The Pennsylvania State University

The Graduate School

Department of Civil and Environmental Engineering

SHRINKAGE CHARACTERISTICS OF ALKALI ACTIVATED FLY ASH-SLAG BINDERS

A Thesis in
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by
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ABSTRACT

Substituting ordinary Portland cement (OPC) with industrial waste such as blast furnace slag (BFS) or fly ash (FA) reduces the amount of CO$_2$ released to the atmosphere by the cement industry. Alkali activated cement (AAC) is a promising new binder, that could serve as an alternative to OPC. Alkali-activated binders, based on slag and fly ash are two prevalent categories of AAC. These binders are composed of a precursor powder (e.g., FA, BFS) and an alkaline solution (activator) as the mixing liquid.

Despite the fact that alkali activated fly ash (AAFA) has comparable or even higher strength than OPC, the curing temperature-dependent mechanical and microstructural properties of AAFA limit the commercial application of these materials. This study shows that adding a small amount of slag can rectify this problem. However, adding slag can lead to larger volumetric instability (i.e., shrinkage potential), causing durability issues in the new binders. This research studies the influence of three volumetric ratios of slag to fly ash (S/FA ratio= 0.1, 0.15 and 0.20) on shrinkage characteristics of alkali activated fly ash/slag blended binders (AAFAS). Three different types of shrinkage deformations, including: chemical, autogenous and drying shrinkage are evaluated in this study. In addition, the effect of activator pH (14.44 vs. 14.04) on early age deformation of blended S/FA binders with the three S/FA volumetric ratios is also studied.

The results of this study indicate that while addition of slag can significantly reduce the time of setting and enhance the compressive strength of blended binders, cured at ambient temperature; larger slag replacement leads to higher autogenous shrinkage. Nevertheless, it was also observed that the greater S/FA volumetric ratio led to the reduction in drying shrinkage of binary mortars and chemical shrinkage of the AAFAS pastes. Comparing the shrinkage measurement of two different pH values of the activators for a given S/FA volumetric ratios, it was found that the higher the pH of the activator, the lower drying and autogenous shrinkage; however the higher pH solution resulted in larger chemical shrinkage.
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Chapter 1

Chapter 1: Objectives and Organization

1.1. Introduction

Over the last few years, cement and concrete industries have experienced significant increase in materials and energy consumption and demand. (Swamy 1998). Portland cement is an essential constituent of concrete and its production increases about 3% annually (McCaffrey 2002). Portland cement production accounts for almost 5 percent of global greenhouse gases emissions; (1kg CO$_2$ per Kg cement), and consumes considerable amounts of natural materials and energy (1.7 KJ per kg cement) (Davidovits 1998, McCaffrey 2002, Mehta 2001, Marland and Boden 1989).

In order to produce environmentally friendly concrete, the use of fewer natural resources, less energy, and minimizing carbon dioxide emissions was proposed (Mehta 2001). In order to reduce the amount of carbon dioxide released by the cement industry, researchers have suggested minimizing the amount of calcined material in the cement by decreasing the cement content in concrete (McCaffrey 2002). While traditionally, Portland cement is “partially” replaced by pozzolanic materials (e.g, FA, BFS, silica fume, glass powder, etc.), it is also possible to “fully” substitute Portland cement with some of these powders. The method is known as alkali activation, where a high pH solution (activator) is used instead of water as the mixing solution.

The two most widely used materials for production of alkali activated cements are fly ash (FA) and blast furnace slag (BFS) and combinations of them; both are industrial wastes requiring

Based on the composition of solid ingredient, three branches of AAC system exists as low-calcium alkali activated materials, high calcium alkali activated binders and intermediate calcium alkali activated systems. The first group is produced by the alkali activation of aluminosilicate materials with low-calcium contents (e.g., alkali activation of metakaolin or class F fly ash). A three-dimensional alkaline inorganic precipitate consisting of a ring structure of Si-O-Al-O bonds (known as geopolymer gel or sodium aluminosilicate hydrate (N-A-S-H)) is formed by activating these materials (Palomo et al. 2007, Duxson et al. 2005). High calcium alkali activated system is obtained by the alkali activation of materials containing high calcium (e.g., alkali activated slag (AAS)). The main reaction product in this case is to some extent similar to the gel formed during the hydration of Portland cement, calcium silicate hydrate or C-S-H gel (Fernández-Jiménez et al. 1999). The C-A-S-H type gel formed by alkali activating slag contains lower content of calcium than the hydrated OPC pastes (Ca/Si ratio in hydrated OPC paste is usually between 1.5 to 2) (Richardson 1999). The intermediate calcium alkali activated binders is formed by alkali activation of aluminosilicate materials with intermediate level of calcium contents (e.g., alkali activation of blended fly ash/slag (AAFAS) or class C fly ash). The hydration product of this group is an intermixed microstructure of C-A-S-H and Na-A-S-H (Shi and Day 1999, Yip et al. 2005).

The alkaline activation of class F fly ash (low calcium content) results in the formation of an inorganic polymer. In these systems, the polymerization starts when alumino-silicate material dissolves in a highly alkaline solution, followed by precipitation of an amorphous products with a
similar structure to zeolites and are known as geopolymers (Davidovits 1988, Palomo et al. 1999, Krivenko, 1997, Palomo et al., 2004). The three dimensional sodium aluminosilicate material, N–A–S–H, is responsible for development of high mechanical strength in this system (Fernandez et al. 2005, Oh et al. 2011). Previous studies show that curing temperature plays an important role in the geopolymerization process of fly ash-based materials (Hardjito et al. 2008, Van Jaarsveld et al. 2002, Palomo et al. 1999), concluding that elevated temperature (through heat curing for example) is needed to achieve desirable strength development. The heat curing process, however, can limit the industrial field applicability to only precast industry (Lee and Lee 2013, Radlinska et al. 2013). It has been observed that curing AAFA mortars at 65°C, 70°C, and 80°C for 24 hours increases the compressive strength, when it is compared to that one ambient temperature. It is also noted that the mechanical and microstructural properties of these materials are highly temperature dependent (Hardjito et al. 2008, Hardjito et al. 2004).

Past studies have concluded that addition of calcium compounds as a fly ash substitute improved mechanical properties at the ambient temperature (Yip et al. 2008, Temuujin et al. 2009). It was concluded that adding slag that contains a high content of CaO to AAFA can improve the strength development of geopolymer systems cured under ambient room temperatures.

Previous research studies reported that AAS had higher drying shrinkage than OPC and addition of FA can help to decrease the drying shrinkage of AAS pastes (Palacios and Puertas 2007, Shi et al. 2006, Yang et al. 2007). The high magnitude of AAS shrinkage, specifically at an early age, induces a risk of premature cracking (Cartwright et al. 2014, Malolepszy et al. 1988, Collins et al. 2000, Kutti et al. 1992, Palacios and Puertas 2007, Sakulich and Bentz 2013). On
the other hand, it was also reported that alkali activated fly ash has low shrinkage characteristics when it is compared to OPC (Malone et al. 1985, Hardjito et al. 2005, Fernández-Jiménez et al. 2006, Rashad 2013). The effect of the addition of slag on early age behavior of AAFA is still in question.

1.2. Objectives and Scope

The goal of this study is to understand the influence of using slag as partial replacement (up to 20%) of fly ash to investigate the early and long-term properties of AAFA. Extensive research has been focused on alkali-activation of fly ash or slag, however an in-depth understanding of the mechanism of incorporation of slag as a source of calcium in activated fly ash binders is still lacking. As this thesis focuses on the engineering characteristics of alkali activated fly ash-slag (AAFAS) binary binders, firstly the mechanical property of AAFA cured under elevated temperature was examined. Then the influence of adding slag on the properties of alkali-activated binary system cured in room-temperature was studied to determine the appropriate replacement ratio of the slag to the fly ash in AAFA. Finally the shrinkage mechanism of the binary system was examined for different slag replacement ratio and PH of the activator solution.

In order to achieve the stated goal, the following main objectives are pursued in this research study:

1. To investigate the mechanical properties of alkali-activated fly ash and fly ash/slag blended mortar cured at elevated and room temperature.
2. To examine the early-age deformation of alkali activated fly ash/slag blended systems to evaluate the effect of slag incorporation on shrinkage characteristics.
3. To investigate the effect of activating solution pH on the shrinkage characteristics of alkali activated systems.

1.3. Outline

The content of this thesis is presented in five chapters. Chapter 2 provides a literature review on alkali activated binder systems. It includes a review of the reaction mechanisms of alkali activated fly ash, slag and binary systems and their mechanical and microstructure properties. It also includes a review of the different testing techniques used in the characterization of alkali activated binders.

Chapter 3 presents the material properties, mixture proportions, mixing procedures and test methods used to evaluate mechanical properties of alkali activated fly ash (AAFA) systems. The results of compressive strength, time of setting and drying shrinkage of AAFA systems are presented and discussed.

Chapter 4 details the material properties, mixture proportions, mixing procedures, setting and mechanical properties, test methods and results of measuring shrinkage and microstructural properties of blended alkali activated fly ash slag systems. Three different forms of shrinkage, including drying, autogenous and chemical shrinkage were studied to explore the susceptibility of AAFAS binary system to shrinkage as a function of slag to fly ash volumetric ratio as well as the activating solution pH. Scanning electron microscopy-coupled with energy dispersive spectroscopy (SEM/EDS) was used to qualitatively and quantitatively study the microstructural and elemental evolution of these AAFAS blended binders. Mercury intrusion
porosimetry (MIP) was also employed to determine the pore structure and pore size distribution of these binary binders to observe how it is affected by activating solution. Static modulus of elasticity of AAFAS concrete was measured to see the influence of bulk elastic modulus of pastes on the magnitude of deformation of AAFAS systems.

Finally, **Chapter 5** discusses conclusions of the studies carried out on the shrinkage characteristics of alkali activated binder systems.
Chapter 2

Chapter 2: Background

In this chapter, past studies on the alkali activated fly ash, slag and binary systems of fly ash and calcium compounds as the binding medium is presented. The microstructural and engineering properties of these materials are discussed.

2.1. Alkali Activation of Cementitious Materials

Alkali activated cement (AAC) is the term applied to a group of binders, formed through dissolution and precipitation reactions, occurring within interactions of some amorphous alumino-silicate or calcium-silicate materials with alkaline solutions. The reaction between the alkaline solution and solid precursor starts when cations from the activating solution (the alkalis or alkali earth ions) cause the reaction or releases the latent cementitious properties form aluminosilicate polymeric gel (Jiang 1992). Roy (1999) reported that alkali-activated cements are those materials with compositions falling in $\text{Me}_2\text{O-}\text{MeO-}\text{Me}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system, where Me is an alkali atom and M is an alkaline earth, Al or Fe atom (Roy and Scheetz 2006).

The inorganic materials (solid precursors) are mostly naturally occurring minerals or industrial by-products including silicates, aluminosilicate and calcium. These source materials have received extensive attention because of their lower environmental impacts, when it is compared to OPC. Utilizing these materials in the concrete production can also decrease the amount of wastes that would be otherwise disposed in the landfill and might contribute to soil and water contamination.
According to Krivenko (1997), alkali activated cementitious material is classified based on the composition of hydration products into two main groups:

1. The alkaline alumino-silicate systems (R-A-S-H, where R=Na or K) which are also known as geo-polymer or geocements, because of the similarity of the formation process of these materials to the geological process of the natural zeolites. According to Davidovits (1994) in these systems the main products form in a polycondensation process rather than hydration. Alkali activation of fly ash is placed in this group.

2. The alkaline calcium aluminosilicate systems (C (N)-A-S-H) where the hydration products contain lower calcium silicate hydrates (C-S-H with low Ca/Si ratio) comparing to Portland cements. These include the alkali activated slag and alkaline Portland cements.

Extensive research has been done with alkaline cement since 1940 or earlier (Chao et al. 2010). In Table 2-1 some important references presenting the steps and the progress of alkali-activated and alkaline cements are chronologically listed (Roy 1999, Chao et al. 2010). In accordance with Roy’s research (1999), three major research opportunities for alkali activated cement are: (1) deep understanding and knowledge of properties and mechanisms, (2) generally good track record of field performance and commercial adoption of these materials in various applications, and (3) according to future expectations that our society must involve in its technological use of waste materials, consuming less energy, generating lower amount of greenhouse gases, and other undesirable product, alkali activated concrete is a future oriented material.
Table 2-1: Bibliographic history of alkali activate cement systems and alkaline cements (after 1939, Chao et al. 2010)

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<th>Significance</th>
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</table>
2.2. Applications of Alkali Activated Binder Systems

A variety of applications, particularly since the 1970s, has been found for alkali activated cement including agricultural, industrial, residential, transportation (e.g., railway ties), mining, various high-volume applications, and oil well cements. This material also plays an important role in the waste management (such as nuclear waste management and immobilization of toxic metals) (Roy 1999). Table 2-2 summarizes the numerous applications of alkali-activated cements up to the present (Krivenko 1994).

| Table 2-2 Applications of alkali activated cement (Krivenko 1994) |
|-------------------|----------------|-----------------|-----------------|-----------------|-----------------|
|                   | Road           | Agriculture     | Industrial       | Residential      | Mining          | Hydraulic       |
| Structural        | Heavy-duty     | Cast in situ    | Acid-resistant   | Pre-cast and     | Oil well        | Irrigation       |
| application       | pavement cast  | and pre-cast    | buildings        | in situ concrete | grouts; ties;   | systems; break   |
|                   | in situ and pre| concrete storage| garages; floor   | buildings; slab  | sealing; prevent| waters           |
|                   | cast reinforced|                 | slabs; foundation| foundation       | water           |                 |
| Nonstructural     | Waste          | Bodies of       |                  |                 |                 |                 |
| application       | immobilization | machine tools   |                  |                 |                 |                 |
|                   |                |                  |                  |                 |                 |                 |

The properties and consequently the application of geopolymeric materials can be specified by the chemical structure and the atomic ratio Si:Al in the polysialate (Davidovits 2005). The molar ratio of Si to Al plays an important role in the application of geopolymer. Table 2-3 presents the possible applications proposed by Davidovits (1988). As it is shown in this table a low Si:Al ratio is suitable for many applications in the civil engineering field.

These geopolymeric concretes provide high strength and good durability characteristics such as reduced ion/liquid transport properties and better acid and fire resistance (Bakharev 2005,
Glifford and Gillot 1997, Kumar et al. 2006), thereby it has the potential of applying as a binder instead of Portland cement.

<table>
<thead>
<tr>
<th>Si/Al</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bricks, ceramics, fire protection</td>
</tr>
<tr>
<td>2</td>
<td>Low CO₂ cements, concrete, radioactive &amp; toxic waste encapsulation</td>
</tr>
<tr>
<td>3</td>
<td>Heat resistance composites, foundry equipment, fiber glass composites</td>
</tr>
<tr>
<td>&gt;3</td>
<td>Sealants for industry</td>
</tr>
<tr>
<td>20&lt;Si/Al&lt;35</td>
<td>Fire resistance and heat resistance fiber composites</td>
</tr>
</tbody>
</table>

Some of the applications of alkali activated cement free concrete are described in the following:

1. Depending on the activator and source material chemistry, they can be used as the repair materials because of their better early age strengths (in most cases) and linking with the substrate material (Hu et al. 2008).

2. Geopolymer is also utilized in the strengthening of concrete materials in the structural elements (Hu et al. 2008).

3. Another application of this material is using them instead of organic polymers, for fastening carbon fabrics to surfaces of reinforced concrete beams. It was reported that geopolymer had an excellent adhesion to both concrete surface and in the interlaminar of fabrics (Balaguru et al. 2002) this material is chemically compatible with concrete.

4. Geopolymers are proper for high temperature applications. Geopolymers have been found to stay structurally stable at temperatures up to 800°C. This material did not degrade under UV and light as reported by Rashad and Zeedan (2011).
5. One of the potential areas of use of geopolymeric materials is in toxic waste management, because their behavior is similar to zeolitic materials that have been known for their ability to absorb the toxic chemical wastes (Davidovits 2005).

2.3. Alkaline Activated Binder’s Constituents

Alkaline liquids and precursor materials are the two main constituents of alkali activated binders, described in more details in the following sections.

2.3.1. Alkaline Agents

Aluminosilicate or calcium aluminosilicate based materials, such as fly ash and slag, are activated using a chemical activating agent to form the resulting binding material.

Typically, caustic alkalis or alkaline salts are used as alkaline activators. Although the use of a single alkaline activator has been reported in some research, the combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate (Na₂O.nSiO₂) or potassium silicate (K₂O.nSiO₂) is commonly used as an alkaline liquid agent (Palomo and Glasser 1992, Van Jaarsveld et al. 2003, Teixeira et al, 2002, Fernandez-Jiménez et al. 2006, Xu and Van Deventer 2000). Table 2-4 shows the classification of alkali activators into six groups, according to their chemical compositions.
Table 2-4 Classification of Alkali activators
(Glukhovsky et al. 1980)

<table>
<thead>
<tr>
<th>Alkali Activator</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxides</td>
<td>MOH</td>
</tr>
<tr>
<td>Non-silicate weak acid salts</td>
<td>M₂CO₃, M₂SO₃, M₃PO₄, MF</td>
</tr>
<tr>
<td>Silicates</td>
<td>M₂O·nSiO₂</td>
</tr>
<tr>
<td>Aluminates</td>
<td>M₂O·nAl₂O₃</td>
</tr>
<tr>
<td>Aluminosilicates</td>
<td>M₂O·Al₂O₃·(2–6)SiO₂</td>
</tr>
<tr>
<td>Non-silicate strong acid salts</td>
<td>M₂SO₄</td>
</tr>
</tbody>
</table>

Komljenovi et al. (2010) confirmed that the type and the nature of the activator have considerable influence on the reaction of alkali activation. It was reported that when an activator has a soluble silicate, the polymerisation process takes place at higher rate than when an alkali hydroxide is used alone. Based on their research, the activation potential of the activators investigated (taking into account equal concentrations) can be represented by the following order (Komljenovi et al. 2010):

\[
\text{KOH} < \text{NaOH} + \text{Na₂CO₃} < \text{NaOH} < \text{Na₂O.nSiO₂}
\]  

(2-1)

Since the alkali hydroxides, silicates and the combination of them are commonly used as activating agents, this section provides more details on the alkali hydroxides and silicates used as activators.

I. Alkali Hydroxides

Alkali hydroxide is a very common activating agent consisting of an alkali metal cation and hydroxide anion (OH⁻). Sodium and potassium hydroxides are the most widely used alkali hydroxides in activation of aluminosilicate materials. NaOH is reasonably cheap when it is...
compared to KOH and largely available, making it an obvious pick for production of alkali activated binders (Palomo and Glasser 1992). The use of high concentrations of NaOH or KOH as the activating agent has been reported to lead to the formation of zeolitic structures after an extensive period of moist curing or a brief period of elevated temperature curing. The dilution of NaOH releases a large amount of heat, thus requiring special precautions to be taken (Chithiraputhiran 2012). One of the concerns related to the applying the high alkalinity in the system is associated with carbonation and leaching of the reaction products activated using alkali hydroxides; so optimal alkalinity needs to be determined when using alkali activated systems.

II. Alkali Silicates

One of the most commonly used activating agents for alkali activated binder systems is sodium silicate. Sodium silicate is the generic name for a series of compounds with the formula \( \text{Na}_2\text{O} \cdot n\text{SiO}_2 \), where the ratio ‘n’ is the modulus of sodium silicate, indicating the molar ratio of \( \text{SiO}_2/\text{Na}_2\text{O} \). Different grades of sodium silicate are generally characterized by their modulus (ratio of \( \text{SiO}_2 \)-to-\( \text{Na}_2\text{O} \) or \( \text{K}_2\text{O} \)); the commonly available sodium silicate has a silica modulus of 1.60 to 3.6 and contains 36-40% solids. Theoretically, different ‘n’ values will result in different properties (such as viscosity of the aqueous solution), that result in many different industrial applications. Sodium silicates are available in solid as well as in liquid forms. Liquid sodium silicates are commercially termed as water-glass or liquid glass. Solid sodium silicate consists of a chain of polymeric anions composed of corner shared \([\text{SiO}_4]\) tetrahedral.

It has been reported that the addition of sodium silicate solution to sodium hydroxide solution (as the alkaline liquid) increase the reactivity between the source material and the
solution and accelerate the setting time of binders (Shi and Li 1989). NaOH is often added to a sodium silicate solution to lower the n modulus to a more desired value. This method allows production of water glass of optimal modulus and concentration.

By comparing the properties of sodium and potassium silicates, the viscosity is one of the main differences between them. Potassium silicate solutions have a remarkably lower viscosity than sodium silicate at the same silica modulus, thereby making mixtures workable at a lower activator-to-binder ratio. However, due to higher costs of potassium silicates, it is less favorable for practical applications. The soluble silicates can influence the effects on the dissolution rate of the precursor powders as well as the properties of final products (Vassilev and Vassileva 2007).

2.3.2. Source Materials

The source materials used for making AAC should be rich in silicon (Si) and aluminium (Al) (Wallah and Rangan 2006) as aluminum and silicon are both network former elements. These could be non-calcined materials, such as kaolin clay, and naturally occurring minerals, whose empirical formula contains Si, Al, and oxygen (O) or calcined materials such as fly ash, silica fume, slag, rice-husk ash, red mud, etc. Many different factors affect the choice of the source material such as cost, availability, or type of application (Davidovits 1988). On the nature of the source material, it was expressed that the calcined source materials, such as fly ash, slag, calcined kaolin, have a higher final compressive strength compared to non-calcined materials, like kaolin clay (Barbosa et al. 2000).
The two widely-used and promising precursor (source) materials are fly ash, slag and blended combinations of them. Alkali activated fly ash (AAFA) is produced by alkali activation of low or intermediate-calcium contents fly ash (class F or C respectively). A three-dimensional alkaline inorganic gel known as geopolymer gel is formed by activating of these materials (Palomo et al. 2007, Duxson et al. 2005). Alkali activated slag (AAS) is obtained by alkali activation of silica-rich slag that also contains high calcium content. The main reaction product formed in AAS is similar to the hydration products of Portland cement, calcium silicate hydrate (C-S-H) (Fernández-Jiménez et al. 1999) that incorporates much more alkalis within the structure. Alternatively, alkali activation of blends of fly ash and slag can be designed to produce a binary precursor (Shi and Day 1999, Yip et al. 2005, Puertas and Fernandez-Jimenez 2003). In the following sections, different characteristics (e.g., raw materials, microstructure and properties of AAFA and AAS) of fly ash, slag are explained in more depth.

I. Fly ash

Utilizing coal as a source of energy in power plant generates tremendous amount of fly ash (FA). It is defined by the American Concrete Institute (ACI) Committee 116R as ‘the finely divided residue that results from the combustion of ground or powdered coal and that is transported by flue gasses from the combustion zone to the particle removal system. The type of fly ash is determined based on the type of coal. The lignite or subbituminous coals produce high calcium fly ash possessing both a cementitious and pozzolanic property and are known as class C fly ash. The anthracite and bituminous coals produce low calcium fly ash, which is a pozzolanic material because of the high content of silica and are called as class F fly ash. Specifications for fly ash types according to ASTM C 618 are presented in Table 2-5.
Fly ash is highly spatially heterogeneous. It may happen even at different batches form the same source. The particle size distribution, chemistry and mineralogy, as well as the reactivity of this material from different sources contribute significantly to the heterogeneity (Favier et al. 2013, Diamond 1986). Variability of the precursor material can affect the microstructure of the hardened binder. The identification of this variation in the hardened matrix (in terms of chemical composition and morphology) can help to better understanding and provide insight into the reaction processes (Lloyd et al. 2009, Provis et al. 2011).

<table>
<thead>
<tr>
<th>Chemical Requirements</th>
<th>Class F</th>
<th>Class C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$ min%</td>
<td>70</td>
<td>50</td>
</tr>
<tr>
<td>SO$_3$ max%</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Moisture Content max%</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Loss on ignition (LOI) max%</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Optional Chemical Requirements Class F</td>
<td>Class C</td>
<td></td>
</tr>
<tr>
<td>Available alkalis max%</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Physical Requirements Class F</td>
<td>Class C</td>
<td></td>
</tr>
<tr>
<td>Fineness (+325 Mesh) max%</td>
<td>34</td>
<td>34</td>
</tr>
<tr>
<td>Pozzolanic activity/cement (7 days) min%</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>Pozzolanic activity/cement (28 days) min%</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>Water requirement max%</td>
<td>105</td>
<td>105</td>
</tr>
<tr>
<td>Autoclave expansion max%</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Uniform requirements : density max%</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Uniform requirements : Fineness max%</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Optional Physical Requirements Class F</td>
<td>Class C</td>
<td></td>
</tr>
<tr>
<td>Multiple factor (LOI x fineness)</td>
<td>225</td>
<td>-</td>
</tr>
<tr>
<td>Increase in drying shrinkage max%</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Uniformity requirements: Air max%</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Cement/Alkali Reaction: Mortar max%</td>
<td>0.02</td>
<td>-</td>
</tr>
</tbody>
</table>
II. Slag

Slag is the by-product of iron manufacturing and it is generated when iron ore is melted and reduced in a blast furnace. Slag can be broadly classified into blast furnace slag and steelmaking slag. The most common cementitious materials for AAS binder is iron blast-furnace slag (Al-Otaibi 2008, Fernandez-Jimenez et al. 1999, Shi & Day 1996, Zivica 2007).

Basicity of a slag or glassy material and hydration modulus are the two mostly used parameters to measure the hydraulic activity of slag. The basicity of a slag or glassy material is defined as the ratio between total content of basic constituents and total content of acidic constituents (McGannon 1971). Based on the basicity coefficient (Eq. 2-2), slag can be classified into three groups: acid slag (the basicity coefficient is less than 1), neutral slag (the basicity coefficient is equal to 1), and basic slag (the basicity coefficient is greater than 1). Neutral and basic slag are preferred as starting materials for AAS binder.

\[
\text{Basicity coefficient} = \frac{\text{Total content of basic constituents}}{\text{Total content of acidic constituents}} \quad (2-2)
\]

To measure hydration properties of raw slag, the hydration modulus (HM) is defined as the ratio of the sum of \(\text{Al}_2\text{O}_3\), \(\text{MgO}\) and \(\text{CaO}\) to \(\text{SiO}_2\) (Eq. 2-2). HM should exceed 1.4 (Chang 2003) to provide proper hydration properties. According to the chemical composition of this waste material, a granulated slag with a \(\text{CaO}/\text{SiO}_2\) ratio between 0.5 and 2.0 and an \(\text{Al}_2\text{O}_3/\text{SiO}_2\) ratio between 0.1 and 0.6 can be used as a source material in alkali activated binders (Talling and Brandstetr 1989).
Hydration modulus (HR) = (sum of Al₂O₃, MgO and CaO content)/(SiO₂ content)  \( (2-3) \)

2.4. Alkali Activated Fly Ash (Class F)

2.4.1. Chemical Structure of Geopolymer and Reaction Mechanisms

The proposed mechanisms of three researchers (Davidovits equations and model, Duxson and Provis flowcharts) for the formation of geopolymeric binders are presented in this section. The molecular structure of geopolymers is termed as polysialate. Sialate was coined as an abbreviation for silico-oxo-aluminate, which has \([-\text{Si-O-Al-O-}]\) as the repeating unit. The network of the sialate is composed of SiO₄ and AlO₄ tetrahedral units, connected by oxygen atoms as displayed in Figure 2-1 (Davidovits 2005). Positive ions Na⁺, K⁺, Ca++, Ba++, NH₃+, H₃O⁺ must be present in the framework cavity to compensate the negative charge of the Al³⁺ in IV-fold coordination. The schematic formation of geopolymer material can be described by the following equation when the aluminosilicate material is activated by alkali hydroxides (Davidovits, 1999):

\[
(\text{Al}_2\text{Si}_2\text{O}_7)_n + n\text{H}_2\text{O} \xrightarrow{\text{MOH}} n(\text{OH})_3 - \text{Si} - \text{Al} - (\text{OH})_3
\]

\[
\xrightarrow{\text{MOH}} \text{M}(-\text{Si} - \text{O} - \text{Al}^{(-)} - \text{O})_n + n\text{H}_2\text{O}
\]

Where M represents the cations (i.e., Na⁺ or K⁺) used to activate the reaction. During this reaction water expels from the geopolymer matrix due to the curing and drying process and it is remained some discontinuous nano pores in the matrix and as a result the geopolymer performance increases. It was observed that water plays no role during the geopolymerization
process and just provides the workability to the mixture during handling (Hardjito and Rangan 2005).

Adding the combination of amorphous silica and alkali hydroxide results in the formation of either the structures of PSS, poly (sialate-siloxo) which has [-Si-O-Al-O-Si-O-] as the repeating unit, or PSDS, Poly (sialate-disiloxo) which has [-Si-O-Al-O-Si-O-Si-O-] as the repeating unite of geopolymers. The reaction for the PSS formation is also provided below (Davidovits 2005):

\[
(\text{Al}_2\text{Si}_2\text{O}_7)_n + n\text{SiO}_2 + n\text{H}_2\text{O} \xrightarrow{\text{MOH}} n(\text{OH})_3 - \text{Si} - \text{Al} - \text{O} - \text{Si} - (\text{OH})_3
\]

\[
(\text{OH})_2
\]

(2-6)

\[
(\text{OH})_3 - \text{Si} - \text{Al} - \text{O} - \text{Si} - (\text{OH})_3 \xrightarrow{\text{MOH}} \text{M}(-\text{Si} - \text{O} - \text{Al}^{(-)} - \text{O} - \text{Si} - \text{O})_n + n\text{H}_2\text{O}
\]

(2-7)

Figure 2-1 Aluminosilicate structure and nomenclature (Davidovits 2005)
In simple words, the polymerization starts when alumino-silicate material is dissolved in a very alkaline solution yields an amorphous zeolitic material, called geopolymer (Davidovits 1988, Palomo and Glasser 1992, Palomo et al. 1999, Palomo et al. 2004). The chemical composition of geopolymer materials is analogous to zeolite but have an amorphous microstructure instead of crystalline (Davidovits 1988). Different research proposed various models for activation of mechanism for aluminosilicate materials. The general mechanism for the alkali activation of materials was suggested by Glukhovsky (1959) which is divided in three steps (a) destruction–coagulation, (b) coagulation–condensation, and (c) condensation–crystallization. Another mechanism of geopolymerisation was also proposed by Duxson et al. (2007) including (a) dissolution, (b) speciation equilibrium, (c) gelation, (d) reorganization, and (e) polymerization and hardening. The general step-wise reaction is shown in Figure 2-2.
Provis (2006) also suggested a simplified model of the reaction processes in the geopolymerisation of aluminosilicate materials that can be seen in Figure 2-3.
2.4.2. Microstructure Model of AAFA

The microstructure development of an alkali activation of class F fly ash is shown in Figure 2-4. Fernandez-Jimenes and Palomo (2005) used SEM to investigate the microstructure of geopolymer mortar. As it is shown in Figure 2-4A, the product is amorphous aluminosilicate gel (points 4 and 5), and the unreacted spheres of fly ash (Figure 2-4A, point 3) and some fly ash spheres partially covered with reaction product (Figure 2-4C). In addition they also discovered some crystalline phases of the aluminosilicate gel (Figure 2-4B, point 6), and a little group of bright particles recognized as zeolite crystals (Figure 2-4D points 7 and 8).
In Figure 2-5, the SEM images of unreacted fly ash powder (Figure 2-5A), fly ash activated with 8 M NaOH for 20 h at 85 °C (Figure 2-5B), and fly ash activated with sodium silicate at 85 °C for 20 hours (Figure 2-5C), are shown (Fernández-Jiménez et al. 2005). It was observed that after 20 hours of curing at elevated temperature a few small fly ash particles reacted with the
alkali solution while some other particles remain unreacted and some of them were partially covered with reaction products (Figure 2-5B). Moreover a very uniform and slightly porous microstructure together with only a few unreacted fly ash particles was detected for the paste activated with sodium silicate (Figure 2-5C).

![Figure 2-5 SEM images of fly ash powder and alkali activated fly ash pastes (A) original fly ash (B) fly ash activated with 8 M NaOH for 20 h at 85 ºC (C) fly ash activated with sodium silicate solutions for 20 h at 85 ºC (Fernandez-Jimenez et al. 2005)](image)

Mechanism of gel formations in alkali activated paste made with fly ash is shown in Figure 2-6. According to the description by Fernandez-Jimenez et al. (2005), the fly ash particles
firstly are attacked by alkaline solution at their surface (Figure 2-6a) and the dissolution process takes place. Then the reaction product is generated both inside and outside of the shell of the particles (Figure 2-6b) until the ash particles are completely consumed (Figure 2-6c).

At the same time, the smaller ash particles inside the bigger particles is dissolved in the alkali solution and the interior of the partially hollow spherical particle becomes filled with reaction product and forming a dense matrix. Sometimes the layer of reaction product prevents more dissolution of fly ash particle and reduces the rate of reaction and after that the reaction continues through a diffusion-controlled process (Figure 2-6e). This process varies among different points inside the matrix. Finally, the result is a microstructure containing several phases and morphologies: unreacted particles, particles attacked by alkali solution while still maintaining their spherical shape, and reaction products.

Figure 2-6 Mechanism of gel formations in alkali activated paste made with fly ash as binder (Fernandez-Jimenez et al. 2005)
2.4.3. Engineering properties of Fly ash Geopolymer

Different factors such as particle size distribution, chemical composition, amount of vitreous phase in FA, nature, concentration and pH of activators and the curing conditions (temperature, curing time, relative humidity) can affect the engineering properties of AAFA. Different research showed that these parameter have significant influence on development of microstructure, and thereafter on the mechanical characteristics of alkali-activated FA (Chindaprasirt et al. 2007, Fernandez-Jimenez and Palomo 2003, Temuujin and van Riessen 2009).

Alkali activated fly ash systems which are properly designed and cured at suitable condition exhibit comparable engineering properties to those of OPC mixtures (Duxson and Provis 2007).

Previous studies have shown that the concentration of the NaOH solution, regardless of curing temperature and age, plays very important role in the strength of alkali activated geopolymers (Bakharev 2005, Palomo et al., 1999, Silva and Thaumaturgo 1998, Hu et al. 2009, Komnitsas et al. 2009). Hardjito and Rangan (2005) reported that geopolymers prepared with a 14 M solution of NaOH showed greater compressive strength than the samples prepared with a 8 M solution of NaOH.

Curing at elevated temperatures is commonly used for synthesis of AAFA. When the activator concentration is enough to initiate the geopolymerization, the curing temperature and
age have significant impact on the mechanical properties of geopolymers. Fernández-Jiménez and Palomo (2005) observed that the compressive strength for some AAFA pastes can reach as high as 90 MPa after only 20 hours cured at 85 °C.

Bernal and Provis (2014) reported that initial carbonation in AAFA, because of the formation of sodium carbonate hepta-hydrate (Na$_2$CO$_3$·7H$_2$O) at the very first days of curing, results in an internal CO$_2$ concentration gradient. It was indicated that carbonation of alkali activated fly ash systems is not just due to the pore solution and it could be caused at the very first days of curing by the alkali ions in the binding gels occurring in the presence of high levels of CO$_2$.

AAFA concrete/mortar has a better resistance against chemical attack when it is compared to OPC concrete. Many investigations (Fernández-Jiménez et al. 2007, Hardjito and Rangan 2005) reported superior resistance of AAFA against sulfate attack. It was observed that there is no significant difference between microstructure of AAFA before and after sulfate exposure. This can be due to the absence of ettringite in AAFA systems (with low-calcium content), while in Portland cement, the formation of ettringite (expansive) leads to cracking of the matrix.
2.5. Alkali Activation of Slag

2.5.1. Hydration Products and Reaction Mechanisms

The formulation of reaction mechanism of alkali activation of slag is different from geopolymeric reaction mechanism explained in the previous section due to the presence of calcium c in slag. In this system, slag particles are attacked by the alkali ions and the outer layer is broken and finally the reaction products undergo polycondensation.

During the initial stage, the reaction takes place on the surface of particles and reaction products due to dissolution and precipitation at later age. The solid state of this mechanism is followed where the reaction occurs (Wang and Scrivener 2003).

According to past research studies (Krivenko 1994, Glukhovsky 1994) in the early stages of hydration, alkaline cations act as a mere catalyst for the reaction to interchange with Ca\(^{2+}\) cations as it is shown in the simplified reactions presented in Eqs. 2-8 to 2-10 (Jiang 1997):

\[
\begin{align*}
=\text{Si-O}^- + R^+ & \rightarrow =\text{Si-O-R} \quad (2-8) \\
=\text{Si-O-R} + \text{OH}^- & \rightarrow =\text{Si-O-R-OH}^- \quad (2-9) \\
=\text{Si-O-R-OH}^- + \text{Ca}^{2+} & \rightarrow =\text{Si-O-Ca-OH}^- + R^+ \quad (2-10)
\end{align*}
\]

As the reaction progresses, the alkalis cataions are involved into the structure to form zeolite-like phases. It was concluded that the alkali hydroxide plays two important roles in the reaction of AAS, firstly provides enough OH\(^{-}\) ions to dissolve the source materials at initial stage and at later stage, it becomes part of the reaction products (Krivenko 1994).
Different investigation showed that the main reaction product in activation of slag is a calcium silicate hydrate (C–S–H) similar to the hydration products of OPC and the major difference is ratio of Ca/Si of final products (Bakharev 2000, Brough and Atkinson 2002, Wang and Scrivener 2003). Taylor (1997) reported the Ca/Si ratios in C-S-H gel of AAS are below 1.5 while in Portland cement the ratio is approximately 2. Figure 2-7 depicts the descriptive model for activation of slag.

![Figure 2-7 Reaction mechanism of alkali activated slag (Fernández-Jimenez and Puertas 2003)](image)

The evolution of hydration of AAS is influenced by the nature of activators and their concentrations. Shi and Day (1995) from calorimeter analysis proposed three models of hydration (for different alkaline solution) which can be distinguished for AAS, shown in Figure 2-8. The Type A model is corresponded to activation of slag with water or Na$_2$HPO$_4$. In this case one peak occurs during the first few minutes due to the initial dissolution of slag and no more peaks appear thereafter. Type B includes two peaks appear before and after the induction hydration of slag, activated by NaOH at 25 and 50°C. This type is very similar to the kinetic reaction of Portland
cement, and contains clearly the five stages. In type C, three peaks can be observed and it takes place when the slag activated with Na$_2$SO$_3$, Na$_2$CO$_3$, Na$_3$PO$_4$ and NaF solutions.

![Diagram of hydration models of alkali activation of slag](image)

**Figure 2-8** Schematic representation of hydration models of alkali activation of slag (Shi and Day 1995)

### 2.5.2. Microstructure of AAS

The microstructure of AAS gel after early hydration includes a homogeneous gel and considerable micro-cracking especially against aggregate interface (Brough and Atkinson 2002). After fully hydration takes place the degree of drying shrinkage cracking is much reduced. The reaction products are formed in the pore space, where originally was occupied by alkali solution (Gruskovnjak et al. 2006, Jiang et al. 1997). The outer product can be seen at the gel matrix where the smaller slag particles have fully hydrated. The product also can be observed as rims around the partially hydrated slag grains. The inner product regions are mostly darker than outer product region (Figure 2-7). Typical SEM microstructures, and BSE, backscattered electron, images after one day of AAS paste are shown in **Figure 2-9**. Based on SEM images, the microstructure of AAS was very smooth, homogeneous and interconnected-solid in all samples.
As mentioned the reaction product of AAS is a homogeneous gel along with substantial cracks in AAS matrix compared to OPC matrix. This cracking phenomenon was also observed in many studies (Escalante-Garcia et al. 2009). Figures 2-9 displays BSE images of activated blend of slag and Portland cement and alkali activated slag concretes. Figures 2-10 shows that the matrix of alkali activated slag concrete is relatively dense with the remaining slag grains, which are smaller than 100 μm.

Figure 2-9 (A) SE (II)BSE images of hydrated AAS paste after one day activator/binder =0.25, T = 20°C, after Wang (2000)
The fine pore structure of the hardened AAS pastes is one of the most important features of this material. The pore structure of AAS mortar is highly influenced by activator used for activating aluminosilicate material, as reported by Shi (1996); activation of slag by Na$_2$SiO$_3$.

Figure 2-10  BSE images of polished samples of Portland cement and slag blended concrete and alkali activated slag (Garcia, et al., 2009)
results in less porosity than OPC, however when activating of slag by NaOH, the porosity is higher. Collins and Sanjayan (2000) observed from the analysis of the incremental pore size distribution data that AAS paste has a much higher proportion of pore sizes within the mesopore limits than OPC paste. This observation can explain the higher magnitude of drying shrinkage of AAS concrete.

2.5.3. Engineering Properties of AAS

Different parameters can affect the strength development of alkali activated slag binders such as type of activator using in this system, proper curing, quality control and dosage of chemical additives. Collins and Sanjayan (1999) observed that AAS concrete achieving higher compressive strength and also higher flexural strengths (at the same activator to binder ratio and equal binder content) compare to that of OPC.

Different research reported that in AAS a large number of micro cracks developed in the microstructure and the magnitude of shrinkage is greater than that of OPC (Andersson and Gram 1987). It was stated the AAS activated by NaOH and Na₂CO₃ may exhibit lower drying shrinkage compare to that of activated by water glass solution because of the formation of silica-rich gel (Wang et al. 1994, Douglas et al. 1992). Collins and Sanjayan (1999) -studied the effect of the curing conditions on drying shrinkage of AAS. They noticed that when the AAS samples sealed occurred at higher relative humidity at the very first age, they gave the lowest shrinkage. It was observed in their research that the highest shrinkage was associated with the samples left to dry at low RH at very early age of curing.
Since the alkalis are bound into the reaction products and are not freely available in the pore solution (this depends on the alkali concentration used), the potential for alkali-silica reaction is reduced (Krizan and Zivanovic 2001).

Bernal and Provis (2014) stated in their research that AAS pastes are less porous than the geopolymer systems (i.e., alkali activated fly ash, AAFA). The pore size distribution can control the transport properties of AAS. They also measured the carbonation depths of some of the AAS concretes after 7 years of natural exposure to carbonation (formulated with 500 kg/m$^3$ of slag) showed carbonation depths of 1.7 mm year, which is lower when it is compared to Portland cement concretes, observed the carbonation depths between 2 and 10 mm after 1 year. Figure 2-11 demonstrates the change in the microstructure of an AAS before and after subjecting to accelerated carbonation. It is noted that after CO$_2$ exposure, carbonated AAS paste is less dense and more porous compared to its initial condition.

Figure 2-11 (A) SE image of a silicate-activated slag binder before exposure to 1% CO$_2$ for 1000 hours(B) SE images of a silicate-activated slag binder after exposure to 1% CO$_2$ for 1000 hours (Bernal and Provis 2014)
2.6. Influence of Calcium Compounds Addition on Alkali Activation of Class F Fly Ash

The application of alkali activated fly ash and alkali activated slag materials has been very limited so far, despite the advantages of these binders. The mechanical and microstructural properties of AAFA are temperature dependent. In this section the effect of calcium compound addition on AAFA properties is reviewed.

2.6.1. Influence of Calcium Compounds Addition on Hydration Products and Reaction Mechanisms of AAFA

García-Lodeiro et al. (2013) evaluated the effect of small portion of OPC on AAFA and proposed a microstructural model which indicates the development of the reaction products forming in these hybrid cements (a model of alkaline activation for cement blends with high silica and alumina and low calcium content). Figure 2-12 depicts different stages of gel formation in binary system as follows:

Stage A: the process starts by dissolution of source materials (fly ash and OPC) in high alkaline solution by breaking the Si-O-Si and Al-O-Al bonds in fly ash and Ca-O and Si-O bonds in OPC.

Stage B: as the concentration of dissolved monomers rises up in the medium, the monomers react with each other and form dimers. As stated before in AAFA, the dimers turn into trimers, tetramers. Initially, N-A-S-H gel is forming around spherical fly ash particles and C-S-H type gel generated around the cement particles.
Stage C: similar to AAFA, as reaction progresses more Si–O groups dissolve from both silicate source binders (fly ash and OPC). The main product of binary system in this stage contains higher silicon content in both N-A-S-H and C-S-H gels.

Stage D and E, the aluminum and calcium monomers start defusing in the hardened gel. In N-A-S-H gel, a few calcium cations replaces the sodium cations through ion exchange (because of the similar ionic radius and electronegative potential of these ions) to form a (N,C)-A-S-H gel. Similarly, the aluminum monomers interact with C-S-H gel to form C-A-S-H gels. The tetrahedral aluminium in C-A-S-H gel aids chain cross-linking, generating two-dimensional structures. The 28-day Transmission Electron Microscopy/Energy-dispersive X-ray spectroscopy (TEM/EDX) analysis of the hybrid cements confirmed the co-precipitation of the two types of gel.

Stage F: after one year of hydration, the hybrid system contains unreacted ash and cement particles co-existed in the matrix along with a (N,C)-A-S-H/C-A-S-H gel mix with a tendency to form C-A-S-H gels (depending on the presence of sufficient amount of calcium cations in the system).

Yip et al. (2008) studied the effects of calcium compounds on geopolymerisation and indicated that the formation of gels on the binary systems are highly dependent on the crystallinity and thermal history of the calcium silicate sources, as well as the alkalinity of the alkaline activator. Seven different calcium silicate sources (Metakaolin, Slag, Portland cement, Wollastonite, Hornblende, Tremolite, Prehnite and Anorthite) were added to geopolymer system. The addition of manufactured calcium silicate (slag and Portland cement) forms higher proportion of calcium aluminosilicate (C-A-S-H) gel while less calcium dissolved from the natural calcium silicate minerals and the smaller amount of C-A-S-H forms in the matrix.
Figure 2-12 Alkaline activation model for cement blends with high silica and alumina and low calcium content (García-Lodeiro et al. 2013)
2.6.2. Influence of Calcium Compounds Addition on Microstructural Properties of AAFA

The binder composition can affect the nature of the main binding gels in these blended calcium compound-fly ash systems. Ismail et al. (2014) reported that the incorporation slag as an additional source of calcium AAFAS binary binders affects the mechanism and rate of formation of the main binding gels. They showed that blended slag-fly ash binders can exhibit the formation of co-existing C–A–S–H and N-A-S-H (geopolymer). Figure 2-13 (Ismail et al. 2014) represents the ternary diagrams of different AAFAS systems based on calcium, aluminum and silicon contents of specimens according to the EDX results obtained for multiple points selected with 28, 90 and 180 days of curing. These ternary diagrams confirm the approximate chemical compositions of the types of gel forming with different AAFAS binder (different proportions of binding material (FA and BFS)). Figure 2-13A depicts that the C–A–S–H type gel forming in the alkali-activated slag binder. The incorporation of fly ash in the slag (Figures 2-13B, C and D) leads to the formation of two distinct products. The C–A–S–H product and N–A–S–H type geopolymer gel are forming in the blended system. As the reaction progresses, The C–A–S–H product seems to show a reduction in the content of calcium and it results in the generation of a hybrid C–N–A–S–H type phase. Figure 2-13E is related to the alkaline activation of pure fly ash. In this system with very low calcium content, the geopolymer-type gel (N–A–S–H) is forming which exhibit very low Ca/Si ratio at different ages.

Figure 2-14 depicts the SEM images of different AAFAS mixtures at 28 days with varying ratios of fly ash to slag. In Figure 2-14A (fly ash/slag ratios of 100/0) the glassy unreacted microspheres were surrounded by a crust of amorphous reaction products. The main product in this case is identified as N–A–S–H geopolymer gel. Figure 2-14B (fly ash/slag ratios of 50/50) illustrates the SEM images of blended mixture (AAFAS) with fly ash/slag of 1/1. This research
Figure 2-13 Ternary representations of EDX data for alkali-activated slag/fly ash binders, as a function of the slag/fly ash ratio and the time of curing:

(A) 100% slag, (B) 75 wt.% slag/25 wt.% fly ash, (C) 50 wt.% slag/50 wt.% fly ash, (D) 25 wt.% slag/75 wt.% fly ash, (E) 100% fly ash.

Compositions included in the black circles correspond to a C–A–S–H type gel, dashed black circles to an N–A–S–H type gel, and black circles filled with dark gray corresponds to an N–(C)–A–S–H type gel (Ismail et al. 2014)

approved the coexistence of two different products for the blended fly ash/slag system; one is a 3D structure as a zeolitic gel type (which is the results of the alkali-activated fly ash) and the other is due to the activation of slag with a dreierketten type structure. This is a low-crystalline
calcium silicate hydrate. This system is mostly dominated by the C-S-H gel (which is the features with a slag-based binder) than N-A-S-H gel (which is a fly ash-based binder product). The important influence of calcium on the gel chemistry is notable in this system (Ismail et al. 2014).

Finally in Figure 2-14C (fly ash slag ratios of 0/100) shows the structure of AAS. This is the only dominated gel in this system (Chi and Huang 2013).

(A) AAFAS mortars with fly ash/slag ratios of 100/0, (B) AAFAS mortars with fly ash/slag ratios of 50/50, (C) AAFAS mortars with fly ash/slag ratios of 100/0 (Chi and Huang 2013)
2.6.3. Influence of Calcium Compounds on Engineering Properties of AAFA

Different research reports that the incorporation of calcium compound significantly change both early and long age properties of AAFA. Researchers reported the mechanical and microstructural properties of AAFA binders are highly dependent on curing temperature (Hardjito et al. 2004). Studies focused on the influence of adding different forms of calcium compounds on the mechanical properties of AAFA have identified that the addition of calcium compounds as a fly ash substitute improved mechanical properties at the ambient temperature (Yip et al. 2008, García-Lodeiro et al. 2013, Lee and Lee 2013). It was proposed that the formation and precipitation of calcium aluminosilicate hydrate accelerates the geopolymerization and it leads to the rapid hardening of the AAFA at ambient temperature.

Strength development in binary binders (such as AAFAS) may be affected by different parameters, including fly ash to calcium compound (e.g., BFS) ratios, the fineness of the slag and the activating solution (Smith and Osborne 1977). The fly ash- calcium compound ratio considerably influences the mechanical properties of the binders. The compressive strength of AAFAS could increases by an addition of more slag, adding more calcium content to the blended system. Lee and Lee (2013) investigated the effect of slag addition on setting and compressive strength development of binary systems. Figure 2-15 indicates the influence of slag addition on compressive strength as a function of time. It is notable that S15 mixture (slag to fly ash ratio is 15%) exhibits greater compressive strength than S15 mixture (slag to fly ash ratio is 10%). Alkalinity of activator solution can also affect the strength of blended mixes. Puertas et al. (2000) reported activating the compressive strength development of the AAFAS with 10 M NaOH solution and curing it at 25°C and the slag to fly ash ratio of one is greater than 50 MPa at 28 days of reaction.
Figure 2-15 Compressive strength development of alkali activated fly ash/slag concrete versus time for S10 and S15 mixtures (Lee and Lee 2014)

As mentioned the setting time of blended system can also be affected with the replacement ratio of the slag for the fly ash. Figure 2-16 shows that a higher replacement ratio of the slag to fly ash accelerated the hydration reaction of the mixture and results in a faster setting time at ambient room temperature which attributed to the formation of higher C-A-S-H gel.

Figure 2-16 Effect of the slag on the setting time of binary AAFAS system (solution/binder: 0.38, water glass/NaOH solution: 0.5 by weight). (Lee and Lee 2014)

It was reported that the carbonation of fly ash-slag blended cements is much faster than AAS and OPC cements. Carbonation can cause the micro cracking, which in turn reduces the strength of these systems (Bijen and Waltje 1989).
Many previous studies investigated the engineering properties of either the alkali-activated slag or fly ash. However few studies were investigated the different characteristics of the blended system. In the present study the influence of different binders (slag to fly ash ratio) and activator (two different pHs) in the mechanical property of materials were considered. The shrinkage characteristic of blended systems for different mixtures was investigated and the optimal activator and ratio of the slag for the fly ash were also studied.
Chapter 3

Chapter 3: Experimental Tests and Results of Alkali Activated Fly Ash Geopolymer Binder

This chapter presents detailed information related to the materials and the experimental methods used to investigate mechanical and setting properties of AAFA. This work was conducted to fulfill as the first step of this research to achieve the objectives outlined in Chapter 1. The goal of this chapter is the determination of the proper activator (by examining different soluble contents) for AAFA binders and measuring the properties of AAFA cured at elevated temperature.

The fresh and hardened property testing consists of setting time (ASTM C191-08), compressive strength (ASTM C 109-11b), and drying shrinkage (ASTM C157-08).

3.1. Experimental Program

3.1.1. Raw Materials

This section discusses the constituents that were used in proportioning the binders. The samples in this study were prepared by alkali activation of a class F fly ash meeting requirements of ASTM C 618-08. The fly ash was obtained from Hatfields Ferry power plant, in Masontown, Pennsylvania, United States. The elemental composition of raw materials was obtained by SEM/EDS. Table 3-1 presents the chemical compositions of the raw materials and some of the physical properties. Table 3-2 shows the particle size distribution of fly ash particles. Quantitative analysis of X-ray diffraction (XRD) showed that the fly ash used in this work
consisted mainly of amorphous material (glassy phase content is more than 70%), and mineral phases, including quartz, hematite, mullite. The sand used in the preparation of mortar was an unreactive sand (unreactive sand, Olay, PA) with the bulk dry specific gravity, bulk SSD specific gravity and absorption of 2.7, 2.72 and 0.46%, respectively.

Table 3-1 Oxide compositions of fly ash powder (mass %)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>SO₃</th>
<th>Loss on ignition</th>
<th>Specific gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash</td>
<td>48.9</td>
<td>25.25</td>
<td>2.54</td>
<td>16.16</td>
<td>0.86</td>
<td>1.04</td>
<td>1.98</td>
<td>1.47</td>
<td>1.58</td>
<td>2.50</td>
</tr>
</tbody>
</table>

Table 3-2 Particle size distribution parameters of fly ash powder (μm)

<table>
<thead>
<tr>
<th>d10</th>
<th>d50</th>
<th>d90</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.18</td>
<td>7.96</td>
<td>31.99</td>
</tr>
</tbody>
</table>

3.1.2. Mixture Design and Specimen Preparation

Three different AAFA mixtures were designed and tested in this work. All mixtures were mixed according to ASTM C 305-11. The cementitious materials were activated with 6M sodium hydroxide combined with sodium silicate. The liquid (activating solution) to binder (solid proportion consisting of fly ash) volumetric ratio of the pastes for all of the mixtures was 0.75.

For preparation of the alkaline solutions, two different alkaline compounds were used: an aqueous sodium silicate (consisting of 18.0% Na₂O, 28.8% SiO₂ and 53.2% H₂O with specific gravity =1.6 g/cm³, pH = 13.7 at 20°C and the modulus n = 1.60) and 6M sodium hydroxide (NaOH). The mass ratio of the sodium silicate solution to sodium hydroxide solution was varying for different mixtures. Table 3-3 represents the activating solution properties of AAFAS pastes.
Mix proportions per liter of AAFA mortars and the activating solution properties are illustrated in Table 3-4. The number in the Mix No. represents the mass ratio of sodium silicate solution to sodium hydroxide, e.g. AAFA-2 mortar was activated with 6M NaOH, when sodium silicate solution to sodium hydroxide mass ratio was 2.

Table 3-3 Activating solution properties for AAFA mixtures

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>n = (SiO₂/Na₂O) molar-based</th>
<th>pH</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAFA-2</td>
<td>1.134</td>
<td>14.44</td>
<td>1.39</td>
</tr>
<tr>
<td>AAFA-1</td>
<td>0.862</td>
<td>14.55</td>
<td>1.31</td>
</tr>
<tr>
<td>AAFA-0.5</td>
<td>0.583</td>
<td>14.65</td>
<td>1.24</td>
</tr>
</tbody>
</table>

*The number in Mix No. represents the sodium silicate to sodium hydroxide mass ratio

Table 3-4 mixture proportions (per liter of mortar)

<table>
<thead>
<tr>
<th>Mix NO</th>
<th>NaOH (g) dry pellets</th>
<th>Na₂O.n(SiO₂) (g) aqueous solution</th>
<th>Water* (g)</th>
<th>Fly ash (gr)</th>
<th>Oven Dry sand (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAFA-2</td>
<td>21.31</td>
<td>200.23</td>
<td>84.78</td>
<td>715.12</td>
<td></td>
</tr>
<tr>
<td>AAFA-1</td>
<td>31.15</td>
<td>146.33</td>
<td>121.16</td>
<td>696.83</td>
<td>1300.00</td>
</tr>
<tr>
<td>AAFA-0.5</td>
<td>40.50</td>
<td>95.12</td>
<td>155.73</td>
<td>679.46</td>
<td></td>
</tr>
</tbody>
</table>

*Note: Water content in the mortar mixtures includes absorption by oven dry sand

3.2. Test Methods

In all of the experiments the mixing procedures corresponding to ASTM C 305-11 were adopted for all paste and mortar mixtures and a steam curing (60°C and 100% RH) was used. For curing the specimens at elevated temperature (60°C and 100% RH), right after casting the
mortars, the molds were placed in a steam curing chamber in an oven at 60 °C for 24 hours (steam curing), as shown in Figure 3-1. The cubic molds were placed on a plastic rack, filled with 5 cm of tap water of the bottom of the container to maintain an appropriate humidity level as saturated. Plastic sheets were placed beneath the closed bin lid to ensure the retention of moisture inside the containers.

Figure 3-1 Curing the cubic specimens in the moist curing apparatus, the containers were stored in an oven at 60°C.

The time of setting of AAFA binary binders was measured using the modified ASTM Standard C191-08 for Portland cement paste (Hardjito et al. 2008). The prepared paste was cast into the conical mold (40 mm height, 80 mm diameter) in two layers. Each layer was compacted
25 times using tamping rod. The specimen was then placed either in the moist room (100RH, 23±0.5 °C) or steam curing chamber and allowed to start setting. The time passed between the initial time of mixing of the pastes and the time when the penetration depth of Vicat needle was 25 mm is identified as the initial time of setting. The final time of setting is when there is no visible penetration of needle into the paste. The penetration depth of the Vicat needle was recorded 15 minutes interval until the initial and final setting times were obtained.

In order to measure the compressive strength of AAFA mortars prepared using different activators, ASTM C109M-11b was followed. The AAFA mortars were cast in two layers of 50 × 50 × 50 mm cube molds immediately after mixing. Each layer of mortar was compacted 25 times with a tamper rod. In order to remove air voids, the specimens were vibrated. All mortar specimens were placed in the moist apparatus (100% RH, 60±0.5°C) for the first 24 hours of the test. After that they were kept in the controlled room (50% RH, 23±0.5°C). Figure 3-2A shows the AAFA cubes after removing from molds.

For drying shrinkage measurement of each mixture, four prisms of size of 2.54 × 2.54 × 25.4 cm were cast into two layers and compacted by a vibrating table and tamping rod. Prism bars were moist cured by using the moist apparatus (100% RH, 60±0.5°C) for one day and after that they were kept in the environmental chamber (50% RH, 23±0.5°C). According to ASTM C490M-11, the drying shrinkage of four AAFA samples was measured by a digital comparator with an accuracy of 0.0025 mm and the weights of samples were recorded in order to determine the moisture loss and degree of saturation. Figure 3-2B shows the AAFA bars before removing their molds.
3.3. Results and Discussion

3.3.1. Time of Setting

The results of the initial and final time of setting are presented in Table 3-4. Figure 3-3 and Figure 3-4 show the influence of different sodium silicate to sodium hydroxide mass ratios (soluble silica) and curing temperature on the setting time of the AAFA pastes. The results are the average of three tests.

The acceleration and retardation of AAFA systems is dependent on the initial solution composition of the alkali solution. A higher pH value of the activating solution may end in a more accelerated dissolution of fly ash powder, whereas the lower concentration of soluble silicon can also retard the rate of setting. When the activating solution is a combination of NaOH and water glass, the setting time of AAFA might be affected by both activator pH and n modulus of the activator. For higher ratio of water glass to NaOH, modulus n (soluble silicon concentration) of
the activator is the dominant factor which can influence the setting property. It may be caused by the fact that mechanical and microstructural property of geopolymers is highly dependent on the amount of soluble silicon in the activating solution. Previous research (Van Jaarsveld and Van Deventer 1997) reported that the addition of soluble silicate could prevent coagulation and polymerization by the initial high solution pH. As the pH starts decreasing to lower than 14 (because of the dissolution of the source materials), polycondensation of both solution silicate and dissolved species will occur very fast and the final product forms inside the system. According to Table 3-3, AAFA-0.5 has the highest pH and the lowest amount of soluble silicon. High pH may lead to the fast dissolution of source material and low soluble silicon may slow down the formation of hydration product. Therefore the notable trend cannot be seen in the setting time of these three mixtures because of the difference between soluble silicon and pH of their activators.

The time of setting of AAFA is significantly influenced by the curing temperature. The results in Figure show that the higher the curing temperature, the shorter the initial and final time of setting. From Figure 3-3, it was observed that AAFA-2 which was cured at ambient temperature had the longest final time of setting (162 hours or about 7 days) while the AAFA-2 cured at elevated temperature (60°C) showed the shorter final setting time (5.42 hours). The dissolution of aluminosilicate source material (fly ash) is temperature dependent. The elevated temperature accelerates the dissolution of these materials significantly and geopolymer gel forms faster.
Table 3-5 Initial and final time of set of the AAFA pastes

<table>
<thead>
<tr>
<th>Mix NO</th>
<th>Curing temperature</th>
<th>Initial time of setting</th>
<th>Final time of setting</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>min</td>
<td>hrs</td>
</tr>
<tr>
<td>AAFA-2</td>
<td>23±0.5°C</td>
<td>6880</td>
<td>114.67</td>
</tr>
<tr>
<td>AAFA-2</td>
<td>60±0.5°C</td>
<td>221</td>
<td>3.69</td>
</tr>
<tr>
<td>AAFA-1</td>
<td>60±0.5°C</td>
<td>223</td>
<td>3.73</td>
</tr>
<tr>
<td>AAFA-0.5</td>
<td>60±0.5°C</td>
<td>204</td>
<td>3.40</td>
</tr>
</tbody>
</table>

Figure 3-3 Comparing the time of setting of different AAFA pastes as a function of sodium silicate to sodium hydroxide mass ratios (soluble silicon) at 60°C, 100%RH
3.3.2. Compressive Strength

Figure 3-5 shows the effect of different sodium silicate to sodium hydroxide mass ratios on compressive strength of the AAFA mortars. Each data set for compressive strength at 1, 3, 7, 28 and 56 days is the average of three test results. All of these mortars were cured at elevated temperature (60°C, 100% RH) for the first 24 hours, followed by curing in an environmental room (23°C, 50% RH).

For different ratios of sodium silicate to sodium hydroxide and invariant solution, a significant improvement in strength development was recorded after the addition of higher amount of sodium silicate. The 56-day strength of AAFA-2 mortar is 43.22 MPa, which is the highest strength achieved on all the mixtures and is 3.3 times greater than the corresponding strength of the AAFA-0.5 mortar.
The larger compressive strength of the AAFA which was activated at higher silicate concentration mortars may be caused by the greater dissolution of fly ash at the larger concentration of soluble silicon. Other investigations of the effect of soluble silicon content on the compressive strength of the AAFA binders have come to the same conclusion which is strength increased with the increases of silica content (by adding more sodium silicate) (Duxson et al. 2007). This could be attributed to the polycondensation possible in the presence of soluble silica. The stability of the structure of geopolymers may improve with addition of soluble silicon to the activating solution.

The compressive strengths of all specimens at 7 days were slightly lower than those of measured at 3 days, respectively. This could be caused by the surface dry condition of the alkali-activated fly ash mortars cured in an environmental room (50% RH, 23±0.5°C) as previously reported by Collins and Sanjayan (1998) and Lee and Lee (2013). This drop also can be derived from the thermal change in the curing condition after the first 24 hrs. As explained before, the specimens were cured at high temperature (60°C) for the first 24hrs and after that they were moved to the environmental room (50% RH, 23±0.5°C). This thermal change in the curing condition can cause generation of thermal stress inside the matrix and formation of micro cracks in these materials. The compressive strength reduction at the first week can be attributed to the existence of these micro cracks. These results are consistent with the findings of other researchers (Hadjito et al. 2004), which investigated the mechanical properties of AAFA and showed that the compressive strength reduces at the very first week of the test.
Figure 3-5 Compressive strength of different AAFA pastes versus time as a function of sodium silicate to sodium hydroxide mass ratios (soluble silicon)
Curing at 60°C, 100%RH for 24hrs

3.3.3. Drying Shrinkage

Figure 3-6 and 3-7 show drying shrinkage and mass loss versus of AAFA mortars at different ages. The specimens were cured for the first 24 hrs at the elevated temperature (60°C, 100% RH) and after that they were placed in the environmental room (50% RH, 23±0.5°C). Both external and internal factors may influence the drying shrinkage. Among these three mixtures, only the internal features were changed, including activating solution. The type and volume fraction of the aggregate were also equal for all AAFA mortars and could not be an influential parameter in this study.

Figure 3-6 shows that the higher the soluble silicon, the lower the drying shrinkage at a given activator. Figure 3-6 indicates the influence of soluble silicon on the drying shrinkage of AAFA mortars. At 63 days, the highest drying shrinkage magnitude was measured for AAFA-
0.5 (about 506 microstrain) and the smallest one for AAFAS-2 (about 277 microstrain). As the previous results relevant to compressive strength show, the lower the silicon concentration leads to the lower the strength and hence the greater tendency to shrinkage.

**Figure 3-7** shows the drying mass loss of all mixtures exposed to an ambient RH of 50% with respect to the first day (after 24 hours curing at 60°C) reference mass. It can be seen from the graph that a higher silicon concentration in activating solution leads to the lower mass losses. The AAFA-2 ultimately lost 6.7% of its mass with respect to the mass of 24 hours moist curing, while the mass loss of AAFAS-0.5 at the same time duration was about 4.9%. These results can be attributed to the effect of water in the hydration process of AAFA binders. Hardjito and Rangan (2005) reported in their research that water plays no role in the AAFA binders within the geopolymerization process and only increases the workability for casting the material and expels from the matrix at an early age. The schematic formation of geopolymer material can be described by the Eqs. 2-2 to 2-5 in chapter two when the aluminosilicate material is activated by alkali hydroxides. It is notable in **Figure 3-7** that the mass change plateaued after three weeks for all mixtures.
3.4. Conclusions

In this chapter, the influence of soluble silicon on the mechanical and setting property of AAFA was investigated. The results showed that if AAFA is cured at ambient temperature, the
final setting time is about 30 times greater than AAFA cured at elevated temperature. It is caused by accelerated dissolution of raw materials at elevated temperature.

The concentration of soluble silicon as well as pH of the activating solution can affect setting time of AAFA. It can be said that the setting properties would be influenced in accordance with the interaction between the NaOH solution and the water glass. The strength increased with the increases of silica content because of the greater dissolution of fly ash at the larger concentration of soluble silicon. It was also indicated that the higher soluble silicate content results in lower drying shrinkage.

In the next chapter (chapter 4), the effect of addition of small portion of slag on setting and mechanical property of AAFA investigated. Different types of shrinkage measured and the effect of activating solution pH and different amount of slag replacement in the shrinkage characteristic of AAFAS binary systems were explored.
Chapter 4

Chapter 4: Experimental Tests and Results of Alkali Activated Fly Ash-Slag Binary Binders

This chapter presents the detailed information on the materials and the experimental methods used to investigate mechanical, setting properties as well as the shrinkage characteristics of alkali activated fly ash/slag (AAFAS) systems. The objective of this chapter is to experimentally investigate the effectiveness of adding small amounts of slag to AAFA binders to develop beneficial properties (i.e., curing AAFA at room temperature) that otherwise could not be possible. This study indeed presents a contribution to the better understanding of early-age cracking of AAFAS based matrices, considering two levels of investigation. The following two specific objectives are defined in this chapter:

1. To explore the effect of adding slag (which contains a high amount of CaO) on setting and mechanical properties of AAFA cured at room for different activators (various pHs).
2. To investigate the influence of the activator pH and the addition of slag on the deformations of AAFAS at a very early age. Different forms of shrinkage characteristics studied include: chemical, autogenous, and drying shrinkage.

To achieve these objectives, the following experimental tasks are employed. The fresh and hardened properties consist of setting time (ASTM C191-08), scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS), compressive strength (ASTM C 109-11b), static modulus of elasticity (ASTM C 469-10), porosity and moisture measurement (ASTM
C642-13), mercury intrusion porosimetry (MIP), chemical shrinkage, autogenous shrinkage (ASTM C1698-09) and drying shrinkage (ASTM C157-08).

4.1. Experimental Program

4.1.1. Raw Materials

This section discusses the constituents that were used in proportioning the binders. The samples in this study were prepared by alkali activation of a class F fly ash meeting requirements of ASTM C 618-08 obtained from Hatfields Ferry power plant (in Masontown, Pennsylvania, United States) and ground granulated blast furnace slag (BFS; grade 120, ASTM C989M-12a). The fly ash and sand are the same material which is used in the last chapter (chapter 3). The elemental composition of raw materials was obtained by SEM/EDS. Table 4-1 presents the chemical compositions of the raw materials and selected physical properties. X-ray diffraction analysis (XRD) indicated that the used slag was mostly composed of amorphous phases with trace amounts of crystalline calcium sulfate (CaSO₄) and tri-calcium silicate (Ca₃SiO₅).

<table>
<thead>
<tr>
<th>Oxide</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>SO₃</th>
<th>Loss on ignition</th>
<th>Specific gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash</td>
<td>48.9</td>
<td>25.25</td>
<td>2.54</td>
<td>16.16</td>
<td>0.86</td>
<td>1.04</td>
<td>1.98</td>
<td>1.47</td>
<td>1.58</td>
<td>2.50</td>
</tr>
<tr>
<td>Slag</td>
<td>30.8</td>
<td>11.45</td>
<td>47.5</td>
<td>1.81</td>
<td>3.65</td>
<td>0.17</td>
<td>0.38</td>
<td>3.03</td>
<td>1.17</td>
<td>2.89</td>
</tr>
</tbody>
</table>
4.1.2. Mixture Design and Specimen Preparation

Six different AAFAS mixtures were designed and tested in this work. All pastes were mixed corresponding to ASTM C 305-11. The cementitious materials with three different volumetric slag-to-fly ash ratios (S/FA = 0.10, 0.15 and 0.20) were activated at two different pH values of the activating solutions. The liquid (activating solution) to binder (solid proportion consisting of fly ash and slag) volumetric ratio of the pastes for all of the mixtures was 0.75.

For alkaline solutions preparation, two different alkaline compounds were used: an aqueous sodium silicate (consisting of 18.0% Na₂O, 28.8% SiO₂ and 53.2% H₂O with specific gravity =1.6 g/cm³, pH = 13.7 at 20°C and the modulus n = 1.60) and either 2M or 6M dissolved sodium hydroxide (NaOH) pellets. The mass ratio of this sodium silicate solution to sodium hydroxide solution for all mixtures was 2. Table 4-2 shows the activating solution properties of AAFAS pastes. The molarity of sodium hydroxide can influence the pH of activating solution as well as the SiO₂/Na₂O molar ratio (n modulus). As the amount of soluble silica is approximately the same for all mixtures, a greater value of n modulus indicates the lower concentration of sodium hydroxide in the activating solution.

The activating solutions were prepared by dissolving NaOH pellets in distilled water at room temperature. After the NaOH solution was stirred for 1 minute, it was covered and set aside for at least 3 minutes. Then the sodium silicate solution was added and stirred for 1 minute. Finally the solution was covered and rested to cool down completely before being added into the pastes (Radlinska et al. 2013).
Mix proportions per liter of AAFAS pastes are shown in Table 4-3. The number in each Mix No. represents the percentage ratio of volumetric fly ash substitution with slag and the symbol 6M or 2M stands for the molarity of the NaOH solution, e.g. AAFAS-20-6M paste was activated with 6M NaOH, when S/FA volumetric ratio was 20 percent.

All pastes were mixed corresponding to ASTM C 305-11. Firstly the alkali solution, fly ash, and slag were placed into an electric mixer (Hobart). Then the paste was allowed to set for 30 seconds followed by 30 seconds of mixing at low speed (140 ± 5 rev/min). The mixture was then allowed to rest for another 30 seconds and finally it was mixed for an additional 1 minute at medium speed (285 ± 10 rev/min).

<table>
<thead>
<tr>
<th>Table 4-2 Activating solution properties for AAFAS mixtures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix No.</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>AAFAS-20-6M</td>
</tr>
<tr>
<td>AAFAS-15-6M</td>
</tr>
<tr>
<td>AAFAS-10-6M</td>
</tr>
<tr>
<td>AAFAS-20-2M</td>
</tr>
<tr>
<td>AAFAS-15-2M</td>
</tr>
<tr>
<td>AAFAS-10-2M</td>
</tr>
</tbody>
</table>
Table 4-3 Mixture proportions (per one liter of pastes)

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>NaOH (g)</th>
<th>Na₂O(SiO₂)n (g)</th>
<th>Water (g)</th>
<th>Fly ash (g)</th>
<th>Slag (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAFAS-20-6M</td>
<td>43.9</td>
<td>411.9</td>
<td>162.1</td>
<td>1166.4</td>
<td>270.6</td>
</tr>
<tr>
<td>AAFAS-15-6M</td>
<td>43.7</td>
<td>410.6</td>
<td>161.6</td>
<td>1220.1</td>
<td>212.3</td>
</tr>
<tr>
<td>AAFAS-10-6M</td>
<td>43.6</td>
<td>409.2</td>
<td>161.0</td>
<td>1279.0</td>
<td>148.4</td>
</tr>
<tr>
<td>AAFAS-20-2M</td>
<td>15.4</td>
<td>400.6</td>
<td>184.9</td>
<td>1161.4</td>
<td>269.4</td>
</tr>
<tr>
<td>AAFAS-15-2M</td>
<td>15.3</td>
<td>399.4</td>
<td>184.4</td>
<td>1214.9</td>
<td>211.4</td>
</tr>
<tr>
<td>AAFAS-10-2M</td>
<td>15.1</td>
<td>392.6</td>
<td>181.2</td>
<td>1287.1</td>
<td>149.3</td>
</tr>
</tbody>
</table>

4.2. Test Methods

In all of the following experiments the mixing procedures corresponding to ASTM C 305-11 were adopted for all paste and mortar mixtures. The setting time of AAFAS binary binder was measured based on modified ASTM Standard C191-08 for Portland cement paste (Hardjito et al. 2008) using Vicat needle apparatus. The prepared paste was cast into the conical mold (40 mm height, 80 mm diameter) in two layers and each layer was compacted using a tamping rod for 25 times. The specimen was placed in the moist room (100% RH, 23±0.5°C) and allowed to start setting. The initial setting time is identified as the time between the initial moment of contact among the paste ingredients and the time when the penetration depth of a Vicat needle is 25 mm. The final time of setting is when there is no visible penetration of the Vicat needle into the paste. The penetration depth of the Vicat needle was recorded at 15 minutes time interval until the initial and final setting times were obtained.
Scanning electron microscopy (SEM) was used to study the microstructural features in AAFAS pastes (two specimens were tested AAFAS-20-6M and AAFAS-20-2M to see just the effect of activating solution on the microstructural development of AAFAS systems) prepared and cured in the moist room (100% RH, 23±0.5°C) for 7 days. Then the specimens were sliced in smaller sizes (about 1-2 mm thick slices), immersed in methanol for 48hrs to halt the hydration, dried in the vacuum and impregnated with a low-viscosity epoxy resin. After resin hardened, a new surface was exposed using a high-precision saw, followed by further grinding and polishing down to 0.05 μm size, using oil-based diamond slurry or pastes. Energy dispersive spectroscopy (EDS) was employed to determine the elemental composition of various spots and area zones within the matrix of different AAFAS binders. The samples were carbon coated prior to SEM analysis. About 100 points were taken for each measurement.

In order to measure the compressive strength of AAFAS-based mixtures, mortars specimens, were cast in 50 × 50 × 50 mm cube molds immediately after mixing according to ASTM C109M-11b. Mortar mixtures were cast in two layers, each one was compacted 25 times with a metal rod. In order to remove air voids, the cast mortar cubes were vibrated on a vibrating table. All mortar specimens were placed in the moist cabinet (100% RH, 23±0.5°C) for the first seven days of the test. After that, the specimens were transferred into an environmental chamber at 50% RH and 23±0.5°C.

The elastic modulus of four different AAFAS mortars was measured at 28 days. Two 100×200 mm cylinders were cast per each mortar mixture. They were demolded at 24 hours and then moist cured until 28-days. At the time of testing, the cylinder was positioned in a dual compressometer-extensometer, connected to a data acquisition system. The cylinder was
compressed and the longitudinal displacement was measured through the use of LVDTs. The LVDT readings were converted to strains. Based on the stress-strain results, the elastic modulus for each specimen was quantified. The loading rate was fixed at $0.25\pm0.05$ MPa/sec.

Measurements of moisture content and porosity were performed according to ASTM C642-13. In these tests, the two unsealed mortars were kept in a moist room for 7 days together with the duplicate pastes that were sealed for the first 7 days after mixing. After 7 days, the samples were weighted and placed in the oven at 105°C until constant mass was obtained. The weights of the oven dried samples were recorded. Subsequently, samples were submerged in water for 48 hours. The samples were surface dried and their weights were recorded again. The specimens were then boiled in water for 5 hours; afterwards, they were surface dried and their weights were measured. Finally, the buoyant weight (suspended weight in a water bath) of each sample was recorded. Figure 4-1 shows the curing/drying procedure for moisture content and porosity measurement. Each step is followed by weighing the specimens.

![Diagram showing the curing/drying procedure for moisture content and porosity measurement.](image)

**Figure 4-1** Test procedure for measuring moisture content and porosity according to ASTM C642-13

The drying shrinkage of AAFAS mortars, the autogenous and chemical shrinkage of AAFAS pastes were also measured. In the present study, the chemical shrinkage was measured using the gravimetry method based on the buoyancy method (Sant et al. 2005).
Figure 4-2 shows the test set up for gravimetry method for chemical shrinkage measurement. From the very first contact between the cementitious binders and the activating solution, the deformation in the paste starts developing. The chemical shrinkage is the difference between the absolute density of anhydrates binder and solution and that of hydrates. Since in a sealed system the cementitious paste does not lose or gain mass, the only change in the buoyancy force of the paste can be assumed to be result of the volume change or chemical shrinkage in the cementitious matrices. The fresh AAFAS paste (about 25 g) was placed in a glass crystallizing dish of 70 mm diameter × 50 mm height (Figure 4-2 A). A 10 ml solution with the same composition of the activating solution was added as the top layer of the paste (Figure 4-2 B). After adding the solution to the surface of the paste, low density paraffin oil (0.863 g/cm³) was placed drop by drop until it covered the entire surface of the solution and roughly filled the crystallizing dish. After that, the dish was positioned on a wire mesh and lowered into a container filled with paraffin oil (Figure 4-2 C). The wire mesh was suspended from the high-precision balance with an accuracy of 0.0001g. The temperature of the sample was held constant during the test by submerging the oil container in a water bath at 23±0.2°C with a water circulation system (Figure 4-2 D). To decrease the amount of water evaporation during the test, a clear acrylic shield surrounded the entire system. The mass of the paste was measured every 5 minutes and recorded by an automatic data acquisition system. Equation 4-1 describes how the chemical the shrinkage can be obtained (Sant et al. 2005).

\[
V_{CS} = \frac{\Delta V_{paste}}{\rho_{fly \text{ ash+slag}}} = \frac{W_{sub}(t) - W_{sub}(30)}{\rho_{oilt} \cdot \rho_{fly \text{ ash+slag}}} \tag{4-1}
\]
In (Eq. 4-1), $g_{\text{fly ash+slag}}$ is the mass of cementitious material content (fly ash and slag) divided by the mass of the AAFAS paste, $W_{\text{sub}(30)}$ is referred to as a reference point (Sant et al. 2005) and it is the recorded submerged weight of the sample 30 minutes after the first contact between the cementitious material and the activating solution, $W_{\text{sub}(t)}$ is the submerged weight of the sample at any time $t$ and $\rho_{\text{oil}}$ is the density of the paraffin oil (0.863 g/cm$^3$ at 23ºC).

Figure 4-2 The test set up for gravimetry method to measure chemical shrinkage of AAFAS pastes, (A) weighing the fresh past (B) Adding the solution as top layer of the paste (C) Filling the dish by paraffin oil (D) submerging the dish in an oil container (Sant et al. 2006)
The linear autogenous deformation of AAFAS pastes was measured by using the corrugated tube protocol based on ASTM C1698-09 procedure (Figure 4-3). The corrugated polyethylene tube (with a length and diameter of 42 cm and 2.9 cm respectively) is designed with a greater stiffness in the radial direction than in the longitudinal direction. This design prevents the deformations while the paste has a lower viscosity and can easily flow. The fresh paste firstly was placed into a corrugated tube and then vibrated. Three specimens were tested for each mixture. After casting, the specimens were kept at a controlled temperature (23±0.5°C) and continuously rotated at a speed of 5 rev/min to prevent bleeding and segregation until the final setting time. The initial length measurement was taken at the final time of setting. The sample mass was measured to obtain the degree of saturation and mass loss of the sealed paste samples based on the results of moisture content and porosity at 7 days.

Figure 4-3 The corrugated tube protocol used to measure linear autogenous strain

(ASTM C1698-09)
For drying shrinkage measurement of each mixture, four prism of $2.54 \times 2.54 \times 25.4$ cm were cast into two layers and compacted at vibrating table and a tamping rod. The prism bars were moist cured (100% RH, 23±0.5°C) for the first seven days of the test and then kept in the environmental chamber (50% RH, 23±0.5°C). Following ASTM C157M-08, the drying shrinkage of four AAFAS samples was measured by a digital comparator with an accuracy of 0.0025 mm and the weights of samples were also recorded in order to determine the moisture loss and degree of saturation.

Figure 4-4 The $2.54 \times 2.54 \times 25.4$ prisms used to measure drying shrinkage

(ASTM C157M-08)
4.3. Brief Theory of Shrinkage in the Cementitious Matrices

This section briefly reviews some of the important theoretical consideration behind the shrinkage mechanism of cementitious system. The rationale of the review is to inform the overall study of the chemical and autogenous shrinkage of pastes and the free drying shrinkage of mortars presented in this research.

Chemical shrinkage results from the reduction in the absolute volume of solids and liquids in the hydrating paste. Measurement of chemical shrinkage exhibits the total potential volume variations of the cementitious system during the hydration process. It is considered as the important reason of autogenous shrinkage (internal drying).

While chemical shrinkage is referred as an internal volume change, the autogenous shrinkage is defined as the external macroscopic volume change within an isothermal sealed system. Before the time of set, the autogenous shrinkage is identical to the chemical shrinkage because of the fluid nature of the paste. Beyond the setting period, however, the magnitude of chemical shrinkage and autogenous shrinkage diverge. This difference could be caused by the solidification of the matrix which could alter the rate of bulk deformation (autogenous strain) compared to the chemical shrinkage rate.

The internal drying causes desiccation shrinkage by means of capillary suction variations (Bazant, and Wittmann 1982), surface energy variations (Wittmann 1982) and disjunction pressure changes (Yurtdas et al. 2004). This study discusses the influence of capillary tension on the volume reduction of the cementitious binders. The Mackenzie-Bentz’s equation (Eq. 4-2) (Mackenzie 1950, Bentz et al. 1998) shows the shrinkage of three dimensional microstructure can
be caused by the formation of menisci in the pores and the generation of the capillary tension in the wall of pores.

\[
\varepsilon_p = \frac{S}{3} \sigma_{cap} \left[ \frac{1}{K} - \frac{1}{K_s} \right] \tag{4-2}
\]

Where:

\( S \) = the volumetric degree of saturation

\( \sigma_{cap} \) = capillary tension on the liquid phase (Pa) which is caused by the formation of vapor-fluid menisci inside the matrix pores.

\( K \) = bulk elastic modulus of the paste (Pa)

\( K_s \) = bulk elastic modulus of the solid skeleton such as anhydrate solid of C–S–H or aluminosilicate gels (Pa)

In the case of autogenous shrinkage, these curved liquid-vapor menisci inside the paste form due to the volume reduction of hydration product. As the hydration continues, the chemical reaction consumes the pore solution and the pores gradually evacuate. This is referred as the self-desiccation. For internal drying in the sealed system, the capillary pressure can be related to the size of the menisci using Young–Laplace equation, (Eq. 4-3) (Adamson and Gast 1997):

\[
\sigma_{cap} = -\frac{2\gamma \cos \theta}{r} \tag{4-3}
\]

Where

\( \gamma \) = surface tension of the pore solution (N/m)

\( \theta \) = solid-solution contact angle (assumed to be 0 radians)
In case of unsealed system, both internal and external drying occur in the paste and fluid-vapor menisci forms both in the interior and at the exposed surface. Kelvin equation (Eq. 4-4) (Adamson and Gast 1997) indicates how driving force (capillary tension) relates to the RH of the cement paste:

\[
\sigma_{cap} = \frac{RT \ln(RH)}{V_m}
\]  

(4-4)

Where

- RH = internal relative humidity (unit less fraction)
- \( V_m \) = molar volume of the pore solution (m\(^3\)/mol)
- \( R \) = universal gas constant (J/mol·K)
- \( T \) = temperature (K)

### 4.4. Results and analysis

#### 4.4.1. Time of setting

*Figure 4-5* presents the influence of different S/FA volumetric ratios and the activating solution on the setting time of alkali-activated fly ash/slag pastes. From each measurement, three specimens were prepared and average of three samples was reported. Increasing the amount of slag replacement decreases the initial and final time of setting for a given activating solution (either solid or dashed lines in *Figure 4-5*). Therefore it could be inferred that higher slag addition results in the formation of more C-A-S-H gel, which coexists with aluminosilicate gels and lead to improved setting properties and higher compressive strength of binary system cured under ambient room temperature.
Figure 4-5 Comparing the time of setting of different AAFAS pastes as a function of S/FA volumetric ratio and PH at 23°C, 100%RH

The acceleration and retardation of geopolymer systems could also be dependent on the initial composition of the alkali solution. The results in Figure 4-5 show that the higher the concentration of hydroxide ions [OH⁻] in the activating solution (the lower n modulus) the greater the initial and final time of setting. From Figure 4-5, it was observed that AAFAS-10-6M had the longest final time of setting (5 hours and 30 minutes) while AAFAS-20-2M showed the shortest final setting time (59 minutes). A lower pH value of the activating solution may result in a more accelerated formation of C-A-S-H gel, whereas the higher concentration of hydroxide ions can also retard the rate of setting. Lee and Lee (2013) investigated the setting properties of AAFAS and their results coincide with the results of the present study.

A sodium silicate solution includes monomeric and polymeric silicate species. When the activating solution is a combination of NaOH and sodium silicate, the pH of the activating solution can influence the form of species, monomeric or polymeric. Four simplified
polymerization reactions in the water glass solution are given in the following equations (Iler, 1979):

\[
\begin{align*}
\text{SiO}_2 + 2\text{H}_2\text{O} & \rightarrow \text{Si(OH)}_4 \quad (4-5) \\
\text{Si(OH)}_4 + \text{OH}^- & \rightarrow \text{HSiO}_3^- + 2\text{H}_2\text{O} \quad (4-6) \\
2\text{HSiO}_3^- & \rightarrow \text{Si}_2\text{O}_3^{2-} + \text{H}_2\text{O} \quad (4-7) \\
\text{HSiO}_3^- + \text{OH}^- & \rightarrow \text{SiO}_3^{2-} + \text{H}_2\text{O} \quad (4-8)
\end{align*}
\]

As seen in Eqs. 4-5 to 4-8, silicic acid reacts with a hydroxide ion and it is converted to a dimeric silicate anion (\(\text{Si}_2\text{O}_3^{2-}\)) via the intermediate formation of a monomeric silicate anion (\(\text{HSiO}_3^-\)). The intermediate monomeric anion can form the silicate dianion (\(\text{SiO}_3^{2-}\)) at the higher concentration of hydroxide ions (higher pH). The lower activator pH may lead to the formation of a greater amount of dimeric silicate anion (\(\text{Si}_2\text{O}_3^{2-}\)) while the higher pH value of activator could cause a greater concentration of silicate dianion (\(\text{SiO}_3^{2-}\)) in the solution.

Once the activator, slag and fly ash materials are mixed, the dimeric silicate anion from solution can quickly react with calcium compound from slag and undergo further polymerization reactions resulting in the set acceleration (Iler 1979). As calcium dissolves from the slag, C-A-S-H can form randomly throughout the microstructure. It can be derived that the lower activator pH may generate the greater amount of C-A-S-H gel at the early age compared to the higher pH. Whereas the initiation of hardening is because of C-A-S-H formation, the lower activator pH can result in the set acceleration.

SEM-EDS was used to investigate the microstructural development of the two different AAFAS pastes after 7 days of moist curing. The slag replacement in both pastes is 20\% while the
activator pH is different. Figure 4-6 shows the BSE images of both pastes. It is notable that the product is an intermixed microstructure of C-A-S-H and Na-A-S-H. A distinctive and segregated phases cannot be distinguished in these BSE images.

![BSE images of (A) AAFAS-20-6M and (B) AAFAS-20-2M pastes at 7 days of moist curing](A) (B)

Quantitative EDS was used to determine the ratio of the different elements in the various regions of the matrix and to study the chemical makeup of reaction products. Table 4-4 and Figure 4-7 represent the average atomic ratios (average of 100 points) of various elements based on the results of the EDS spot analysis. It is noticeable that in the case of the lower activator pH (AAFAS-20-2M), the Ca/Si atomic ratio is higher (greater C-A-S-H gel), while the (Na+K)/Al ratio is lower (less N-A-S-H gel). Table 4-4 demonstrates that a higher pH has a higher Si/Ca ratio but a lower pH shows a higher Al/Ca atomic ratio. Comparing different atomic ratios of two pHs, the lower activator pH leads to larger amount of C-A-S-H gel at the age of 7 days.
### Table 4-4 Average atomic ratio in the hydration products of AAFAS binary pastes at 7 days using EDS spot analysis

<table>
<thead>
<tr>
<th>Mixture ID</th>
<th>Activator pH</th>
<th>Ca/Si</th>
<th>Al/Si</th>
<th>(Na+K)/Al</th>
<th>Al/Ca</th>
<th>Mg/Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAFAS-20-6M</td>
<td>14.44</td>
<td>0.48</td>
<td>0.31</td>
<td>1.04</td>
<td>1.66</td>
<td>0.07</td>
</tr>
<tr>
<td>AAFAS-20-2M</td>
<td>14.04</td>
<td>0.57</td>
<td>0.36</td>
<td>0.97</td>
<td>1.70</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Figure 4-7 BSE images of AAFAS-20-6M and AAFAS-20-2M pastes at 7 days of moist curing

### 4.4.2. Compressive strength

Figure 4-8 shows the effect of different S/FA volumetric ratios and activators on compressive strength of the AAFAS mortars. Each data set for compressive strength at 1, 3, 7 and 28 days is the average of three test results.

For different volumetric ratios of S/FA and invariant activating solution, a significant improvement in strength development was recorded after the addition of a larger amount of slag. It could be noted that a higher content of slag increased the compressive strength. The 28-day
strength of AAFAS-20-6M mortar is 57.88 MPa (20% slag replacement), which is the highest strength achieved on all the mixtures and is 75% greater than the corresponding strength of the AAFAS-10-6M mortar (10% slag replacement). Other investigations of the effect of the slag content on the compressive strength of the AAFAS binders have come to the same conclusion, which is that strength increases with the increases of calcium content (by adding more slag) (Lee & Lee 2013, Bentz et al. 1998, Maochieh & Ran 2013]. The higher content of fly ash reduces the accelerated hydration of slag and strength at ambient room temperature (Shi and Day 1999).

![Figure 4-8](image_url)

**Figure 4-8** Compressive strength development of AAFAS mortars as a function of age, mortars were cured at 23°C, and 100 %RH for the very first week and then moved to environmental chamber at 23°C, and 50 %RH

Experimental results shown in **Figure 4-8** indicate that, in general, the AAFAS mortars activated at the higher activator pH (solid lines) show marginally greater strength than those activated at the lower pH value (dash lines). At the same slag substitution, there is a slight difference between the compressive strength of AAFAS mortars that were activated at higher versus lower pHs during the first 7 days of the experiment. At the later age (after 7 days) the
strengths of mortars activated at different pHs are not as similar. Between 7 and 28 days, the strength gain rates of AAFAS-20-6M, AAFAS-15-6M, and, AAFAS-10-6M (the mixtures activated at higher pH) are 49%, 43% and 40% respectively. In the case of the lower activator pH, the strength gain of mortars (AAFAS-20-2M, AAFAS-15-2M, and, AAFAS-10-2M) levels off after 7 days. The greater compressive strength of the AAFAS mortars may be caused by the better and slower dissolution of cementitious materials (fly ash and slag) at the higher pH. It was shown in the previous section that the lower activator pH accelerates the dissolution of calcium from slag and causes rapid geopolymerization of fly ash. A rapid initial dissolution of the reference binders (fly ash and slag) leads to the precipitation of the hydration product (N-A-S-H and C-A-S-H gels) on the surface of slag or fly ash particles. This is a diffusion barrier which could halt or slow down more dissolution of initial binders (Ben Haha et al. 2011) and create coarser and higher porosity matrix, which may cause the loss of strength of the binder activated at the lower activator pH. On the other hand, a slow dissolution of calcium from slag at the higher activator pH effectively increases compressive strength because of the prolongation of geopolymerization.

The results of the 28 day static elastic modulus for four AAFAS mortars (two different S/FA volumetric ratios were activated at two different pHs) are presented in Table 4-5. Each data point is an average of 2 duplicate cylindrical specimens. The results show the same trend as the compressive strength.
Table 4-5 Static modulus of elasticity of AAFAS mortars after 28 days of curing at 23°C and %100 RH

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>Elastic Modulus (GPa)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAFAS-20-6M</td>
<td>42.04</td>
<td>0.28</td>
</tr>
<tr>
<td>AAFAS-10-6M</td>
<td>31.85</td>
<td>1.56</td>
</tr>
<tr>
<td>AAFAS-20-2M</td>
<td>36.70</td>
<td>1.79</td>
</tr>
<tr>
<td>AAFAS-10-2M</td>
<td>21.72</td>
<td>0.07</td>
</tr>
</tbody>
</table>

4.4.3. Chemical Shrinkage

The evolutions of chemical shrinkage (per gram of binders) of the six studied AAFAS pastes measured with the gravimetry system at constant temperature (23±0.5°C) are plotted in Figure 4-9 as a function of time. Figure 4-9A shows the chemical shrinkage of AAFAS pastes at an early age (within 24 hours) of the test while Figure 4-9B illustrates the results of chemical shrinkage during the first 10 days. This results show the degree of chemical reaction that had taken place. In these figures, two mix parameters are considered: the S/FA volumetric ratio and the activating solution pH. Chemical shrinkage results from the reduction in the absolute volume of solids and liquids in the hydrating paste. Measurement of chemical shrinkage exhibits the total potential volume variations of the cementitious system during the hydration process. It is considered as an important reason for autogenous shrinkage (internal drying). Chemical shrinkage is mostly measured as an indicator to quantify the extent of a chemical reaction (Sant et al. 2005) and it is directly proportional to the degree of hydration (Tazawa et al. 1995).
Results obtained at a constant S/FA volumetric ratio show that the lower concentration of hydroxide ions in the activator (or lower activator pH) at the very first day of the test resulted in the marginally higher degree of hydration (Figure 4-9A). The reason for this behavior probably lies in the difference between the setting times of the paste activated with different pH values. As indicated in Figure 4-5, the higher the pH of the activator solution, the greater the initial and final time of setting. According to Figure 4-9A, during the first 24 hours of the test, the lower activator pH could accelerate the formation of hydration product and show the higher degree of reaction (or higher chemical shrinkage) at this specific time. The differences between chemical shrinkage of the pastes activated at the higher and lower pH may also be attributed to the difference between the natures of their hydration products. After 3 days, the chemical shrinkage of the pastes activated at the lower pH becomes constant (approximately 0.017 ml/gecm) while the chemical shrinkage of the higher pH of the activating solution keeps increasing even up to 10 days (Figure 4-9B).
In the constant activating solution pH, the S/FA volumetric ratio has a relatively insignificant influence on the value of chemical shrinkage obtained up to 10 days (Figure 4-9B). The experimental results show that lower S/FA volumetric ratios led to higher chemical shrinkage at any given age of hydration. It is likely because different S/FA volumetric ratios result in various hydration products with varying volumes. Considering the variation of hydration product in microstructural scale of different mixtures may explain the slight difference between the values of chemical shrinkage at different slag replacements. Further work is needed to fully explain the reasons that may influence the chemical shrinkage and estimate the approximate complete hydration of these alkali activated binary binders.

The previous research (Tazawa et al. 1995) stated that chemical shrinkage of OPC is associated with compressive strength development. The general trend of compressive strength results of the lower and higher pH is consistent with the trend of chemical shrinkage results within the first 10 days. The strength gain of mortars activated at the lower molarity of NaOH (lower pH of the activating solution) begins to plateau at an earlier age. It may be derived that the higher pH value of the solution could retard the chemical reaction in these systems (because it retards the formation of C-A-S-H gel) as a consequence strength development still has a steady increase after 10 days. Figure 4-10 illustrates the relation between compressive strength development and chemical shrinkage evolution of different AAFAS pastes at three different ages (1, 3 and 7 days). This figure reveals that at the lower activator pH (dash lines), the compressive strength and chemical shrinkage are roughly related linearly. In contrast, there is nonlinear trend in the compressive strength over chemical shrinkage of pastes activated at the higher activator pH at different ages (solid lines). At the same slag substitution and constant chemical shrinkage (the
same degree of chemical reaction), the AAFAS mortars activated at the lower activator pH (dashed lines) generally show greater strength than those activated at the lower pH value (dash lines). This finding is likely due to the greater formation of C-A-S-H gel at the early age of the pastes activated at 2M sodium hydroxide (lower activating solution pH). Experimental results also indicate that at the early age (7 days) the higher activator pH showed greater chemical shrinkage which can be attributed to the slow dissolution of calcium from slag and also the longer duration of geopolymerization in these binders.

Figure 4-10 Compressive strength development as a function of the chemical shrinkage of different AAFAS pastes at the age of 1, 3 and 7 days

4.4.4. Autogenous Shrinkage

Autogenous shrinkage is macroscopic volume reduction of different sealed pastes is cause by self-desiccation due to solution (liquid phase) consumption inside the matrix. Figure 4-11 shows the autogenous shrinkage and mass loss of six different sealed AAFAS pastes, used to investigate the effect of S/FA volumetric ratio and the pHs of activator solution. It can be
observed in Figure 4-11 that the magnitude of autogenous shrinkage is increasing as a function of time. The ultimate recorded amount of shrinkage for these different mixes is between 1300 to 3100 microstrain. It should be noted that the variations of autogenous shrinkage over time generally follow the similar trends for all the mixes. Table 4-7 provides the results of the degree of saturation, absorption and porosity of the pastes at 7 days (after casting the sealed specimens), which were measured according to ASTM C642-13. Since the mass loss in the sealed system is insignificant, degree of saturation of the sealed pastes did not change considerably over time.

The Mackenzie-Bentz’s equation (Eq. 4-2) shows the shrinkage can be caused by the formation of menisci in the pores and the generation of the capillary tension in the wall of pores. According to the Young–Laplace equation (Eq. 4-3), the capillary pressure can be associated with the size of the menisci. In order to describe the pore size distribution of AAFAS pastes, an MIP (mercury intrusion porosimetry) test was performed. Figure 4-12 shows the 7 day results of MIP test for two different pastes (AAFA-20-6M and AAFA-20-2M) to investigate the effect of

![Figure 4-11](image-url)  
Figure 4-11 Autogenous shrinkage of sealed AAFAS pastes as a function of age at 23°C (reference point is at the final setting time)
activator pH on the pore size distribution of AAFAS pastes at the constant S/FA volumetric ratio (20% slag replacement). Figure 4-12 displays the relation between mercury intrusion and pore size distribution by two different lines for each mixture. The solid line indicates the cumulative pore volume of pore size whereas the dashed line reflects the incremental intrusion. Comparing the MIP results of the two different pastes, there is a slight difference between their capillary pore sizes at 7 days (different activator pH). Based on the results of the cumulative pore volume (solid lines), the paste activated at the lower pH has a slightly greater porosity which may contribute to the higher shrinkage in these pastes compared to the pastes activated at the higher pH. The difference is related to the pores smaller than 1000nm.

Figure 4-12 Variations of mercury intrusion value as a function of pores size (MIP test results)

Results of autogenous shrinkage (Figure 4-11) obtained indicate that at a constant pH, by increasing the S/FA volumetric ratio from 10 to 20 percent, the magnitude of autogenous shrinkage is roughly increased. The higher autogenous shrinkage can be attributed to the higher degree of saturation, the finer porous matrix (increasing the capillary stresses), and the lower
stiffness based on Eq. 4-2 and Eq. 4-3. Table 4-5 and 4-6 show the results of degree of saturation and stiffness. It seems the capillary stress mechanism is not likely to explain the cause of large autogenous shrinkage for the higher S/FA volumetric ratio.

As seen in Figure 4-11, variations in activators for constant S/FA volumetric ratios lead to different autogenous shrinkage. For mixture with invariant S/FA volumetric ratio, the magnitude of autogenous shrinkage decreases by increasing the molarity of NaOH in the activating solution (the higher value of the activator pH). This drop may be explained by the higher elastic modulus caused by the higher pH of the activator or lower porosity (the MIP results). Other mechanisms such as creep or carbonation shrinkage may also contribute to the larger autogenous shrinkage of mixtures activated at the lower solution pH.

Table 4-6 Degree of saturation, absorption and the water permeable porosity of pastes at 7 days after casting sealed AAFAS pastes

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>Degree of Saturation (Vol%)</th>
<th>Absorption (Vol%)</th>
<th>Water Permeable Porosity (Vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAFAS-10-6M</td>
<td>96.079</td>
<td>15.190</td>
<td>28.224</td>
</tr>
<tr>
<td>AAFAS-15-6M</td>
<td>96.544</td>
<td>13.752</td>
<td>26.725</td>
</tr>
<tr>
<td>AAFAS-20-6M</td>
<td>96.705</td>
<td>13.745</td>
<td>26.033</td>
</tr>
<tr>
<td>AAFAS-10-2M</td>
<td>93.250</td>
<td>15.220</td>
<td>29.175</td>
</tr>
<tr>
<td>AAFAS-15-2M</td>
<td>93.313</td>
<td>15.718</td>
<td>28.836</td>
</tr>
<tr>
<td>AAFAS-20-2M</td>
<td>94.070</td>
<td>15.740</td>
<td>28.280</td>
</tr>
</tbody>
</table>
4.4.5. Drying shrinkage

Figures 4-13A and Figures 4-13B illustrate the drying shrinkage and mass loss over time for AAFAS mortars as a function of time. These figures show that moist curing (23±0.5°C, 100%RH) of AAFAS bars within the very first week results in weight gain and slight expansion of the mortar prisms (less than 500 microstrain). Both external and internal factors may influence the drying shrinkage. In this study only the internal features were changed, including paste constituents and activating solution. The type and volume fraction of the aggregate were also equal for all AAFAS mortars and would not be an influential parameter in this study.

The moisture, absorption and porosity of the mortars at 7 days (after exposure to 100% moist curing) were measured according to ASTM C642-13. Table 4-7 illustrates the results of this test for different mixtures. The percentage of the degree of saturation at the end of the moist curing was slightly lower than 100%. This small drop may be due to the self-desiccation inside the matrix during the external moist curing time and also low permeability, which is likely to reduce the entry of water into the mortars. Base on the information given in Table 4-7 and Figure 4-13B, the saturation degrees of different mixtures after exposure to drying at 50%RH were obtained as a function of age. The results are presented in Figure 4-13C. The mix with 20% slag shows the greatest ultimate degree of saturation, about 36.5%, while the lowest degree of saturation is reported for 10% slag replacement and is about 19.6%.

Figure 4-13A indicates the influence of S/FA volumetric ratio as well as the activating solution on the drying shrinkage of AAFAS mortars. Although each type of mixture results in different compressive strength, the drying shrinkage at constant activator pH does not show a significant difference. At 14 weeks the highest drying shrinkage magnitude was measured for the
AAFAS-10-2M (about 2750 microstrains) and the smallest one corresponds to the AAFAS-20-6M (about 2060 microstrains). Figure 4-13A shows that the higher the slag replacement, the lower the drying shrinkage for a given activator. The present findings seem not to be consistent with other research (Maochieh & Ran 2013) which indicates that the drying shrinkage increased as the slag content increased. This difference also could be caused by the fact that in this study just a small amount of slag was added to the AAFA binders and the drying shrinkage of different S/FA volumetric ratios (0.10, 0.15 and 0.20) are somewhat close to each other. Therefore, the drying shrinkage of different S/FA volumetric ratios activated at a constant activator pH is close to each other and it is identical after the reaction progressed (10 weeks). For 6M NaOH activating solution (higher pH), the drying shrinkage of 10% and 15% became the same at week 5 and beyond, while for 2M NaOH activating solution (lower pH) the identical drying shrinkage was recorded at 15% and 20% after 2 weeks.

At the same S/FA volumetric ratio, the higher activator pH value shows a lower magnitude of drying shrinkage. As the previous results relevant to compressive strength and elastic modulus of mortars showed, the smaller the solution pH, the lower the strength and the modulus of elasticity and hence the greater tendency toward shrinkage. Similar to the results of compressive strength and chemical shrinkage, the drying shrinkage of the binders activated at the lower activator pH reaches a plateau at an earlier age than mortars activated at the higher pH. This can be attributed to the difference between the degrees of chemical reaction of different binders.

According to Eq.4-2, the shrinkage is a function of capillary tension, degree of saturation and stiffness of the pastes. As the RH is constant during the test, the capillary tension related to
external drying is invariant in the test duration (4-4) and the magnitude of internal drying might be proportional to the autogenous shrinkage of the matrix. Thus the effective parameters for explanation of the drying shrinkage variations could be caused by the magnitude of autogenous shrinkage, degree of saturation and elastic modulus (which is proportional to stiffness in Eq. 4-2. Comparing the results presented in Table 4-5, Table 4-7, Figure 4-11 and Figure 4-13, the capillary stress mechanism could not fully explain the results of drying shrinkage. Other mechanisms like creep and carbonation shrinkage may also help to analyze these results.

**Figure 4-13B** shows the drying mass loss of all mixtures exposed to an ambient RH of 50% with respect to the 7th day reference mass. This loss of water is mainly caused by changes in humidity above the curved meniscus surface of the capillary water in the pores and partially adsorbed water in the surface of hydration products. The amount of adsorbed water is influenced by the structure of hydration products, and this moisture could hardly evaporate at ambient room temperature. As the C-A-S-H gel has a large surface area, more water gets adsorbed on the surface of this hydration product. It can be seen from the graph that a higher replacement of the slag leads to a lower mass loss because of a higher formation of C-A-S-H gel. The AAFAS-10-2M ultimately lost 5.5% of its mass with respect to the mass of 7 day moist curing, while the mass loss of AAFAS-20-2M at the same time duration was about 4.0%.

These results (**Figure 4-13B**) could also result from the effect of water in the hydration process of AAFAS binders. It can be interpreted from these results that water has a lower influence during the chemical reaction and development of gel for the binders containing a higher fly ash content. Hardjito and Rangan (2005) reported in their research that water plays no role in the AAFA binders within the geopolymerization process and only increases the workability for
casting the material and expels from the matrix at an early age. The schematic formation of geopolymer material can be described by the following equation when the aluminosilicate material is activated by alkali hydroxides (Davidovits 1999).

$$\text{(Al}_2\text{Si}_2\text{O}_7)_n + n\text{H}_2\text{O} \overset{\text{MOH}}{\longrightarrow} n(\text{OH})_3 - \text{Si} - \text{Al} - (\text{OH})_3$$

(4-9)

$$\text{n(OH)}_3 - \text{Si} - \text{Al} - (\text{OH})_3 \overset{\text{MOH}}{\longrightarrow} \text{M}(-\text{Si} - \text{O} - \text{Al}^- - \text{O})_n + n\text{H}_2\text{O}$$

(4-10)

Since the water releases during the formation and development of geopolymer gel, the larger content of fly ash led to the greater mass loss. For the lower activator pH (2M NaOH), the mass change roughly plateaued after 3 weeks, whereas the higher value of activator pH (6M NaOH) resulted in the gradual mass drop until week 7 and after that the mass became approximately constant. These results coincide with the general trend of compressive strength and chemical shrinkage results of the binders activated at the lower and higher activator pHs. It was observed that the chemical shrinkage and the strength gain of the mortars activated at the lower pH (2M NaOH) reach a plateau at an earlier age. This is likely due to the slower reaction of the binders activated at the higher pH (6M NaOH).
Figure 4-13 Variations of shrinkage parameters of different unsealed mortars as a function of age at 23°C, 50%RH (A) Drying shrinkage of AAFAS mortars (reference point is day 1: time of demolding) (B) Mass change (%) with respect to day 7 (after moist curing) of AAFAS mortars (C) Degree of saturation (vol%) with respect to day 7 (time of moist curing) of AAFAS mortars
Table 4-7 Degree of saturation, absorption and the water permeable porosity of pastes at 7 days after casting unsealed AAFAS mortars

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>Degree of Saturation (Vol%)</th>
<th>Absorption (Vol%)</th>
<th>Water Permeable Porosity (Vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAFAS-10-6M</td>
<td>99.250</td>
<td>6.376</td>
<td>15.369</td>
</tr>
<tr>
<td>AAFAS-15-6M</td>
<td>94.869</td>
<td>6.480</td>
<td>15.581</td>
</tr>
<tr>
<td>AAFAS-20-6M</td>
<td>94.388</td>
<td>6.588</td>
<td>15.586</td>
</tr>
<tr>
<td>AAFAS-10-2M</td>
<td>97.956</td>
<td>6.967</td>
<td>16.986</td>
</tr>
<tr>
<td>AAFAS-15-2M</td>
<td>93.231</td>
<td>6.931</td>
<td>16.904</td>
</tr>
<tr>
<td>AAFAS-20-2M</td>
<td>92.510</td>
<td>7.140</td>
<td>16.880</td>
</tr>
</tbody>
</table>

4.5. Conclusions

The mechanical and microstructural properties of alkali activated fly ash (AAFA) are temperature dependent which can limit the commercial application of these materials. Adding a small amount of slag can rectify this problem. However adding slag can lead to volume instability and thus potential loss of durability in the new binders. This chapter of this research studied the influence that adding three different volumetric ratios of slag-to-fly ash (0.1, 0.15 and 0.20) has on the shrinkage deformations of alkali activated fly ash/ slag blended binders. The effect of activating solution (different activator pH) on the early age deformation of these binary systems was also investigated.

It was observed, addition of small portion of calcium compound (e.g., 20 percent fly ash substitution) can considerably improve the setting properties of AAFA cured at room
temperature. Comparing the results of this chapter with previous chapter, it is notable that setting time of the AAFA (cured at ambient temperature) after adding slag, reduces 74 times (by comparing the final setting time of AAFA-2, which is 9720 mins, with the final setting time of AAFAS-20-6M which is 32 mins).

The results of this section of study indicate that addition of slag can significantly enhance the compressive strength of the blended binders at ambient room temperature. Higher slag replacement and higher activating pH leads to greater compressive strength.

It is notable that adding slag as well as activator pH both can influence the shrinkage characteristics of AAFAS binders. After measuring different types of shrinkage, it is observed that larger slag replacement demonstrated higher autogenous shrinkage. The two different pH values of the activators for a given S/FA volumetric ratio indicate that the higher activator pH resulted in lower drying and autogenous shrinkage and greater chemical shrinkage.
Chapter 5

Chapter 5: Conclusions and Future Research

5.1. Conclusions

The mechanical and microstructural properties of alkali activated fly ash (AAFA) are temperature dependent which can limit the commercial application of these materials. Adding a small amount of slag can rectify this problem. However, adding slag can lead to volume instability and thus loss of durability in the new binders. In chapter 3, the mechanical and setting property of three different AAFA systems cured at elevated temperature (60°C for 24hrs) were measured. Chapter 4 studies the influence that adding three different volumetric ratios of slag-to-fly ash (0.1, 0.15 and 0.20) has on the setting and mechanical properties and shrinkage deformations of alkali activated fly ash/slag blended binders (AAFAS) cured at room temperature. This research also investigated the effect of activating solution (different activator pH) on the early age deformation of these binary systems. Specific conclusions drawn from the present study are following:

1. Curing temperature plays an important role in setting properties of AAFA system. Curing at elevated temperature can significantly accelerate the dissolution of precursors in the alkaline solution.

2. In pure AAFA binders, the lower the concentration of the soluble silica in the activating solution results in smaller compressive strength of the AAFA mortars.

3. Increasing the soluble silica in the activator solution can lead to the reduction in the magnitude of drying shrinkage of AAFA cured at elevated temperature.
4. In AAFAS binary binders, for any given activating solution, the greater slag addition leads to improved setting properties and compressive strength under ambient room temperature.

5. The lower S/FA volumetric ratio leads to the higher drying shrinkage and lower magnitude of autogenous shrinkage at any given activating solution in AAFAS binary binders.

6. The effects of slag addition on the setting time and strength development of AAFAS binary binders depends on the pH of the activating solution. The higher pH value results in greater initial and final time of setting in the presence of high concentration of soluble silicate.

7. In the presence of sodium silicate in the activating solution, the higher hydroxide ion concentration can retard the chemical reaction in the AAFAS binders. This causes the chemical shrinkage, the strength gain, the drying shrinkage and mass change of binary binders reach to plateau at a later age.

8. Activation at higher activator pH can lead to reduction in the magnitude of autogenous and drying shrinkage.
Following table summarizes the results obtained in this research.

Table 5-1 Summary of the results obtained in chapters 3 and 4

<table>
<thead>
<tr>
<th>Slag/FA</th>
<th>Activator pH</th>
<th>$n = (\text{SiO}_2/\text{Na}_2\text{O})$</th>
<th>Curing method (the first 24 hrs)</th>
<th>Final time of set (hrs)</th>
<th>Compressive strength (28 days)</th>
<th>Chemical shrinkage (ml/gcem) (10 days)</th>
<th>Autog. shrinkage ($\mu$e) (63 days)</th>
<th>Drying shrinkage ($\mu$e) (63 days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>14.44</td>
<td>1.134</td>
<td>Steam curing (60 $^\circ$C)</td>
<td>3.69</td>
<td>36.32</td>
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<td></td>
<td>14.55</td>
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<td>-</td>
<td>507</td>
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<td>0.10</td>
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<td>Moist curing (23$^\circ$C and %100 RH)</td>
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<td>2790</td>
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<td>52.54</td>
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<td>2307</td>
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<td></td>
<td>14.04</td>
<td>1.443</td>
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<td>2.20</td>
<td>57.58</td>
<td>0.034</td>
<td>1475</td>
<td>2002</td>
</tr>
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</table>

5.2. Future Research

This study showed the viability of adding slag as a source of calcium to the AAFA and improving the mechanical and setting property of new binders by curing them at the room temperature. However, more research is necessary to understand the effect of other calcium compounds on the mechanical and microstructural properties as well as the durability of alkali activated binary binders. A list of future work is listed as follow:

1. As the shrinkage characteristics of pure AAFA are still in question, investigation is needed to measure the shrinkage characteristics of AAFA.

2. Study is necessary to investigate the influence that addition of different calcium compounds (such as OPC, calcium hydroxide, gypsum) to AAFA has on the shrinkage characteristics of alkali activated blended binders.

3. More research is needed to investigate the mechanisms behind the volumetric instability of these binary binders.
4. Additional work is needed to explore how to mitigate the large magnitude of shrinkage in these alkali activated binary binders.
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