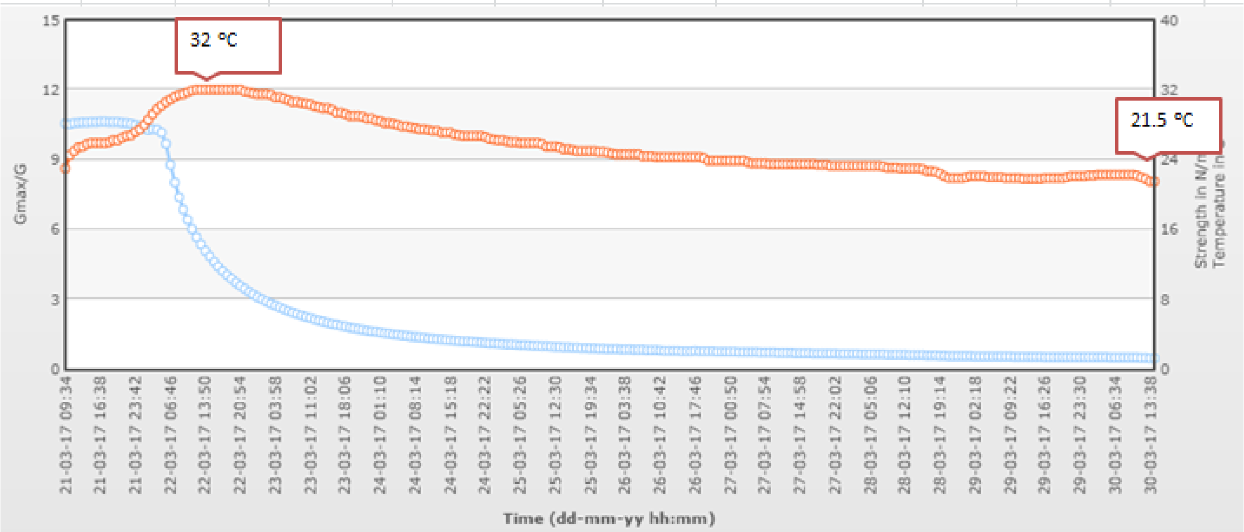

Figure 40: ConSensor 2.0 data: Temperature and conductivity

4. Conclusion

From the different experiments on pastes and concrete mixtures, it can be concluded that:

- Sodium hydroxide concentration and the ratio between sodium hydroxide and waterglass affect the hydration process; Parallel to that the bond between aggregates and the binder.
- A higher liquid to binder ratio (l/b) makes the mixture more workable and delays the setting time, but it also lowers the mechanical properties of the mixture depending on the curing conditions and curing time.
- A higher sodium hydroxide concentration in the mixture fastens the setting time and provides a higher mechanical strength of the cured specimens.
- The addition of CUGLA admixtures did not prolong the workability and setting time. However additions of 0.5% wt. barium chloride dehydrate retarder to the mixture prolonged the workability and setting time for 40 minutes. It is important to mention that adding more than 0.5% wt. of retarder can cause segregation of the aggregates.
- The study also shows that the use of barium chloride dehydrate retarder has not affected the compressive strength at 7, 28 and 90 days.
- The drying shrinkage results indicate that when shrinkage tests start from 28 days of curing, no any cracks were observed on the surface of the prisms, while at other ages the cracks were visible.
- It seems that geopolymer concrete is more sensitive to curing and drying conditions compared to the traditional concrete. From drying shrinkage measurements, the proper curing period of 28 days is recommended for the alkali-activated FA and BFS concrete for the structural applications.

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