Utilization of By-products for Concrete: Development of One-part Mixing of Fly Ash, GGBFS and Silica Fume AAM and Applicability of Paper Sludge Ash

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Abstract

OPC (ordinary Portland cement) is not an environmentally friendly construction material and it is a major contributor to global warming. AAM (alkali-activated material) which is mainly produced by aluminosilicate precursors and AA (alkaline activators) can be a substitute for the OPC due to its extraordinary properties such as high strength and durability. Moreover, AAM contains some by-products such as fly ash and slag, and compare to the OPC lesser amount of CO2 is emitted for their production. Therefore, they are adopted as environmentally friendly materials. Corrosive and viscosity effects of alkaline materials cause difficulty in handling the materials by common people and make it tough to cast them on site. Therefore, they are made as precast elements which increases the cost of their production. To overcome the problem, a one-part mixing method is proposed by some researchers but they found that the quality of AAM made by the one-part mixing method is lower than the one made by the two-part mixing method. Furthermore, low-calcium fly ash-based AAM has some problems such as a long setting time and low compressive strength when cured at ambient temperature curing. This research aimed to solve the aforementioned problems and develop a one-part mixing method of AAM.

The properties of one-part mixed AAM mortar were characterized. It was found that the quality of the AAM made by the aforementioned method was much lower than the conventional and OPC mortar. The compressive strength of the AAM was increased with an increase in slag amount but the flowability of the AAM was much lower due to the quick setting of the fresh mortar. The higher reactivity of the slag caused the problem. Therefore, sucrose was added to the mortar to delay the setting time. Sucrose increased the setting time and improved the flowability, compressive strength, and drying shrinkage of the AAM.

The flow and compressive strength properties of AAM made by one-part and two-part mixing methods were tested and compared. It was found that the AAM made by the two-part mixing method had much better flowability and compressive strength than the one-part mixed AAM. Therefore, the solubility test of solid alkaline activators was conducted and it was revealed that sodium metasilicate couldn’t be dissolved well in a solvent at a temperature around 25°C. So, it was concluded that when 32% sodium metasilicate is used for making AAM using one-part mixing method, water or a solvent need to have a temperature of around 40°C. In addition, the properties of AAM made by sodium metasilicate were investigated. The AA solution made by sodium metasilicate was smooth and fluent but it was susceptible to a lower temperature than 30°C as a crystallization of the solution could easily occur. Hot mixing conditions played a positive role in increasing the flowability of the mortars. Compressive strength of 40MPa and flexural strength of 6.1 MPa were achieved by AAM using granular sodium metasilicate.

As mentioned before that low-calcium fly ash-based AAM has a much longer initial and final setting time and low compressive strength when cured at ambient temperature conditions. So, in this experiment, the influence of the type and concentration of sodium silicate was studied on the setting time, flowability, and compressive strength of low-calcium fly ash-based AAM. It was found that the decreased concentration of sodium disilicate had a considerable positive effect on the setting time and compressive strength of AAM cured at ambient temperature.

In addition, this research also aimed to study the influence of recycled waste materials such as recycled coarse aggregate produced by pulsed power technology, paper sludge ash and silica fume on properties of ordinary Portland cement concrete. It was found that both silica fume and paper sludge ash showed their pozzolanic reactivity and improved some of the properties such as compressive strength of both conventional and recycled concrete. furthermore, high-quality recycled aggregate was produced by pulsed power technology and using the aggregate didn't have a negative effect on the properties of concrete.

Keywords: Alkali-activated material, One-part mixing, Alkaline activators, Fly ash, Slag, Solubility, Recycled Aggregate, Paper sludge ash.

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Chapter 1

Introduction

1.1 Background

Portland cement (PC) concrete has some remarkable properties such as the ability to cast in different shapes and sizes, high compressive strength, and reasonable cost. Moreover, its reinforcement by steel makes it an extraordinary construction material. According to these facts, Portland cement concrete is the most commonly used construction material in the world. Annual global production of ordinary Portland cement (OPC) reaches 4 billion tons [1]. But according to the statistics OPC is responsible for the emission of 8% CO_2 of the globe [2]. Therefore, they are not environmentally friendly materials and one of the major causes of global warming which is a serious issue nowadays.

Moreover, waste materials such as concrete debris, waste paper and by-products of energy production power plants such as coal ash have a negative impact on the environment because the majority of them are disposed of in landfills. Therefore, recycling waste materials not only has environmental benefits but, in some cases, it has economic advantages as well.

When aluminum silicate materials such as fly ash and slag react with an alkali source, it produces a material that has binding properties (3,4). These kinds of materials are called Geopolymer or alkali-activated materials (AAM). Compared to OPC, AAM is a more environmentally friendly material because they emit a much lower amount of CO_2 to the atmosphere [5, 6]. Moreover, they contain some by-products as their primary constituents, such as fly ash and slags [7].

Besides being environmentally friendly materials, AAMs have some other advantages, such as obtaining high early strength and superior mechanical properties [8,9]. They have better resistance to fire, acid attack, and alkali-silica reaction [10, 11,12].

AAM and geopolymer are made conventionally by the reaction of aluminosilicate precursors such as fly ash and slag, and aqueous alkaline solutions such as hydroxides, silicate and carbonate. This method of making the materials is called the two-part mixing method [13, 14, 15]. Handling and working with corrosive and viscous alkaline solutions cause difficulty in its application, and there is a need for special skill and caution for working with it. This limits the material's production in factories for precast purpose (16-18).

One-part mixing method or dry mixing method is being studied by some researchers [16, 17, 18] in which aluminosilicate precursors and alkali materials are used in solid-state, and water is just added for their reaction purpose. Cast-in situ or cast-in-place, and secure application of the materials are the main aims of studying this method [16-18].

Some researchers reported [19, 20] that the AAM made by the one-part mixing method had lower mechanical strength than the one made by the two-part mixing method. Moreover, Ouyang et al [19] found some undissolved particles of sodium metasilicate pentahydrate by studying the microstructure of the samples. This may negatively influence the properties of the product. Basically, the alkaline solution is the main part of geopolymer and AAM for geopolymerization and activation of the aluminosilicate precursors to make the binder [21]. It is essential that the solid alkali activators dissolve well to obtain the aqueous solution during the mixing procedure. Hence, modification of the mixing method is required by studying the alkaline materials' solubility in different solvent temperatures.

One of the aims of this study is to identify the existing problem in the one-part mixing method, modify it to equalize the quality of the one-part mixed AAM to the one made by a two-part mixing method.

Low calcium fly ash-based AAM has some extraordinary advantages. They possess geopolymeric characteristics such as low shrinkage and high fire resistance [1]. But they have much higher setting times, and it is due to their slow reactivity. Therefore, they are cured at higher temperatures [22,23]. Incorporating the slag with fly ash improves the reactivity of the aluminosilicate precursors that result in hardening of the samples at ambient temperature and modify some other properties such as compressive strength, flexural strength, and density of concrete [24]. As the slag is very active and increases the reactivity and hydration of the materials [25], this causes the materials to emit a higher amount of heat during the reaction process than fly ash-based AAMs [26]. Therefore, the drying shrinkage of alkali-activated materials with slag is much higher than the other types [24, 27].

The retarding behavior of sucrose on ordinary Portland cement materials is reported by some researchers, and they also concluded that sucrose improves the microstructure of ordinary Portland cement concrete [28,29]. Therefore, the drying shrinkage of the slag-based alkali-activated materials may be amended by using sucrose. Moreover, to better understand the retarding influence of sucrose on alkali-activated materials, the setting time test needs to be conducted.

As mentioned before, low calcium fly ash-based geopolymer or the alkali-activated material has a longer setting time when cured at ambient temperature conditions, but they have relatively low drying shrinkage compared to the slag-based AAM [23]. The longer setting time, make it almost impossible to be used and cast at the site of the construction. The viscosity of the water glass and the rheological problem of traditional geopolymer and AAM [30,31,32] are other problems that have a negative influence on the applicability of the material. However, different methods need to be applied such as preheating of the materials, changing the type and concentration of the alkaline solution to overcome both the setting time and rheological problems. Therefore, this research also aims to solve the problem related to the low-calcium-based AAM and make the material to be cured at ambient temperature conditions and appropriate for use in the structural field.

As stated above, materials such as concrete debris and waste paper have a negative influence on the environment. Modification of this kind of materials and using them in construction can reduce their disposal in landfills. Therefore, in this study, the effect of high-quality recycled aggregate produced by pulsed power technology and paper sludge ash as a pozzolan on some of the properties of OPC concrete will be investigated.

1.2 Objectives

a) Properties characterization of AAM using one-part mixing method or dry mixing method.

b) Evaluation of the retardation effect of sucrose on AAM.

c) Comparison of the properties of AAM made by the one-part and two-part mixing method.

d) Solubility test of sodium metasilicate pentahydrate ($Na_2SiO_3.5H_2O$) by a solvent with different temperatures.

e) Characterization of an aqueous solution made by sodium hydroxide and sodium metasilicate pentahydrate.

f) Evaluation of the effect of sodium silicate concentration and modulus, and the temperature of the mixing materials on properties of low-calcium fly ash-based AAM cured at ambient temperature.

g) Study the influence of the paper sludge ash, silica fume and recycled aggregate on properties such as strength and AE behaviour of OPC concrete.

1.3 Thesis Outline

Chapter 1 presents the introduction section of this thesis, which is consists of the background, objectives, and outline of the thesis. The chapter illustrates environmental issues created by OPC concrete and the environmental and structural importance of AAM and geopolymer as an alternative for OPC. Moreover, problems associated with the application of the alkali-activated materials and the need for this study to solve the problem were discussed in this section.

Chapter 2 is an introduction to geopolymer and alkali-activated materials, and their constituent materials: aluminosilicate precursor and alkaline materials. This chapter will also explain the mechanism of geopolymerization, dissolution of the precursors by the alkaline materials, and consolidation process of the product.

Chapter 3 discusses the properties of the AAM made by the one-part mixing method. The influence of different ratios of aluminosilicate precursors such as fly ash, the slag and silica fume, the concentration of NaOH and Na_2SiO_3: NaOH ratio on the flowability, mechanical strength, and drying shrinkage properties of the materials were discussed here. Moreover, the effect of sucrose on the properties of the AAM especially drying shrinkage explained in this chapter here.

Chapter 4 presents the retardation behaviour of sucrose. Moreover, the admixture's influence of the flowability, compressive strength and drying shrinkage is discussed here.

Chapter 5 of the thesis explains the solubility problem of sodium silicate in the one-part mixing method of alkali-activated materials. The solubility test of sodium metasilicate pentahydrate (Na2SiO3.5H2O) was conducted to reveal the optimum temperature of a solvent for totally dissolving the sodium metasilicate. Moreover, characterization of AAM made by the Na2SiO3.5H2O and NaOH solution is discussed.

Chapter 6 describes the influence of sodium silicate modulus and concentration on setting time, flowability and compressive strength of low-calcium fly ash-based AAM cured ambient (around 20°C) and in an incubator at 45°C. In addition to this, the influence of the raw material temperature, and sucrose on the aforementioned properties of the material are also presented in this chapter.

Chapter 7 discusses the properties of OPC concrete using pulsed powered recycled aggregate, waste paper sludge ash and micro-silica. Those properties are flowability, mechanical strength and acoustic emission behaviour.

Chapter 8 summarizes all the chapters in this dissertation.

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Chapter 2

A Review on Alkali-activated Materials

2.1 History

Alkali-activated material (AAM) was first reported by H. Kühl. He explained that when aluminosilicate (blast furnace slag) reacts with an alkali source produces a material that has cementitious and binding properties [1]. After that, Purdon [2] published his work regarding the material in 1940. He used blast furnace slag (BFS) and sodium hydroxide (NaOH) as an alkali activator. According to him, the process was in two steps, first, the liberation of silica aluminum and calcium hydroxide happens followed by the formation of silica and alumina hydrates. Later in 1950, the material was commercialized in Belgium and several buildings were made by the AAM [3].

In the mid-1950, Glukhovsky [4] developed the AAM and used low-calcium or calcium-free aluminosilicate precursors. These precursors were activated by alkaline solutions. He named the binder “soil cement” and the concrete “soil silicate”. The binder was developed at a time when there was a shortage of Portland cement and need for an alternative in the former Soviet Union. The soil-cement was used widely in construction fields such as infrastructure and commercial fields [5]. Moreover, the AAM was commercialized and used in Northern Europe and China [6,7]. Glukhovsky [10] also investigated the alkali-activated blast furnace slag and described the hydrated products as calcium silicate hydrates and calcium and sodium aluminosilicate, considering that when clay mineral is activated by an alkali, converts to aluminum silicate hydrate(zeolite). He [11] categorized the alkaline activator into the 6 groups, where M is an alkali ion:

1. Alkalis, MOH
2. Weak acid salt, M_2CO_3, M_3PO_4, MF
3. Silicate, M_2O
4. Aluminates, $M_2O.nAl_2O_3$.
5. Aluminosilicate, $M_2O.Al_2O_3$. (2-6) SiO_2.
6. Strong acid salts, M_2SO_4.

Davidovits [8] from France, developed the metakaolin AAM and started to commercialize the material as a fire-resistant product. His effort led to the commercialization of a high-early strength hybrid Portland/ alkali-activated concrete named Pyrament in North America [8]. Wastiels et al. were the first to show the activation of fly ash by the alkaline solution. A binder from the activation of fly ash and blast furnace slag (BFS) by an alkali was discovered and commercialized in the 1990s. This material was used as an acid resistance for pipe production [9]. Since then, studies on AAM have grown dramatically. This is to modify the material and to increase their applicability so as to be an alternative for Portland cement [12].

2.2 Reaction mechanism

The reaction mechanism of alkali-activated materials has not been fully understood till now. But researchers agree that the mechanism is much dependent on the prime materials such as aluminosilicate precursors and the activator solutions [13]. According to Glukhovsky [10], the mechanism is based on a destruction-condensation reaction. As first the aluminosilicate materials are destructed by the high PH of the alkaline solution, the destructed materials are transformed in a colloid phase, and then the destructed product is accumulated and interaction happens between them to form a condensed structure. So, the reaction mechanism occurs in three-stage of destruction, accumulation and condensation.

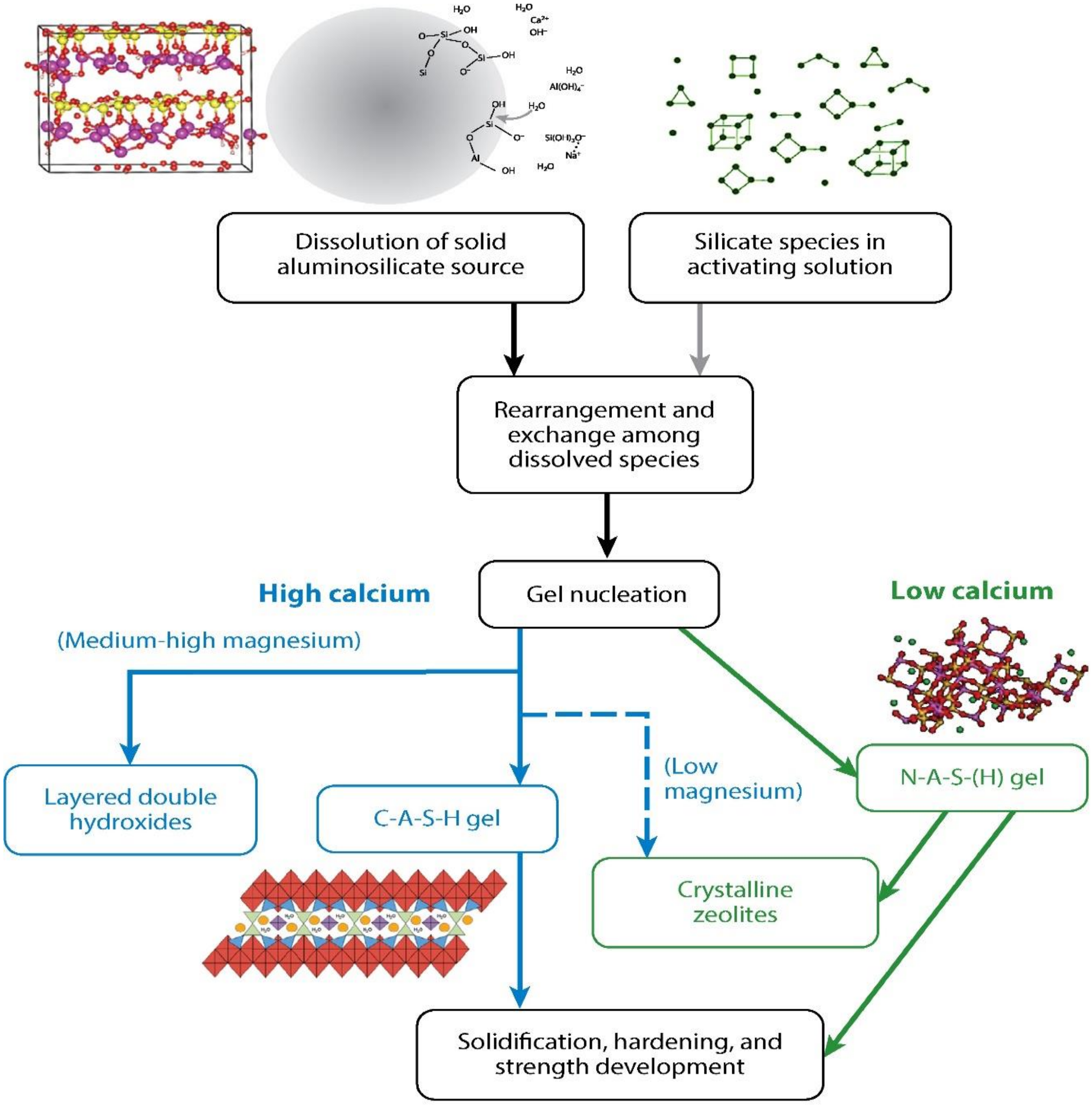
Other authors [14,15] also agree with the proposed stage of the reaction mechanism by Glukhovsky. As all stage occurs simultaneously, it makes it difficult to precisely study the mechanism [16]. Alonso and Palomo [17] studied the heat evolution of metakaolin-based alkali-activated materials in which NaOH was used as an alkaline material. They found several phase peaks. One related to the dissolution of metakaolin, followed by the induction stage that had low heat release, and the last peak belonged to the final structure formation of the AAM. Jaarsveld et al. [18] concluded that the formation of geopolymer follows the same reaction procedure of zeolite: dissolution of the prime materials (aluminosilicate precursors) to the hydroxide ions, the orientation of the separated ions, and condensation of the structure in the polymeric system.

The difference between the reaction mechanism of OPC binder and AAM is that OPC is dissolved in water with an initial PH of 0, however, the alkalinity of water is reached around 13 when the dissolution is proceeding [5]. But in the case of AAM, the aluminosilicate precursors cannot be dissolved in neutral water but need a solution with high alkalinity to dissolve the prime materials [8,11,16]. Soluble silicates are often added to the alkaline solution to get the final product with good strength and durability, high alkalinity of the solution prevents the silica reaction in the mixture thus the setting is delayed but when the pH of the solution decreases, coagulating and polymerization occur [20].

Garcia-Lodeiro et.al [21] characterized the reaction mechanism of low and high calcium-based AAMs. According to them, the reaction procedure for both types of alkali-activated materials consist of three stages. first, dissolution of Si-O-Si, Al-O-Al, and Al-O-Si. This stage is called the nucleation stage. Followed by the polycondensation or coagulation stage, in which coagulated structure between dissolved composition from the precursor form, and at the last stage, C-A-S-H (calcium aluminum silicate hydrate) is produced for a high calcium-based system. In which calcium decrease the setting time of the product and provide higher early strength. But in the case of the low calcium system, the inorganic hardened and 3-dimensional polymer structure is built by the development of the crystals in the final stage of the reaction process. The final product is N-A-S-H (sodium aluminum silicate hydrate) gel which has a higher setting time and often requires thermal curing to develop strength.

For the activation of the high calcium-based aluminosilicate precursors, a solution with moderate alkalinity is required to obtain a calcium silicate hydrates-like phase as a reaction product. But for the dissolving or activating low-calcium and calcium-free prime materials, moderated or high alkaline activating solution is required to produce a zeolite-like phase material [16].

John L. Provis and Susan A. Bernal [21] summarized the reaction process of low and high calcium-model;



Provis JL, Bernal SA. 2014.
Annu. Rev. Mater. Res. 44:299–327

Figure 2.1 Reaction mechanism and final product of AAM consisting of high and low calcium-based aluminosilicate precursors [21]

2.3 Geopolymer as a subset of alkali-activated materials

Alkali activated material is widely categorized: as any binders produced by the reaction of an alkaline salt with a silicate material [22, 23]. The silicate materials can be calcium silicate or aluminosilicate precursors such as fly ash and blast furnace slag. The alkaline activators consist of alkali hydroxide, silicates carbonate, sulfates, aluminates, or any other materials that can accelerate the dissolution of the prime materials such as aluminosilicate precursors [24].

Inorganic polymers [25] belong to the alkali-activated materials group. They are formed through a disordered silicate network. For their formation compare to CaO and Na2O, a high amount of silica or alumina is required. BFS based alkali-activated material, combined fly ash and slag and aluminosilicate-based binders are all can make inorganic polymers. As alkaline activators, silicates, hydroxides or, carbonate can activate slag and make it an inorganic polymer. But sulfate can't be used for making the binder [24].

Geopolymers [8] belong to inorganic polymer, a subset of the alkali-activated material. Geopolymers are formed by aluminosilicate precursor and are highly coordinated and make probably a Q4 network structure (a network which contains 4 atoms of Al in each repeating subunit) [26]. The calcium content is usually low for making geopolymer that possesses a zeolitic network structure [27]. The alkaline activators in such kinds of AAM are hydroxides and silicates [28]. Low calcium-based fly ash and calcined clay are usually used as prime materials for making geopolymer binders.

van Deventer, J.S.J., Provis, J.L., Duxson, P. et.al [24] describe each type of the binders such as alkali-activated material and geopolymer in the following graph.

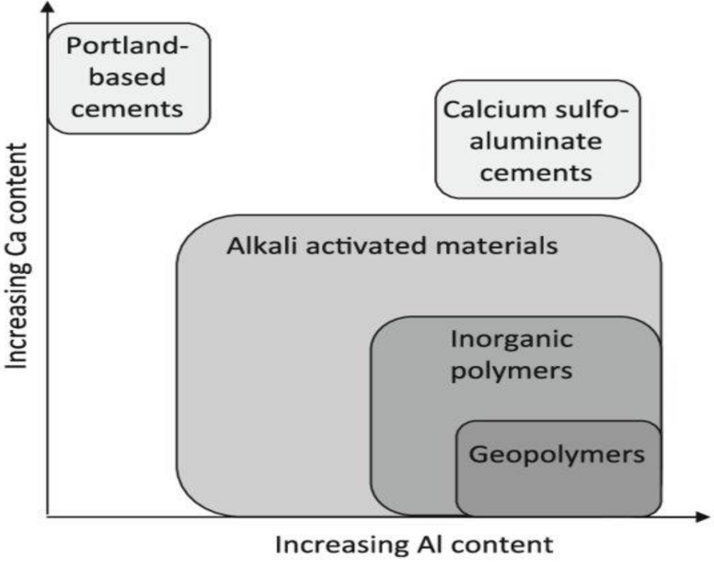


Figure 2.2 AAM and its subsets according to Ca and Al contents [24]

2.4 Alkali-activated materials constituents

Alkali-activated materials are mainly consisting of aluminosilicate precursors and alkaline activators.

2.4.1 Aluminosilicate precursors

Aluminosilicate precursors are the prime materials of AAM [10]. They are fly ash, GGBFS, metakaolin, rice husk ash, and other materials which are rich in silica and alumina. They are dissolved by alkaline activators so as to rearrange and become reactive to produce gel [21]. Since the invention of the AAM, many kinds of aluminosilicate precursors have been introduced to the field.

Fly ash, GGBFS, and metakaolin are commonly used as aluminosilicate precursors [29]. Moreover, silica sources, such as rice husk ash [30, 31], silica fume [32], and some others [33] are occasionally used with the precursors in the AAM.

2.4.1.1 Fly ash

Fly ash which is also called coal ash or flue ash is a by-product of coal-based thermal power plants. They are fine particles that exhaust together with the flue gas during the combustion of coal. They are acquired by means of electrostatic precipitators. The ashes which fall under the combustion chamber are called bottom ash. Compare to the fly ash, they are coarser and heavier. Fly ash that is utilized in AAM has a glassy, hollow, spherical shape, and are mainly consisted of SiO2, Al2O3, Fe2O3 and CaO [34]. The particle size of the fly ash ranges from 1 to 20 µm. The majority of the fly ash is disposed of in landfills [35]. However, some countries such as the USA recycle about 43% of waste material [36]. In Portland cement, fly ash is not just used as a pozzolan but is also used to modify the rheology of the fresh mortar and concrete and prevent alkali-aggregate reaction [37, 38].

Commonly fly ash is divided into two types, low-calcium fly ash or class F and high-calcium fly ash or class C [34]. Chemical composition of each type is illustrated in Table 1. Class F type of fly ash is more used due to its availability and better performance such as improvement of workability and shrinkage [39]. The other type is less available and has unstable properties, therefore, it is not often used in cementitious material. One of the major drawbacks related to class F or low-calcium fly ash is its slow reactivity that causes a delay in the consolidation of the material. To enhance the reaction and intensify the hardening process, thermal curing or incorporation with another High-Ca component is recommended [40,41].

Fly ash contains a significant amount of silica (SiO2) and alumina (Al2O3), especially the F class. Both of the materials have an influence on the properties of fly ash-based AAM. De Silva et.al reported that SiO2 content in the fly increases the setting time of the paste while alumina Al2O3 decreases it [42]. However, the silica content in the fly ash tends to decrease the porosity and modify the microstructure of AAM and therefore, the strength of the material is increased [42].

Ferrite oxide is another component of fly ash. This material mainly specifies the color of the fly ash. Moreover, it also increases the specific gravity of the final product [43]. However, Jimenez and Palomo state that the exact behavior of iron oxide on AAM is not well understood [44].

Both MgO and SO3 are present in low amounts in AAM. They are allowed at a maximum range of 5% [45,46]. MgO has an influence on increasing the pH and accelerating the setting of the AAM [47].

LOI or loss of ignition is the residue of the unburnt coal in the fly ash. The increased amount of unburnt coal has a higher demand for water, therefore, the compressive strength and microstructure of the AAM is negatively influenced [48]. Because of this, ASTM recommends that the amount of the LOI not to be exceeded over 6% by the weight of the fly ash.

Table 2.1 Chemical composition of high and low-calcium fly ash [49]

Compound	**Class F (%)**	**Class C (%)**
SiO_2	47.2-54	18-24.8
Al_2O_3	27.7-34.9	12.1-14.9
Fe_2O_3	3.6-11.5	6.3-7.8
CaO	1.3-4.1	13.9-49
Free lime content	0.1	18-25
MgO	1.4-2.5	1.9-2.8
SO_3	0.1-0.9	5.5-9.1
Na_2O	0.2-1.6	0.5-2
K_2O	0.7-5.7	1-3

2.4.1.2 Ground granulated blast-furnace slag

Ground granulated blast-furnace slag or GGBFS is another by-product that can be used as an aluminosilicate precursor in alkali-activated material. This material is produced by the grinding of molten slag that is obtained from the steel-making factory. The term slag is also used for GGBFS in some countries [50]. GGBFS or slag is a cementitious material and possesses a high amount of Ca that helps in modifying the mechanical strength and durability of a product [10,51]. Moreover, GGBFS also contains a significant amount of silica and alumina in its content that makes it suitable for use as cementitious material [52]. chemical composition of slag is depending on the type of steel and the manufacturing process [53]

Table 2.2 Chemical composition of GGBFS [53]

SiO_2	**CaO**	**Al_2O_3**	**MgO**	**Fe_2O_3**	**S**	**Cr_2O_3**	**Na_2O +K_2O**	**MnO_2**	**P_2O_5**	**TiO_2**
27-40 %	30-50%	5-33%	1-2.1%	<1%	<3%	0.003-0.007%	1-3%	<2%	0.02-0.09%	<3%

The particle size of the GGBFS or slag play important role in its reactivity. Particle size below 2 μm is considered to have good reactivity while the particles with a higher size than 20 μm are slow in reaction [54]. Therefore, for the better performance of GGBFS in the AAM system, the specific surface of the material needs to be in the range of 400 m^2/kg to 600 m2/kg [53].

Using GGBFS in alkali-activated materials has some prominent advantages such as high early strength and durability [55], high resistance against fire, and little environmental effect [56]. But there are some disadvantages associated with the use of the material including the formation of cracks, high shrinkage, and volumetric instability [57].

2.4.1.3 Metakaolin

Metakaolin is produced by the hydroxylation of kaolinite Si_2O_5, Al (OH)4 which occurs at around 750°C. Metakaolin has a significant amount of silica and alumina in the range of around 44.4 to 73% and 14.5 to 47.43 respectively, the particle size of metakaolin varies from 1.20 to 38 μm and surface area of 2.16 to 22 m2/g [58]. Metakaolin is effective when used with low calcium-based AAM such as fly ash Class F that provides an increase in the polycondensation rate to make denser nano-and micro-structure, that cause improvement in the mechanical properties of the AAM [59].

2.4.2 Alkaline Activators

Alkaline activators are one of the main parts of alkali-activated materials. They are essential in dissolving aluminosilicate sources and produce a binder or cementitious material. PH of the alkaline activator plays important role in the dissolution process, and a PH value of higher than 11.5 is required for this purpose, for slag-based AAM, the value is around 13-13.6 [61]. Alkali hydroxide and silicate generated higher alkalinity while sulfate and carbonate produce moderate PH values [61]. Sodium hydroxide and sodium silicate are the two prominent activators that are more available and usually used in making AAM [60]. However, sodium hydroxide creates higher alkalinity than sodium silicate, but sodium silicate contributes in developing the mechanical strength because they provide additional silica to the (C-S-H) gel [16]

2.4.2.1 Sodium silicate

Sodium silicate is belonging to the family of soluble silicate [34]. Soluble silicates are formed by alkali metal oxide M2O, silica, and water. M2O can be Na2O, K2O, or Li2O. The general formula of the soluble silicate is xSiO2:M2O. zH2O, x is the degree of polymerization and z is the number of water molecules [34].

According to the molar ratio (MR) (SiO_2:Na_2O), sodium silicate falls into the following categories.

Table 2.3 Molar ratio for commercial silicates [34]

NO.	Name of the silicate	Formula	MR (SiO_2:Na_2O)
1	Sodium orthosilicate	Na_4SiO_4	0.5
2	Sodium metasilicate	Na_2SiO_3	1.0
3	Sodium disilicate	$Na_2Si_2O_5$	2
4	Sodium polysilicate	$Na_2O.3.3SiO_2$	3.3

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Chapter 3

Characterization of the Alkali-activated materials Made by the One-part mixing Method

3.1 Introduction

Geopolymer and the Alkali-Activated Material (AAM) possess some excellent characteristics [1-4]. They are traditionally produced by a two-part mixing method, in which aluminosilicate precursors and alkaline aqueous solution are mixed [5-7]. But due to some drawbacks such as the corrosive effect of alkaline solution and workability problems related to the viscosity of alkaline materials especially water glass or sodium silicate solution, cause difficulty in the applicability of the material, and this cause making of the AAM to be just related to the expert people of this field [8].

Therefore, the one-part mixing method has been studied by some researchers to make ease in application of the AAM, in which aluminosilicate precursors and alkali materials are used in solid-state, and water is just added for their reaction purpose [8,9,10]. This is the same as making ordinary Portland cement materials. But some found the quality of the AAM made by the one-part mixing method to be lower than the one made by the traditional or conventional method [11,12].

The traditional AAM has been well characterized by researchers since its invention. The influence of many factors such as the mix proportion of aluminosilicate precursors, NaOH molarity, Na_2SiO_3: NaOH ratio and others on their properties are well studied. For the better characterization of the AAM made by the one-part mixing method, it's also necessary to study the effect of the aforementioned factors on the properties such as flowability and mechanical strength of the materials.

Aluminosilicate precursors are the major component of aluminosilicate materials. Their reaction with the alkaline materials results in making a cementitious material. Fly ash and GGBFS or slag are the two prominent aluminosilicate precursors [13]. Each of them has a significant influence on the properties of AAM. Low calcium fly ash improves some properties of AAM such as workability [14] and provides volumetric stability [15-17], but their setting needs a longer time [18]. Incorporation of slag with fly ash not only decrease the setting time [14] but can also improve the strength [14;19-20], and durability [21] of the material but shrinkage of the AAM is increased with the increment of slag in the mixture [22]. Therefore, an optimum mix proportion is needed to be considered to overcome the aforementioned problem. Besides fly ash and slag, silica fume is also used to modify the properties of the AAM [19].

Alkaline activators (AA) have a key role in making AAM as they react with the precursor and dissolve their compounds into smaller molecules. Sodium hydroxide or NaOH is one of the prominent and frequently used AA, its concentration or molarity influence has been studied on the traditional AAM. Workability, mechanical strength and shrinkage are increased with the increment of the AA concentration [23], but some research shows that workability of the AAM is decreased with the higher molarity of AA [24].

Sodium silicate is used together with NaOH as an alkaline material. They provide extra SiO_2 to the AAM and improve some properties of the AAM. Therefore, the Na_2SiO_3: NaOH ratio has some significant influence on the properties of the AAM. A study [25] concluded that the compressive strength is improved with the increase in the ratio, they found the maximum compressive strength at the ratio of 2.5, but after that, the strength was declining. Nur Hamzah et al found the same result [26].

To study the effect of the production method and to compare the properties of AAM made by the one-part mixing method and the conventional AAM which is made by the two-part mixing method, the result of the flowability, the 28-day compressive and flexural strength, and drying shrinkage was taken from the research conducted by the Yuyun [27].

In this study, all the influence of all aforementioned factors will be evaluated on AAM made by the one-part mixing method.

3.2 Objectives

The objective of the chapter is to study the influence of the following factors on flowability, compressive and flexural strength, and shrinkage of the AAM made by the one-part mixing method;

- Aluminosilicate precursors mix proportion
- Molarity of NaOH
- Na_2SiO_3: NaOH
- Production method

3.3 Experiment

3.3.1 Materials

a) Fly ash

Two types of fly ash were used in this study, fly ash type F and PFBC type fly ash. Fly ash type F conforms to the JIS standard called fly ash A 6201. This type of fly ash which is also called low calcium fly ash was achieved from Kyushu Electric Power Co., Ltd. The other type which is called PFBC type fly ash was received from the Kyushu Electric Power Kanda Power Plant. The difference between both types of fly ash is in their composition and burning temperature. The PFBC fly ash burns at a lower temperature than the fly ash type F, and PFBC fly ash contain more CaO than the other type. Table 3.1 shows the composition and other specifications of both types of fly ash.

b) Ground granulated blast furnace slag

The specific surface area of the slag was 4000-4120 cm2 /g. The composition of the Ground Granulated Blast Furnace Slag (GGBS) or slag is shown in Table 3.2.

c) Silica fume

Silica fume conforming JIS A 6207 with a density of 2.22 g/cm^3 was used in this study. The particle shape of the material was spherical.

d) Ordinary Portland Cement (OPC)

Ordinary Portland cement was not used in an alkali-activated material but was used for comparison purposes.

e) Standardized sand

Standardized sand conforming to the JIS R5201 standard was used as a fine aggregate.

Table 3.1 Specific gravity (S.G.), the chemical composition of materials in weight percentage (wt. %) by XRF, and chemical analysis of standardized sand.

Materials	Chemical composition (% weight)							SG(g/cc)
	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	H_2O	K_2O	
Fly ash type F	55.19	25.35	7.57	4.06				2.33
PFBC	34.2							2.64
Slag	33.8	13.4	0.7	41.7				2.91
Micro-silica	93.67	0.83	1.3	0.31	0.4			2.22
OPC	17.9	4.2	3.4	69	0.28			3.15
Standardized sand	98.4	0.41	0.36	0.16	0.01	<0.2	0.01	2.64

e) Sodium hydroxide (NaOH)

While making the conventional alkali-activated material, solid sodium hydroxide is dissolved in water to form an aqueous solution. But in this research, for the one-part mixing method, the solid NaOH was used together with the aluminosilicate precursors.

d) Sodium silicate

Granular sodium metasilicate pentahydrate ($Na_2SiO_3.5H_2O$) was used to make AAM using a one-part mixing method. Sodium oxide (Na_2O) and silicon dioxide (SiO_2 with amounts of 28 to 30% and 27 to 29% were used respectively. This means that Na_2O: SiO_2 modulus was around 1. For the AAM made by using a two-part mixing method, sodium silicate gel was used. Na_2O with 17 to 19% and SiO_2 35 to 38% composed the material and the modulus was set to around 2.

3.3.2 Mix proportion

Table 3.2 Mix design of AAM and OPC mortars

Mortar name	**Aluminosilicate mix proportion**	**PFBC (%)**	**Fly ash Type II (%)**	**GGBFS (%)**	**Silica fume (%)**	**OPC (%)**	**NaOH (mol/L)**	**AA ratio (g)**	**Extra water (%)**	**AA state**
GM1	PFBC100	100	0	0	0	0	16	1.0	10	Solid
GM2	FA100	0	100	0	0	0	16	1.0	10	Solid
GM3	FA80/GGBFS20	0	80	20	0	0	16	1.0	0	Solid
GM4	FA45/GGBFS45/SF10	0	45	45	10	0	16	1.0	10	Solid
GM5	FA42.5/GGBFS42.5/SF20	0	42.5	42.5	20	0	16	1.0	10	Solid
GM6	FA40/GGBFS40/SF20	0	40	40	20	0	16	1.0	10	Solid
AAM-16	FA42.5/GGBFS42.5/SF15	0	42.5	42.5	15	0	16	1.5	10	Solid
AAM-8	FA42.5/GGBFS42.5/SF15	0	42.5	42.5	15	0	8	1.5	10	Solid
AAM-8C	FA42.5/GGBFS42.5/SF15	0	42.5	42.5	15	0	8	1.5	0	Solution
OPC	OPC mortar	0	0	0	0	100	8		0	Solid

Note: In the aluminosilicate mix proportion column, FA, GGBFS and SF stand for fly ash, slag and silica-fume or micro-silica respectively. The right-side value is the percentage of the material.

Table 3.3 Mix proportion (kg/m^3)

Mortar	**Sand**	**PFBC**	**Fly ash Type II**	**GGBFS**	**Micro-silica**	**OPC**	**NaOH**	**$Na_2SiO_3.5H_2O$**	**Water glass (Sodium disilicate)**	**Water**	**AE water reducing agent**	**L/B***
GM1	1536	511	0	0	0	0	61	76	0	190	0	0.6
GM2	1536	0	511	0	0	0	61	76	0	190	0	0.6
GM3	1536	0	417	104	0	0	62	77	0	193	0	0.6
GM4	1536	0	240	240	53	0	64	79	0	198	0	0.6
GM5	1536	0	226	226	80	0	64	79	0	197	0	0.6
GM6	1536	0	212	212	106	0	63	78	0	197	0	0.6
AAM-16	1536	0	229	229	81	0	52	96	0	197	0	0.6
AAM-8	1536	0	229	229	81	0	30	96	0	218	0	0.6
AAM-8C	1536	0	229	229	81	0	30	0	170	83	0	0.5
OPC	1536	0	0	0	0	512	0	0	0	256	10	0.5

*Liquid/Binder. L: AA solution, B: Aluminosilicate materials (Fly ash + GGBFS +Micro-silica).

3.3.3 Mixing, casting and curing

For each type of the mixture, four sets of 3 molds were prepared for the strength test (7, 14, 28 and 56 days), and one set of molds for the shrinkage test were prepared.

For the making of the mortar samples the following mixing procedure was applied;

First of all, the bowl of the mixer was cleaned with a dry cloth, in the case of one-part mixing method, aluminosilicate precursor and solid alkaline materials such as NaOH and $Na_2SiO_3.5H_2O$ were mixed for one minute to make a paste, standardized sand was then added to the mixture and was mixed in low and high speeds, the duration for each was 30 seconds. Then, the mixing was stopped for 90 seconds followed by a high-speed mixing of 60 seconds. The same procedure of mixing was also used for making the ordinary Portland cement mortar.

For the two-part mixing method, the aluminosilicate precursors were first mixed for 2 minutes, then the alkaline solution and AE water reducing agent were added and mixed for two minutes to make a paste followed by the addition and mixing of standardized sand for 3 minutes. After the mixing procedure, the mortar was poured into the molds and vibrated for 2 minutes.

The surface of the molds was covered by plastic and put inside in a room with a temperature of around 20 °C. After 24 hours, the samples were demolded and each was wrapped and covered with plastic and cured at the aforementioned temperature until the day of the testing. But the samples which contained 100% fly ash couldn’t be demolded due to their slow setting. Therefore, they were demolded at the age of 9 days.

OPC samples were demolded as same as AAM, but they were cured inside the water until the strength test day. But for the shrinkage test, they were cured for 7 days inside water and then cured at the same temperature that was used for the other type.

3.3.4 Flowability test

Flowability test was conducted according to JIS R 5201. The detail is as follow;

A flow table was used for measuring the flowability of the mortars. First of all, the flow table was put on a flat surface, and the steel plate and the cone were cleaned with a dry cloth. After the mixing procedure, the mortar was put in a flow cone which was properly fixed in the center position on the steel plate of the flow table. The mortar was put in the cone in two equal layers. Each layer was tamped 15 times by a tamped rod. Then the excessive mortar was cut off and the surface of the cone was flattened. Then the cone was slowly lifted upward. The plate was then risen and dropped 15 times. Next, the mortar was spread. The maximum direction and the opposed direction which was perpendicular to the maximum direction was measured. This procedure was done twice and the average value in millimeter (mm) was taken as a flow value of a mortar.

3.3.5 Flexural and compressive strength test

The flexural and compressive strength tests of the materials were carried out according to the Physical Testing Method for Cement, JIS R 5201. Each of the specimens was first tested for flexural strength, then the two broken parts were taken for the compressive strength test, and the average value was taken as a value of the strength.

3.3.6 Drying shrinkage test

A dial gauge with an accuracy of 0.005 mm was used to test the drying shrinkage of samples. First of all, a reference rod with a specific length was measured. Then the specimen with attached pins with a length of 20 mm on both sides of its length was measured. This procedure was carried out twice for each sample. For the calculation of the drying shrinkage, first, the average length of the rod was subtracted from the average length of a sample to find the difference in their length. Deducting this length from the previous day’s amount was the drying shrinkage value for each type of sample.

The measurement of the sample was started after 2 days to 7 days of demolding. GM2 which had 100% fly ash took a long time for setting, therefore, its measurement started after 9 days of the mixing.

For the drying shrinkage test, the specimen was kept uncovered at a temperature of around 20°C in a controlled temperature room. The samples were measured every day until they become 28 days old, then, the measurement was taken 2 to 3 times a week.

3.4 Result

3.4.1 Effect of aluminosilicate precursors mix proportion

3.4.1.1 Flowability

Figure 3.1 and Table 3.2 show the effect of the aluminosilicate mix proportion on the flowability of mortars.

GM2 which is composed of 100% fly ash had the highest flow value of 256 mm. GM7 and OPC which stand in the second and third positions have flow amounts of 163 mm and 149 mm respectively. The flowability of the other types is much lower.

From the flow result, it can be concluded that fly ash increased the flowability of mortars, and as the amount of fly ash is decreased and the amount of the slag is increased the flow value of the mortar is decreased. This is due to the spherical shape of the fly ash particles and their packing effect that causes low water retention. On the other hand, the angular particle shape of slag and also the presence of Ca cause low flowability of the material.

GM1, a PFBC fly ash mortar has much lower fluidity compared to the GM2. This is also due to the irregular particle shape of PFBC fly ash which results in high retention of water inside the particles.

Table 3.4 The mix proportion and flowability specification of the samples

Mix	The Mix proportion	Flow value (mm)
GM1	PFBC100	101
GM2	FA100	256
GM3	FA80G20	163
GM4	FA45G45M10	107
GM5	FA42.5G42.5M15	100
GM6	FA40G40M20	107
OPC	PC Mortar	149

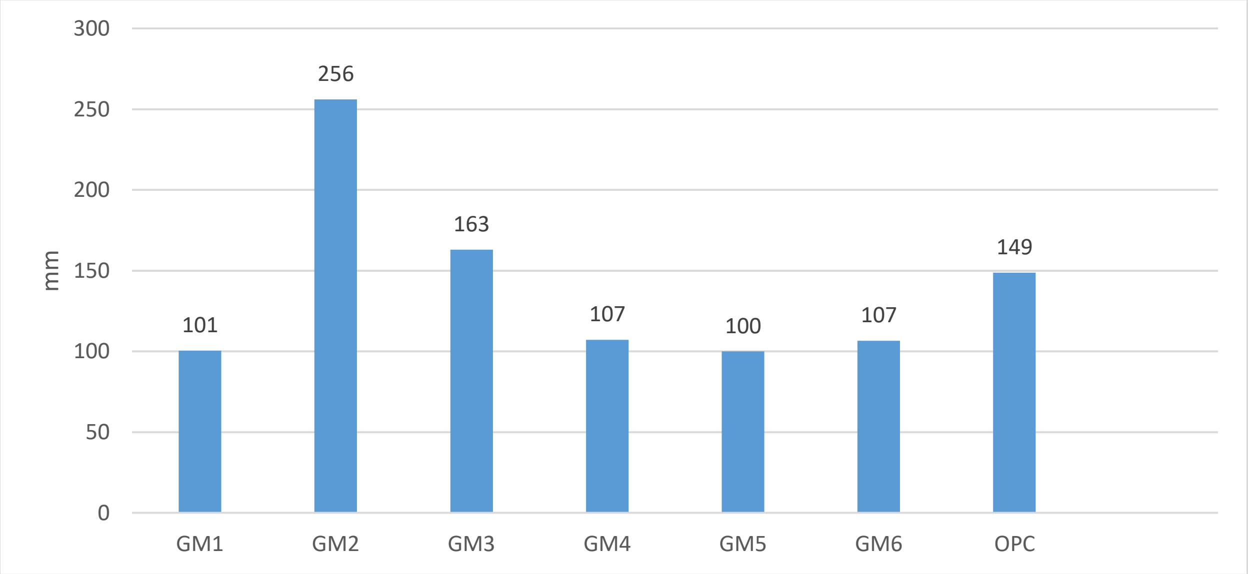

Figure 3.1 Effect of aluminosilicate mix proportion on the flowability

3.4.1.2 Strength

Figures 3.2 and 3.3 show the effect of aluminosilicate mix proportion on the compressive and flexural strength of the materials.

The compressive and flexural strength of both GM1 and GM2 are much lower in all ages. However, GM2 gained some strength at ages of 28 and 56 days which are 8.9 and 7.7 MPa for compressive strength and 1.8 and 1.5 MPa for flexural strength. However, the 56-day compressive and flexural strength of GM2 was lower than the 28-days', which is maybe attributed to the loss of mesopore water during curing at 18°C–20°C and 30%–50% relative humidity in the control temperature room, that loosens the mesopore walls. GM1's strength was not improved significantly at the later ages. The slow reactivity of the fly ash causes both the GM1 and GM2 to have lower mechanical strength.

Both the compressive and flexural strength of the material was increased with the increment of the slag in the mixture. Replacement of 20% fly ash with slag significantly improved both the initial and final strength of the samples. Moreover, GM4, GM5 and GM6 had the almost same value of compressive and flexural strength for all ages which is significantly higher than the other type of AAM with the lower amount of GGBFS or slag. This is due to the presence of a higher amount of Ca element in the slag which contributes to the higher reactivity of the material and formation of C-A-S-H gel which reduces the porosity and condense the microstructure of the AAM [28].

Incorporation of the micro-silica in the mixture couldn't improve the strength of the AAM, in addition, the 56-day flexural strength was reduced with the increase of the material.

The compressive and flexural strength of all the alkali-activated materials made by the one-part mixing method was lower than the OPC mortar. This is in contradiction with the compressive result of the conventional AAM or the AAM made by a two-part mixing method [29]. Which indicates AAM's higher strength. A study shows that some even with the same mix proportions of GM4, GM5, and GM6 had the compressive strength higher than 65MPa which was higher than the OPC [27]. The decrease in strength in the one-part mixed method may be attributed to the deficiency in the reaction process between AA and the aluminosilicate precursors.

Moreover, the compressive strength result shows that the 56-day compressive strength of the OPC was decreased slightly from 62.1 MPa to 57.4 MPa. This is may be due to the enlargement of mesopores during the curing process. This defect is not usual in OPC concrete.

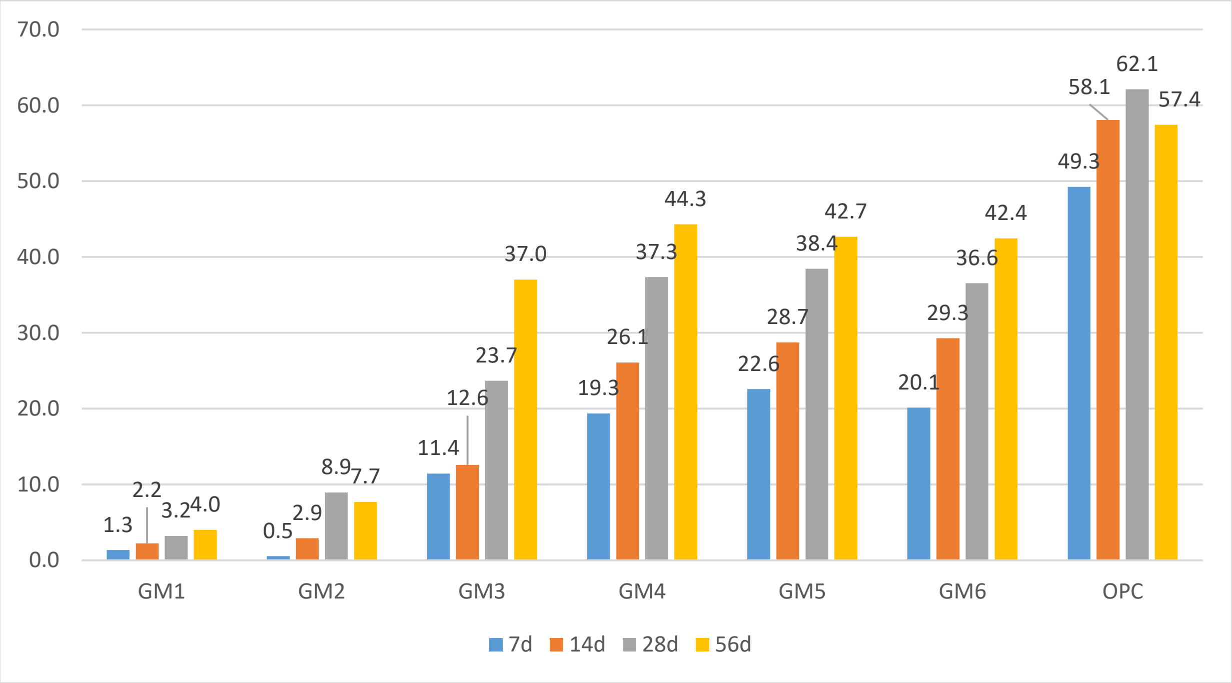

Figure 3.2 Effect of aluminosilicate mix proportion on the compressive strength

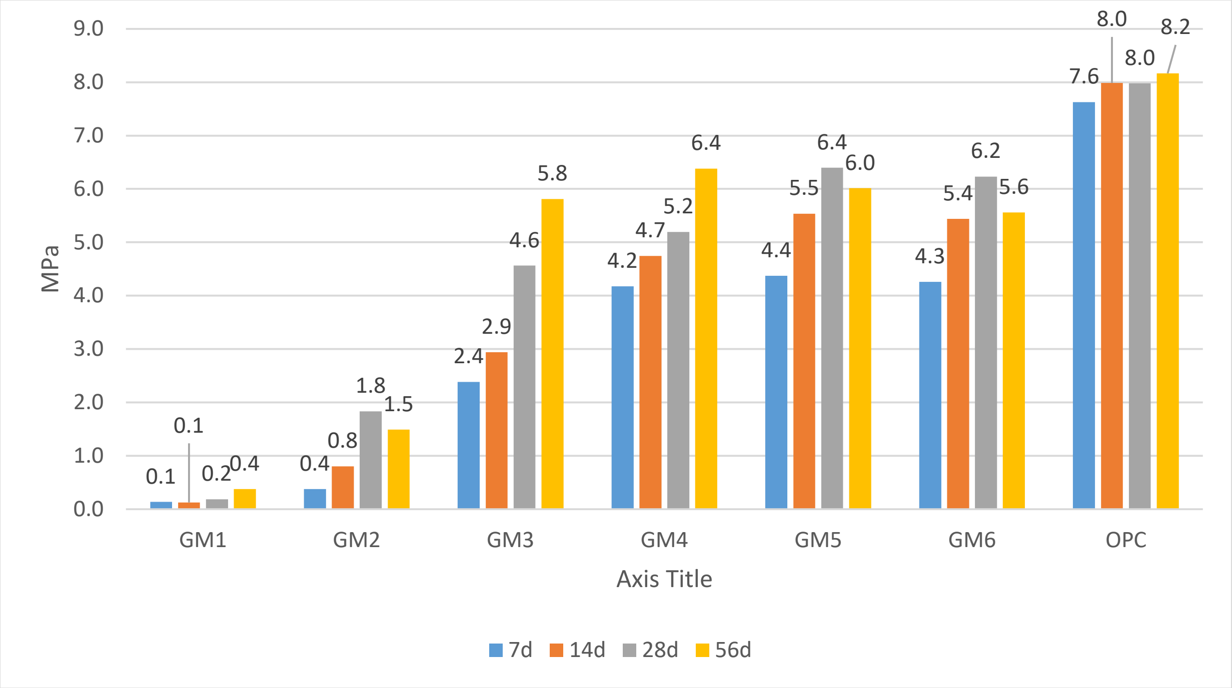

Figure 3.3 Effect of aluminosilicate mix proportion on the flexural strength

3.4.1.3 Drying shrinkage

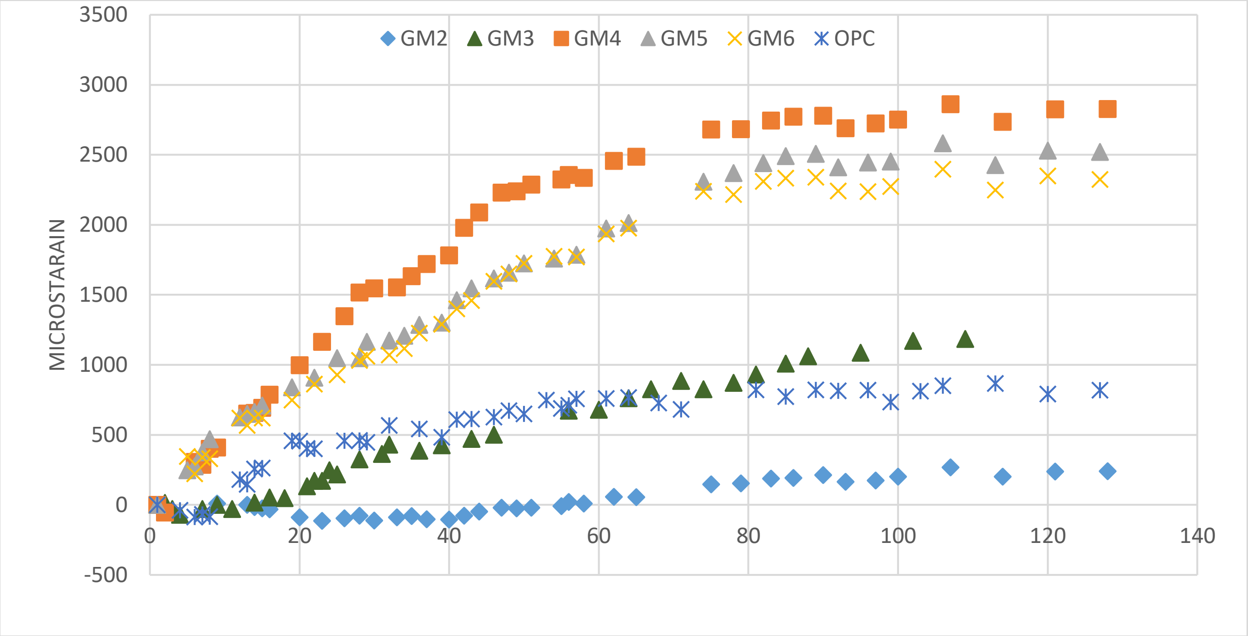

Figure 3.4 Effect of aluminosilicate mix proportion on the flexural strength

The GM2 which has 100% fly ash had the lowest shrinkage value. The amount of shrinkage was less than 300 microstrain (με). This is due to the low hydration rate of the fly ash mortar, moreover, the unreacted particles of fly ash can play a significant role in restraining the deformation of the material.

As far as GM1 is concerned, due to the increment of their length, the measurement couldn't be continued after the age of 7 days. This may be attributed to the accumulation of the high number of unreacted particles that cause enlargement in the size of the samples.

The shrinkage of the AAM is increased with an increase in the amount of slag. GM4 which had the highest amount of slag and micro-silica had the largest value of shrinkage that is around 3000 με. This shrinkage value was more than twice of the OPC sample. GM5 and GM3 had the equal shrinkage value of 2000 με. GM3 had a slightly lower drying shrinkage value compared to OPC samples. The high shrinkage of slag-based AAM is due to their high hydration rate that causes the retained water to evaporate quickly and result in capillary stress inside the samples.

3.4.2 Effect of AA ratio

3.4.2.1 Flowability

The mix proportion which was consisted of 42.5% fly ash, 42.5% slag, and 15% micro-silica was used to study the influence of the AA ratio, NaOH molarity, and extra water on the properties of the AAM.

Figure 3.5 shows the effect of the AA ratio on the flowability of the samples.

AAM-16 with a flow value of 111 mm had a slightly higher flowability compared to GM5's 100 mm. This indicates that the flowability of AAM made by the one-part mixing method is improved with the increase in AA ratio ($Na_2SiO_3.H_2O$: NaOH).

Table 3.5 Mix proportion, AA ratio and flow value specification of the samples

Mix	The mix proportion	Flowability	AA ratio ($Na_2SiO_3.5H_2O$: NaOH)
GM5	FA42.5G42.5M15	100	1
AAM-16	FA42.5G42.5M15	111	1.5

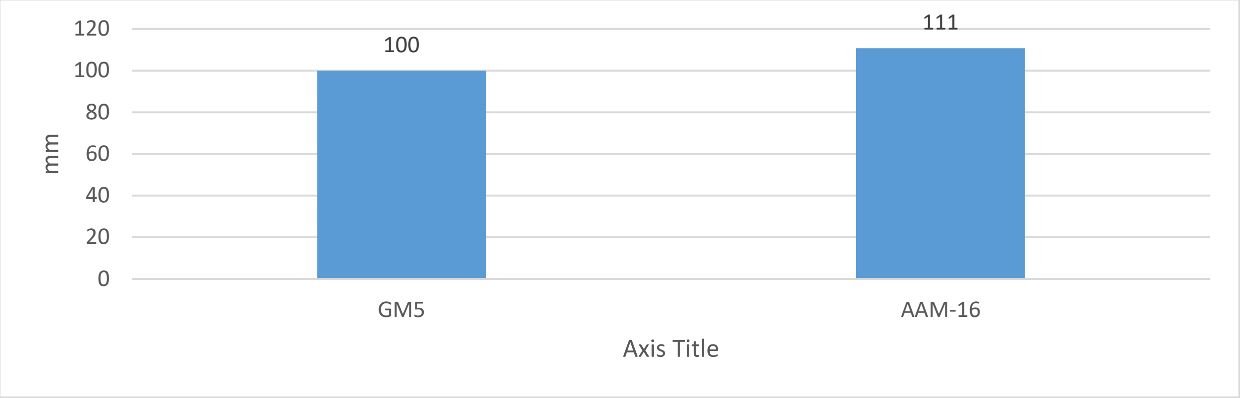

Figure 3.5 Effect of AA ratio on the flowability

3.4.2.2 Strength

The compressive and flexural strength of the AAM-16 was higher than the GM4 at 7 days. At 14 days, both types of samples had an almost similar compressive strength of around 29 MPa. But for 28 and 56 days, the compressive and flexural strength of the sample with an AA ratio of 1.5 was lower than its counterpart. The result is in conflict with the previous finding [25,26] which indicates that the strength is improved with the increase in AA ratio. Compare to the GM5, the lower strength of AAM-16 may be attributed to the poor dissolution of the $Na_2SiO_3.5H_2O$ particles which caused a lack in providing enough SiO_2 and PH to the matrix.

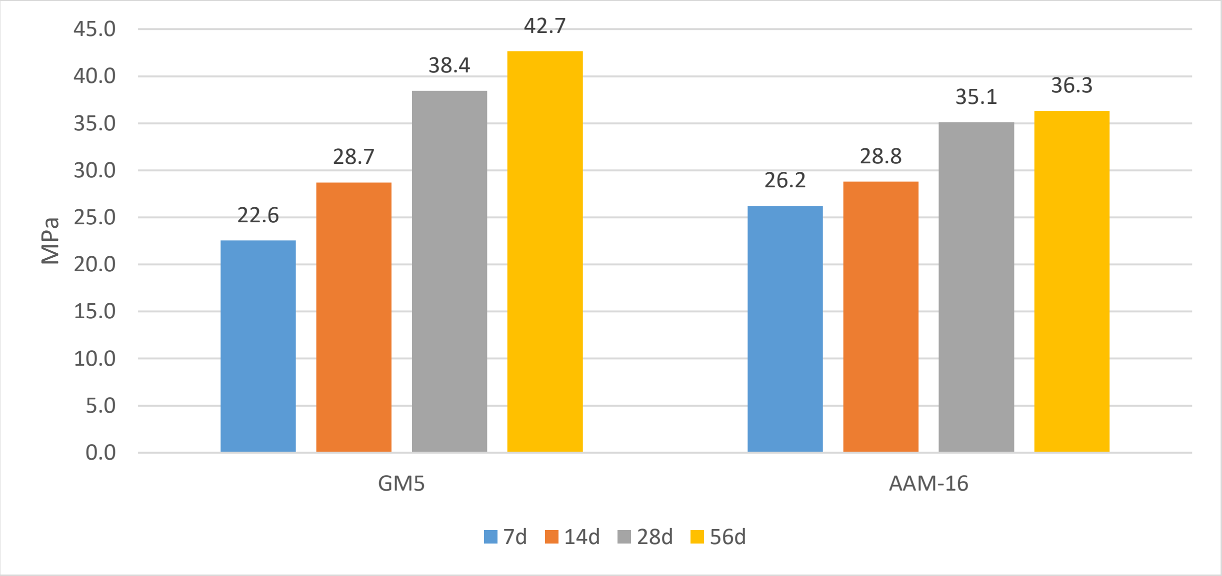

Figure 3.6 Effect of AA ratio on the compressive strength

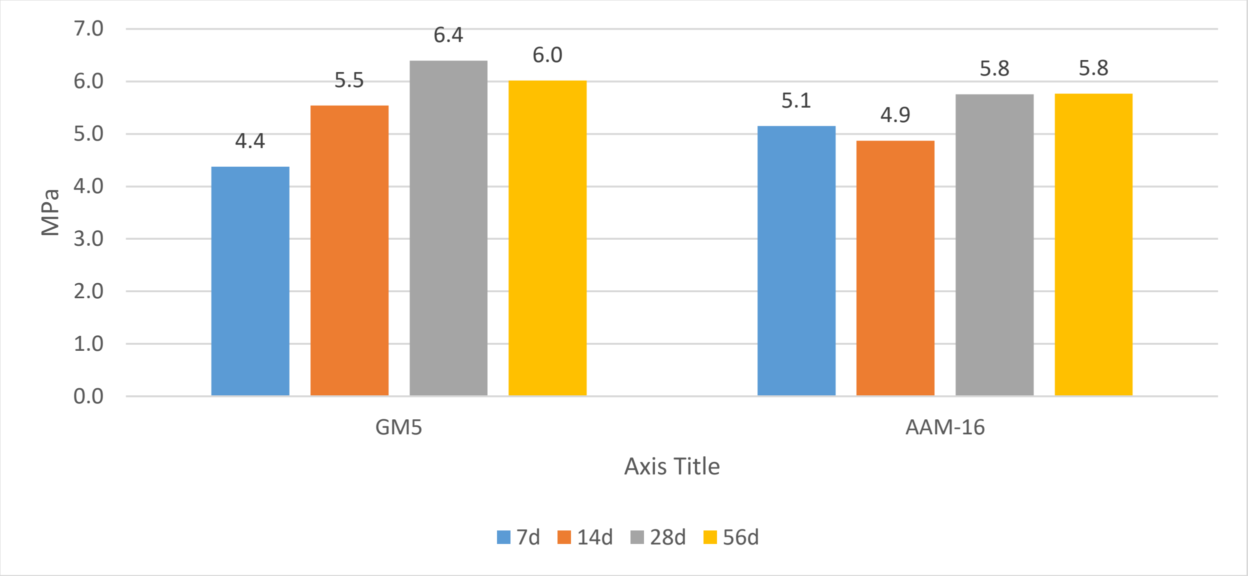

Figure 3.7 Effect of AA ratio on the flexural strength

3.4.2.3 Drying shrinkage

Figure 3.8 shows the effect of the AA ratio on drying shrinkage of the AAM made by the one-part mixing method. Both of the materials had higher drying shrinkage than OPC. The drying shrinkage was decreased with an increase in the AA ratio. This may be due to the presence of the unreacted sodium metasilicate particles which played a role to keep a stable skeleton.

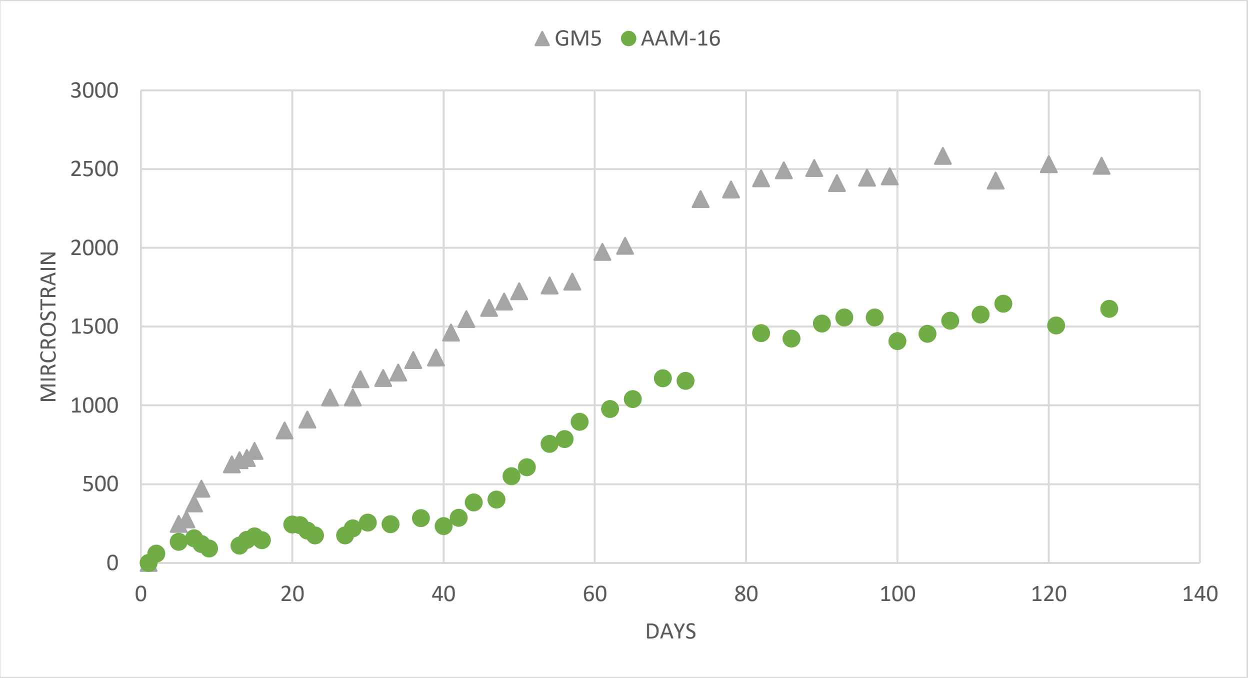

Figure 3.8 Effect of AA ratio on the drying shrinkage

3.4.3 Effect NaOH molarity

3.4.3.1 Flowability

Figure 3.9 shows the influence of the NaOH solution molarity on the flow properties of the samples.

When the molarity increased from 8M to 16M, the flow of the mortar decreased by around 21%. This result confirms the finding of [24]. As higher molarity increased the viscosity and improved the reactivity of the constituent, the solidification of the mortar proceeded in quick time that reduced the flowability.

Table 3.6 Mix proportion, NaOH molarity and flow value specification of the samples

Mix	The mix proportion	Flowability	NaOH molarity
AAM-8	FA42.5G42.5M15	128	8M
AAM-16	FA42.5G42.5M15	111	16M

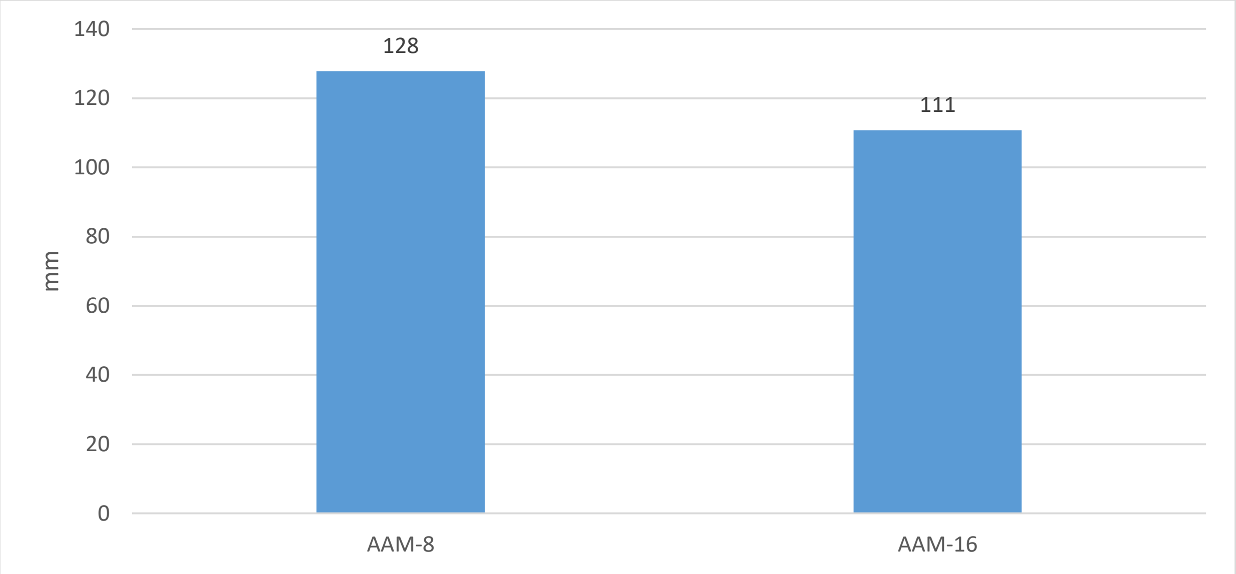

Figure 3.9 Effect of NaOH molarity on the flowability

3.4.3.2 Strength

The initial compressive and flexural strength of the mortar was increased with an increase in molarity of NaOH in the mixture. But the 28 and 56 days compressive and flexural strength of AAM-16 was lower than AAM-8. The maximum compressive strength of 41 MPa was achieved by the AAM-8 at 56 days. The higher strength of the mortar with lower NaOH concentration is perhaps due to their higher flow rate which helps the aluminosilicate precursors and other constituents to disperse well through the mortar.

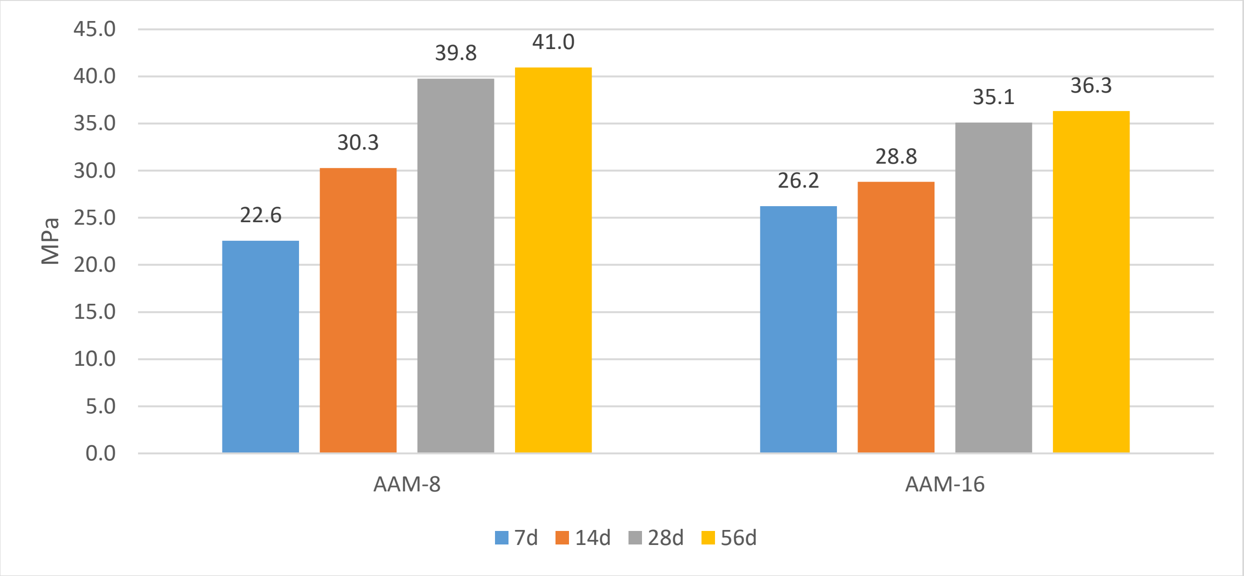

Figure 3.10 Effect of NaOH molarity on the compressive strength

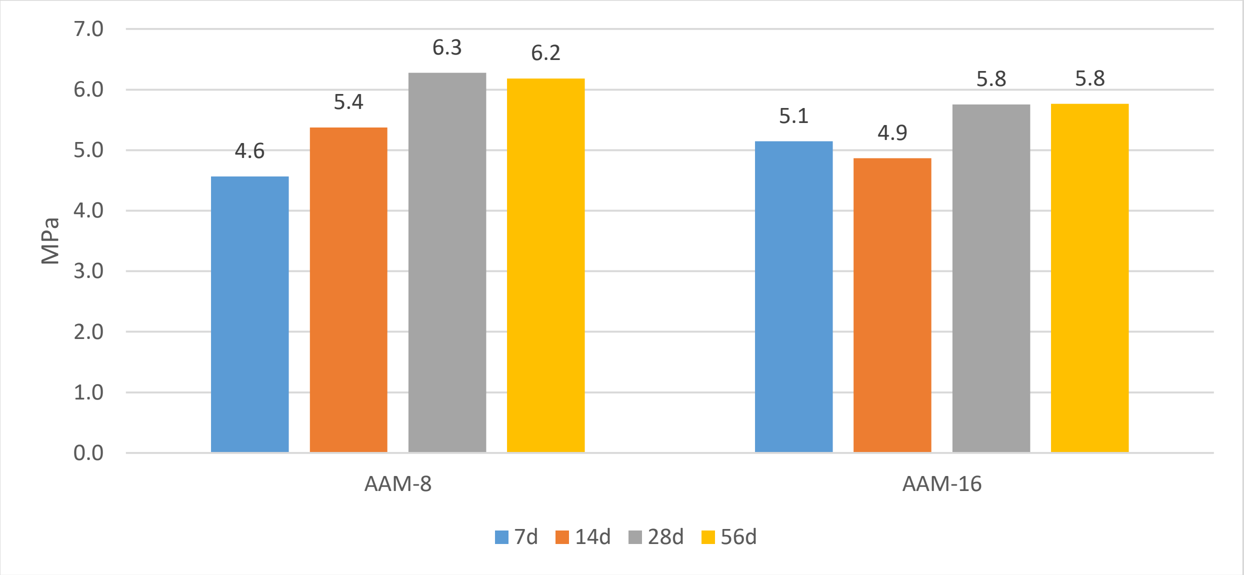

Figure 3.11 Effect of NaOH molarity on the flexural strength

3.4.3.3 Drying shrinkage

Figure 3. 11 shows the effect of the NaOH molarity on the drying shrinkage of the AAM. There isn't any significant difference in the drying shrinkage amount between AAM-8 and AAM-16. But drying shrinkage of both types of mortar was much higher than the shrinkage of OPC. From the result, it can be perceived that the AA molarity doesn't have any influence on the drying shrinkage of AAM made by the one-part mixing method.

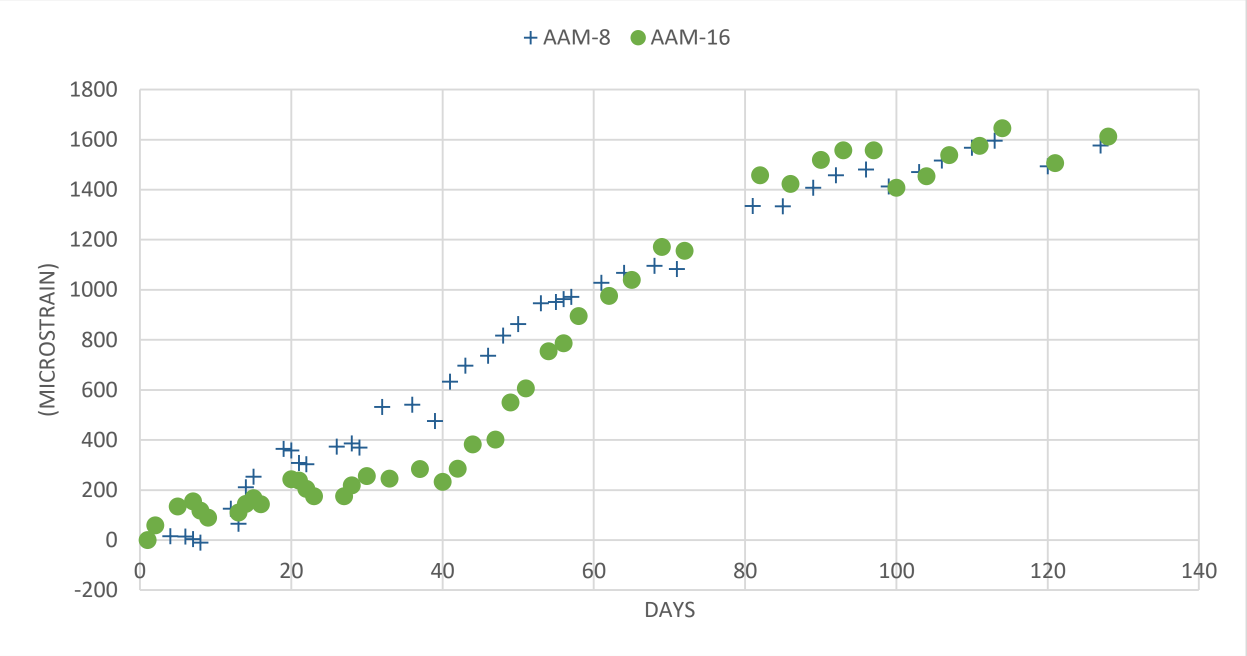

Figure 3.12 Effect of NaOH molarity on the drying shrinkage

3.4.4 Effect of the production method

This section compares AAM made by the one-part mixing method and conventional method. The conventional AAM was made with 54% sodium disilicate solution and a two-part mixing method was used for its production but the one-part AAM was made by 32% sodium metasilicate pentahydrate and the AA were mixed in a dry state.

The SiO_2:Na_2O ratio in sodium disilicate solution is 2, where this ratio is one for the sodium metasilicate. For comparing the compressive strength and flexural strength, a 28-day strength result was used. The 28-day strength result of the AAM-8C which is the conventional AAM was taken from the research conducted by Yuyun et.al [27]

3.4.4.1 Flowability

The flowability of AAM-8C was 181mm, and it is 41% more than the flowability of AAM made by the one-part (dry) mixing method. After the mixing of AAM-8, the hardening or consolidation of the mortar was quicker. This problem caused the fresh mortar to lose its workability.

Table 3.7 Mix proportion, production method and flow value specification of the samples

Mix	The mix proportion	Flowability	Production method
AAM-8	FA42.5G42.5M15	128	One-part mixing (dry mixing)
AAM-8C	FA42.5G42.5M15	181	Conventional

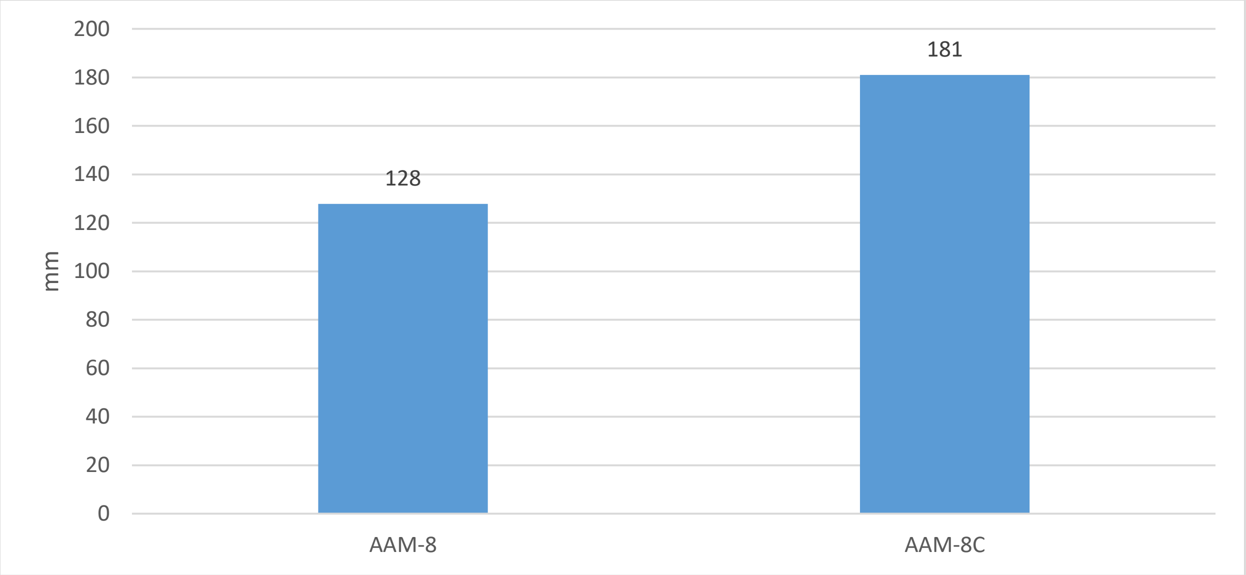

Figure 3.13 Effect of the production method on the flowability of AAM

3.4.4.2 Strength

Figures 3.13 and 3.14 show the influence of the AAM production method on the 28-day compressive and flexural strength of the AAM. AAM-8C which is a conventional type alkali-activated material had much higher mechanical strength than the other type. The compressive and flexural strength of AAM-8C were 68 MPa and 39.8 MPa respectively. While AAM-8 had a compressive strength of 39.8 MPa and flexural strength of 6.3 MPa.

The higher compressive and flexural strength of the conventional type AAM was due to the higher SiO_2:Na_2O ratio of the water glass than the granular sodium metasilicate used in the AAM made by the one-part. Secondly, because of the low flowability and quick hardening of the AAM-8 mortar, the constituents of the mixture were not well dispersed in the mixture and cause lower strength of the material. This problem of a lower strength in the one-part mixing method is further analyzed in chapter 5 of this thesis.

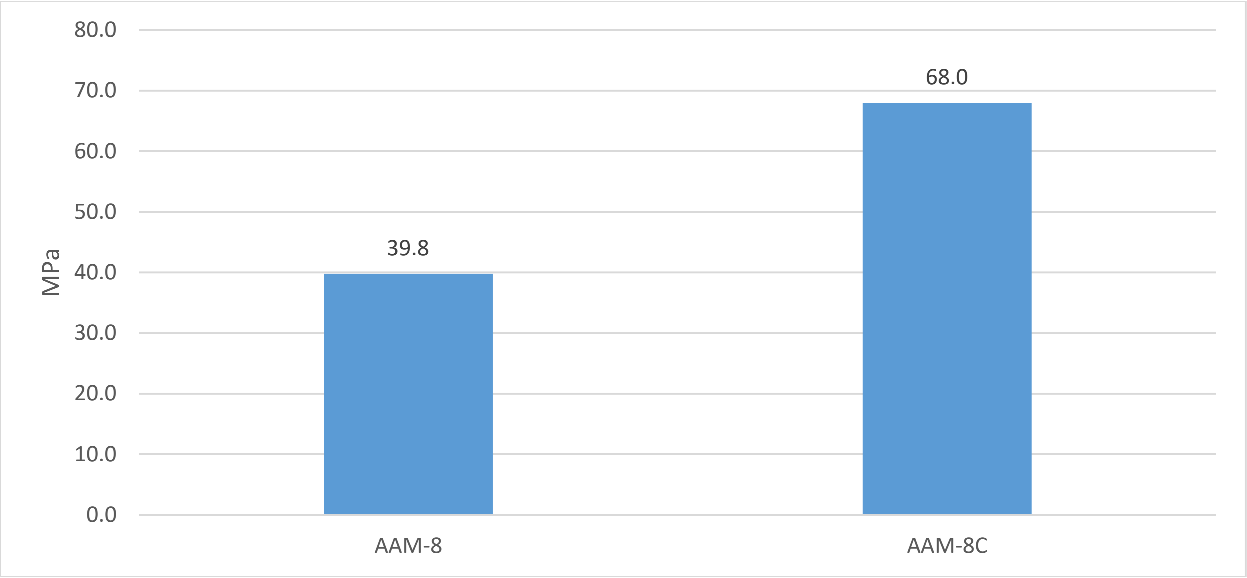

Figure 3.14 Effect of the production method on the 28-day compressive strength of AAM

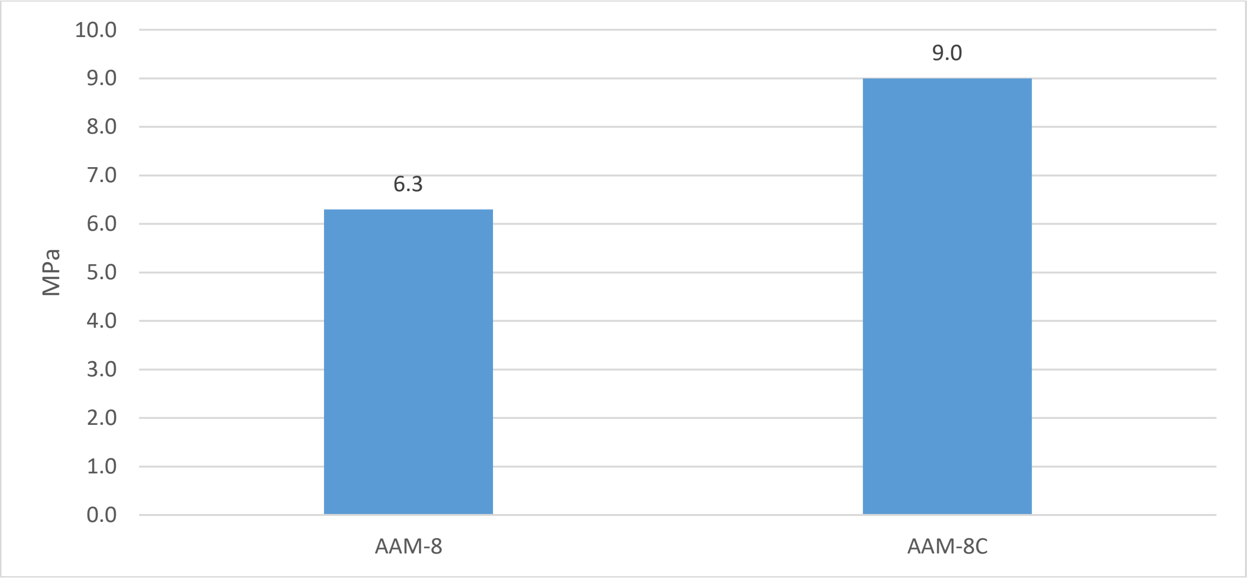

Figure 3.15 Effect of the production method on the flexural strength of AAM

3.4.4.3 Drying shrinkage

Figure 3.15 shows the effect of the production method of AAM on the drying shrinkage of the AAM.

The drying shrinkage of AAM-8C was significantly higher than AAM-8 until 60 days. But since then, the shrinkage of the AAM made by the conventional method was stopped and the length remained stable for the rest of the days. On the other hand, the drying shrinkage of AAM-8 was slower until around 40 days but the pace of the shrinkage was increased after that.

The higher shrinkage of AAM-8C at initial days was due to the higher hydration rate between the aluminosilicate precursors and AA solution. On the other hand, the low shrinkage value of the AAM-8 at the earlier time may be attributed to the shortage in dissolution rate of AA material which may result in a low reaction speed between the constituents of the material.

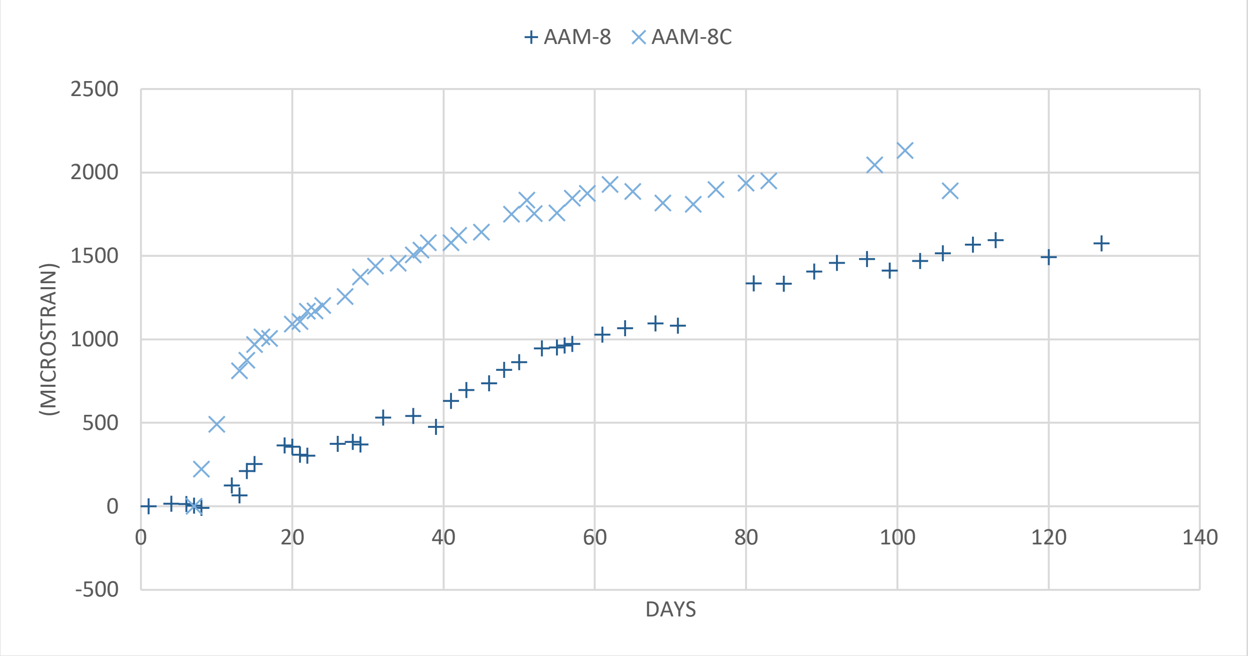

Figure 3.16 Effect of the production method on the drying shrinkage of AAM

3.5 Conclusion

AAM is conventionally produced by the two-part mixing method. The procedure of making is done by expert people. Handling the AA solution is difficult for common people as they are corrosive and cause danger to humans. Furthermore, the higher viscosity of AA solution used in making AAM by conventional method cause workability problem. With the aim to solve the aforementioned problems, a one-part mixing method was studied by some researchers. However, this kind of material has not been comprehensively characterized. Therefore, in this study, the effect of aluminosilicate precursors type and ratio, Na_2SiO_3: NaOH ratio, NaOH molarity, and the production method were studied. The following conclusion can be drawn from the result of this research;

1. Fly ash increases the flowability of AAM made by a one-part mixing method. This is due to the spherical shape and packing effect of its particles.
2. Overall, the compressive and flexural strength of all one-part mixed AAM made by different mix proportions of aluminosilicate precursors are lower than the OPC mortar.
3. GGBFS (slag) increases the early and final compressive and flexural strength of the AAM. Micro-silica doesn’t have any significant influence on the strength of the materials.

4. PFBC and fly ash have lower initial and final strength. However, fly ash-based mortar slightly gain strength at the final ages, but still, that is much lower than the slag-based mortars.
5. 100% fly ash mortar has the lowest drying shrinkage among all samples and this is because of the low reactivity of their particles. But the drying shrinkage of the samples is increased with an increase in the amount of slag.
6. A higher hydration rate of slag causes the early loss of the mesopore water and creates capillary stress that results in drying shrinkage.
7. AA ratio doesn't have any significant influence on the flowability of the fresh mortars.
8. Both the compressive and flexural strength of AAM made by the one-part mixing method are decreased with the increase in AA ratio.
9. The drying shrinkage of AAM made by the one-part mixing method is increased with an increase in AA ratio.
10. The concentration of the NaOH has a slight influence on the flow and the strength properties of the materials. The flowability, compressive and flexural strength are improved with a decrease in the concentration of NaOH. But there isn't any effect on the drying shrinkage of the materials.
11. Conventional AAM has much higher flowability, compressive and flexural strength than the AAM made by the dry mixing method.
12. The drying shrinkage of the dry mixed AAM is lower in the early days but it is increased as the samples get older. This is in contradiction with the drying shrinkage result of conventional AAM, but after 100 days, the drying shrinkage amount of both types reach the almost same value.

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Chapter 4

Retardation Behaviour of Sucrose on Alkali-activated Materials

4.1 Introduction

In chapter 3, it was mentioned that the hardening of the mortar samples containing 40% or more GGBFS was very quick, so technically it can be said that they had a very short setting time. The result confirms the previous research [1,2]. The problem causes a workability problem as it was difficult to cast the fresh mortar into the molds. Therefore, it was decided to use an admixture to retard the setting process. Sucrose is an organic material. Its retardation influence on ordinary Portland cement materials was studied by several researchers in the past [3,4]. They concluded that sucrose has the ability to delay the setting process. Moreover, some of them also reported that besides the retarding effect, sucrose improves the microstructure of the OPC-based materials.

The retardation mechanism of the sucrose is not fully understood up to now, but it is generally accepted that sucrose adsorbs to the surface of hydrating particles to delay the production of the main hydrated material such as the C-S-H product [3]. Baruere [5] suggested that when mono-saccharides and disaccharides convert to the saccharinic acids by dilute alkali, these acids have retarding ability through adsorbing onto cement particles. Also, Milestone [6] has concluded that sugar and sugar acids adsorb onto the Ca ions which form tri-calcium silicate particles. So, blockage of hydration is occurring when the calcium silicate hydrate nucleation site surface is poisoned by the adsorption of sugar-acid anions.

This research aims to study the retardation effect of sucrose on AAM. The retardation effect of sucrose will be studied by the setting time test. Moreover, other properties of the AAM which have been studied in the previous experiment such as workability, compressive and flexural strength, and drying shrinkage test will be investigated in the presence and absence of sucrose.

4.2 Objective

This research will focus on the effect of sucrose on the initial and final setting time of AAM. Moreover, one of the mixes from the previous experiment which contains a higher amount of GGBFS will be chosen and 2% of the mass of aluminosilicate precursors, sucrose will be added as an admixture. The material’s flowability, compressive and flexural strength and drying shrinkage will be studied, and the result will be compared with the one which doesn’t have sucrose.

4.3 Experiment

4.3.1 Materials

Aluminosilicate precursors such as fly ash type F, GGBFS and silica fume, Alkaline activators (AA) such as NaOH pellets and granular $Na_2SiO_3.5H_2O$ were used in this experiment. For the mortars, one-part mixing and for the making of the paste two-part mixing was adopted. Standardized sand which conforms to JIS A 6207 was used as fine aggregate in mortar preparation. Sucrose was used as an admixture to retard the reaction process and to delay the solidification of the materials.

4.3.2 Mortar preparation and experimental program

Table 4.1 Mix design of the mortar used in this experiment.

Mortar	**Aluminosilicate mix proportion (%)**	**PFBC (%)**	**Fly ash Type II (%)**	**GGBFS (%)**	**Silica fume (%)**	**Sucrose (%)**	**NaOH (mol/L)**	**AA ratio (g)**	**AA state**
AAM-8	FA42.5/GGBFS42.5/SF15	0	42.5	42.5	15	0	8	1.5	Solid
GM7	FA42.5/GGBFS42.5/SF15	0	42.5	42.5	15	2	8	1.5	Solid

FA=fly ash, S=silica fume

The AAM-8 mortar which was prepared and tested in the previous experiment was chosen as a reference sample. The difference between AAM-8 and GM7 is the addition of sucrose. GM7 has sucrose by 2% of the mass of aluminosilicate precursors in its composition while AAM-8 is made without using sucrose.

For each type of mixture, four sets of 3 molds were prepared. 3 sets for the strength test (7, 14, 28, and 56 days), and one set for the shrinkage test.

The mixing procedure of both mixtures was the same as explained in the previous chapter. In GM7 the sucrose was mixed together with the aluminosilicate precursors and AA materials. Casting, vibrating, curing of the samples were the same as in the previous study.

The flowability, compressive and flexural strength and drying shrinkage of the samples were measured.

4.3.3 Paste preparation and setting time test

Paste samples were made to study the influence of sucrose on the setting time of alkali-activated materials. Table 4.3 shows the mix proportion of aluminosilicate precursors and composition characteristics of the materials.

Table 4.2 Mix design and composition characteristics of pastes.

Pastes	**Aluminosilicate mix proportion (%)**	**PFBC (%)**	**Fly ash Type II (%)**	**GGBFS (%)**	**Silica fume (%)**	**Sucrose (%)**	**NaOH (mol/L)**	**Sodium metasilicate (%)**	**AA ratio (g)**	**AA state**
P1	FA100	0	100	0	0	0	8	32	1.5	Solution
P1S	FA100	0	100	0	0	2	8	32	1.5	Solution
P2	FA80/GGBFS 20	0	80	20	0	0	8	32	1.5	Solution
P2S	FA80/GGBFS20	0	80	20	0	2	8	32	1.5	Solution

For the setting test time test, the maximum amount of the GGBFS was chosen to be 20%. Because the hardening of the paste and mortar with a higher percentage of GGBFS than the aforementioned percentage was occurring quickly soon after the mixing. This problem was obvious during testing the flowability. As for each type, two times flow measures were conducted, for the higher GGBFS based AAM, there was a significant difference of flow of each measure. Therefore, for studying the setting time, 100% fly ash-based and 20% slag-based AAM paste were chosen.

For making the pastes, an AA solution from NaOH pellets and $Na_2SiO_3.5H_2O$ was made. The AA solution to the binder or aluminosilicate materials ratio was kept to 0.4 for the P1 and P1S, and 0.35 for the P2 and P2S paste.

A Vicat apparatus was used to test the setting time. Vicat apparatus consisted of units that were equipped with a frame and backlight platform, graduated scale, 10mm (0.4in) dia. plunger assembly, adjustable indicator, mold, glass plate and needle for testing the initial and final setting time.

For testing the initial setting time, a needle with a cross-sectional area of 1 mm^2 and for the final setting test, a needle with an annular (5mm diameter) attachment was used.

The mixing procedure was conducted according to the JIS R501. A paddle mixer was used to mix the materials. First, the aluminosilicate precursor and AA solution were mixed for 60 seconds. Then the mixing was stopped for 30 seconds, followed by the mixing for 90 seconds. The paste was then poured into the mold of the Vicat apparatus.

For the initial setting time test, the needle was lowered until it touched the surface of the AAM paste. Then the needle was gently released. This procedure was continued in different intervals of time until the needle was stopped 1 mm above the glass plate or the reading from the bottom of the scale was 1 mm. For the finding final setting time, the needle with an annular attachment was used. The needle was first lowered to contact the surface of the paste. Then it was released. The procedure was continued until the was no sign of the annular or circular attachment on the surface of the paste. The setting time was calculated from the starting period of the mixing until the time of the initial and final set was achieved.

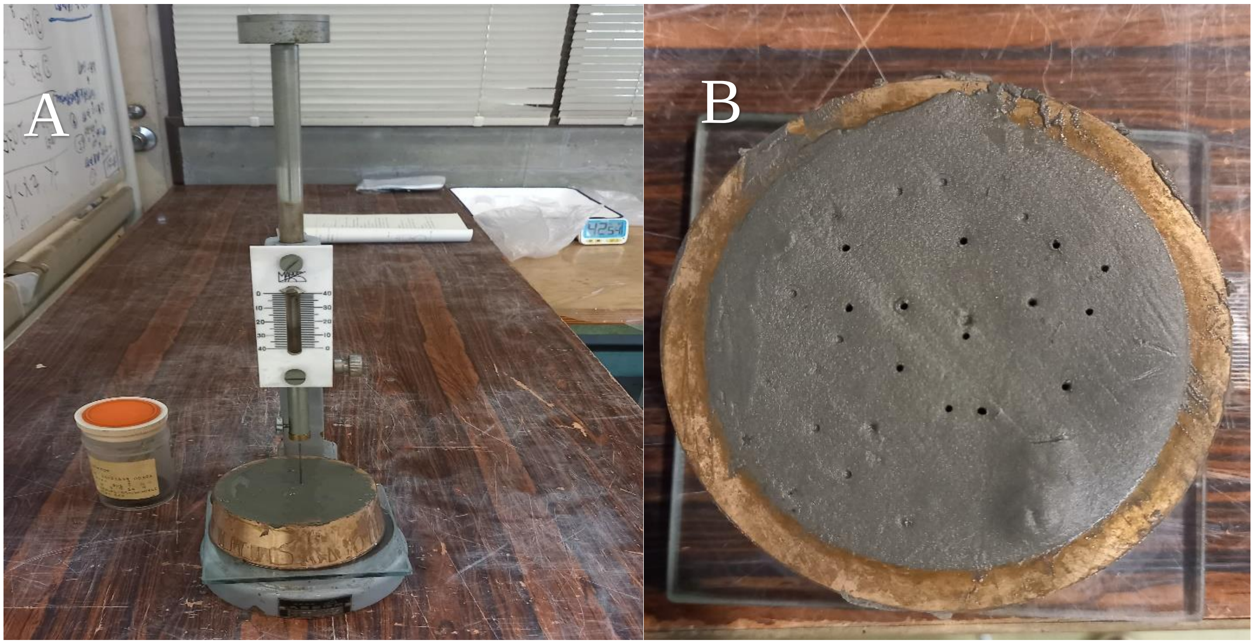

Figure 4.1 Setting time test: (A) Vicat apparatus, (B) Paste with marks of the needles

4.4 Result

4.4.1 Setting time

Figure 4.2 shows the initial and final setting time result of the P1 and P1S pastes. The result shows that sucrose retarded the initial and final setting time of the pastes significantly. Sucrose increased the initial setting time of P1S from 310 minutes to 515 minutes and the final setting time from 433 minutes to 990 minutes.

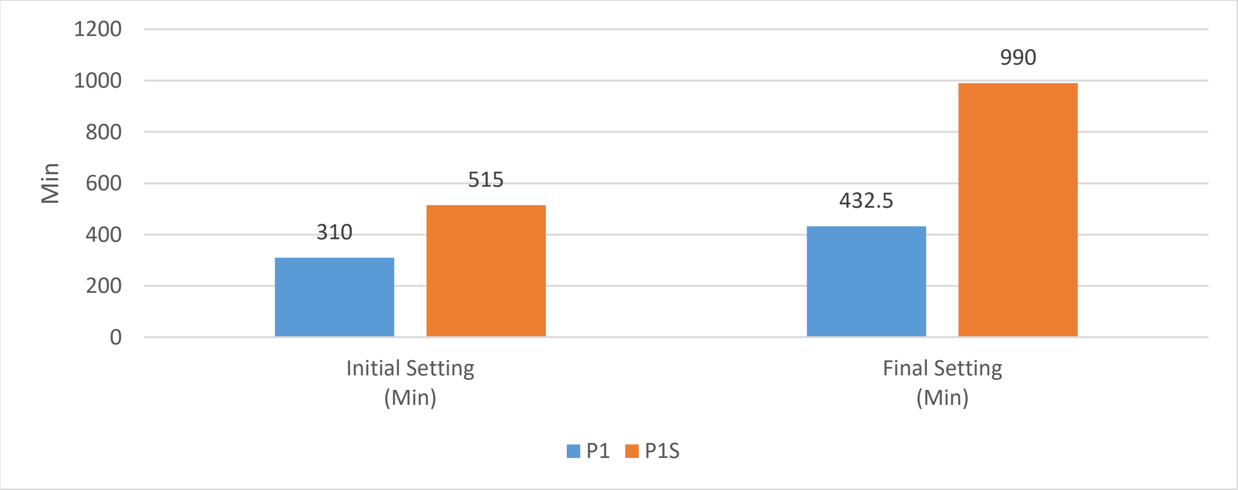

Figure 4.2 Setting test result of the P1 and P1S

Figure 4.3 shows the initial and final setting time to P2 and P2S. The result followed the same trend as the previous one. P2, which didn't have sucrose, had very short initial and final setting times of 10 and 30 minutes, respectively, but adding the 2% sucrose increased the paste's initial and final setting time to 23 and 48 minutes, respectively.

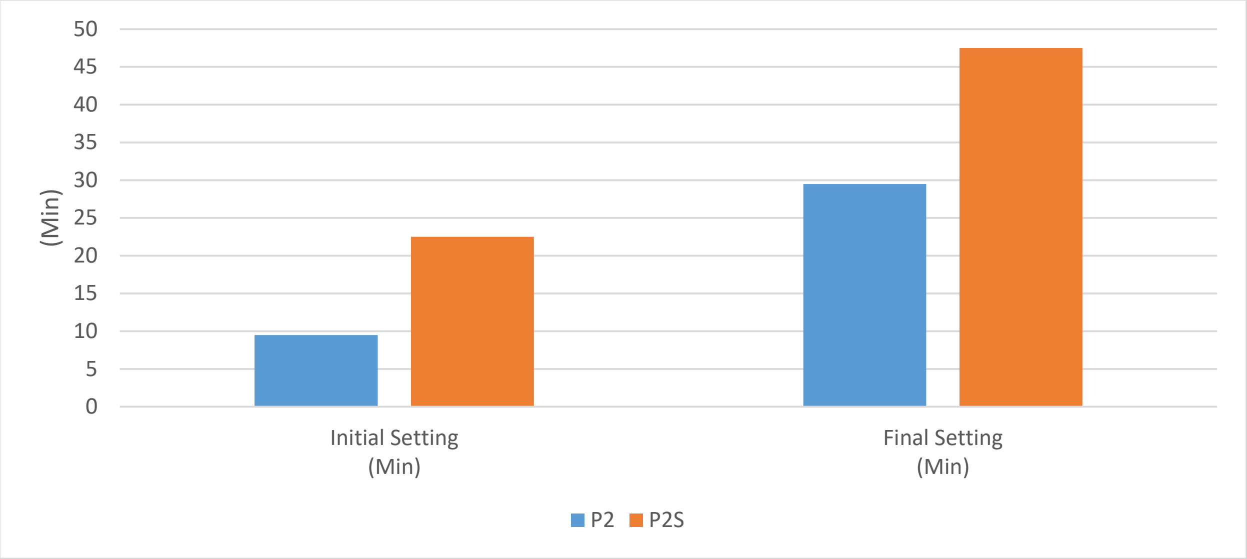

Figure 4.3 Setting test result of the P2 and P2S

The initial and final setting time test results of both kinds of pastes revealed that the retarding behavior of sucrose can also be observed on alkali-activated materials. As many researchers confirmed its retarding effect on ordinary Portland cement materials in the past [3,4].

4.4.2 Flowability

Figure 4.4 shows the flowability result of AAM-8 and GM7. The addition of 2% sucrose increased the flowability by 14%. AAM-8 had a flowability value of 128 mm while GM7 had 146 mm. This significant increase in flowability is attributed to the retarding behavior of sucrose. Because AAM-8's flow was quickly decreasing after the mixing time. But sucrose maintains the flow rate of the GM7 longer than the AAM-8.

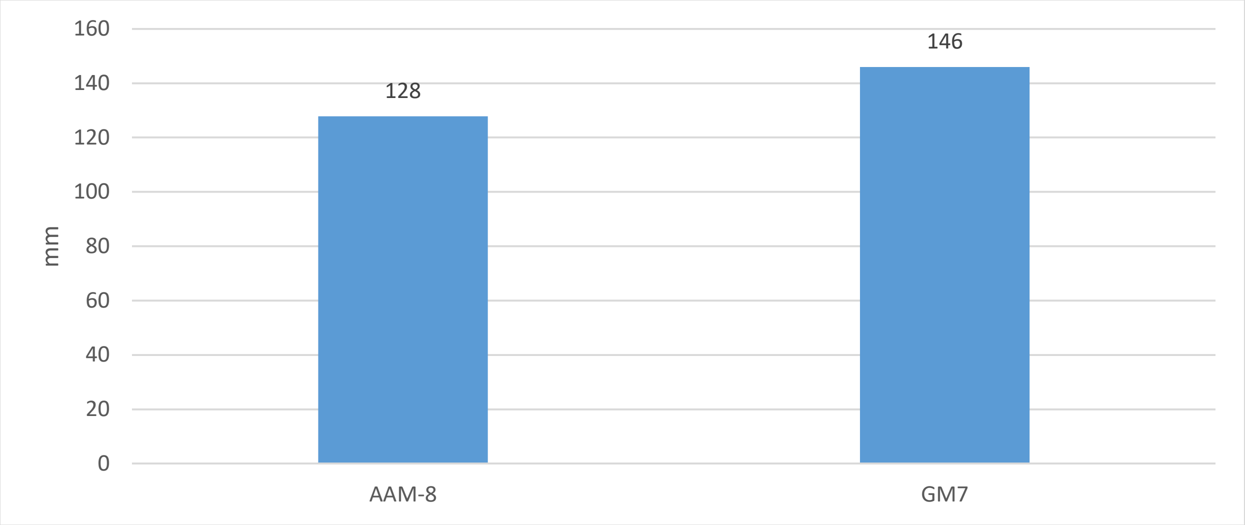

Figure 4.4 Flowability test result

4.4.3 Strength

Figure 4.5 and Figure 4.6 show the compressive and flexural strength results.

Sucrose increased the compressive strength. The compressive strength of G7, for 7, 28, and 56 days was increased by 30.5, 16.4, and 8% respectively. Importantly, sucrose had a significant influence on increasing the early compressive strength of the material.

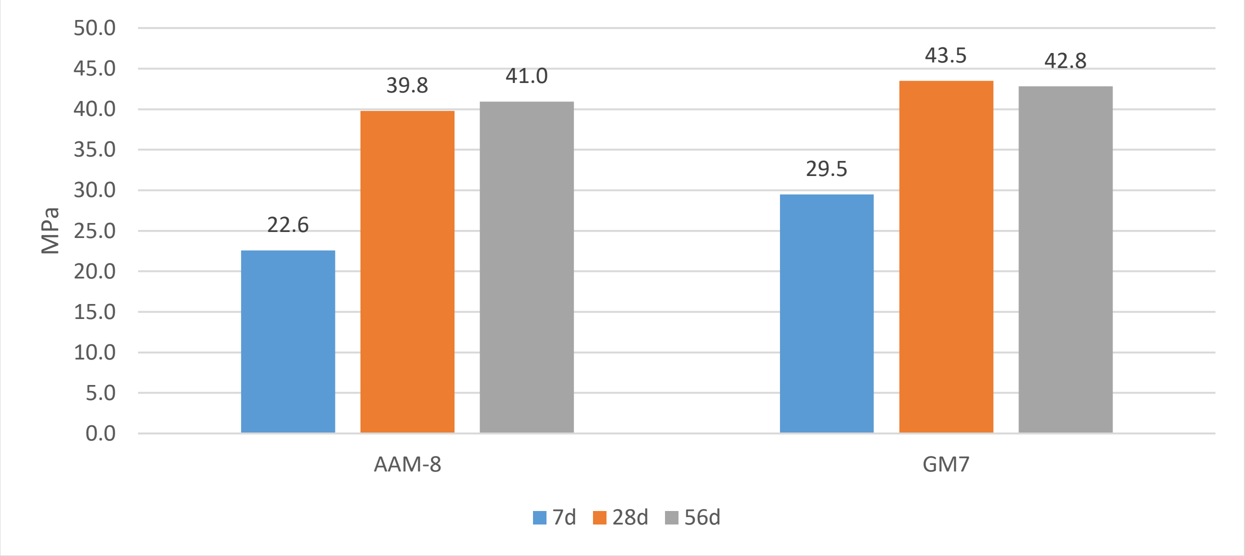

Figure 4.5 Compressive strength result

The flexural strength result followed the same trend as the compressive strength. Sucrose improved the flexural strength as well. AAM-8 had a flexural strength of 4.6, 6.3, and 6.2 MPa for 7, 28, and

56 days respectively, while GM7 had a strength of 4.6, 7.1, and 7.6 MPa for 7, 28, and 56 days respectively.

The increase in strength of the AAM using sucrose was due to their better flowability, which caused the aluminosilicate precursors and solid AA to better disperse through the mortar. Sucrose has the ability to improve the reaction process between the binders [3], this can also be a factor of the strength increment.

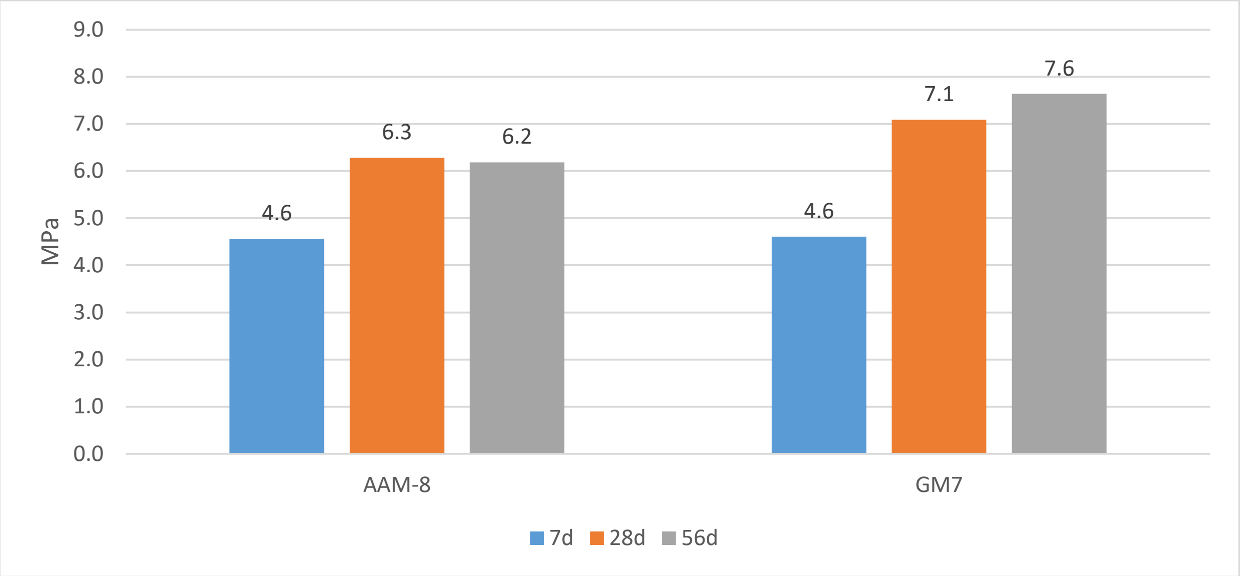

Figure 4.6 Flexural strength result

4.4.4 Drying shrinkage

Figure 4.7 shows the drying shrinkage of the AAM-8, G7, and OPC mortars. The shrinkage result of the OPC is included and used as a reference sample.

Sucrose had a significant influence on decreasing the drying shrinkage of the material. The drying shrinkage of GM7 was almost half of the AAM-8 and slightly lower than the OPC.

The higher drying shrinkage of AAM-8 was due to the larger amount of GGBFS in its composition which caused a high rate of hydration inside the mortar. But using sucrose significantly reduced the hydration intensity and improved the reaction process.

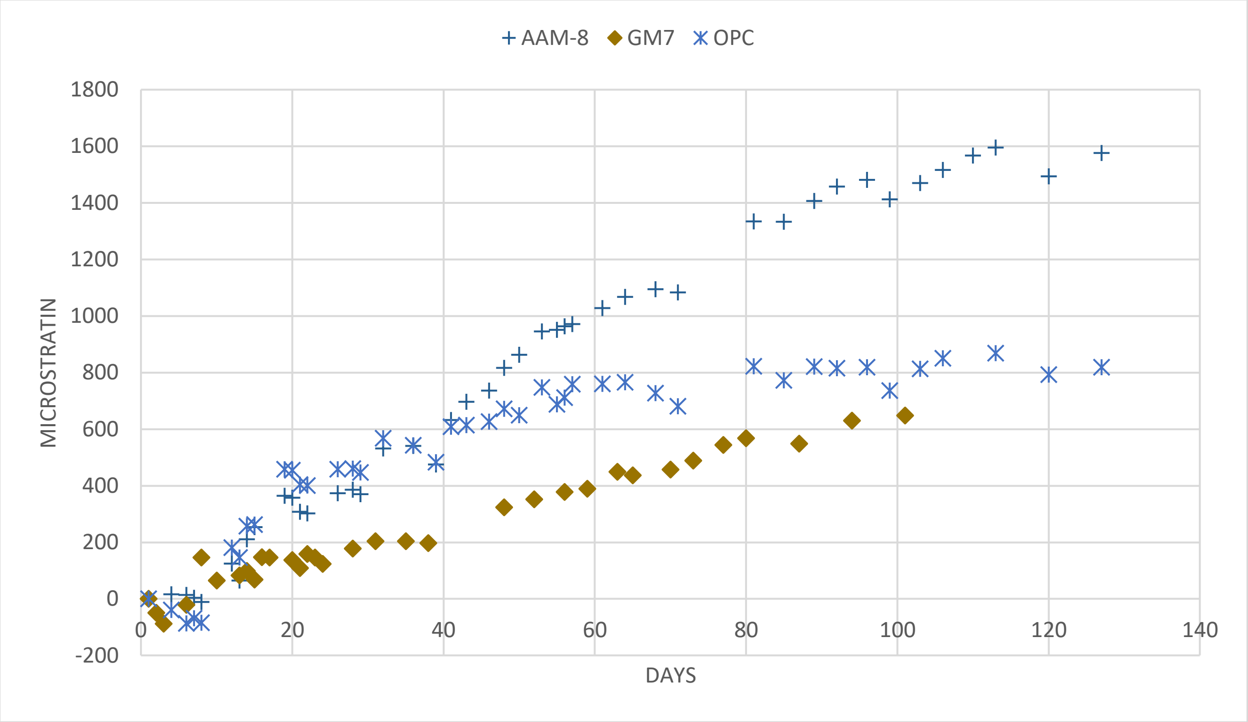

Figure 4.7 Drying shrinkage result

4.5 Conclusion

In the previous experiment, it was noticed that the mortars with higher percentages of GGBFS had a very quick setting time that creates difficulty in handling and casting them into the molds. Therefore, this research aimed to use sucrose as an admixture to retard the reaction process and delay the setting time. The following conclusion can be acquired from this study;

1. Using sucrose has a significant influence on the setting time of the AAM. It increases both the initial and final setting time of the materials.
2. Sucrose improves the flowability of AAM made by the one-part mixing method.
3. Both the compressive and flexural strength can be increased by using sucrose as an admixture in the AAM. The more significant effect can be seen in the increment of early compressive strength. The higher strength of the AAM with using sucrose is attributed to the better dispersion of the aluminosilicate precursors and AA all over the mortar.
4. AAM with sucrose has a much lower drying shrinkage than the one without sucrose. This is due to the reduction in the hydration rate and reaction process of AAM containing the admixture.

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Chapter 5

A Consideration on the One-part Mixing Method of Alkali-activated Materials: Property Comparison with the Two-part Mixing Method and Solubility Problem of Sodium Silicate

5.1 Introduction

Some researchers reported [1,2] that the AAM made by the one-part mixing method had lower mechanical strength than the one made by the two-part mixing method. Ouyang et al [1] found some undissolved particles of sodium metasilicate pentahydrate by studying the microstructure of the samples. Therefore, inappropriate dissolution of the alkaline source may cause the problem. Basically, the alkaline solution is the main part of geopolymer and AAM for geopolymerization and activation of the aluminosilicate precursors to make the binder [3]. Hence, there is a need for studying the solubility of both kinds of alkaline activators. NaOH pellets and granular $Na_2SiO_3.5H_2O$ in different solvent temperatures. The result will help the further development of the method.

Granular sodium metasilicate pentahydrate was used for making AAM by one-part mixing method in the previous experiment, moreover, some other researchers also used the material while adopting the same mixing method [1,4,5]. This is maybe due to the higher solubility [6, 7] and availability of the material compare to the other types of solid sodium silicate. So, there is a need for studying the properties of sodium metasilicate aqueous solution and its influence on the characteristics of AAM. Because there isn’t any study available regarding this. Moreover, this experiment characterizes the applicability of sodium metasilicate solution in a two-part mixing method. Traditionally, in a two-part mixing method, AAM is produced by using water glass gel that has a modulus (SiO_2:Na_2O) of around 2 which make the AAM viscose and cause application problem [8,9,10]. But sodium metasilicate has the modulus of 1. And according to Davidovits [11], the viscosity of the water glass is decreased when reducing the molar (SiO_2:Na_2O) ratio.

In the previous experiment, the authors observed the problem of the quick setting of the mortar which had a significant amount of slag in their composition, but using sucrose delayed the solidification of the mortar and facilitate the casting of the mortar. Therefore, sucrose was used as an admixture in the mortars which were produced to characterize the properties of the AAM made by $Na_2SiO_3.5H_2O$ solution.

5.2 Objective

The objectives of this study can be defined as follow;

1. Comparison of the flowability and compressive strength of the samples made by a one-part and a two-part mixing method. Remember that the chemical composition of both types is the same.

2. Solubility test of sodium metasilicate pentahydrate ($Na_2SiO_3.5H_2O$) by a solvent with different temperatures.

3. Characterization of an aqueous solution made by sodium hydroxide (NaOH) and $Na_2SiO_3.5H_2O$.

4. Study the properties of mortars using $Na_2SiO_3.5H_2O$ aqueous solution as a water glass.

5.3. Experiments

5.3.1 Material

The materials utilized were fly ash type II, slag with a Blaine size of 6000 cm^2/gr, and micro-silica as aluminum silicate precursors. Alkaline materials used were NaOH pellets and granular $Na_2SiO_3.5H_2O$. Sucrose was used as an admixture to improve the reaction process. Standardized sand conforming to JIS standard was used as fine aggregate. The chemical composition and other properties of the materials are explained in chapter 3 of the thesis. AA aqueous solution was made for making mortars by a two-part mixing method. The procedure of making an AA solution is explained in the next section.

5.3.2 Making alkali solution

The Water Bath Shaker was used to make an alkaline activator (AA) solution. It was equipped with a heater to control the temperature of the water inside, wires that can hold the flasks, and a shaking mechanism. For the making of the alkaline solution, firstly, the shaker's tub was half-filled with water. Then, flasks with a specified amount of distilled water were placed inside it and tightened by its wires. The temperature of the water inside the tub was set to 30°C. The frequency of the shaking was at 120 rounds/min. Specific NaOH pellets were put inside each of the flasks in two sets, then shook for 3 minutes for complete dissolution. Granular $Na_2SiO_3.5H_2O$ were placed inside the flasks in 3 equal sets of shakings. During the dissolution of NaOH pellets in water, the solution's temperature increased. It helped the first set of granular $Na_2SiO_3.H_2O$ to be dissolved well in the NaOH solution. When the temperature decreased, the $Na_2SiO_3.5H_2O$ could not be dissolved well. Therefore, in the second and third sets, the tub water temperature was increased to 40 and 45°C, respectively.

After $Na_2SiO_3.5H_2O$ was dissolved entirely in NaOH solution, they were put in a larger flask and stored at room temperature. After some while, it was noticed that the solution was susceptible at normal temperature, and crystallization of the solutes could quickly occur inside the solution. Therefore, the solution was put in an incubator at 45°C. After that, the crystallization of the solute disappeared, and the solution became transparent, smooth, not viscose, and looked like water

Figure 5.1. Making alkaline solution: (A, B) Water Bath Shaker, (C) AA solution after dissolution process, (D) Crystallization of the solutes, (E) An incubator, (F) AA solution after heat treatment in the incubator.

5.3.3 Comparison of the properties of samples made by the one-part and two-part mixing method

To compare the properties of the AAM mortars made by one-part and two-part mixing methods, low calcium-based fly ash was used as aluminosilicate precursor and 8M NaOH and 32% $Na_2SiO_3.5H_2O$ were used as AA. The AA/ aluminosilicate materials ratio was set to around 0.6 for all the samples. For the one-part mixing method, the AA was used in the dry state while in the two-part mixing method, they were used in the solution state. The AA solution was made by using Water Bath Shaker.

Table 5.1 The specification of each type of mortar

Sample	Fly ash (%)	AA	Mixing Method
GO	100	NaOH+$Na_2SiO_3.H_2$0	One-part
GT	100	NaOH+$Na_2SiO_3.H_2$0	Two-part

For the one-part mixing method, the water temperature was set to 24 to 25°C. while for the two-part mixing method, the temperature of the AA solution was around 40°C, because as it was mentioned in the previous section that crystallization could occur at a lower temperature. The mixing procedure was the same as explained in the previous chapters. For the mortars made by the one-part mixing method, they were vibrated just after the casting. But for the two-part mixing method, the flow was higher enough that vibration was not required. The samples made by the two-part mixing method were demolded after 48 hours but the sample made by the one-part mixing method took a long time for the consolidation and setting, therefore, they were demolded after 7 days. After the demolding procedure, they were sealed with plastic and were cured at around 20 °C in a controlled temperature room until their compressive strength test.

The flowability and the compressive strength properties of the mortars were studied and compared. The flowability was tested according to JIS R 5201. To study the 7-, 28- and 56-days' compressive strength, cylindrical samples were made. The test procedure was carried out according to JIS R 5201.

5.3.4 Experimental program for characterization of AAM made by sodium metasilicate pentahydrate solution

For this experiment, four types of mortar samples were made as shown in Table 1. NaOH solution's molarity was 8M. The concentration of the sodium metasilicate solution was 32%, and the ratio of the alkaline solutions (Na_2SiO_3: NaOH) was set to 1.5 for all types of mortar and paste samples.

Table 5.2 Percentages of the aluminum silicate precursors in each type of the sample

Sample	**Fly ash (%)**	**GGBFS (%)**	**Silica fume (%)**
M1	80	20	0
M2	70	30	0
M3	75	20	5
M4	100	0	0

Table 5.3 Mixture proportions of AAM mortars (kg/m^3)

Mix	**Aluminosilicate materials**			**Sand**	**Alkali activator (AA) aqueous solution**			**Mixing Water (10% of aluminosilicate materials)**	**Sucrose**	**L/B***
	Fly ash	**GGBFS**	**Silica fume**		**NaOH**	**$Na_2SiO_3.5H_2O$**	**Solvent water**			
M1	422.8	105.7	0	1536.2	29.8	93.9	160.8	52.9	10.6	0.64
M2	373.9	160.2	0	1536.2	31.0	97.2	166.4	53.5	10.7	0.65
M3	397.9	106.1	26.5	1536.2	29.8	93.9	160.8	53.0	10.6	0.64
M4	517.6	0.0	0	1536.2	29.2	92.1	157.5	51.8	10.4	0.64

*Liquid/binder. L: Solvent water + Mixing water (10% of aluminosilicate precursors) + NaOH + Na2SiO3.5H2O. Binder: Aluminosilicate materials.

5.3.4.1 Preparation of the aluminosilicate precursors

To improve the reaction process for making the AAM, fly ash, slag and silica were premixed in a mixer called OMNI mixer.

The authors used an Omni mixer with a 5L capacity and rotation speed of 2.5Hz (2.5 spin or round per second) to mix the materials. Three liters of the materials were premixed, and they were covered by plastic bags and put inside the bucket with a lid. The duration time of the mixing was first set to 2 hours. But when the materials were not appropriately mixed and some white slag particles were apparent, then the mixing duration time was increased to 3 hours. After the 3-hour mixing, the materials were well mixed than before.

5.3.4.2 Mixing, casting and curing

The experiment prepared prisms of 160x40x40 mm for compressive and flexural strength and shrinkage tests. The materials were mixed in a paddle mixer. The mixing procedure was the same as described in chapter 3.

The M2 mortar required 10% more water to have a flow with sufficient workability, so it was decided to use 10% added water to all samples. The 10% extra water was added together with standardized sand in the mixing process.

During the mixing procedure, as the solution's temperature decreased due to the solute crystallization, the flow and the workability of the mortars decreased. Therefore, it was too difficult to cast them in the molds. This mixing condition was called the ambient mixing condition.

To solve the workability problem, it was decided to keep the mixing materials at 45°C in the incubator for at least 24 hours. And then mix the materials at a constant temperature of 24-26 °C. This mixing condition was named a hot mixing condition. The crystallization of the solution was not observed in the hot mixing condition and the mortar had sufficient workability. The mixing procedure was done at the temperature above inside a tent. The study observed significant improvement in the flow and rheology of the mortar.

The flow rate was measured according to JIS (R5201). After that, the mixtures were poured inside prisms, then vibrated for 2 minutes. To avoid the crystallization of the solution during the curing and facilitate the reaction process between aluminum silicate precursors and the alkaline solution, the prisms were put at 45°C and 94% relative humidity inside an incubator for 2 days.

5.4 Result and discussion

5.4.1 Comparison of the properties of samples made by the one-part and two-part mixing method

5.4.1.1 Flowability

Figure 2 shows the flowability of the mortar made by the one-part and two-part mixing methods. In the two-part mixing method, the flow value of the mortar is 244 mm which is significantly higher than the one made by the two-part mixing method. The flow value of GO which is made by the one-part mixing method is 159 mm. The lower flow rate of the GO is due to the poor solubility of $Na_2SiO_3.5H_2O$, the detail of the solubility of the material is described in the forthcoming section. Whereas, in GT, the AA is in a solution state and all the materials were well dissolved in the solvent.

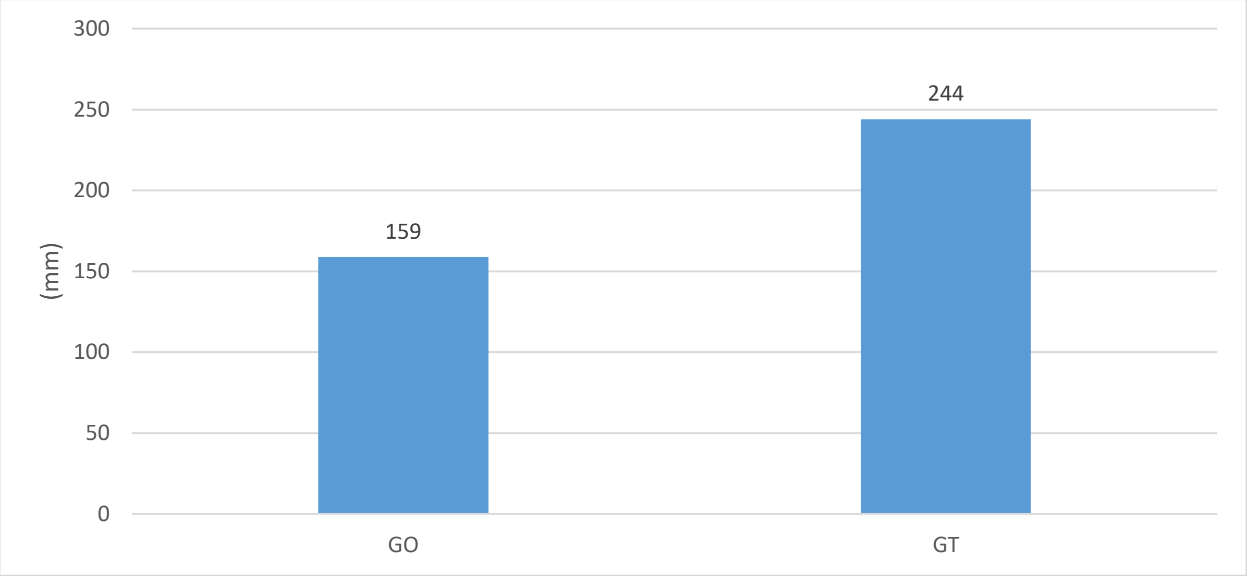

Figure 5.2 Comparison of the flowability

5.4.1.2 Compressive strength

The samples made by the two-part mixing method had significantly higher compressive strength than the samples made by the one-part mixing method at 7, 28, and 56 days. The compressive strength of the GT was higher than the GO by 104% at 7 days, by 357% at 28 days, and by 725% at 56 days' test. This indicates that the AA solubility had a serious and important effect on the properties of the materials. Furthermore, the AA solution's temperature in GT may also have an impact on the increasing strength of the AAM.

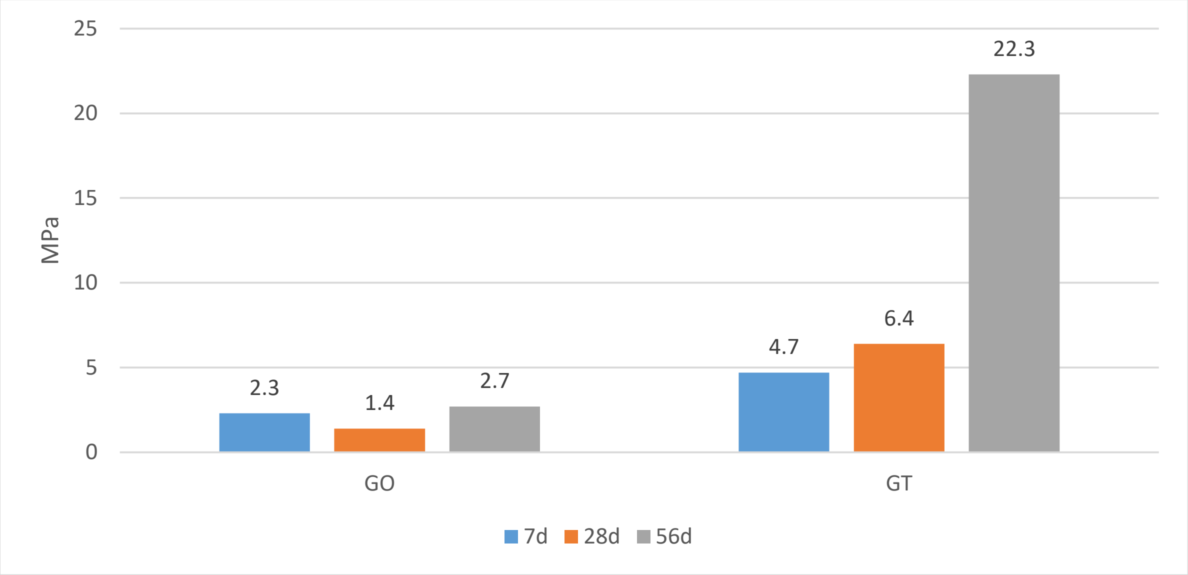

Figure 5.3 Comparison of the compressive strength

5.4.2 Solubility of the solid alkaline materials

The reaction between aluminosilicate precursors and alkali-activated materials is vital for producing Geopolymer and AAMs. Therefore, it is important that in a one-part mixing method solid alkaline materials such as NaOH and sodium silicate are well dissolved to achieve the material with the required properties.

A solubility test of the materials was conducted to better understand the alkaline materials' solubility mechanism in the one-part mixing. One batch mixing amount of NaOH pellets, granular sodium metasilicate pentahydrates, and water was put inside a flask. The $Na_2SiO_3.5H_2O$: NaOH ratio was set to 1.5. Water Bath Shaker was used to mix the materials. The shaking frequency was set to 120 rounds/min.

The temperature of the water before mixing with the alkaline materials was 26°C. NaOH pellets and $Na_2SiO_3.5H_2O$ were put inside the flask and shook for 5 minutes. The duration of shaking was chosen according to the estimated mixing timing of making mortar or concrete in a mixer. After 5 minutes of mixing, the temperature of the solution increased to about 34°C. As the dissolution of NaOH in water is an exothermic reaction, it rose the temperature of the solution to about 8 degrees Celsius. The majority of the particles couldn't be dissolved in water and those particles were the sodium metasilicate since NaOH quickly dissolved in water, this was confirmed by another attempt, in which less than 5 minutes were required for the NaOH to be fully dissolved inside the solvent.

Therefore, the solution was mixed for two more minutes, but still, there was no improvement observed in the dissolution rate, and the temperature of the solution decreased to 31°C. Thus, to increase the temperature of the solution, the temperature of the water tub bath shaker was set to 35 °C and then to 40°C, and each was mixed for 5 minutes. The temperature of the solution increased to 32 and 36.5 °C respectively. A significant improvement in the dissolution rate of the sodium metasilicate was observed. However, there were still some particles that remained undissolved. When the temperature of the solution was kept to 41 °C, total dissolution of the particles occurred.

This study shows that dissolution of the sodium metasilicate by a solvent with a lower temperature is difficult and couldn't be fully dissolved when adopting the drying mixing method to make geopolymer and alkali-activated materials. A temperature of around 40°C for the solvent is required to dissolve the material thoroughly. Concerning increment of some degrees of temperature by the NaOH, a solvent slightly lower than the temperature mentioned above can also be enough for solubility of the sodium metasilicate. The temperature of the aluminum silicate precursors and aggregates may also influence the solubility of the materials. Therefore, the hot mixing condition will have a significant effect on the one-part mixing method. Moreover, besides maintaining the proposed temperature, increasing the mixing duration and reducing the $Na_2SiO_3.5H_2O$: NaOH ratio may also play important role in the dissolution of the material in the one-part mixing method.

5.4.3 Characterization of AAM made by the sodium metasilicate pentahydrate solution

5.4.3.1 Flowability

This test was carried to observe the influence of the aluminosilicate precursors and change in mixing conditions on the flow of the samples. Moreover, the flow and rheology of the alkaline solution made by the sodium metasilicate are discussed in this section.

The alkaline solution made by NaOH pellets and sodium silicate pentahydrate was smooth and fluent and there was no sign of viscosity. But as mentioned before, the alkali solution was very sensitive to the temperature variation as the crystallization of the alkaline activator solution occurred at a temperature lower than 30°C. Therefore, the workability and flowability of the mortars were decreased at the aforementioned temperature. The same phenomena of crystallization of water glass can also happen while adopting the one-part mixing method using sodium silicate pentahydrate. The crystallization in the solution may reduce the reaction process between the alkali and the aluminosilicate precursors. Hence the properties of the alkali-activated product can be reduced.

In this study, it was decided to change the temperature of the materials and the mixing condition. All the materials were kept at 45 °C for 24 hours, and the mixing was done at a controlled temperature of 24-26 °C. When the mixing condition changed to the hot mixing condition, significant improvement in the workability of fresh mortar was observed and crystallization was disappeared.

Before applying the hot mixing condition, the M1 mix was made in an ambient mixing condition, and the flow of the mixing was so low that it couldn't be easily put inside the molds. The flow value of the M1 was 102.5mm. There was about a 15% increment in the flow value of the mixture when the hot mixing condition was applied. A higher flow rate was achieved due to a reduction in the mix's cohesiveness at a higher temperature.

The M4 (fly ash 100%) sample had the highest flowability among the samples, and its flow value could not be measured due to its overflow from the flow table. Figure 4 shows the flow of M4. While some studies [8,9,10] show low workability and high viscosity for fly ash-based geopolymer using Na-based silicate as an activator. They also reported that admixtures such as superplasticizers did not significantly improve the flowability and rheology of paste or mortar. However, this experiment shows that all the fresh mortars were smooth, fluent, and without viscosity. This was achieved due to the use of sodium metasilicate and adopting hot mixing conditions.

Figure 5.4 Flow value of M4

The slag and micro-silica decreased the flowability. The mortar with 30% of the slag had the lowest flow value of 114 mm. M3 and M1 had a flowability of 122 and 120 mm, respectively.

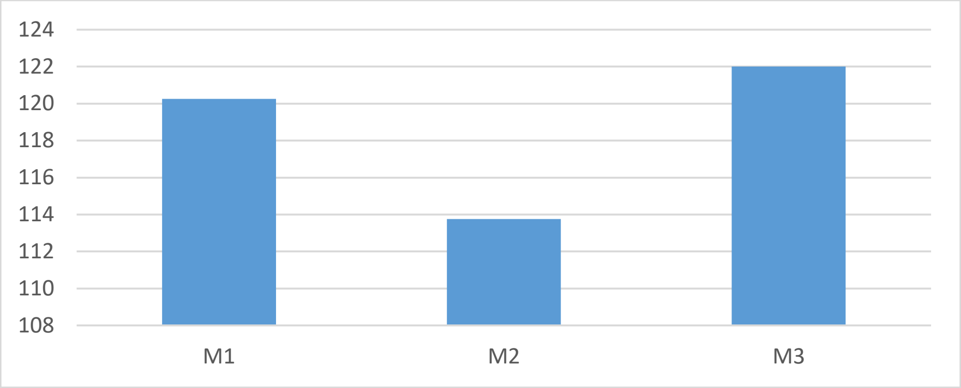

Figure 5.5 Flow value (mm)

5.4.3.2 Compressive and flexural strength

Compressive and flexural strength is an important characterization of AAM. As sodium silicate improves the reaction process between the precursors and alkali [12], the result of compressive and flexural will reveal if a reasonable early strength is achieved by using the sodium metasilicate. Therefore, each sample type was tested for compressive and flexural strength at 7, 28, and 56 days. The test used a Universal Testing Machine (UTM) with a capacity of 200 tons.

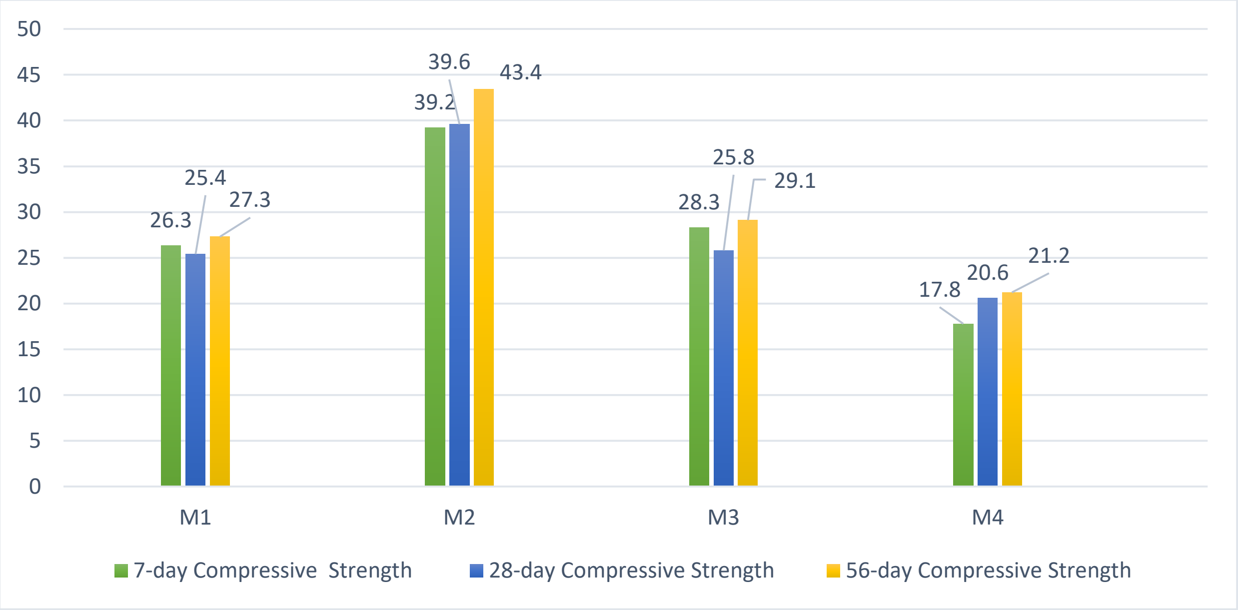

Figure 5.6 The compressive strength (MPa)

Slag had a significant influence on the compressive strength of the samples. M2, which had 30% slag, had the highest compressive strength at the age of 7, 28, and 56 days which are 39.2MPa, 39.6 MPa, and 43.4MPa, respectively, followed by M3 and M1.

M4, made of 100% fly ash, had the lowest compressive strength of all ages. M4 had a compressive strength of 17.8 MPa, 20.6MPa, and 21.2MPa for the ages of 7, 28, and 56 days respectively. The flow of M4 was much higher than the other types, decreasing the liquid/binder ratio can improve the strength of M4.

In accordance with the compressive strength result, M2 had the highest 7, 28, and 56-day flexural strength, which is around 6MPa—followed by M1 and M3, which had the flexural strength of around 5 MPa for all ages. In comparison, M4 had a flexural strength of 3.7 MPa for seven days, 4.2 MPa for 28 days, and 4.7 MPa for 56 days.

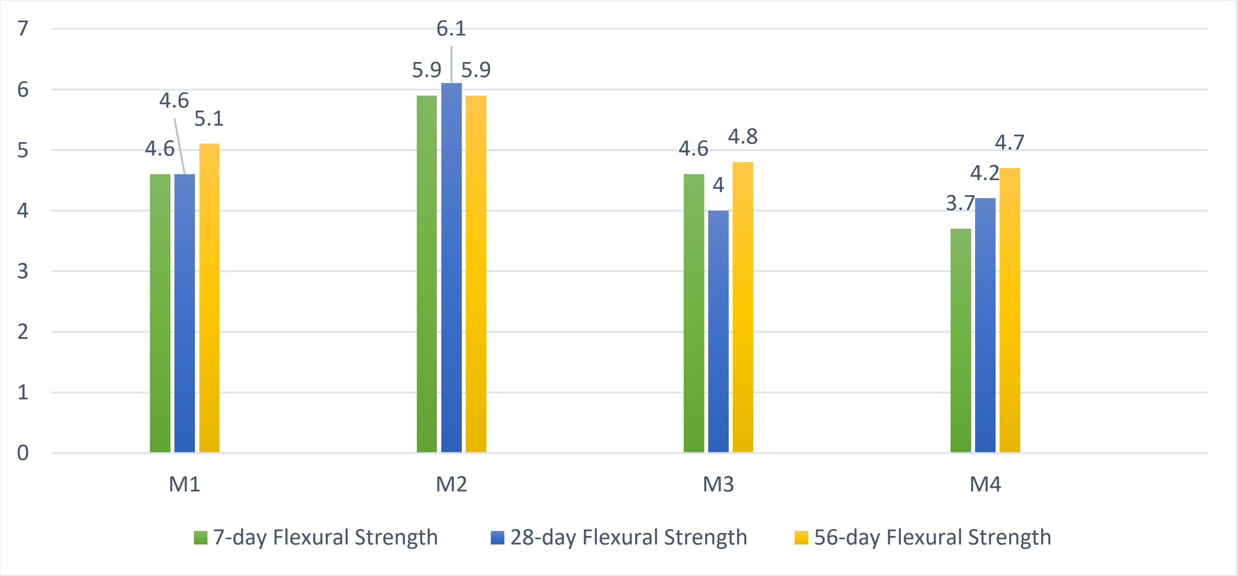

Figure 5.7 The flexural strength (MPa)

All the samples achieved reasonable early compressive and flexural strength by the age of 7 due to the Ca element's presence in the slag [6] and the influence of the sodium metasilicate as a source of silica.

Both compressive strength of more than 40 MPa and flexural strength of 6 MPa can be achieved by using 32% concentrated sodium metasilicate solution, which is much lower than the concentration of water glass or sodium silicate solution used in making traditional geopolymer and alkali-activated materials [13,14,15,16,17].

5.4.3.3 Drying shrinkage

Drying shrinkage of the samples was studied according to [18]. The test was conducted to study the influence of the mix proportion of the aluminosilicate precursors activated by the alkaline activator solution made by the sodium metasilicate and sodium hydroxide on the drying shrinkage property of the AAM.

M3, M2, and M1 had higher amounts of shrinkage compared to M4. It was due to the presence of the slag and silica fume in their composition. Which caused the quick reaction and early loss of water in the mixture. The shrinkage of samples containing slag was increased until 50 days, after that, it was decreased and then flattened. On the other hand, the shrinkage of the 100% fly ash sample was nearly 0 microstrain at the age of around 90 days. This is attributed to the slow reactivity of the precursor.

The shrinkage of all samples was below 0.07 percent, within the range of allowable shrinkage defined by the ACI 209R, which is 0.05 to 0.078% [19]. This is maybe due to the curing of the samples at 45°C in the incubator. Which conforms to the result of [17].

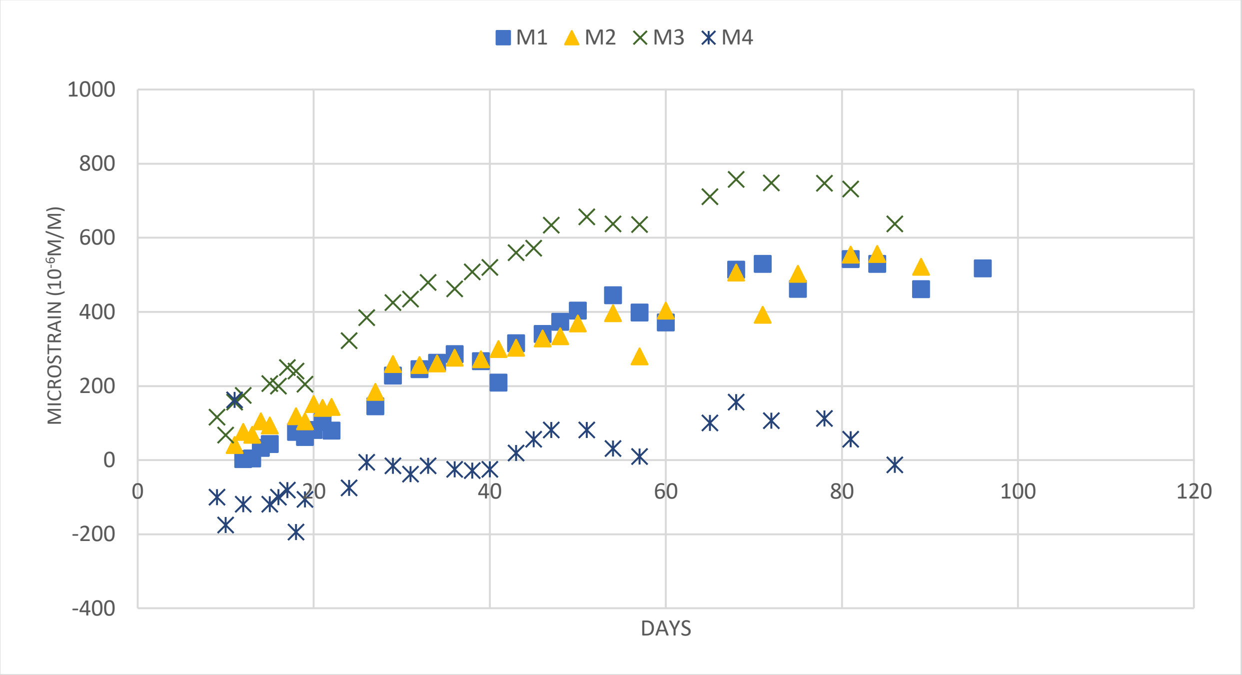

Figure 5.8 Shrinkage test result

5.5 Conclusion

One-part mixing method was studied by many researchers to make ease in the production of alkali-activated materials and geopolymers and to generalize the materials. But some researchers found the quality of the materials made by the one-part mixing method is lower than the one made by the two part-mixing methods. Therefore, this research reconfirms the properties of materials made by both kinds of mixing methods. Furthermore, none of the researchers checked the solubility of the alkaline materials used in the aforementioned mixing method. Therefore, this research studied the dissolution mechanism and solubility of the alkaline materials used in a one-part or dry mixing method. Moreover, the aqueous solution from sodium metasilicate and NaOH were made to overcome workability and rheological problems. This study concludes as follow:

1. Granular sodium metasilicate pentahydrate cannot be dissolved totally in a solvent with a temperature of around 25°C in 5 or more minutes of mixing. The problem of solubility can decrease the mechanical strength and other properties of AAM.
2. The dissolution of the sodium metasilicate increases with an increase in temperature. Total dissolution of the material occurs at a temperature of around 40°C. Hot mixing conditions can play a significant role in the material's solubility in the one-part mixing method.
3. The alkaline solution made by the sodium metasilicate is more fluent and smoother. This is due to the lower amount of SiO2 and concentration of the water glass. But the alkaline solution is more sensitive to the lower temperature. Crystallization of the solution can easily happen at a temperature below 30°C. The same phenomena of crystallization of water glass can also occur while adopting a dry mixing method. This can reduce the reaction process between the alkali and the aluminum silicate precursors and reduce the properties of the alkali-activated product. To avoid crystallization and to retain it smooth, keeping the solution at a higher temperature is recommended.
4. Mixing materials at the ambient condition method decreases the flow rate of the fresh mortar made by the sodium metasilicate solution due to the sensitivity of the solution at a lower temperature. Therefore, the hot mixing condition improves the flow rate of mortars
5. AAM samples made by the sodium metasilicate solution can acquire shape according to the molds, and the surfaces of the samples are the same as other types of alkali-activated material made by the traditional method.
6. Incorporating slags in AAM material has advantages such as improving the reactivity between aluminum silicate precursors and modifying the compressive and flexural strength and density. A compressive of around 40 MPa can be achieved by combined fly ash and slag-based AAM activated by a low concentrated sodium metasilicate and NaOH solution.
7. Using sodium metasilicate solution in the two-part mixing method can solve the viscosity problem created by sodium silicate gel.

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Chapter 6

A Study on The Influence of Sodium Silicate Concentration and Modulus Ratio, Temperature of the Raw Materials, Sucrose and Curing Conditions on the Properties of Low-Calcium Fly Ash-Based Alkali-activated Materials

6.1. Introduction

Low calcium fly ash-based AAM has some extraordinary advantages. They possess geopolymeric characteristics such as low shrinkage and high fire resistance [1]. But compared to the slag-based AAM they have lower strength [2,3] and longer setting time [4] when cured at ambient temperature conditions. The high setting time of the material is considered one of the major problems, this means that they can't set or harden well at ambient temperature curing conditions. They sometimes need more than 40 hours to achieve their final setting [4].

Incorporating the slag with fly ash improves the reactivity of the aluminosilicate precursors that result in hardening of the samples at ambient temperature and modify some other properties of concrete such as compressive strength, flexural strength, and density of the AAM [5]. As the slag is very active and increases the reactivity and hydration of the materials [6], this causes the materials to emit a higher amount of heat during the reaction process [7]. Therefore, the drying shrinkage of alkali-activated materials with slag is much higher than the other types [5, 3].

This research aims to solve the problem related to low calcium fly ash-based AAM. Therefore, the influence of the concentration and molar ratio of sodium silicate, etc. is studied on the setting time, flowability, and compressive strength of AAM.

Conventionally, for the production of fly ash-based AAM or for other types, sodium silicate is used at a concentration of around 50% [8, 9, 10] In the previous experiment while characterizing the one-part mixing method of AAM, granular sodium metasilicate was used with a concentration of 32%. A quick setting of the mortar consisting of 100% low-calcium fly ash was observed. Hence, the role of concentration and types of sodium silicate on the setting time of the AAM is considered to be studied in this experiment.

6.2. Objectives

Study the influence of the following factors on the setting time, flowability and compressive strength of the low-calcium fly ash-based AAM:

1. Sodium silicate molar ratio (SiO_2:Na_2O ratio).
2. Sodium silicate concentration.
3. The addition of sucrose
4. Raw material (fly ash and sand) temperature

5. Curing condition.

6.3. Experiment

6.3.1 Materials

Fly ash type II was used as an aluminosilicate precursor, the composition and other properties are illustrated in Table 1. Sodium silicate and sodium hydroxide were used as alkali activators (AA). The concentration of NaOH was 8 molars. Sodium silicate: NaOH ratio was set to 1.5 for the paste and mortar samples. According to the SiO_2:Na_2O modulus, two types of sodium silicate were used: Sodium metasilicate pentahydrate ($Na_2SiO_3.5H_2O$) which has the modulus of 1, and sodium disilicate ($Na_2O.2SiO_2$) with the SiO_2:Na_2O ratio of around 2. The sodium metasilicate was in the granular solid state, while sodium disilicate was used in form of solution gel. The granular sodium metasilicate consisted of 28% SiO_2, 28% Na_2O, and 54% H_2O, and sodium disilicate aqueous solution was composed of 36% SiO_2, 18% Na_2O, and 46% H_2O. Standardized sand conforming JIS R 5201 was used as a fine aggregate for making the mortars. Sucrose was used as an admixture in this experiment.

Table 6.1 Specific gravity (S.G.), the chemical composition of materials in weight percentage (wt. %) by XRF, and chemical analysis of standardized sand

Materials	Chemical composition (% weight)							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	H_2O	K_2O	SG(g/cc)
Fly ash	55.19	25.35	7.57	4.06				2.33
Standardized sand	98.4	0.41	0.36	0.16	0.01	<0.2	0.01	2.64

6.3.2 Mix proportion and samples detail

In this research, 7 types of paste and 11 types of mortar samples were made. Table 2 and Table 3 show the chemical composition and other characteristics of the pastes and mortars respectively. AA solution was composed of NaOH and sodium silicate.

To investigate the effect of the sodium silicate solution (water glass) on the setting time, flowability, and compressive strength of the AAM, 3 patterns of sodium silicate solution were utilized. Sodium metasilicate solution with a concentration of 32% and sodium disilicate solution with concentrations of 32% and 54% were prepared. Each type of aforementioned solution was then mixed with 8M NaOH to make AA solutions. Granular sodium metasilicate pentahydrate was dissolved in water to make the solution. The procedure was conducted by a Water Bath Shaker. Sodium disilicate solution (a commercial name) with 54% concentration which is available commercially was provided, and for the making of 32% concentration, the estimated amount of water was added to the solution. In the previous experiment, the solubility of $Na_2SiO_3.5H_2O$ was investigated. It was found that the granular sodium metasilicate couldn't be dissolved well in a solvent with a temperature below 40°C. Moreover, below the aforementioned temperature, the solution was sensitive and crystallization of the solute could easily occur. So, it was recommended to use water or a solvent at around 40°C temperature while adopting a one-part mixing method. Therefore, for better characterization, all the AA solutions were used at 40°C in the experiment.

To study the influence of the temperature of the mixing materials on the properties of the AAM, the materials were used in two different temperature conditions, hot conditions and ambient conditions. In hot conditions, all the materials were used at 40 °C. But at the ambient conditions, except for the AA solution, the temperature of the raw materials such as fly ash and sand was around 20°C. There was a difference of 20 °C between those two mixing conditions. As mentioned before, AA solution was used at a temperature of around 40 °C both for ambient and hot mixing conditions.

The effect of sucrose on the properties of the paste and mortars was also studied. The amount of sucrose was set to 2% by the mass of fly ash.

For the characterization of the curing condition of the mortars, they were cured at ambient conditions and in an oven or incubators. At ambient condition, they were put at a controlled temperature room where the temperature was set to around 20 °C, but for the others which were cured inside incubators, the temperature was set to 45°C and was kept for 24 hours and then they were put inside the controlled temperature room until the compressive strength test day.

Table 6.2 Mix proportion and detail of each paste type

No	Samples	Fly ash (g)	SiO_2/Na_2O	32 % Sodium metasilicate concentrated +8M NaOH AA Solution (g)	32 % Sodium disilicate concentrated +8M NaOH AA Solution (g)	54 % Sodium disilicate silicate concentrated +8M NaOH AA Solution (g)	Sucrose (g)	Solution/Fly ash	Raw material (fly ash, sand) temperature
1	PA	400	2	0	0	166	0	0.42	20°C
2	PH	400	2	0	0	166	0	0.42	40°C
3	P1A	400	1	140	0	0	0	0.35	20°C
4	P1H	400	1	140	0	0	0	0.35	40°C
5	P2A	400	2	0	140	0	0	0.35	20°C
6	P2H	400	2	0	140	0	0	0.35	40°C
7	P3A	400	1	140	0	0	8	0.35	20°C

Table 6.3 Mix proportion and the details of each mortar type

No	Fresh mortar	Cylindrical samples	Fly ash (kg/m^3)	Sand (kg/m^3)	$Si_2O:Na_2O$	32 % Sodium metasilicate concentrated+ 8M NaOH AA Solution (kg/m^3)	32 % Sodium disilicate concentrated+ 8M NaOH AA Solution (kg/m^3)	54 % Sodium disilicate silicate concentrated+ 8M NaOH AA Solution (kg/m3)	Sucrose (kg/m$_3$)	Solution /Fly ash	Fly ash and sand temperature	Curing Condition
1	GA	GAO	517.6	1536.2	2	0	0	278.7	0	0.54	20°C	O
2	GH	GHO	517.6	1536.2	2	0	0	278.7	0	0.54	40°C	O
3	G1A	G1AA	517.6	1536.2	1	278.7	0	0	0	0.54	20°C	A
4		G1AO	517.6	1536.2	1	278.7	0	0	0	0.54	20°C	O
5	G1H	G1HA	517.6	1536.2	1	278.7	0	0	0	0.54	40°C	A
6		G1HO	517.6	1536.2	1	278.7	0	0	0	0.54	40°C	O
7	G2A	G2AA	517.6	1536.2	2	0	278.7	0	0	0.54	20°C	A
8		G2AO	517.6	1536.2	2	0	278.7	0	0	0.54	20°C	O
9	G2H	G2HA	517.6	1536.2	2	0	278.7	0	0	0.54	40°C	A
10		G2HO	517.6	1536.2	2	0	278.7	0	0	0.54	40°C	O
11	G3A	G3AA	517.6	1536.2	1	278.7	0	0	10.4	0.54	20°C	A

Note: A= ambient temperature condition, O= Curing at 45°C

6.3.3 Paste preparation and setting time test

Preparation of the paste and setting time test was done according to the JIS R 5201[25]. For the mixing, a paddle mixer was used. First, fly ash and AA solution were mixed for 1 minute. Then the mixing was stopped for 90 seconds followed by a 1-minute mixing. Next, they were poured into a mold. The pouring procedure was required to be completed within a minute. Then initial and final setting times of the pastes were tested.

6.3.4 Mortar preparation, flow and compressive strength test

The fly ash was first mixed with the alkaline solution for 1 minute, followed by the addition and mixing of standardized sand for 30 seconds each at low and high speed. Then the mixing procedure was stopped for 90 seconds and the next high speed mixed for 1 minute.

Except for samples containing 54% sodium disilicate, all other mortar had enough flow and smoothness that didn’t require a vibrator for the compaction. Samples with a 54% concentration of sodium disilicate were compacted by a vibrator.

Two patterns of curing were applied. At ambient condition and inside incubator. As mentioned before, for the ambient condition, the samples were cured inside a controlled temperature room in which the temperature was kept to around 20 °C. The other types were cured inside incubators for 48 hours and then cured at the controlled temperature room until their compressive strength test.

Flow test was conducted twice and the procedure was done according to the JIS R 5201 [11]. Cylindrical molds with a diameter of 5 cm and a height of 10 cm were used to study 7-, 28-, and 56-days’ compressive strength. The compressive strength test was also conducted according to JIS R 5201[30].

6.4 Result

6.4.1 Influence of the sodium silicate concentration

In this experiment, sodium disilicate solution was used in two concentrations, 32 and 54%. In PA and GA, the concentration of the water glass was 54% while in P2A and G2A it was 32%.

6.4.1.1 Setting time

Figure 1 shows the setting time of AAM with different concentrations of sodium silicate. PA which was made by a conventional method had 54% water glass in its composition. The initial and final setting time of PA was around 35 hours, which was notably high and the result confirmed the previous research [4]. This type of AAM is not applicable on site. The slow reactivity of low-calcium fly ash in an alkaline environment is the factor behind the delayed setting time. Therefore, they need to be cured at higher temperatures or partially replaced with slag to reduce the setting time. But using slag increase the shrinkage of the material. Interestingly, when the concentration of the water glass was reduced to 32%, there was a significant development in the initial and final setting time of the paste. The initial and final setting time of the P2A was 5.8 and 7 hours respectively. The increase in the amount of water might improve the reactivity of the fly ash and cause the paste to set quickly.

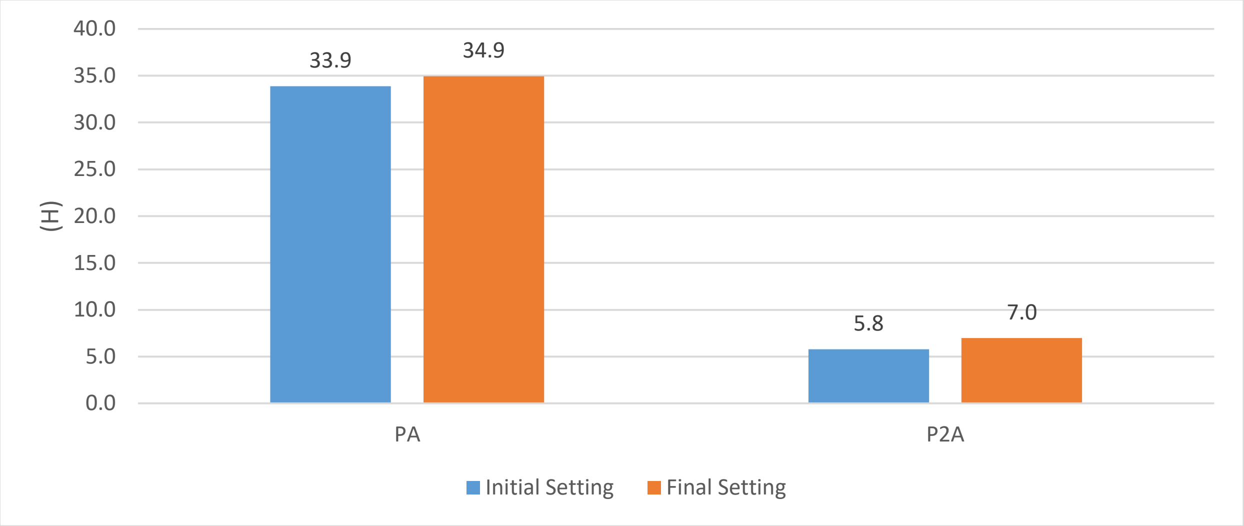

Figure 6.1 Influence of the change in concentration of sodium silicate solution on the setting time of the pastes

6.4.1.2 Flowability

Figure 2 shows the effect of the sodium silicate concentration on the flow properties of AAM. GA, a mortar that was made of 54% sodium silicate has a flow value of 145 mm which was much lower than the 32% sodium silicate concentrated AAM. G2A had a flow rate of 250 mm. As mentioned in the introduction section, conventional alkali-activated mortar and concrete have a higher viscosity. This viscosity is caused by the presence of SiO_2 in the sodium silicate solution. In this experiment, increasing the water amount in the solution reduced the viscosity and improved the flowability of the fresh mortars.

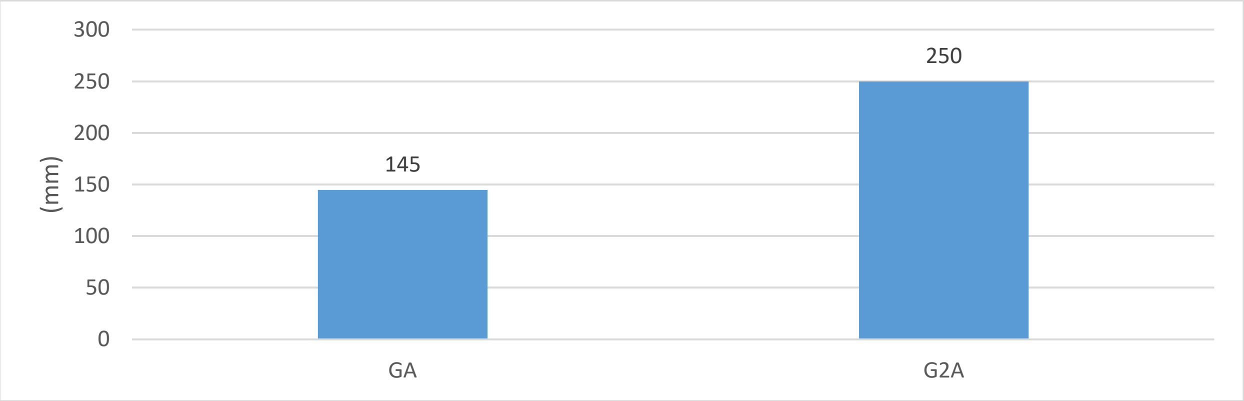

Figure 6.2 Influence of the change in concentration of sodium silicate on the flowability of AAM

6.4.1.3 Compressive strength

Figure 6.3 shows the influence of the water glass concentration on the AAM mortar compressive strength. GAA and G2AA were made by 54 and 32% sodium disilicate solution respectively. Both of them were cured at ambient temperature conditions. In this study, GAA which had almost the same composition as GA of this experiment was taken from another research [10]. The result shows that G2AA with 25.8 MPa, significantly had higher compressive strength than the GAA. The compressive strength of the GAA was 8 MPa.

Using sodium silicate with the lower concentration decreased the setting time and increased the compressive strength of the AAM in ambient temperature conditions. This indicates that the reactivity of the fly ash was increased with an increase in the amount of water or a decrease in the PH value of the alkaline solution.

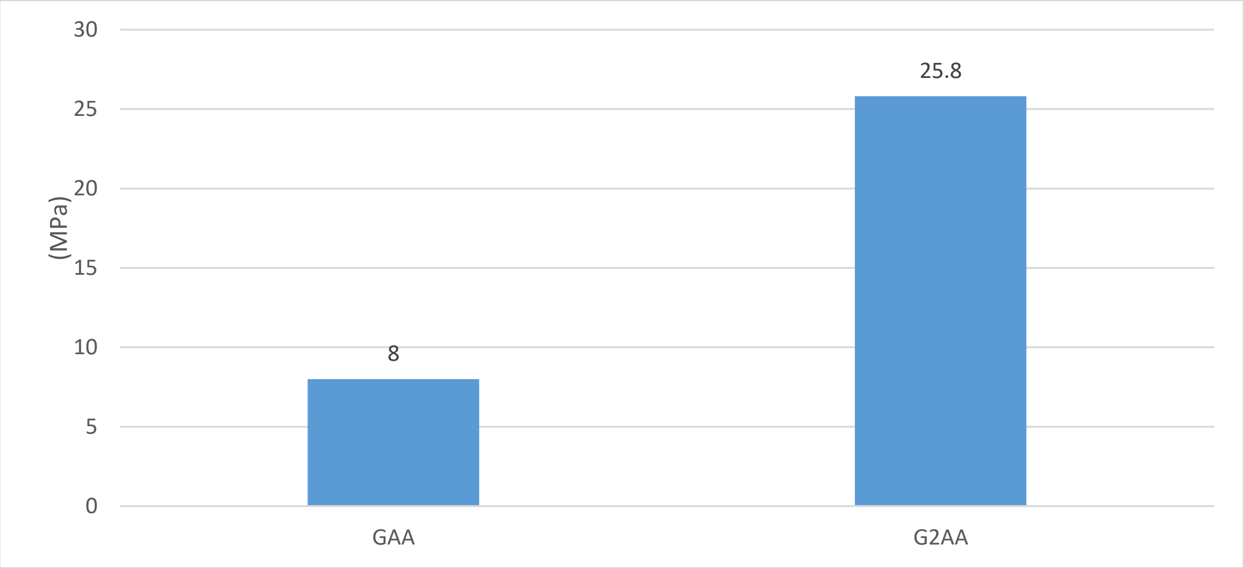

Figure 6.3 Influence of the change in concentration of sodium silicate on the compressive strength of AAM

6.4.2 Influence of the SiO_2:Na_2O ratio

6.4.2.1 Setting time

Figure 6.4 shows the influence of the sodium silicate molar ratio (SiO_2:Na_2O) on the initial and final setting time of P1A and P2A samples which was made by each 32% sodium metasilicate and sodium disilicate solution respectively. P1A had an initial setting time of 6.3 hours and a final setting time of 8.4 hours. Both the initial and final setting time of P1A was slightly higher than P2A which had initial and final setting times of 5.8 and 7 hours respectively. This indicates that the SiO_2:Na_2O ratio of sodium silicate solution with the same concentration doesn’t have any significant influence on the setting properties of low-calcium fly ash-based AAM. The final setting time of both kinds of material was slightly lower than OPC paste. OPC paste has a final setting time of around 10 hours [26]. This means that in terms of the setting time, both kinds of materials are reasonable for the cast-in-situ condition.

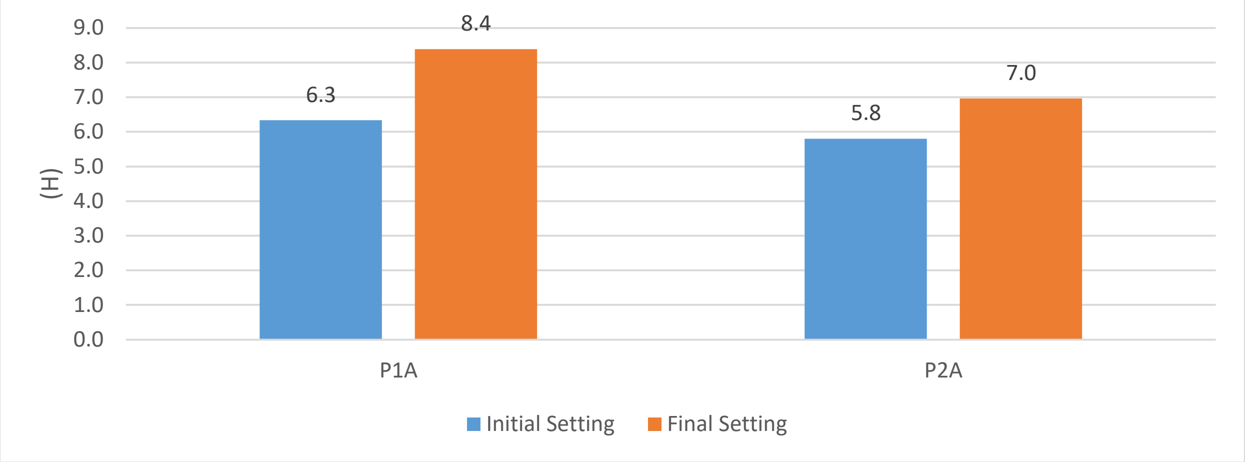

Figure 6.4 Influence of the SiO_2:Na_2O ratio on the setting time

6.4.2.2 Flowability

Same as the setting time test, the change in the SiO_2:Na_2O ratio didn’t have any significant effect on the workability and flow rate of both types of AAM. Both types, G1A and G2A had good flow rates of 244 mm and 250 mm respectively.

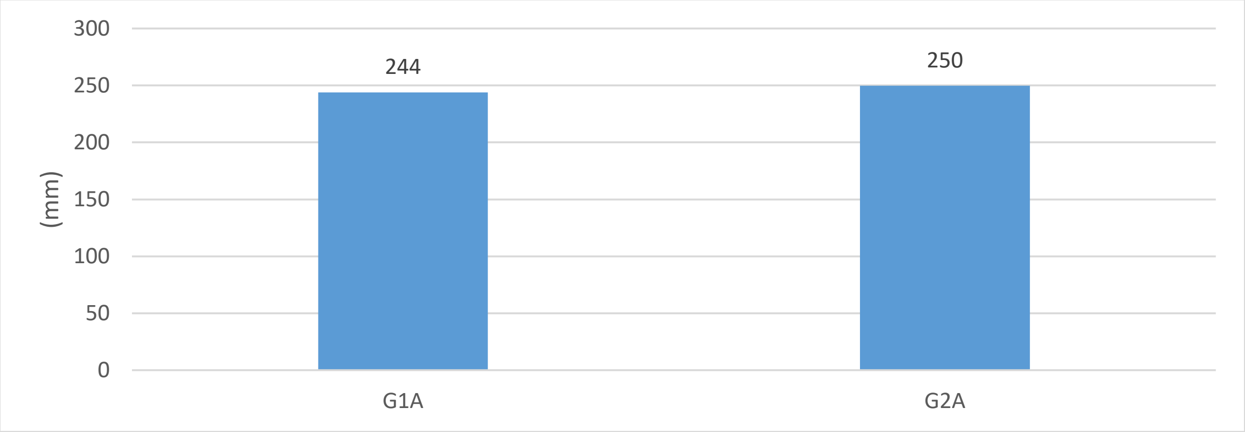

Figure 6.5 Influence of the SiO_2:Na_2O ratio on the flowability

6.4.2.3 Compressive strength

Figure 6.6 shows the influence of the SiO_2:Na_2O on the compressive strength of both types of AAM. G1AA had a compressive strength of 4.7 MPa, 6.4 MPa, and 23.2 MPa at 7,28 and 56 days respectively. Whereas G2AA's 7-, 28- and 56-days’ compressive strength were 4 MPa, 25 MPa, and 46 MPa respectively. This indicated that both types had almost the same compressive strength at 7 days but for 28 and 56 days, the compressive strength of the G2AA was increased by 403 and

719% respectively. This revealed that the increase in SiO_2 content of sodium silicate solution improved the compressive strength remarkably at ambient temperature curing.

This result indicates that with using 32% sodium disilicate, remarkable 28 and 56-day compressive strength can be achieved, which is appropriate for use in the structural field. However, the 7-day compressive was much lower, but that may be increased by a slight increase in the concentration or reducing the solution: fly ash ratio, as the flow value of the mortar, was high enough for the reduction.

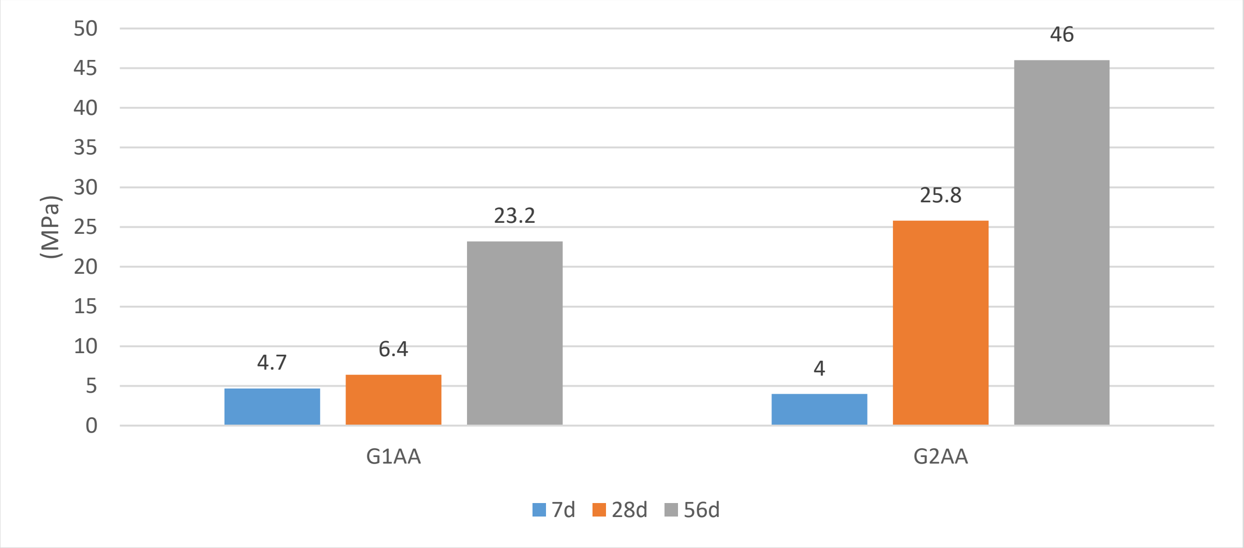

Figure 6.6 Influence of the SiO_2:Na_2O ratio on the compressive strength

6.4.3 Influence of using sucrose

6.4.3.1 Setting time

There was a significant increment in the initial and final setting times of the AAM when sucrose was added to the mixture. P1A had the initial and final setting time of 5.2 and 8.6 hours respectively, but when sucrose was added to the mixture the initial and final setting times were increased to 7.2 and 16.5 hours respectively. Figure 6.7 shows the effect of sucrose on the initial and final setting of low-calcium fly ash-based AAM.

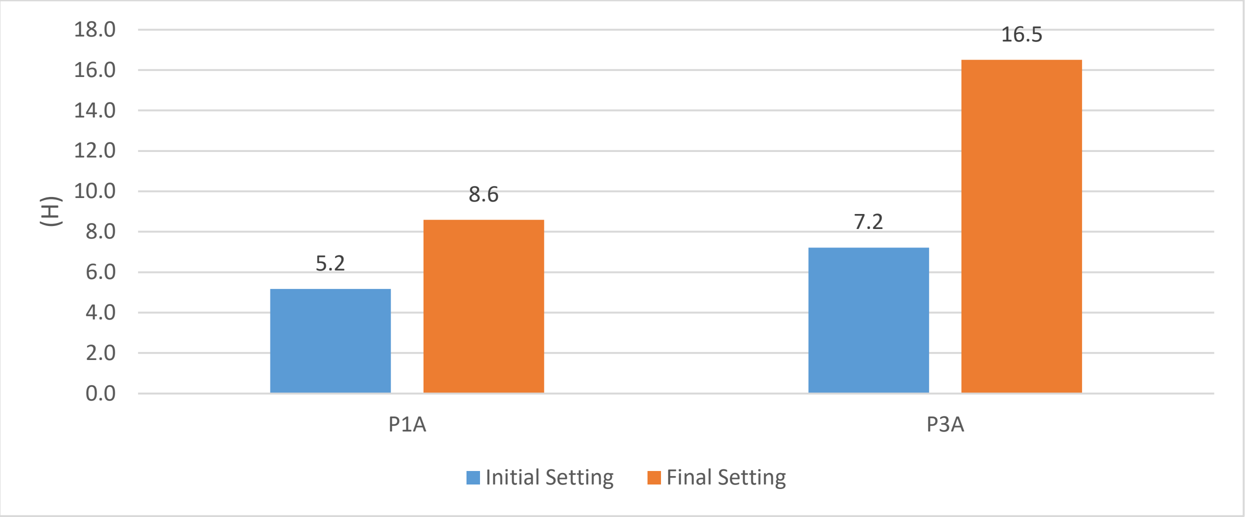

Figure 6.7 Influence of sucrose on the setting time

6.4.3.2 Flowability and compressive strength

In chapter 4 while characterizing the effect of sucrose on AAM made by the 42.5% fly ash, 42.5% slag, and 15% slag, it was found that adding 2% sucrose to the mixture increased the flowability and compressive strength. As the mixture without the sucrose had a quick setting, adding the admixture delayed the setting time, therefore, the mixture maintained its initial flow, and this cause the fly ash and other materials to disperse well through the mixture. Hence the flow value and compressive strength of the AAM with sucrose were higher than the AAM without sucrose. But in this experiment 100% fly ash was used and the flowability of the mortar was better after the mixing procedure, and quick setting did not occur. Therefore, sucrose didn’t have a positive influence on the flowability and compressive strength of the AAM, instead, the flow value and the compressive strength were decreased with the addition of sucrose.

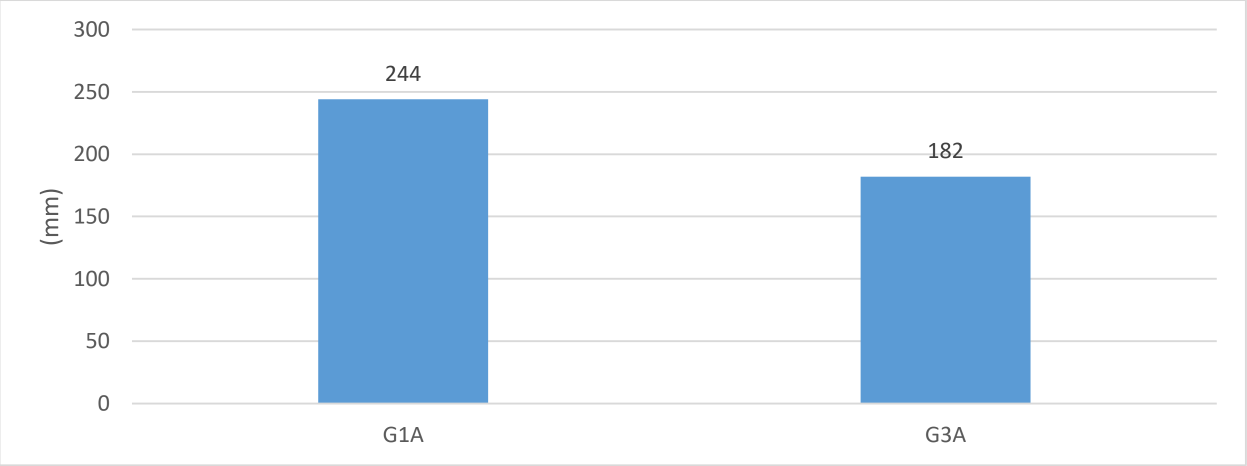

Figure 6.8 Influence of sucrose on the flowability

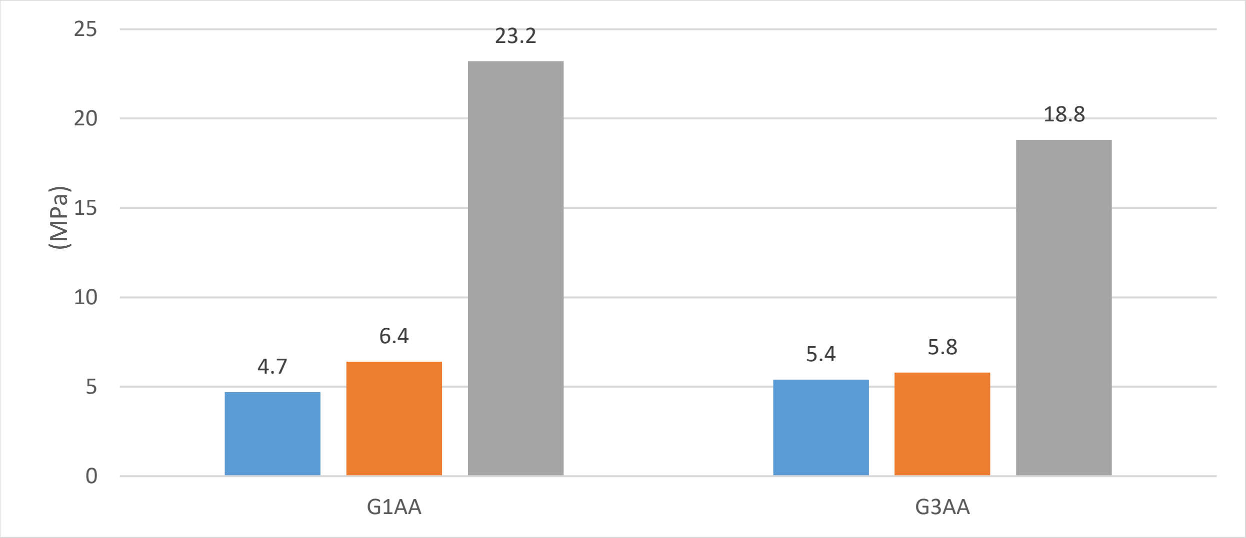

Figure 6.9 Influence of sucrose on the compressive strength

6.4.4 Influence of the temperature of the raw materials

To study the influence of the temperature of raw materials such as fly ash and sand on the properties of the AAM. They were studied in two different temperatures, an ambient temperature which was around 20°C, and hot conditions. In hot conditions, fly ash and sand were used at temperatures around 40°C.

6.4.4.1 Setting time

Figure 6.10 shows the influence of the fly ash and sand temperature on the initial and final setting time of all three types of AAM.

The temperature of the materials didn’t have any significant influence on the initial and final setting time of the conventional type of fly ash-based AAM. P2H followed the same trend, the hot condition or temperature of the mixing materials did not decrease the setting time of the AAM. But, conversely, the final setting time of the P2H was increased by almost 1 hour. This result indicated that the temperature of the materials didn’t have any obvious effect on the setting properties of AAM using sodium disilicate that has a SiO_2:Na_2O ratio of 2.

But the temperature of the materials and hot mixing method had a significant influence on the setting time of AAM using sodium metasilicate. The initial and final setting times of P1A were 6.3 and 8.4 hours respectively and after heating the material at an incubator, the initial setting and final setting times were decreased to 2.6 and 6.9 hours respectively. There was a decrease of 58% for the initial setting time and 18% for the final setting time.

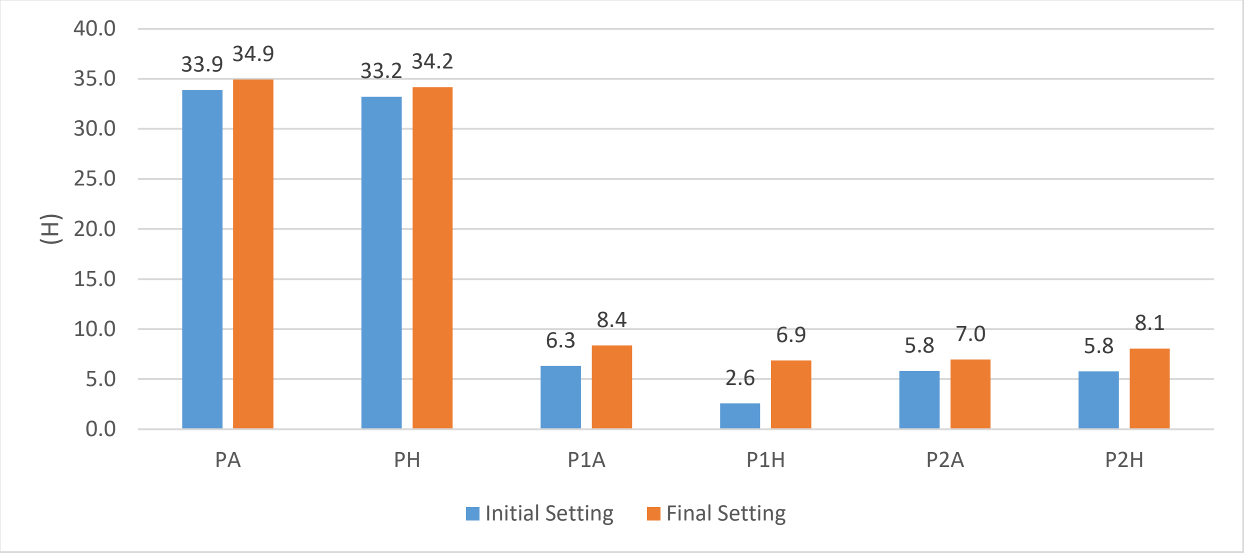

Figure 6.10 Influence of the temperature of the raw materials on the setting time of AAM

6.4.4.2 Flowability

The hot mixing condition or preheating of the materials in the incubator increased the flow value of conventional fly ash-based AAM. GAO had a flow of 145mm and the other one (GHO) in which the aluminosilicate precursor and the fine aggregate were heated before the mixing had a flowability of 157 mm. This improvement of the flow was due to the breaking of the sodium silicate solution viscosity by the application of heat. The viscosity of the GHO was lower than the GAO. This result can help to overcome the viscosity problem of AAM which is created by the alkaline solution. Some researchers tried to solve the workability problem using some admixture, but none of them had apparent and considerable influence to reduce the viscosity and solve the workability problem [12, 13, 14].

G1AA and G2AA both had better workability and the viscosity had been already reduced by a decrease in the concentration of sodium silicate solution. Application of hot mixing conditions or heating of the mixing material decreased the flowability of both kinds of AAM. G1AA and G2AA had flow rates of 244 mm and 250 mm respectively, but after the application of the heat, the flow rates were decreased to 236 mm and 232 mm respectively. The decrease in the flow rate was due to the activation and increase in the reactivity of the fly ash by the application of the heat. This phenomenon was also confirmed by the compressive strength result.

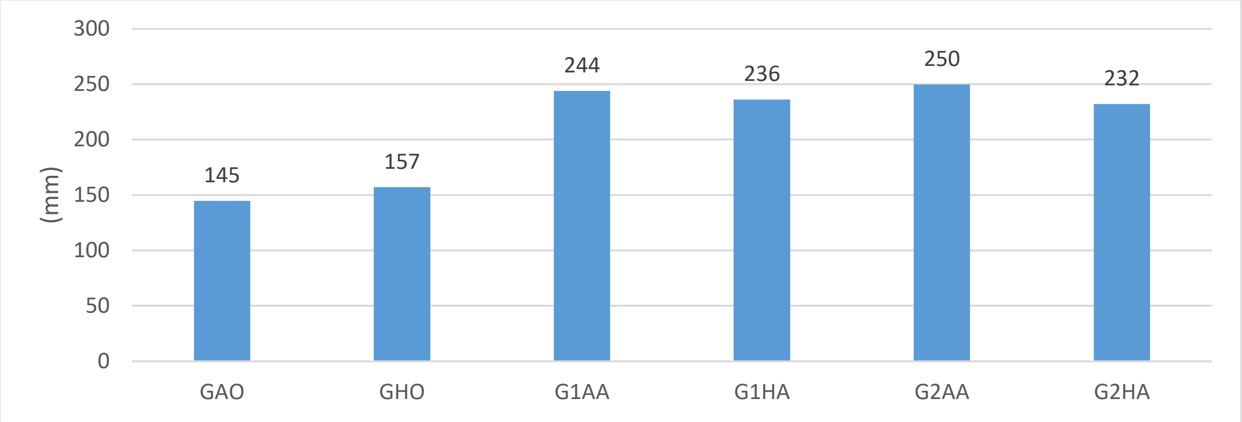

Figure 6.11 Influence of the temperature of the raw materials on the flowability

6.4.4.3 Compressive Strength

Figure 9 shows the influence of the aluminosilicate precursor and fine aggregate temperature on the compressive strength of the fly ash-based AAM.

There was a slight increase in the compressive strength of the conventional AAM by applying heat on the mixing material. GAO had a compressive strength of 96.2 MPa at 28 days, while the compressive strength was increased to 99.9 MPa after the application of heat to the materials. The curing of both GAO and GHO was done at 45°C in an incubator.

The same trend of the conventional AAM result was followed by the G2HA, there wasn’t any significant improvement in the compressive strength of the material at 7, 28, and 56 days.

However, there was a decrease in the strength of the AAM made by the 32% sodium metasilicate at 7 days, but there was a remarkable improvement of 34% at 28 days and an increase of 39% at 56 days’ compressive strength of the aforementioned material.

The result clearly indicated that the compressive strength sodium disilicate was less influenced by the heat than AAM made by the sodium metasilicate. The finding confirmed the setting time result.

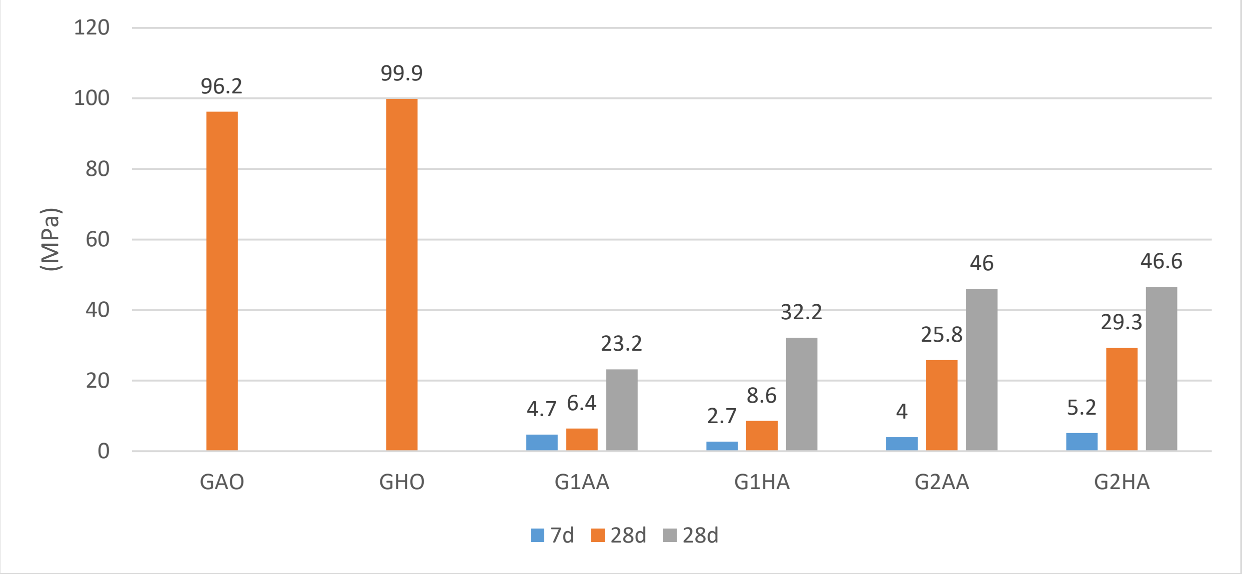

Figure 6.12 Influence of the temperature of the raw materials on the compressive strength

6.4.5 Effect of the curing condition on compressive strength

The heat curing had a significant influence on the 28-day compressive strength of AAM made by 54% sodium disilicate. Because of this, the conventional type of low-calcium fly ash AAM is cured at a higher temperature. At ambient curing conditions, GAA had a compressive strength of 8MPa at 28 days, and with the curing at 45°C for two days, the compressive strength was increased by around 12 times.

Moreover, the heat curing had a remarkable effect on the 7, 28, and 56-day compressive strength of the AAM made by the 32% sodium metasilicate. When applying the heat curing at 45°C for 48 hours, the compressive strength of G1A was increased by 326%, 400%, and 78% at 7, 28 and 56 days respectively. The G2H mortar followed the same trend of G2A, by applying the heat curing, there was an increase of 770%, 312%, and 32.3% at 7-, 28- and 56-days' compressive strength respectively. This result indicates that heat curing had a significant influence on the 7 and 28-day compressive strength of the AAM made by the sodium metasilicate, but the improvement of 56-day strength was lower than the earlier strength.

For G2A and G2H mortars, while applying heat curing, there was a remarkable increase in the 7-day compressive strength. Improvement of 583% and 462% was observed in the compressive strength of G2AO and G2HO respectively at the aforementioned age. At 28 days, there was a slight increase but at 56 days, the heat curing had a negative impact on the compressive strength. The compressive strength was dropped from 46 MPa to 39.9 for G2A and from 46.6 MPa to 43.3 MPa for G2H. This result showed that heat curing had a significant influence on the early strength of G2A and G2H mortar but for the later ages the compressive strength of the samples cured at ambient temperature and at incubator had very little difference. This may be due to the higher content of SiO2 which helped the mortar to achieve its late strength without curing at the higher temperature. Therefore, sodium disilicate with a lower concentration than the conventional one will be effective for making AAM for the sake of improving compressive strength at ambient temperature curing.

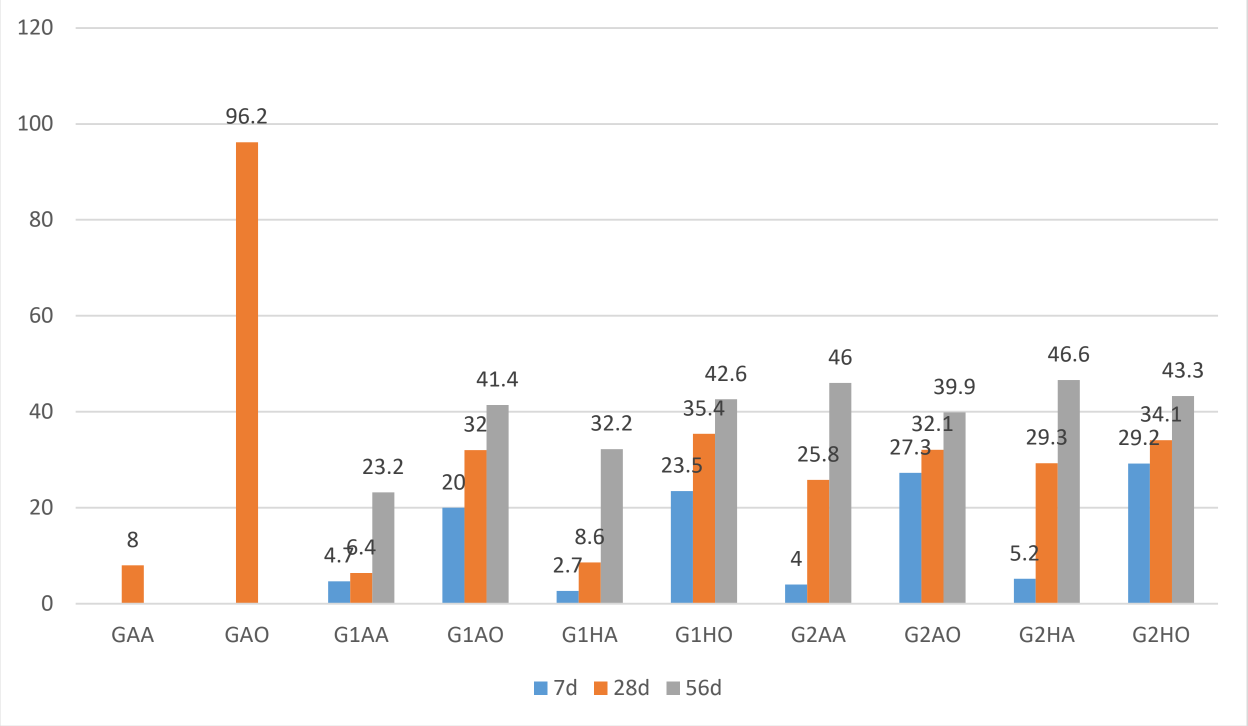

Figure 6.13 Effect of the curing condition on the compressive strength

6.5 Conclusion

This research was conducted to develop the one-part mixing method using low calcium fly ash-based AAM at ambient curing conditions. Low-calcium fly ash-based AAM has some drawbacks such as high setting time and low compressive strength when cured at ambient temperature. Replacing some percentage of fly ash with slag can solve the problems but using slag increase the shrinkage of the materials.

Therefore, this research studied the influence of the types and concentration of the sodium silicate solution on the setting time, flowability and compressive strength properties of the AAM. These two types of sodium silicate were sodium metasilicate with a SiO_2:Na_2O ratio of 1 and sodium disilicate with a modulus of 2. Moreover, the effect of the sucrose, temperature of raw materials and curing conditions were also investigated.

From the study the following conclusion can be written;

1. SiO_2:Na_2O ratio of the 32% concentrated sodium silicate solution doesn't have a significant influence on the setting and flowability of the paste and mortar samples. The final setting time of the materials was lower than OPC.
2. The influence of the SiO_2:Na_2O is prominent on the compressive strength of the AAM. The compressive strength at 28 and 56 days are increased 4 and 2 times respectively when sodium disilicate is used instead of sodium metasilicate.

3. The concentration of the sodium silicate has a considerable influence on the setting time of the AAM paste. Using 54% sodium disilicate increase the initial and final setting time to more than 30 hours. But while reducing the concentration, the initial and final setting is reduced to less than 10 hours. Conventionally fly ash-based-AAM made by around 50 concentrated sodium silicate solutions.
4. The 54% concentrated or the conventional type AAM has a much lower flow rate than the one which is made by a lower concentration of sodium silicate solution.
5. For the ambient temperature curing, a higher concentrated sodium silicate-based AAM has much lower compressive strength at 28 days. But when heat curing is applied, the compressive strength is much higher for the AAM made by a higher concentrated sodium silicate solution.
6. Sucrose significantly increased the initial and final setting times of the AAM.
7. Using sucrose decreases the flow rate and compressive strength of low calcium fly ash-based fly ash AAM
8. The preheating of the fly ash and sand reduces the initial and final setting time of AAM using sodium metasilicate.
9. Hot mixing condition breaks the viscosity of the conventional AAM, hence improving the flow rate.
10. The temperature of the materials has a significant influence on the compressive strength of the AAM made by the sodium metasilicate but for the sodium disilicate-based AAM, the effect is not so obvious.
11. Heat curing has a significant influence on the initial strength of both sodium metasilicate and sodium disilicate-based AAM. But the AAM made by the sodium disilicate solution has higher compressive strength at ambient temperature curing conditions than in heat curing conditions.
12. Sodium silicate with SiO_2:Na_2O ratio of 2 (sodium disilicate) with a lower concentration than the conventional one, can set earlier and acquire higher compressive strength at ambient temperature curing conditions. Using this material can be effective both in one-part and two-part mixing methods. Dry sodium disilicate solubility needs to be checked while using it for making one-part AAM.

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Chapter 7

Fundamental Investigation of Recycled Concrete using Paper Sludge Ash and Silica Fume

7.1. Introduction

Portland cement concrete is the most used construction material in the world. Annually, a huge amount of waste concrete is generated due to the demolition and reconstruction process. It is estimated that 900 million tons of waste concrete are generated in the USA, India, Europe, and Japan. Most of this waste is trashed and disposed of in landfills which creates environmental problems [1].

Recycled Concrete Aggregate (RCA) is a concrete material that is produced by modification of waste concrete, this material is not widely used as aggregate due to its higher water absorption and lowers specific gravity, consequently, strength and durability are negatively affected. Different kinds of substances such as silica fume, fly ash, and steel fiber are used as an admixture or as partial cement substituents to enhance the strength and durability of recycled aggregate concrete [2], [3] [4].

Waste paper sludge is another material that can be recycled like other pozzolans such as ash fly ash [5], after incinerating paper sludge at approximately 800 °C, ash will be produced that have reactive silica and can chemically react will cement and can improve some properties of concrete [6].

Silica fume (SF) is an ultrafine by-product of silicon processing industries. It has an amorphous shape and highly reactive silica. Silica fume has a surface area of 15-25 m^2/gram. This by-product increases the Si/Ca ratio in the binder which improves the permeability of the paste and hence, increases the strength and durability of concrete [7]. This research will further study the by-product by conducting an Acoustic emission (AE) behavior test on concrete samples containing 5 and 10% silica fume.

Each of the binder (SF and PSA) need to be used together with RCA to study their influence on some properties of recycled aggregate concrete. Moreover, each of the binders and recycled aggregate also need to be used separately to understand their single effect on the properties of Portland cement concrete.

This experiment aims to study the influence of silica fume and paper sludge ash on some of the properties such as flowability and compressive strength of recycled aggregate concrete. Moreover, the acoustic emission behavior of these kinds of concrete will also be investigated as there isn't any past experiment of studying the AE behavior of concrete or recycled concrete using paper sludge ash and silica fume.

7.1.2 Significance of the research

- Enhance the tendency of people to utilize paper waste and concrete waste effectively to reduce disposal amount for landfills.
- Energy and heat can be produced while burning paper sludge, and by secondary ignition and incineration at a temperature of about 800, it can be converted to pozzolan, which can be partially replaced with cement.
- Consequently, the rectification and exploitation of both wastes can have economic and environmental advantages.

7.2 Objectives

The following properties of concrete with different percentages of paper sludge ash, silica fume, and recycled aggregate are investigated and then compared with the conventional or reference concrete.

- Workability
- Compressive strength
- Acoustic Emission behavior

7.3 Experiment

7.3.1 Materials

The materials which were used for the making of the samples consisted of the binders, aggregates, water, and admixture. The specifications of the materials are explained as follow:

7.3.1.1 Binders

Ordinary Portland cement (OPC), Paper sludge ash, and silica fume with specific gravities of 3.15, 2.43, and 2.22 respectively, were used as binders for making the samples.
Figures 1 and 2 show the SEM (scanning electron microscope) of OPC and PSA. Both the materials have an amorphous molecular structure.

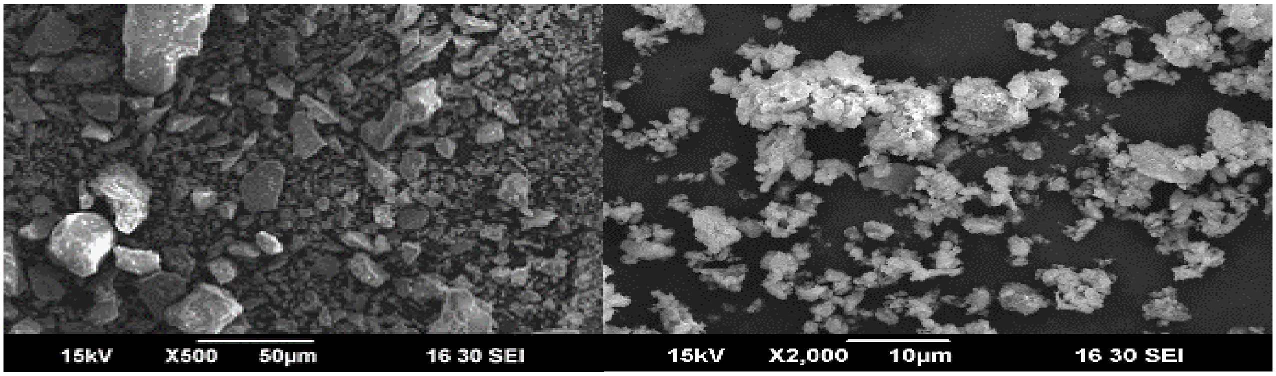


Figure 7.1 SEM of OPC and PSA

XRF (X-ray fluorescence) was conducted on each of the binders to find chemical compositions and the result is shown in Table 1.

Table 7.1 XRF of the cement, paper sludge ash, and silica fume

Oxides	**OPC (%)**	**PSA (%)**	**Silica Fume (%)**
Na_2O	0.217	0.372	0.213
MgO	0.964	2.968	0.390
Al_2O_3	4.234	12.282	0.237
SiO_2	17.899	16.906	96.536
P_2O_5	0.174	1.162	0.082
SO_3	3.009	2.412	0.223
K_2O	0.517	0.314	0.837
CaO	69.045	61.068	0.222
TiO_2	0.279	0.615	1.079
MnO	0.076	n/a	n/a
Fe_2O_3	3.411	1.611	0.100
CuO	0.041	0.063	0.017
ZnO	0.070	0.068	n/a
SrO	0.048	0.039	n/a
ZrO_2	0.017	0.016	n/a

7.3.1.2 Aggregates

Aggregate is an important component of concrete. It has a major role in the specification of the properties and quality of concrete. In this experiment, around 80% of the mass of the concrete was occupied by the aggregate. Both fine and coarse aggregates are described as below;

a) Fine aggregate

Sea sand was used as fine aggregate with oven-dry density and water absorption of 2.5 and 2.87 respectively

Table 7.2 Size distribution of fine aggregate

Size of sieve openings (mm)	**Passing (%)**
9.5	100
4.75	100
2.36	98.42
1.18	81.82
0.6	52.26
0.3	24.74
0.15	7.1

b) Coarse aggregate

Crushed stones and recycled aggregates were used as coarse aggregate. Specific gravity and water absorption are shown in Table 3 below.

Table 7.3 Properties of coarse aggregate

Physical property	Crushed stone	Recycled aggregate
Oven-dry density (g/cm^3)	3.02	2.76
Water absorption	0.56	2.4

The pulsed power apparatus was used to produce recycled aggregate. A high grade of recycled aggregate can be discharged when this apparatus is used [8] (Shigeishi, et al., 2013). The recycled coarse aggregate was obtained by applying energy of E/N=6.4 kJ per pulse at a capacitance of 0.8 μF and the applied voltage of 400 kV satisfied the oven-dry density criterion and the water absorption coefficient criterion when using applied energy of 384 kJ. Thus, the frequency of pulsed discharge was 60 times underwater. Consequently, the high-grade recycled aggregate was produced which satisfied JIS regulation class H (A 5021) for high-grade recycled concrete aggregate, as this regulation requires oven-dry density for recycled aggregate to be at least 2.5 gr/cm^3 and maximum water of absorption of 3%.

Figure 7.2 Recycled aggregate

Table 7.4 Size distribution of coarse aggregate

Size of sieve opening (mm)	**Passing (%)**	
	Crushed stone	**Recycled aggregate**
25	100	100
20	96.31	100
15	84.07	94.66
10	27.74	56.71
5	0.71	0.42
2.5	0.04	0.05
1.2	0.035	0.03

7.3.2 Procedure and experiment

The procedure of the sample preparation and conduction of the experiment are described in the following subsections.

7.3.2.1 Mix proportion

The w/c ratio was maintained to 0.55, while sand/ aggregate was kept to 0.48. 15 types of samples were prepared. The mix proportion is described in Table 5. To study the effect of paper sludge ash on the properties of concrete, it was replaced with 5 and 10 percent of cement, and the same amount of cement was replaced by another pozzolan which is silica fume. Silica fume is a widely used material in the world for the enhancement of some characteristics of concrete. To investigate the influence of recycled aggregate on the properties of concrete samples, they replaced 10 and 20 percent of natural aggregates. Polycarboxylate superplasticizer was used as a water-reducing agent, and to increase the flowability of concrete, the amount of usage was kept the same (1 percent of the weight of cement) for all sample types.

Table 7.5 Mix proportion (kg/m^3)

No.	Sample name	Cement	PSA	Silica fume	Fine aggregate	Coarse aggregate	RCA	Water
1	CON	318	0	0	841	1070.00	0	175.00
2	CA5	300.50	15.82	0	841	1070.00	0	173.97
3	CS5	299.90	0	15.78	841	1070.00	0	173.63
4	CA10	283.20	31.47	0	841	1070.00	0	173.07
5	CS10	281.90	0	31.32	841	1070.00	0	172.27
6	10RC	318	0	0	841	956.00	106.00	175.00
7	10RA5	300.50	15.82	0	841	956.00	106.00	173.97
8	10RS5	299.90	0	15.78	841	956.00	106.00	173.63
9	10RA10	283.20	31.47	0	841	956.00	106.00	173.07
10	10RS10	281.90	0	31.32	841	956.00	106.00	172.27
11	20RC	318	0	0	841	842.00	212.00	175.00
12	20RA5	300.50	15.82	0	841	842.00	212.00	173.97
13	20RS5	299.90	0	15.78	841	842.00	212.00	173.63
14	20RA10	283.20	31.47	0	841	842.00	212.00	173.07
15	20RS10	281.90	0	31.32	841	842.00	212.00	172.27

7.3.2.2 Mixing

A concrete mixer was used to mix the materials. At first OPC, the fine and coarse aggregate was blended for 1 minute and after adding water and the superplasticizer, they were mixed for 1.5 minutes. But in the case of using PSA and SF, cement was first blended with sand, then for effective mixing, the cement substituents were poured in different points and blended for 1 minute. Afterward, coarse aggregate and then water was added to the mixer for mixing.

Figure 7.3 Slump test and samples after casting in molds

7.3.2.3 Slump test, specimen casting, and curing

The slump test was conducted according to JIS A 1101. The test was done to study the workability of fresh concrete. A cone with a height of 30 cm, with a bottom diameter of 20 cm and an upper 10 cm was used. For each slump test, the cone was filled by mortar in 3 layers and each layer was tempted 25 times by a 16 mm rod. Afterward, the cone was carefully removed and the height difference is measured as a slump. All the samples were cylindrical, with a dimension of 100 mm diameter and 200 mm height. The molds were removed after 24 hours and samples were immersed in water for curing at 18-22 °C temperature until the day of their testing.

7.3.2.4 Compression test

The compressive test was carried out on hardened concrete samples to find compression strength. Loads were applied on each of the samples until their failure, and the peak loads were then recorded. This test was performed on all 150 cylindrical samples (100 mm*200 mm) after 28 and 56 days of curing.

7.3.2.5 Acoustic Emission (AE) behavior test

An AE sensor was attached to each of the samples during the compressive strength test. Due to the compression, stresses occurred inside the samples. The micro-cracks were produced by the stresses emitted by sound waves with different intensities. Above 40 decibels acoustics or elastic wave were considered to be produced by those cracks are called acoustic emission (and abbreviated as AE). AE waves propagate through concrete and can be detected on a surface by an AE sensor, which turns the vibrations into an electrical signal. The propagation of fracture sound was originally referred to as AE since it is acoustic and audible [9] (Ohtsu, 1995).

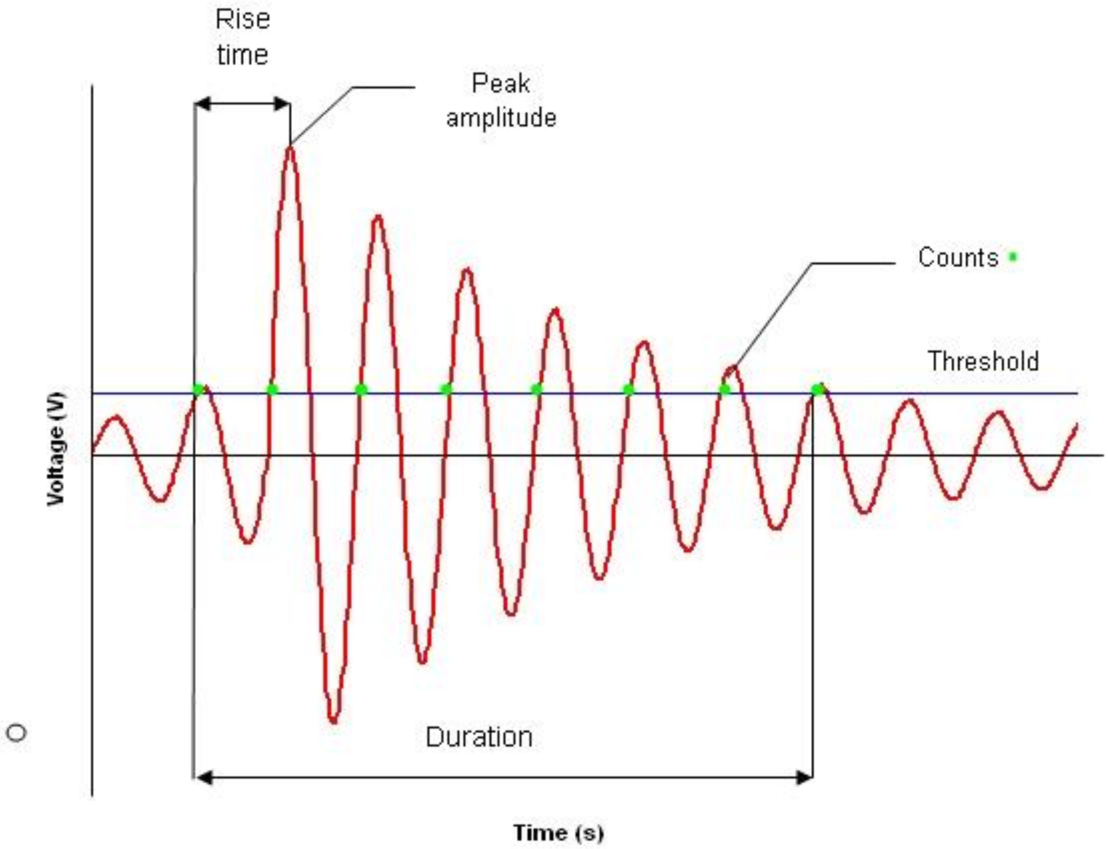


Figure 7.4 Parameters of acoustic emission waveform [10]

7.4 Result and discussion

7.4.1 Workability

Figure 7.6 shows the slump value of each sample. The workability of concrete was increased with the 5% silica fume but slightly decreased with the 5% PSA. Both the 10% PSA and 10% silica fume significantly decreased the slump of concrete. The 10 and 20% RCA improved the workability of the samples. The 5% silica fume didn’t decrease the flowability of the 10 and 20% recycled concrete but the workability of the samples was notably decreased with PSA and 10% silica fume concrete.

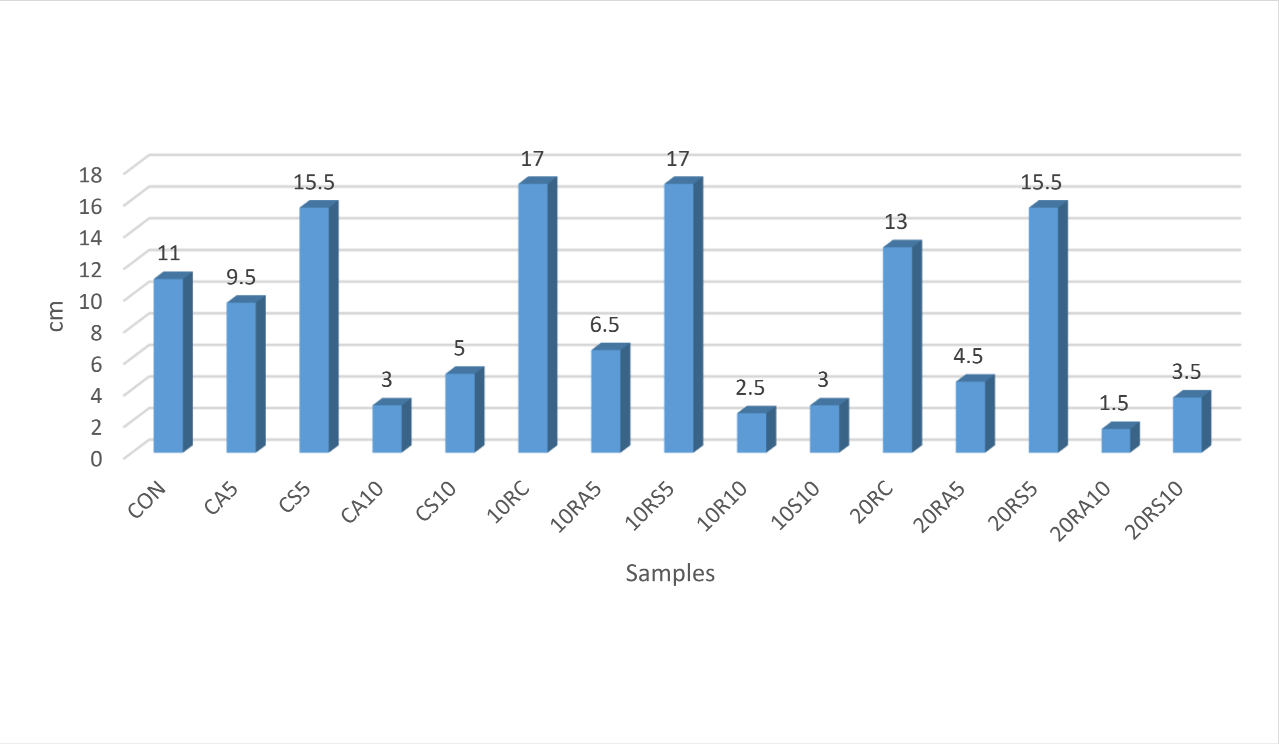
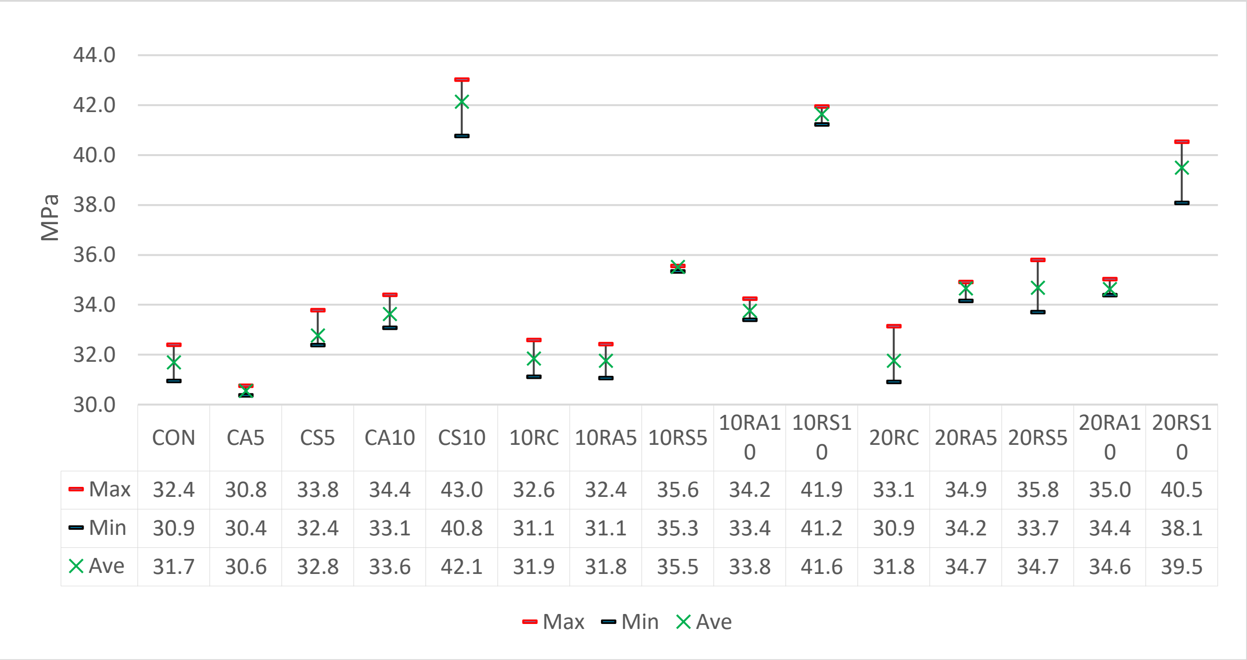


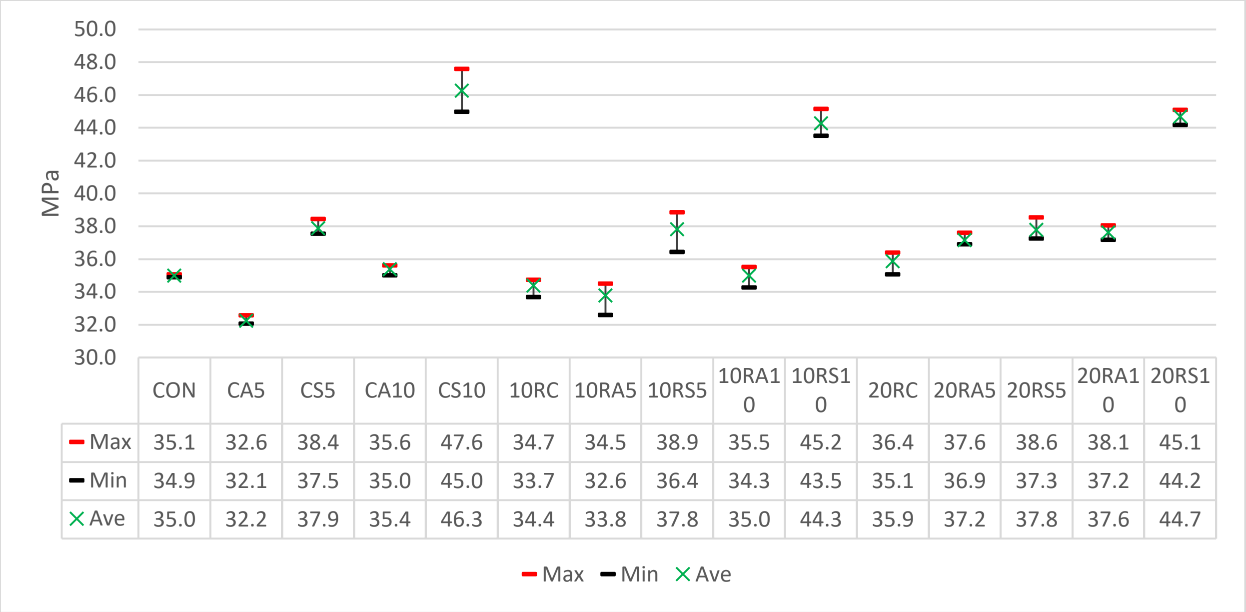
Figure 7.5 Slump value of the concrete samples

7.4.2 Compressive strength



	CON	CA5	CS5	CA10	CS10	10RC	10RA5	10RS5	10RA10	10RS10	20RC	20RA5	20RS5	20RA10	20RS10
– Max	32.4	30.8	33.8	34.4	43.0	32.6	32.4	35.6	34.2	41.9	33.1	34.9	35.8	35.0	40.5
– Min	30.9	30.4	32.4	33.1	40.8	31.1	31.1	35.3	33.4	41.2	30.9	34.2	33.7	34.4	38.1
× Ave	31.7	30.6	32.8	33.6	42.1	31.9	31.8	35.5	33.8	41.6	31.8	34.7	34.7	34.6	39.5

Figure 7.6 The 28-day compressive strength



	CON	CA5	CS5	CA10	CS10	10RC	10RA5	10RS5	10RA10	10RS10	20RC	20RA5	20RS5	20RA10	20RS10
— Max	35.1	32.6	38.4	35.6	47.6	34.7	34.5	38.9	35.5	45.2	36.4	37.6	38.6	38.1	45.1
— Min	34.9	32.1	37.5	35.0	45.0	33.7	32.6	36.4	34.3	43.5	35.1	36.9	37.3	37.2	44.2
× Ave	35.0	32.2	37.9	35.4	46.3	34.4	33.8	37.8	35.0	44.3	35.9	37.2	37.8	37.6	44.7

Figure 7.7 The 56-day compressive strength

Figures 7.7 and 7.8 show the compressive strength of the samples at 28 and 56 days. Maximum, minimum, and average strengths are shown on the charts and an average value is accepted as compressive strength for each type of sample.

Both the silica fume and the PSA increased the 28 and 56-day compressive strength. It can be said that pozzolanic reaction between ingredients of the PSA, SF, and the OPC. From the figures, it can be understood that there wasn’t any significant decrease in compressive strength when recycled aggregate was used, but on the other hand, the 20% RCA increased the 56-day strength. This may be due to previously attached mortar on the surface of the RCA which helped to strengthen the bond between the cement and the RCA. Both the SF and the PSA improved the strength of the RCA concrete, especially, when they were used with the 20% recycled aggregated concrete.

7.4.3 Acoustic Emission (AE) behavior

Hits vs stress diagrams of the concrete samples were drawn to study the robustness of the samples. Hits which are the accumulation of acoustic data that exceed the threshold were achieved throughout the loading process. Generally, sound concrete has low numbers of AE hits at the initial stage of stress production and the amount exceeds at the final stage. Figure 9 shows the relation between AE hits and stress levels during compression loading for all types of concretes. There is no significant difference in AE behavior between conventional concrete, silica fume concrete, and both the 10% and 20% RCA concrete. AE hits were found to be consistently low at the beginning of loading and were higher when the stress reached around 100%. Moreover, AE activity and number of cumulative hits were lower in the PSA concrete, this indicates the robustness of this kind of concrete.

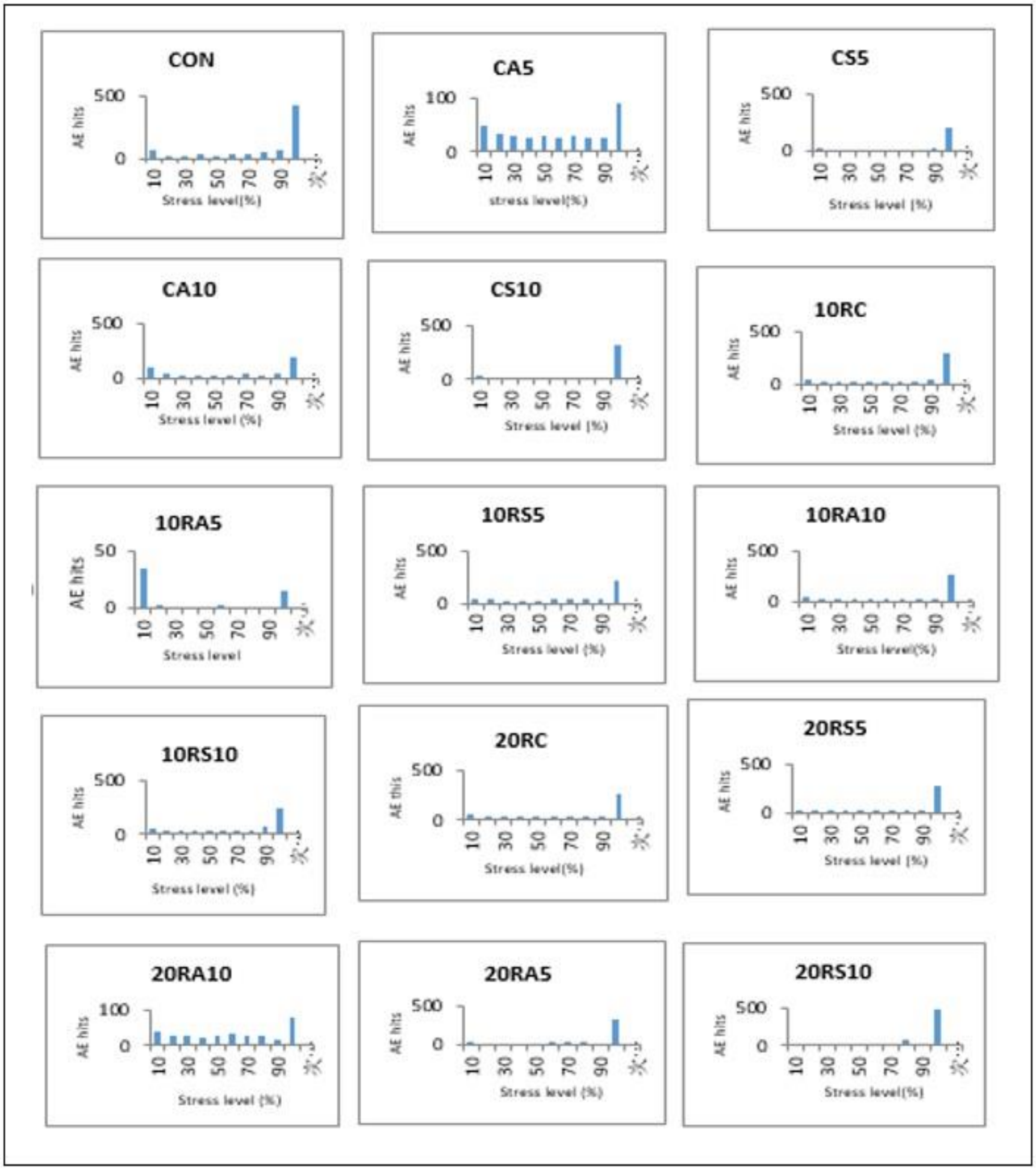


Figure 7.8 Relationship between AE hits and stress level for the concrete samples

7.5 Conclusion

According to literature, recycled aggregate has a higher porosity and lower density has a negative influence on some properties such as strength and durability of recycled aggregate concrete. In this experiment, paper sludge ash and silica fume were used to modify the properties of recycled concrete, moreover, the effect of both pozzolans are also investigated on OPC concrete. The following conclusion was acquired from the study;

1. The workability of concrete is decreased with an increase in the amount of silica fume and paper sludge ash.
2. The recycled aggregate produced by pulsed power improves the workability of fresh concrete.
3. Both PSA and SF improve the compressive strength of conventional and recycled aggregate concrete. This indicates that both of the materials have shown their pozzolanic activity inside the mixture.
4. Both the 10 and 20% recycled aggregate concrete improve the compressive strength of the samples. And this is maybe because of the surface roughness of the RCA due to the previously attached mortars.
5. The acoustic emission activities of all types of samples were lower at the early stage of loading. The cumulative hits in PSA concrete were lower and this shows that PSA concretes were denser and had higher robustness than the other type of concrete samples.
6. From this research, it can be concluded that both silica fume and paper sludge ash can improve the properties of concrete. although, the workability is negatively affected by a higher percentage of the substituents, therefore, there is a need for studying the influence of other types of admixtures on the workability of such kinds of materials.
7. High-quality recycled aggregate didn’t have a negative influence on the properties of concrete but can improve some of the properties of the concrete.
8. The effect of the pozzolans on properties of concrete made by a lower or medium quality of recycled aggregate is also essential to be evaluated.

Future research

In this research, the workability of the samples decreased when the percentage of the PSA and silica fume increased to 10%, therefore, other types of admixtures need to be used and to be studied to overcome this drawback. Moreover, other properties such as durability properties also need to be investigated while using these kinds of cement and aggregate substituents.

There are some kinds of by-products such as rice husk which shows pozzolanic properties when they are burnt at high temperature. These kinds of materials are also better to be studied comprehensively.

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Chapter 8

Conclusion

Global warming is a major issue nowadays. Ordinary Portland cement (OPC) production is responsible for the emission of 8% CO2 of the world. Moreover, some by-products such as fly ash are disposed to landfills which create an environmental problem. Using alkali-activated material (AAM) as an alternative for OPC can have both environmental and economic advantages. Moreover, they have some extraordinary properties such as high strength, high resistance to fire, heat, and acid, and low shrinkage. With having all the aforementioned properties, their usage is still limited. Difficulties in handling corrosive alkaline solution and high viscosity of sodium silicate and complicated technology are the problems that make the material to be made in factories as a precast element. This causes huge costs and a massive reduction in the production of AAM.

Efforts have been made to make ease in the production of AAM, therefore, a one-part mixing method has been studied by some researchers in which solid alkaline activators are premixed with aluminosilicate precursors and then water is added to them for making the binder. This method is the same as making an OPC binder. But some studies concluded that the AAM made by the one-part mixing method has lower quality than the one made by the conventional or two part-mixing method. Therefore, this research aims to find the root of the problem and find a solution for that. Furthermore, this study aims to develop the properties of low-calcium fly ash-based-AAM cured at ambient temperature conditions.

In chapter 3, the properties of AAM made by the one-part mixing method were characterized. The influence of the mixed proportion of aluminosilicate precursors such as ash fly ash, slag, and silica fume, the molarity of sodium hydroxide, AA ratio was studied. Furthermore, the properties of AAM made by the one-part mixing method were compared with the OPC mortar and AAM made by the conventional method in which sodium silicate solution was used with a higher concentration. Although compressive strength of the AAM made by the one-part mixing method increased with the increment of the slag in composition their quality was lower than the OPC and conventional type AAM. Moreover, there was a quick setting occurred with the one-part mixed AAM containing a high percentage of slag. This cause workability problem in casting the material into the molds.

Chapter 4 focuses on the retarding influence of sucrose on the AAM. As it was mentioned in the previous paragraph, the workability problem that occurred with the AAM contained a high amount of slag. This chapter revealed that using sucrose retards the setting time of the AAM, hence the flowability and compressive strength of the material was improved. A better spread of the aluminosilicate and alkaline activators through the mixture due to the better flowability of the fresh mortar was mentioned as a reason for the improvement of strength by sucrose.

In chapter 5, the flowability and compressive strength comparison of AAM made by one-part and two-part mixing methods were discussed. Both kinds of materials had the same mix proportion and composition. The result revealed that AAM made by the one-part mixing method had much lower flowability and compressive strength than the one made by the two-part mixing method. In the literature review, it was found that undissolved particles of sodium metasilicate were observed while studying the microstructure of one-part mixed AAM.

Therefore, the solubility of solid alkaline activators such as sodium hydroxide pellets and granular sodium metasilicate was studied. The duration of mixing was set to 5 minutes. The result showed that sodium hydroxide pellets were quickly dissolved at 25 °C but the sodium silicate couldn't be dissolved in the solvent at the aforementioned temperature. Then the temperature of the solvent was increased and improved the solubility of the material was observed. The total dissolution occurred when the temperature of the solvent was reached 40°C. So it was concluded that the temperature of a solvent needs to be at around 40°C while the one-part mixing method is applied. Remember that the aforementioned temperature is adopted when 32% sodium metasilicate is used. For the lower and higher concentration of sodium silicate, the temperature can be changed.

Moreover, in this chapter, a solution made by granular sodium metasilicate was characterized. It was found that sodium metasilicate was fluent and without viscosity. But it was susceptible to a temperature around 25°C. Because crystallization could occur inside the solution. But after putting it inside an incubator at a higher temperature the crystallization could disappear. The fresh mortar of AAM made by sodium metasilicate was much influenced by the ambient temperature and quick hardening or setting had a negative influence on the flowability of the mortar. Therefore, it was decided to use the hot mixing method. In the hot mixing method, all the raw materials were used at a temperature of around 40°C. Improvement in workability was observed after adopting the method.

Low-calcium fly ash-based-AAMs have some extraordinary geopolymeric properties such as high fire resistance and low shrinkage. But it is conventionally made by curing at a higher temperature inside an oven and also sodium silicate with a concentration of around 50% is used in the material. But they have a very high setting time and low compressive strength when cured at ambient temperature. In chapter 6, the influence of sodium silicate types and concentration on the setting time, flowability, and compressive strength properties of the AAM was discussed. The concentration of 32% and 56% were investigated. In addition, the influence of the raw material temperature, sucrose, and curing condition was studied on the aforementioned properties of low-calcium fly ash-based AAM. This study aimed to solve the high setting time and low compressive strength problem of low-calcium fly ash-based AAM cured at ambient temperature conditions.

The concentration of sodium silicate had a significant influence on the setting time, flowability and compressive strength of the AAM cured at ambient temperature conditions. 32% sodium disilicate considerably improved all the aforementioned properties of the AAM. This was maybe due to the better reactivity of fly ash in an alkaline environment with a decreased PH value. There is a need for some further study to find the reason related to the phenomenon. In this study, sucrose didn’t improve the properties of the AAM. This was contrary to the previous study in which sucrose improved the flowability, compressive strength, and drying shrinkage of AAM containing a high amount of slag. But in this experiment, as the reactivity of low-calcium fly ash is very low, and the flowability of the AAM was good enough for the dispersing of the main constituents, the use of sucrose was not required.

As it was found that sodium disilicate with a lower concentration than 50% can be effective for decreasing the setting time and improvement of flowability and compressive strength of low-calcium fly ash-based AAM cured at ambient condition, the solubility of this type of sodium silicate is also required to be studied before using its solid form for the making of one-part mixed AAM.

Chapter 7 investigated the influence of recycled concrete aggregate produced by pulse power technology, Silica fume, and paper sludge ash on the workability, compressive strength, and acoustic emission behavior of concrete. In the experiment, 5 and 10% of cement were replaced by PSA and silica fume, and 10 and 20% of coarse aggregate were replaced by recycled aggregate. Both the PSA and SF showed their pozzolanic activity as both the OPC substituents improved the Strength and acoustic emission behaviors of concrete. Moreover, the high-quality recycled aggregate also modified the properties of concrete.