UNDERSTANDING THE ROLE OF CALCIUM ON THE REACTION MECHANISM OF GEOPOLYMER CEMENTS THROUGH ADDITION OF NUCLEATION SEEDS

BY

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DISSEPTION

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Geopolymer cement is an innovative binder proposed by Davidovits as an alternative to conventional Portland cements for construction use. It is made from minimally processed industrial byproducts (fly ash, slag) activated by a low concentration alkaline solution (Na, K) and cured at room temperature. The use of low concentration alkaline activators (2 M), unlike the high concentration used for conventional geopolymer binders (8-12 M), makes these cements environmentally friendly (using industrial waste products) and user-friendly. Geopolymer cements gain strength quite rapidly and have been formulated to achieve nearly 100 MPa in 28 days, however, at the cost of low workability. The loss of workability is usually attributed to the presence of free calcium. It is predicted that calcium silicate hydrate/calcium aluminosilicate hydrate gel (C-S-H/C-A-S-H, a main binding phase of fly ash modified Portland cements binder) and aluminosilicate gel ((Na,K)-A-S-H, a main binding phase in geopolymer binders) co-exist in these systems. The precipitation of C-S-H/C-A-S-H is known to initiate the rapid hardening which then is hypothesized to act as a nucleation site for the precipitation of aluminosilicate gel.

This study verified the hypothesis through the addition of synthesized C-S-H/C-A-S-H as an external seed during the processing of geopolymer cement. Isothermal conduction calorimetry, scanning electron microscopy, shear wave ultrasonic wave reflection method, and Fourier Transform Infrared spectroscopy are employed to study the effects of seed on reaction kinetics, extent of product formation, nature of reaction products, and dissolution of raw materials. Through the addition of seeds, it has been concluded that the reaction mechanism in fly ash-slag cements depends on the activator solution. In hydroxide acti-
vated fly ash-slag geopolymers, the rate controlling step is the nucleation-growth controlled reaction, early age hardening behavior in these systems can be controlled via mechanisms that increases or decreases the rate of nucleation and growth of C-S-H. The reaction can be accelerated by adding synthesized C-S-H seed or a small percentage of nanoparticles which will promote nucleation of the product in the pore space. In silicate activated systems, the rate determining step is gelation which depends exclusively on the extent and the rate of aluminosilicate oligomers formation in the solution. Any factor that will affect the availability of silicate species or the rate of aluminosilicate oligomer formation will effect the reaction mechanism. Retarders that will selectively polymerize with silicate species in the pore solution can be used to develop retardation in these cements.

The addition of nucleation seeds to study reaction kinetics is shown to effectively capture the shift in the reaction mechanism from nucleation-growth controlled to the gelation with varying silica concentration in the solution. The protocol developed in the study to separate the responses of two amorphous gels (C-A-S-H and (Na,K)-A-S-H) from the amorphous precursors can be extended to understand the structural evolution of phases in other alkali activated blends of complex chemistry. The fundamental understanding gained through this research can pave a way for large-scale adaptation of alkaline cement technology. The research output will enable engineers to understand the early age reaction mechanism, the knowledge of which will provide greater control over the length of induction period, setting time, and workability of geopolymer cements. Research will provide a unique tool for tailoring the nanostructure of the reaction products through the addition of synthetic seeds for optimizing engineering performance.
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vii
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<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>LITERATURE REVIEW</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>MATERIALS AND METHODS</td>
<td>43</td>
</tr>
<tr>
<td>4</td>
<td>UNDERSTANDING STRUCTURAL EVOLUTION OF ALKALI ACTIVATED ALUMINOSILICATES</td>
<td>56</td>
</tr>
<tr>
<td>5</td>
<td>SEED SYNTHESIS AND CHARACTERIZATION</td>
<td>91</td>
</tr>
<tr>
<td>6</td>
<td>HYDROXIDE AND SILICATE ACTIVATED FLY ASH-SLAG BINDERS</td>
<td>105</td>
</tr>
<tr>
<td>7</td>
<td>INFLUENCE OF NUCLEATION SEEDS IN HYDROXIDE ACTIVATED FLY ASH-SLAG BINDERS</td>
<td>120</td>
</tr>
<tr>
<td>8</td>
<td>EFFECT OF C-S-H NUCLEATION ON THE FORMATION OF K-A-S-H GEL</td>
<td>146</td>
</tr>
<tr>
<td>9</td>
<td>CONCLUSIONS</td>
<td>172</td>
</tr>
<tr>
<td></td>
<td>REFERENCES</td>
<td>178</td>
</tr>
</tbody>
</table>
Concrete, made from Portland cement, is the single most widely used man made material and second-most-used commodity in the world (behind only water) [1]. It is predicted that by 2050, due to the booming construction industry in developing countries, the amount of concrete produced will be four times that of the level in 1990 [2]. High volumes of cement are produced every year because of the ubiquitous use of concrete for infrastructure development.

Each ton of Portland cement releases nearly 0.8 tons of carbon-di-oxide (CO$_2$) gas into atmosphere. The combustion of limestone (main source material for cement production) and the burning of fossil fuels (to generate heat) contribute to 5-8% of anthropogenic CO$_2$ emissions [2]. The concrete industry is attempting to reduce its carbon emissions by partially replacing cement with supplementary cementitious materials (SCMs) that are derived from industrial by-products, such as fly ash, which is a by-product of coal burning. Every year in the United States, coal plants produce 60-70 million tons of fly ash. Among these, a few million tons (<38%) are used by the construction industry; the remainder is landfilled [3]. For every ton of fly ash used in the place of Portland cement, nearly a ton of CO$_2$ is prevented from entering the earth’s atmosphere [2].

With current levels of SCMs used to replace cement, the volume of Portland cement globally required in 2020 is predicted to be 3 times the volume used in 1990 [4]. After considering the significant efforts made by cement plants to reduce their carbon footprint, the CO$_2$ emissions associated with cement production will still be significant unless the cement usage is reduced. One way to reduce the usage is by using increasing the amount of SCMs as a replacement for cement. However, to substantially reduce the cement use,
possibly to the level used in 1990, SCM replacement levels will be too high to be activated through cement hydration product (calcium hydroxide) only (see Figure 1.1) [4]. Therefore, external alkali activation becomes unavoidable. Alkali activated binders are obtained by the reaction of an alkali metal source (alkali hydroxides, silicates, carbonates) with solid silicate/aluminosilicate powders (metakaolin, fly ash, metallurgical slag, natural pozzolan). Binders prepared through alkali activation of fly ash and slag offer an immediate solution to reduce the use of OPC, CO₂ emissions (by 80-90%), and the utilization of industrial waste products [5,6].

![Figure 1.1: Trends in cement production, SCM utilisation and CO₂ production based on 1990 and 2005 (adapted from [7] data)](image)

1.1 Geopolymer Binders and Geopolymer Cements

“Geopolymer binders” are a special class of alkali activated binders that are obtained from the chemical reaction of aluminosilicate oxides with alkali hydroxides-alkali silicates, yielding polymeric Si-O-Al bonds [8]. “Geopolymer” is a primary binding phase in these cements which is a three dimensionally (3D) cross-linked amorphous alkali aluminosilicate gel. Geopolymer gel is composed of tetrahedral aluminum and silicon atoms with alkali
metal cations charge balancing the tetrahedral Al(II) sites. According to Davidovits, the empirical formula of geopolymers is $M_n\left[(-Si-O_2)_z-Al-O_2\right]_{n+}\cdot wH_2O$ (abbreviated as M-A-S-H), where $M$ is a monovalent/divalent cation such as $K^+$, $Na^+$ or $Ca^{2+}$; $n$ is the degree of poly-condensation, and $z$ is 1, 2 or 3 [8]. Low-calcium fly ash and calcined clay are the most prevalent precursors used in geopolymer binder synthesis. Geopolymer binders, especially those made from fly ash, are usually cured at temperatures between 60 and 90°C for several hours and activated with solution of $SiO_2:Na_2O$ (molar ratio) <1.20 (8–14 M). The handling of 14 M concentration solutions is hostile to the ordinary labor force employed on the field. To avoid the usage of corrosive solutions, Davidovits developed a new class of innovative cements by using a low concentration activator solution called “geopolymer cements” or “user-friendly geopolymers” [8,9].

Geopolymer cements are medium-calcium binders that harden (set) at room temperature (much like regular Portland cement) and are different from geopolymer binders that require high temperatures to set [8,12]. Geopolymer cements rely on the use of minimally processed natural materials or industrial by-products (60-80% by weight) as the aluminosilicate source. It is activated through a user-friendly reagent (sodium or potassium soluble silicates with a molar ratio $SiO_2:M_2O >1.25$, $M$ is Na or K) and water. Room temperature hardening is achieved through the addition of calcium cation in the form of a ground granulated blast furnace slag (or slag in short term). The handling conditions of these cements are user-friendly and not caustic because of the use of a low concentration activator; and, thus they are named user-friendly cements.

1.2 Current Field Applications of Geopolymer Cements and Limitations

Geopolymer cements made from fly ash-slag blends were recently commercialized by the Australian company Zeobond, under the product name “E-crete”, thus demonstrating a
strong commercial interest in these cements [13]. Figure 1.2 shows one of the many E-crete applications.

![E-crete retaining wall at the Swan Street bridge in Melbourne, Australia](image)

Figure 1.2: E-Crete retaining wall at the Swan Street bridge in Melbourne, Australia [13].

A study on geopolymer cements by Nugteren et al. reported the successful development of a very high strength (100 MPa) binder, however, at the cost of low workability [11]. The loss of workability was attributed to both the presence of free lime in the system and the fineness of fly ash particles. The type, dosage, concentration of alkali metal activator (Na or K), temperature of curing, and the presence of various ionic contaminants are several parameters known to affect the hardening rate of fly ash geopolymer cements and change the setting time from a few minutes to a few days [14-16]. Therefore, the consequence of using waste materials as precursors results in an additional challenge because the properties of the final product vary significantly with the extreme variability of the raw materials.

The presence of a soluble form of calcium was known to effect early age (loss of worka-
bility) as well as later age properties (high strength) of alkali-activated binders made from metakaolin and fly ash [17,19]. Davidovits et al. proposed that the matrix of geopolymer cements is (K, Ca)-poly(sialate-siloxy) geopolymer of Si/Al ratio 2 [10]. However, Yip and van Deventer reported the co-existence of sodium aluminosilicate gel ((N,K)-A-S-H) and calcium silicate hydrate/calcium aluminosilicate gel (C-S-H/C-A-S-H) when metakaolin and slag blends are activated at a pH not high enough to precipitate all the reactive calcium as portlandite [20–22]. The presence of calcium was proposed to be critical to the early strength development and accelerated hardening due to an enhanced amount of aluminosilicate gel formation [17,23,24]. The accelerated setting observed in the presence of soluble calcium is hypothesized to be due to multiple reasons such as [17,23,27]:

- Precipitation of calcium silicate hydrate initiates rapid hardening
- Precipitation of calcium silicate hydrate or Ca(OH)$_2$ from the solution provides nucleation sites which triggers rapid aluminosilicate gel formation and accelerated hardening

However, there is little to no direct evidence present to explain the reasons behind accelerated hardening evidenced in the presence of calcium. The interaction between calcium, silicate, and aluminate species is very complex, and the role of calcium on the reaction mechanism during early ages needs further verification to optimize the workability and strength of geopolymer binder.

### 1.3 Objectives and Organization of thesis

The main objective of this study is to understand the role of calcium on the low-workability and rapid hardening seen in user-friendly geopolymer cements. The focus is to verify the above mentioned two hypotheses which are believed to be the reasons for the accelerated hardening observed in the presence of soluble calcium. The first hypothesis will be verified by quantifying the amount of C-S-H and K-A-S-H forming in the binder during early stages
of hardening. The ages for quantification will be chosen based on the shear wave ultrasonic wave reflection (UWR) results. A protocol is developed to effectively characterize and quantify these products and monitor their structural evolution through time by using selective dissolution techniques and Fourier transform infrared (FTIR) spectral subtraction corroborated through Scanning electron microscopy - Energy dispersive spectroscopy (SEM-EDS) results.

The second hypothesis will be verified through the addition of appropriate seeding agents during the processing of geopolymer cements. The research tasks are developed to first gain a fundamental understanding of the effects of the addition of external seeding agents on the reaction mechanism by adding non-product based seeds (nano-\(\text{Al}_2\text{O}_3\), nano-\(\text{SiO}_2\), nano-\(\text{ZnO}\), and finely powdered \(\text{CaCO}_3\)). As the hypothesis is that the C-S-H that forms in the presence of soluble calcium in geopolymer cement can act as nucleation site, seeding agents related to the reaction product, such as C-S-H (of varying Ca/Si ratio) and C-A-S-H are used. For this study, most of the seeding agents will be synthesized using laboratory chemicals. Tasks have been developed to study the influence of addition of C-S-H/C-A-S-H gel on the reaction kinetics, microstructure, the extent of product formation, and fly ash dissolution of raw materials on geopolymer cements activated through potassium hydroxide and potassium silicate solutions.

In this thesis, a detailed literature of current understanding of geopolymer binder formation, factors that influence the reaction kinetics, and the characterization techniques used in this study are presented in chapter 2. Materials used and experimental methods used in this study are summarized in chapter 3. The first hypothesis will be verified by quantifying the amount of C-S-H and K-A-S-H forming in the binder during early stages of hardening in chapter 4. Chapter 4 also presents a protocol to successfully characterize the evolution of reaction products with time when C-(A)-S-H and K-A-S-H co-exist in the binder. Synthesis of seeds, characterization of seeds, and the protocol of mixing are discussed in chapter 5. The differences in reaction kinetics, phase formation, and microstructural development be-
tween hydroxide and silicate activated cements are explored in chapter 6. Hypothesis 2 will be verified in hydroxide activated binders and silicate activated binders by monitoring the reaction kinetics and microstructure development through the addition of nucleation seeds in Chapter 7 and chapter 8, respectively. Chapter 9 presents conclusions.
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Alkali-Activated Binders (AABs) are defined as any binder formed through a reaction using alkali metal solutions to convert alumina- and silica-containing solid precursors to a hardened solid material \[28-30\]. Alkali-activated binders are made from a wide range of aluminosilicate containing raw materials, and the most commonly used are calcined kaolin (metakaolin), fly ash, ground granulated blast furnace slag (GGBFS). A wide variety of alkali-activated binders have been developed in the last twenty years from different raw materials, but the discussion in this thesis is mainly limited to three main categories based on the nature of the solid precursors \[31,32\]:

- High-calcium binders namely alkali-activated slag binders
- Low-calcium binders namely geopolymer binders
- Medium-calcium binders namely geopolymer cements

The primary focus of this thesis is to understand the reaction mechanism of medium-calcium binders called geopolymer cements. The other two binders (low- and high-calcium) have been studied in the literature. The reaction mechanism in those binders will be discussed in detail here in this chapter to help us understand the reaction mechanism in geopolymer cements. The formation mechanism in alkali-activated binders in general terms will be discussed first before we move into discussing formation mechanism in each of the above-mentioned cements.
2.2 Reactivity and Product Formation in Alkali-activated Binders

The formation of alkali-activated binders was initially described by Glukhovsky as a series of destruction-condensation transformations that take place in the starting solid precursor to give rise to a range of coagulated structures that will ultimately condense to generate the binder [4, 32, 33]. The formation of aluminosilicate structures during the alkali activation can simply be described as follows:

- Gradual dissolution of aluminosilicates to form reactive aluminate and silicate monomers called hydrolysis
- Mutual condensation of the monomers units to form oligomeric intermediates
- Polymerization of aluminosilicate oligomers to form a three-dimensional (3D) network resulting in the gelation of the system. Water gets expelled during poly-condensation reactions, and the gel reorganizes and restructures to form a stable 3D network

2.2.1 Hydrolysis

Hydrolysis is the first disaggregation process where R-O (R-metal cation in the precursor), Si-O-Si, Al-O-Al, and Al-O-Si bonds in the starting aluminosilicate material break upon the addition of alkaline activator solution. The hydroxide ions (OH\(^-\)) in the solution initiate the reaction by breaking Si-O-Si, Al-O-Al, and Al-O-Si bonds thus promoting dissolution of raw materials (Figure 2.1a) [7]. The attack on Si-O-Si bonds result in silanol (-Si-OH) and sialate (-Si-O\(^-\)) species at high pH values. The attack on Al-O-Al and Al-O-Si bonds result in aluminate anions. At pH >10, Al is almost exclusively is present as Al(OH)\(_4^+\) ion in the solution (Figure 2.1b) [34]. Depending on the SiO\(_2\)/R\(_2\)O ratio of the activating solution, speciation of Si can be either smaller monomeric entities or higher order oligomers.
At high pH values, silica exclusively present as partially deprotonated monomers (Si(OH)$_4$) (Figure 2.1b) [34]. The presence of alkali metal cations (R) neutralizes and stabilizes the deprotonated silicate species to form Si-O-R$^+$ bonds, hindering reversibility [7]. So, alkali metal cations promote dissolution and also stabilize solution species. During hydrolysis, one mole of silica can take up to four moles of hydroxide ions. As a result, the dissolution process can lower the pH of the solution, slowing the reactions which are dependent on high OH$^-$ ion concentration. Most of the hydroxide is released later in the reaction.

![Chemical reactions](image)

Figure 2.1: a: Hydrolysis of aluminosilicates to form aluminate and silicate monomers, b: Common silicate and aluminate monomers present in solutions with pH $>$12 (adopted from [7]).
2.2.2 Condensation

As the silicate and aluminate species increase in the solution, they start interacting with each other. Due to its polymerizability, silica displays a complex solution chemistry. Silica monomers from the precursor interact to form dimers, which in turn react with other monomers to build higher-order polymers called oligomers. Iler found that silica polymerization happens in a way to maximize siloxane (Si-O-Si) bonds and minimize uncondensed Si-OH groups (non-bridging oxygens(NBO)) \[35\]. The degree of polymerization of silicate species in a solution depends on the silica concentration as well as on the ratio of silica to alkali hydroxide (SiO\(_2\)/M\(_2\)O, M-alkaline metal cation) \[36,37\]. At a low silica concentrations or low silica to alkali ratio, the silica species is predominantly monomeric. But, at a high silica concentration and high silica to alkali ratio, silica is present as a higher order species \[38,39\].

The aluminates participate in the polymerization by replacing silicon tetrahedra in growing oligomers. The Al(OH)\(_4^-\) is tetrahedral, and so the aluminosilicate polymerization can grow in all directions producing colloids. McCormick and Bell have found that the aluminate anions react more readily with large linear silicate oligomers than smaller silicate polymers \[40\]. Alkali cations influence the condensation of silicate and aluminate anions, with larger cations increasing the extent of condensation \[41,42\]. The hydroxide ion consumed during the hydrolysis reaction is released back into the solution during condensation. The newly released hydroxyl ions participates in further hydrolysis and liberate more silicate and aluminate species into the solution and keep reaction continuing.

2.2.3 Gelation/precipitation

Hydrolysis and condensation reactions lead to the growth of monomers. Polymerization or growth of monomers in a solvent could lead to two possible outcomes: gelation and precipitation \[43\]. Kallala et al. define gelation as the mechanism when the polymers grow
with a fractal dimension lower than 3 and precipitation when a fractal dimension equals to 3 (denser structures) \[43\]. Relative reactivities of monomers with chemical environment defines the final state and the growth process (gelation vs. precipitation). One of the important factors that influence the reaction mechanism (gelation Vs. precipitation) is the chemical modifiers. Chemical modifiers (such as cations) that can bind to the monomers and modify the partial charge of reaction groups have a strong influence in determining the reaction mechanism \[43\].

The factors that influence the rate and the extent of aluminosilicate polymerization will determine the nature of the final product and the reaction mechanism of alkali-activated binders. The composition and structure of the product are determined by the nature of the precursors used, alkaline activator, and the reaction conditions. Therefore, this step will be discussed in more detail while discussing the three types of cements.

### 2.3 Effect of Alkali Cation on the Reaction Mechanism

Cations in an aqueous solution establish an association between their positive charge (Lewis acid) and partial negative charge on oxygen atoms (Lewis base) of surrounding water molecules.
forming large aqueous complexes. Sodium ions have relatively high charge density and holds water molecules very tightly. Whereas larger alkali metal ions are less strongly hydrated and can shed water molecules to associate with negatively charged silicate surface sites. It has been suggested that smaller ions promote gelling because surrounding water molecules coordinate hydrogen bonding between silicates and the ability to promote gelling decreases with the increasing size of the cation [44].

During hydrolysis, alkali cations promote dissolution and stabilize deprotonated silicate and aluminate species (dissolved from precursor) in the solution to promote condensation through what is called as ion pairing. Silicate-ion pairing decreases the electrostatic repulsion between different silicate species promoting interaction between them and making condensation favorable. Ion pairing is enhanced at high alkalinites, low temperatures, and with smaller alkali cations. McCormick suggested that the Coulombic interactions between cations and silicate/aluminosilicate anions lead to selective stabilization of particular structures relative to others [40]. For small anionic monomers, the extent of ion pairing of anions with cations decreases with increasing cation size (Na$^+$ < K$^+$) [40,45]. For larger anions, preferential pairing occurs with the larger cations due to the high polarizability of such ions. Therefore, an increase in the concentration of large silicate ions is seen with increasing cation size [40,45].

Alkali cations also accelerate gelation by reducing electrostatic repulsion between aluminate and silicate anions. Ion pair becomes less reactive as cation size decreases. Small cations bind strongly with silicate ions so that the pair is relatively inert to condensation with another silicate. It means that the smaller cations like sodium can break the precursor bonds faster and result in more gel forming species in the solution but condensation might be slower due to strong ion pairing. Swaddel and Kinrade showed that sodium stabilizes the monomer and potassium increases the amount of dimer and trimer [36]. Potassium can more readily associate and stabilize larger silicate and aluminosilicate anions than sodium through ion pairing. Therefore, potassium based geopolymer does not induce the gelation step to
proceed unless there is a sufficient supply of large aluminosilicate anions for gel growth [14].

2.3.1 Effect of Calcium on Phase Formation

The nature of available cations strongly influences the degree of condensation. The role of calcium in complexing silicates/aluminosilicates is principally driven by the strong polarizing power (higher charge/ion radius ratio) of the aqueous Ca ion relative to the alkali metal ions Na\(^+\) and K\(^+\) [46]. Alkaline earth metals (Ca) stabilize non-bridging oxygen more efficiently than alkaline metals (Na, K). Therefore, the inclusion of calcium ion would favor the formation of less polymerized species [46].

Increasing pH increases polarization of electron density into M-O (M - Na, K, Ca) bond which weakens O-H bonds releasing a proton by hydrolytic dissociation. Release of proton leads to the formation of M-OH ion-pair species such as [CaOH]\(^+\). At high pH, Ca\(^{2+}\) tends towards precipitating silicates (or aluminosilicates) from solution and its aqueous complex size limits the higher degree of directional polymerization forming only two dimensional sheet polymers such C-(A)-S-H [7].

2.4 Reaction Mechanism in Alkali-activated Slag Binders: High-calcium Binders

Alkali-activated slag binders are obtained through the activation of ground granulated blast furnace slags (GGBFS) under moderate alkaline conditions. The main reaction product is a two-dimensional C-S-H / C-A-S-H gel, similar to the gel obtained through the hydration of Portland cement binders. Alkali-activated slag binders were one of the first non-Portland cement binders to get commercialized in former USSR back in 1960. A 20-storey residential building (shown in Figure 2.3) in Lipetsk Russian Federation was the first building to be made entirely of alkali-activated slag concrete built in 1987-1989 [32,47].
Figure 2.3: The first residential building made entirely of alkali-activated slag concrete built in 1987-1989 (adopted from [32, 47]).

The usual components of slag are CaO (35-40%), SiO$_2$ (25-35%), MgO (5-10%), and Al$_2$O$_3$ (5-15%) along with S, Fe$_2$O$_3$, MnO, and K$_2$O in weight percentages lesser than 1%. Slag is made of 90-95% (by weight) of amorphous depolymerized calcium silicate and rest as minor crystalline phases namely gehlenite (2CaO.Al$_2$O$_3$.SiO$_2$) and akermanite (2CaO.MgO.2SiO$_2$) [32, 47]. Vitreous phase contains both network-forming anions (SiO$_4$)$^{4-}$, (AlO$_4$)$^{5-}$, and (MgO$_4$)$^{6-}$ and network modifying cations, Ca$^{2+}$, Al$^{3+}$, and Mg$^{2+}$.

Fernandez-Jimenez reported that the type of activator (anion) solution plays an important role during the early hydration stages and setting of alkali-activated slag binders [48]. The reaction mechanism in alkali-activated slag depends on the nature and dosage of activators [48]. Along with the main reaction product, C-S-H/C-A-S-H, a number of secondary products may form, like hydrotalcite, calcite, and Afm, depending on the type and concentra-
tion of the activator. Slag can be activated using alkali hydroxides or alkali silicates. Nature of activator also influences the rate of strength development and the long-term strength. It has been observed that the hydroxide activated binder, shows high compressive strength after one day whereas silicate activated binders develop strength slowly and have no measurable strength after one day.\[29,49\].

Sodium hydroxide and sodium metasilicate (also known as waterglass) are the two most common activators used. When slag is activated with highly concentrated alkaline hydroxide solutions, the heat evolution curve of hydroxide activated slag binders shows one initial peak corresponding to the wetting and dissolution of slag particles followed by an induction period and a second peak due to the accelerated hydration. Based on the earlier discussion on hydrolysis and condensation, alkali-activated slag paste reactions can be described as follows and is shown in Figure 2.4\[29,32\]:

- The hydroxide ions (OH\(^{-}\)) in the solution break Ca-O bonds, Si-O, and Al-O bonds of slag particles leading to a variety of dissolved silicate and aluminate monomers and hydrolyzed calcium aqueous complexes
- Alkali cation in silicate monomer does a cationic exchange with the Ca\(^{2+}\) ions
- Silicate monomers condense to form low Ca/Si ratio C-S-H of very low solubility and precipitates very quickly through the solution. C-S-H gel embeds aluminate ions into its structure forming C-A-S-H gel. Alkali cations (R\(^{+}\)) are then uptaken by C-S-H/C-A-S-H later into the structure.

In hydroxide activated binders, the C-S-H/C-A-S-H gels form on the surface of slag particles and products grow outward into the pore space (shown in Figure 2.4b). Sodium metasilicate was found to be the most efficient activator resulting in rapid hardening and high compressive strength (comparable to Portland cements).\[49,50\]. When slag is activated by alkaline silicate solutions, calcium ions dissolving from slag particles react with
Figure 2.4: a: Hydrolysis of slag releasing partially deprotonated silicate monomers. Silicate anions are stabilized by calcium cation and condensation of cation-anion pairs give calcium silica hydrate gel (C-S-H), b: Reaction mechanism in an hydroxide activated slag particle [32].

Silicate ions in the activator to form foil-like C-S-H phase in the pore space away from the raw materials [51, 52]. NMR analysis by Brough et al. has confirmed that the C-S-H formation in silicate activated slag pastes is due to reaction between Ca dissolving from slag and silicate anions from the activator solution [51]. In sodium silicate activated slag pastes, the microstructure is characterized as gel-like material filling the space between slag particles (from SEM micrographs shown in Figure 2.5). In hydroxide activated pastes, uniform hardened structure is seen in the microstructure with scattered voids indicative of product growing from the particle surface out into pore space and impinging with each other [29]. The addition of C-S-H seed accelerates reaction kinetics in alkali (hydroxide and silicate).
activated slag paste and thus proved to be a nucleation-growth controlled reaction \([53]\). In the absence of alkaline activator solution, the slag paste hydrates very slowly and the addition of C-S-H seed does not have any effect on the reaction kinetics. The non-responsivness in the presence of C-S-H was indicated to be because hydration rate was controlled by slag dissolution \([53]\).

Figure 2.5: Microstructure development of hydroxide and silicate activated slag pastes at 2 hours and 3 days (adopted from \([29]\)).

(a) 2 hours
(b) 3 days
Hydroxide activated

(c) 2 hours
(d) 3 days
Silicate activated

Figure 2.5: Microstructure development of hydroxide and silicate activated slag pastes at 2 hours and 3 days (adopted from \([29]\)).
2.4.1 Structure of C-S-H/C-A-S-H

The main reaction product in alkali-activated (hydroxide and silicate) slag binders is calcium silicate hydrate with aluminum in its structure (C-A-S-H) with low Ca/Si ratio (Ca/Si= 0.9-1.2). The C-S-H formed in alkali-activated slag binders has foil like morphology owing to low Ca/Si ratio compared to C-S-H in Portland cement pastes, which has fiber-like morphology indicative of high Ca/Si ratio [29].

The evolution of C-A-S-H gels in slag binders is shown in Figure 2.6. Calcium and silicon ions precipitate very quickly out of the solution to form a 1-D C-S-H gel. Initially formed C-S-H gel takes up more and more Si dissolving from raw materials which enhances gel polymerization. Polymerization increases the chain length from three silica tetrahedra to chains with five or more links as percentage of $Q^2$ (Si atoms with two Si neighbors) increases at the expense of $Q^1$ (edge Si atoms with one Si neighbor). Trimethylsilation studies of C-S-H phases have shown that the C-S-H structure contains dimeric, pentameric, and higher polymeric species of SiO$_4$ tetrahedra resulting in chains of 2, 5, 8, .. SiO$_4$ tetrahedra [54]. The $^{29}$Si MAS NMR studies have shown the evidence of pentameric unit where a bridging SiO$_4$ tetrahedron connects two dimers which results in two SiO$_4$ end groups and two paired SiO$_4$ sites [55]. The $^{29}$Si MAS NMR studies have proved the presence of dimeric ($Q^1$) and chain ($Q^2$) SiO$_4$ tetrahedra and the absence of ($Q^3$) SiO$_4$ tetrahedra (double chains of SiO$_4$ tetrahedra) [55].

In the presence of aluminum ions, aluminum preferentially substitutes a non-bridging SiO$_4$ tetrahedron in C-S-H gel forming C-A-S-H gels [56,57]. Andersen et al. proposed that Al incorporates into the C-S-H phase, for a pentacoordinates Al site, where Al $^{3+}$ substitutes for Ca$^{2+}$ ions in the interlayer structure of the C-S-H [58]. Andersen et al. demonstrated that the quantity of Al in the C-S-H increases with increasing hydration time [58].

The EDS microanalysis studies have revealed that the pastes made with silicate activator form C-(A)-S-H gels with lower Ca/Si ratio than the gels in hydroxide activated binders [18].
Figure 2.6: Schematic showing the transformation of C-S-H (1D) gel into C-A-S-H gel (2D) in alkali-activated slag cements (adopted from [32]).

Lower Ca/Si in C-S-H is attributed to the excess silica in the activator solution that becomes part of the C-S-H gel structure. The charge imbalance caused by Al substitution promotes C-(A)-S-H gels to take up higher amounts of alkalis than C-S-H gels [59, 59, 60].

2.5 Reaction Mechanism in Geopolymer Binders:

Low-calcium Binders

Geopolymer binders involve activation of low-calcium aluminosilicate precursors ((Na,K)$_2$O-Al$_2$O$_3$-SiO$_2$-H$_2$O binder) such as calcined clays (metakaolin), class-F fly ash using highly alkaline solutions (8-14 M) and cured at high temperatures (60-200°C) [10, 61]. The primary binding phase in low-calcium geopolymer binders is a highly disordered and a highly cross-linked three-dimensional aluminosilicate polymer called geopolymer gel ((N,K)-A-S-H gel) [10, 61]. The geopolymer binders are among the most investigated class of AABs and have garnered interest as a potential sustainable replacement to Portland cement binders. However, due to the use of highly alkaline corrosive solutions, the geopolymer binder usage...
is limited to applications where the handling conditions of solutions can be carefully monitored. Some applications involved the use of geopolymer binders for stabilizing/solidifying radioactive wastes and as capping agents for highly saline mine tailings [62,63].

Geopolymer binders made from metakaolin are studied extensively in the literature [8,16,64]. The present discussion about reaction mechanism will only be confined to geopolymer binders made from class F fly ash. The use of class C fly ash is categorized as a medium-calcium binders due to the presence of significant amount of CaO in the vitreous phase. Class F fly ash consists of an amorphous phase and a few minor crystalline phases such as quartz (SiO$_2$;5-13%), mullite (Al$_6$Si$_2$O$_1$3;8-14%), and magnetite (Fe$_3$O$_4$;3-10%) [65]. The composition of fly ash is quite variable and depends on the source of coal and the incineration process used at the power plant. When fly ash comes in contact with the activator solution, hydrolysis and condensation happen according to the procedure described in hydrolysis and condensation sections earlier with some differences. The microstructure and the phase composition depends on the activator (hydroxide or silicate) much the same way as in alkali-activated slag binders.

In hydroxide-activated binders, when a solution comes into contact with fly ash surface, silicate and aluminate monomers are released into the solution. The silicate monomers react with each other to form dimers which in turn react with other monomers to form trimers, tetramers, and so on. Also, silicate monomers react with growing aluminosilicate species. When the solution reaches aluminosilicate saturation, nucleation of Al-rich gel is observed to take place in the region immediately outside of fly ash particles (only available nucleation site) [66-68]. As more silica and alumina ions are released into the solution, they will condense with the product formed on the surface already. Gradually as the layer of the gel thickens, further dissolution of the underlying precursor material will be hindered [67]. In general, the kinetics of aluminosilicate gel formation in fly ash-based binders is modeled as nucleation, followed by gel growth based on the similarities with zeolite formation [66,67,69,70].
The presence of appreciable amounts of silica in the activating solution has important implications on the reaction mechanism. The effects are mainly attributed to the solution chemistry of silica [66][70]. In silicate activator solution, as the silicon and aluminum are released from the fly ash surface, they can either precipitate on the surface of the fly ash surface as in the case of hydroxide-activated samples or react with dissolved silica (present as oligomers in the solution) to form aluminosilicate oligomers [66]. At high dissolved silica concentrations, dissolving species are taken away from the surface of the fly ash into the solution. Before precipitation, there is an even distribution of material in the solution, and due to the lack of product build up on the surface, the dissolution of fly ash is unrestrained [66]. The aluminosilicate oligomers in the solution condense and result in the growth of larger polymeric units of colloidal dimensions, which are often seen in SEM/TEM studies [61,66].

The presence of silicates in the activating solutions have been reported to have both an accelerating and a retarding effect on geopolymer binder formation and strength development and the information in the literature is quite conflicting [71–73]. At low soluble silicate concentrations, the dissolution was found to be inhibited by secondary precipitates on the surface of the fly ash. Lee and van Deventer observed that there exists a threshold silica concentration in the solution (200mM in their study) below which precipitation onto the particles surfaces is the dominant mechanism [74].

The microstructure of aged geopolymer binders activated with hydroxide and silicate is shown in Figure 2.7. Reaction products in hydroxide activated binders have formed preferentially on the surfaces of the ash particles, and gel in the silicate-activated samples is formed uniformly in the pore space and consists of numerous roughly similar-sized globular units. The microstructure of the binder is much less uniform in hydroxide-activated binders compared to microstructure that forms in a corresponding silicate-activated binder. According to Lloyd and Provis, this is due to the more uniform gelation process in the silicate-activated binders as nucleation is seen in bulk regions [66]. Increased homogeneity results in a lower porosity and higher compressive strength of silicate-activated samples.
compared to hydroxide-activated samples as observed by many researchers [66,70,75].

Figure 2.7: Microstructure of aged hydroxide activated and silicate activated geopolymer binders (adopted from [23]).

2.5.1 Structure of (N,K)-A-S-H

The main reaction product formed in the alkaline activation of low-calcium precursors is an amorphous alkaline aluminosilicate hydrate \((M_n-(SiO_2)_z-AlO_{2n}-wH_2O)\) known as R-A-S-H gel, where R is Na or K, commonly referred as (N,K)-A-S-H gel. The gel is characterized by a three-dimensional (3D) structure in which the Si is found predominantly in \(Q^4(nAl)(n=0,1,2,3 \text{ or } 4)\) units. The Si\(^{4+}\) and Al\(^{3+}\) cations are tetrahedrally coordinated and joined by oxygen atoms (shown in Figure 2.8). The negative charge generated by substitu-
tion of aluminum for silicon tetrahedra is balanced by Na\textsuperscript{+} or K\textsuperscript{+} cations. Cations are not
directly bound to the Al atom but with negatively charged oxygens surrounding Al atom and
cations are free to move about within the pores of the structure \[76\]. Water is not chem-
ically bound to the structure unlike in the case of C-A-S-H/C-S-H gel but resides within
the nano- and micro-pores of the gel. In the presence of excess alkalis or partially cured
gels, the non-bridging oxygens form in the structure which is charge neutralized by alkali
cations. Kriven et al. investigated the nanostructure of potassium-based-geopolymer and
through TEM-EDS, they determined that fully-reacted regions correspond to a Si:Al ratio of
2:1 \[64\]. Criado et al., and Rahier et al., also concluded that regardless of initial conditions,
the composition of fully-reacted geopolymers tends toward Si:Al ratio of 2:1 \[77,78\].

Figure 2.8: 2D and 3D view of three-dimensional N-A-S-H gel structure (2D-adopted
from \[79\] , 3D-adopted from \[32\]).

A combined work of several authors proposed that N-A-S-H gel evolution in geopolymer
binders includes a series of stages (shown in \(\text{Figure 2.9}\) \[31,61,80\]). In hydroxide activated
binders, reactive aluminum dissolves faster than silicon followed by congruent dissolution of
Si and Al ions. Aluminum dissolves faster because Al-O bonds are weaker than Si-O bonds
and are readily attacked by hydroxide ions during hydrolysis. So, in the first few minutes to
few hours when aluminate ion concentration is higher in the solution, precipitated N-A-S-H
gel is rich is Al (gel 1) and has low Si/Al ratio. As the reaction progresses, more Si-O groups
dissolve raising the silicon concentration in the solution which increases the amount of Si
in N-A-S-H gel forming gel 2. Whereas in silicate activated binders, due to the presence of high concentration of silicon in the activating solution, initially precipitated N-A-S-H gel has high silicon content (Si/Al) which will gradually decrease as more aluminum dissolves from the raw materials.

![Model proposed for N-A-S-H gel formation](image)

**Figure 2.9:** Model proposed for N-A-S-H gel formation (adopted from [61]).

The structure of geopolymer gel and the extent of polymerization depends on curing time, curing temperature, and the activator solution. Long curing times are known to give rise to the formation of silica-rich products. Criado reported that the degree of polymerization in sodium silicate solution, which depends on SiO$_2$/Na$_2$O ratio, determines the structure of gel 1 and gel 2 [75].

### 2.6 Structure of Reaction Products and Fourier Transform Infrared Spectroscopy (FTIR) Characterization

Gels that are formed in alkali-activated materials (C-A-S-H and N-A-S-H) are amorphous, and so are the precursors that are used as raw materials. Classical characterization techniques such as X-ray diffraction (XRD) produces a broad halo rather than sharp diffraction peaks for amorphous materials. Therefore, their structure cannot be investigated by using XRD alone. Advanced techniques such as Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) spectroscopy in conjunction with XRD provides
better insight into the molecular framework of these materials. Because of its sensitivity
to amorphous products, FTIR has been used extensively to characterize synthesized N-A-
S-H gels as well as to monitor the reaction progress of alkali-activated fly ash, fly ash-slag,
metakaolin, metakaolin-slag activated geopolymers, and slag binders [67,71,74,81,87].

2.6.1 Nature of Chemical Bonds from IR

When a compound of two or more atoms is exposed to external energy, thermal or elec-
tromagnetic, the atoms are excited to vibrate about their equilibrium position [88]. The
energies needed to vibrate the atoms are quantized meaning molecule can only absorb ener-
gies at some well-defined, and discrete energy pockets called photons. The energies absorbed
are characteristic of an individual molecule, or group of atoms which is the basis for molec-
ular identification using a molecular vibration technique such as infrared spectroscopy. In
infrared radiation region (12800-200 cm\(^{-1}\)), a vibrating molecule absorbs energies every time
there is an oscillating dipole moment [88]. Hence, molecules without a center of symmetry,
like large molecules or amorphous solids, are infrared active making it an extremely valuable
technique to study complex amorphous solids such as aluminosilicate gels [88].

The vibrational frequencies observed in an infrared spectrum are a function of masses of
constituent atoms, the magnitude of interatomic force constants (strength of intermolecular
bonding), and the molecular geometry [89,90]. In aluminosilicates, the most prominent
bands occur in the ranges from 1250 to 950 cm\(^{-1}\), from 790 to 650 cm\(^{-1}\) and from 500 to 420
cm\(^{-1}\). Bands in 1250 to 950 cm\(^{-1}\) are assigned to asymmetric stretching mode of Si-O-T,
(T- Si, Al), bands in 790 to 650 cm\(^{-1}\) are assigned to symmetric stretching mode of Si-O-T,
and 500 to 420 cm\(^{-1}\) to Si-O bending mode of SiO\(_2\) tetrahedra [91].

In aluminosilicates, the substitution of aluminum into silicate structure has a significant
impact on the intermolecular bonding strength. The Al-O bond in aluminate has a bond
energy of 125 kJ mol\(^{-1}\) compared to that of the Si-O bond of silica with a bond energy of
466 kJ mol\(^{-1}\). Therefore, as aluminum substitution increases in silicate network, it takes

26
lesser and lesser energy to induce framework vibrations. A fused silica or silica gel without any aluminum substitution or any other impurities is known to exhibit an IR asymmetric stretching Si-O-Si band centered around 1100 cm\(^{-1}\) \cite{92}. The IR asymmetric stretching bands of Al\(^{IV}\)-O-Al\(^{IV}\) are situated at lower frequencies at 900-650 cm\(^{-1}\) \cite{92}. With increasing Al substitution, the Si-O-T (T = Si or Al) asymmetric stretching vibration band shifts to lower frequencies from the original 1100 cm\(^{-1}\).

The band positions are also affected by the degree of polymerization in silicate/aluminosilicates. As the polymerization in silicate units increase from Q\(^0\) to Q\(^4\), the amount of energy required to vibrate the bond increases and the band position that corresponds to asymmetric stretching vibration of Si-O-Si moves to higher wavenumbers. Table 2.1 shows IR peak positions in 1700-450 cm\(^{-1}\) range for typical bonds seen in aluminosilicates as identified from the literature.

Table 2.1: IR peak positions in 1700-450 cm\(^{-1}\) for typical bonds seen in aluminosilicates

<table>
<thead>
<tr>
<th>Peak position (cm(^{-1}))</th>
<th>Chemical bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>680-400</td>
<td>Asymmetric stretching (Al-O-Al, Al(^{IV})O(_4) octahedra, pure aluminite)</td>
</tr>
<tr>
<td>900-650</td>
<td>Asymmetric stretching (Al-O-Al, Al(^{IV})O(_4) octahedra, pure aluminite)</td>
</tr>
<tr>
<td>1100</td>
<td>Asymmetric stretching (Si-O-Si, pure silica)</td>
</tr>
<tr>
<td>1100-1000</td>
<td>Asymmetric stretching (Si-O-Si, alkali cation-modified silicate)</td>
</tr>
<tr>
<td>1100-900</td>
<td>Asymmetric stretching (Si-O-Si, Si-O-Al)</td>
</tr>
<tr>
<td>1390-1450</td>
<td>Asymmetric stretching (C-O)</td>
</tr>
<tr>
<td>1640</td>
<td>Bending (H-O-H in H(_2)O)</td>
</tr>
</tbody>
</table>

FTIR can also yield valuable qualitative information of a molecule through examination of spectral bandwidths. Highly heterogenous and highly amorphous materials usually have very broad bandwidths \cite{54,92}. As material acquires an increasing degree of structural order through crystallization, bands become sharper \cite{92}. FTIR offers an accurate detection of not only crystalline phases but also amorphous phases. It can be used to gather information about the structure of compounds and can be used as an analytical tool for determining the
qualitative and quantitative analysis of mixtures. FTIR is also very sensitive to compounds present in tiny quantities which could perhaps not be detected by XRD. High sensitivity to small quantities is especially useful for early age reactions where reaction products are present in tiny amounts.

### 2.6.2 FTIR Characterization of C-S-H/C-A-S-H

IR spectroscopy has been used to study the structure of synthesized C-S-H gels of varying Ca/Si ratio \[89,93,94\]. The local structure of C-S-H gels was evaluated by comparing the spectra with those of naturally occurring crystalline equivalents, tobermorite and jennite. Figure 2.10 shows IR spectra of C-S-H gels with varying Ca/Si ratios. C-S-H gels exhibit bands in the range of 800-1200 cm\(^{-1}\) corresponding to asymmetric and symmetric stretching vibrations of Si-O bonds and a band around 660 cm\(^{-1}\) due to Si-O-Si bending vibrations. The band at 1640 cm\(^{-1}\) is due to H-O-H bending vibration of molecular H\(_2\)O. The sharp band at 980 cm\(^{-1}\) and the shoulders at 1060 and 900 cm\(^{-1}\) are due to Si-O-Si stretching vibrations at Q\(^2\) sites. The 1200 cm\(^{-1}\) seen in 1.1 nm tobermorite is attributed to Si-O-Si stretching vibrations in Q\(^3\) sites. As noted earlier, the band position shifts to higher wavenumber as silicate network becomes more polymerized. In C-S-H gels, the frequency of Si-O-Si bands is seen to be centered around 970 cm\(^{-1}\) coming from Si-O-Si stretching vibrations of Q\(^2\) tetrahedra. It has been observed that the position of this band shifts to a lower frequency with increasing Ca/Si ratio due to progressive depolymerization of silicate chains.

The effect of aluminum on C-S-H gel structure was studied by Garcia et. al. by adding synthesized and dried C-S-H gel to a solution containing sodium hydroxide and aluminum nitrate \[60\]. The control C-S-H gel was synthesized with CaO/SiO\(_2\) ratio of 1.9 and C-A-S-H gel was synthesized by mixing C-S-H gel with a solution of SiO\(_2\)/Al\(_2\)O\(_3\) = 1 and Na\(_2\)O/SiO\(_2\) = 4. After 72 hours of mixing, the gel was filtered, and FTIR was performed which is given in Figure 2.11. FTIR of control C-S-H gel shows an intense band at 966 cm\(^{-1}\) which corresponds to asymmetric Si-O-Si stretching vibration (will be referred as the main
Figure 2.10: Mid-IR spectra of C-S-H samples with varying Ca/Si ratio compared with tobermorite and jennite (adopted from [89]).

band) from Q² units. In FTIR spectrum of C-A-S-H gel, the main band becomes broader which is attributed to the formation of Si-O-Al cross-links. The study has confirmed that the main band position shifts to higher wavenumber due to increasing cross-linking with Al substitution into the C-S-H structure (for a given Ca/Si ratio).

2.6.3 FTIR Characterization of (N,K)-A-S-H

FTIR has been used extensively to understand the structural evolution of (N,K)-A-S-H gels formed through alkali activation of fly ash [67][71][74][81][87]. Criado et. al. have used FTIR to understand the effect of activator solution (hydroxide vs. silicate) on the reaction mechanism of fly ash based geopolymer binders [84]. Figure 2.12 shows a time-dependant shift in the Si-O-T bond asymmetric stretching band in N-A-S-H gel formed in fly ash geopolymer binders activated with sodium hydroxide (N) solution and sodium silicate solution (W15, W50, and W84). In hydroxide activated binders (N), the main band position of the product first shifts to lower wave numbers and later shifts back to higher wave numbers indicating the
Figure 2.11: Mid-IR of control C-S-H gel (CaO/SiO$_2$ = 1.9), C-A-S-H gel (SiO$_2$/Al$_2$O$_3$ = 1 and Na$_2$O/SiO$_2$ = 4) showing the effect of Al on the Si-O-T asymmetric stretching peak position (adopted from [60]).
formation of two gels, one Al-rich gel which eventually transforms to Si-rich gel as Si/Al ratio increases. Formation of two gels was in consensus with the reaction model developed for alkali activation of fly ash binders [31, 61, 80].

FTIR is also often used as a quick method to validate synthesized gels. Figure 2.13 shows typical IR spectra of synthesized N-A-S-H gels of varying Si/Al ratio. The position of the main band in gel G1 (Si/Al = 1) is at 1007 cm\(^{-1}\) and in gel G2 (Si/Al = 2) is at 1020 cm\(^{-1}\). The position of main band in N-A-S-H gels (1000±5 cm\(^{-1}\)), shifts toward higher wavenumbers with increasing Si/Al ratio (decreasing Al content).

From the above discussion it can be seen that the FTIR is a powerful and versatile technique that can be used to monitor the structural evolution of (N,K)-A-S-H gel as well as C-(A)-S-H gel. Because of easy sample preparation and short collection times (unlike NMR), it has become an invaluable tool for not only quick characterization but also sophisticated structural analysis.
2.7 Reaction Mechanism in Geopolymer Cements:

Medium-calcium Binders

Geopolymer cements are formed as a result of the alkaline activation of precursors with intermediate/medium calcium content. Medium calcium blended precursors such as class F-fly ash and slag binders are activated with solutions of low alkalinity and cured at room temperature [9,10,12]. The cements are expected to have the highest potential for applications as the blended binders (fly ash + slag) provide a good synergy between mechanical strengths and durability [32,95].

The mechanism of geopolymer formation differs significantly in the presence of calcium and the exact mechanism controlling the process remains largely elusive. In many studies, it was observed that in binders of compositions similar to geopolymer cements, the presence of small amount of slag accelerates setting and gives a higher compressive strength [17,19,25,27].
In hydroxide activated binders, the initial rapid release of Ca into the solution can lead to supersaturation with respect to Ca(OH)$_2$ [96]. However, when appreciable amounts of silica is present in the activating solution, calcium complexes with silica rather than reaching supersaturation with respect to a hydroxide phase [97].

The presence of soluble calcium is known to significantly accelerate the hardening process [17,23]. The rate of hardening of various geopolymer pastes with and without calcium was monitored using the Proctor penetration method as well as S-wave UWR measurements [25,26]. Figure 2.14 shows the variation in S-wave reflection coefficient with time of fly ash geopolymers with varying slag replacement (0, 1, 5, 10, 15%) and fly ash with 1% of weight replaced with CaO. Cement paste of w/c = 0.33 (similar to the water-to-solids ratio of the geopolymer pastes used in this study) is also presented for comparison. In the case of fly ash geopolymer with 0% slag replacement (0S), S-wave reflection coefficient changes slowly and remains roughly around 0.6 even after 1000 minutes and it offers nearly zero resistance to proctor penetration until 300 minutes, indicating an extremely slow rate of hardening and microstructure development. In the mix with higher slag replacement, the onset of proctor penetration resistance as well as drop in S-wave reflection are observed to initiate within 5-15 minutes after the reaction initiation. As calcium is known to alter the hardening rate of geopolymer, the effects of slag as mentioned above can be assumed to be mainly due to calcium coming from slag (as the CaO content of class F fly ash used in this study is very low) [17,18]. The presence of calcium rapidly initiates the formation of products resulting in the accelerated setting.

UWR and Proctor penetration results indicate that the hardening is accelerated in the presence of soluble calcium. The accelerated setting observed in the presence of soluble calcium is hypothesized due to an enhanced aluminosilicate gel formation [17,23,27]. However, the exact mechanism remains unknown due to the complex interaction between calcium, silicate, and aluminate species. Therefore, there is a need for further investigation of CaO-Na$_2$O-SiO$_2$-Al$_2$O$_3$-H$_2$O systems, to provide a more detailed insight into the effect of
Figure 2.14: S-wave reflection coefficient vs. time plot for fly ash geopolymers with varying slag content (0, 1, 5, 10, 15%), fly ash replaced with 1% CaO and cement paste of w/c =0.33. The plot describes the change in the rate of hardening with the varying amount of slag. As the amount of slag increases, the rapid drop in R value gets initiated earlier indicating accelerated hardening [26].
C-S-H/C-A-S-H precipitation on the formation of geopolymer cements.

2.7.1 Co-existence of (N,K)-A-S-H and C-(A)-S-H

The binder in geopolymer cements is a complex mixture of products characteristic of alkali-activated slag binders (2-D C-S-H/C-A-S-H gels) and geopolymer binders (3-D (N,K)-A-S-H gel) \[20–22\]. Microprobe analysis of geopolymer cements, conducted by Davidovits et al. concluded that the bulk geopolymer composition is 4SiO$_2$.Al$_2$O$_3$.CaO.0.3K$_2$O ((Ca, K)-(Si-O-Al-O-Si-O-), with Si:Al =2) \[9, 12\]. However, in silicate-activated binders, several researchers reported that C-A-S-H, (C,(N,K))-A-S-H, and (N,K)-A-S-H co-exist as reaction products in fly ash/metakaolin geopolymers in the presence of any soluble form of calcium \[17–22,25–27,98\]. The percentage of different reaction products depends on various factors, such as alkalinity, temperature, a ratio of aluminosilicate to calcium sources, the rate of dissolution of ions from aluminosilicate, and calcium sources \[17,99–101\].

Recent studies on laboratory synthesized gels by Garcia-Lodeiro explored the compatibility between the C-A-S-H and N-A-S-H gels at different pH values \[98\]. Dried gels were added at 50/50 wt% in the water keeping pH>12 and were left to interact with each other over time. Figure 2.15 shows FTIR data of combined gels over time, and typical spectra for C-A-S-H and N-A-S-H have also been included. The main band for C-A-S-H is around 960 cm$^{-1}$ associated with asymmetrical stretching vibrations of Si-O-Si bonds. The main band for N-A-S-H gel is around 1060 cm$^{-1}$ which corresponds to asymmetrical stretching vibrations of Si-O-T (T - Si or Al) bonds. Upon mixing of two gels, the broader peak corresponding to N-A-S-H gel is seen to gradually diminish with time leaving peaks corresponding to C-A-S-H. Disintegration of N-A-S-H gel in the presence of calcium was associated with the strong polarizing effect of Ca$^{2+}$ to form Si-O-Ca bonds as discussed in the section 2.3 on the effect of cations. The polarizing effect of Ca$^{2+}$ distorts Si-O-Al bonds by inducing stress and ultimately rupturing Si-O-Al bonds. Based on detailed compositional analysis using TEM-EDS, XRD, and FTIR and from precipitation/solubility experiments, it was proposed that
Figure 2.15: FTIR study on the direct mixing of pre-synthesized C-A-S-H and N-A-S-H gels for up to 7 days at pH >12. FTIR of starting C-A-S-H and N-A-S-H gels are included as a reference (adopted from [7]).


In another study, when the Ca was added to synthesized N-A-S-H gel at pH<12, calcium ion partially replaced sodium ion in N-A-S-H gel structure by ion exchange mechanism until all available Ca was exhausted [46]. At low pH values, N-A-S-H behaved like a zeolite with calcium replacing sodium without affecting the 3D structure. At high pH values in the presence of sufficient calcium, C-A-S-H gel is favored over N-A-S-H gel formation. Based on the above studies, Gracia et al. proposed a model to define the stability of N-A-S-H gel as a function of pH and calcium content, shown in Figure 2.16 [46]. It should be remembered that
2.7.2 Challenges in Characterizing Co-existence of (N,K)-A-S-H and C-(A)-S-H

Due to a complex interaction between C-A-S-H and R-A-S-H (R - Na, K) gels, the phase characterization gets even more complicated for geopolymers cements (medium-calcium). Many different phases form as reaction products and their response to various characterization techniques is difficult to isolate as they are all amorphous. The co-existence of C-A-S-H and R-A-S-H in the microstructure has been studied by scanning electron microscopy, elemental analysis through energy dispersive spectroscopy (SEM-EDS), and XRD [20, 23, 26]. The presence of C-(A)S-H has been suggested by the synchrotron XRD results and by average elemental analysis on several points of a geopolymer microstructure [20, 22]. However, a segregated C-S-H phase in the microstructure is not found in SEM-EDS studies [22, 23]. It has been found to be always intermixed with geopolymer phases, possibly owing to a large interaction volume of EDS [22, 23, 26]. Differentiation between phases is difficult if they are smaller than interaction volume which is mostly the case in early age samples. Furthermore,
EDS study involves time-consuming sample preparation that can be avoided in an infrared spectroscopic method. However, the characterization and interpretation of the results are difficult even while using FTIR as the Si-O-T (T =Al, Si) vibrations from the initial ash, geopolymer product, unreacted slag, and calcium silicate hydrate yield an overlapping spectrum \cite{81}. As the development of geopolymers suitable for practical applications becomes important, there is an increasing need for rigorous characterization of binders often made from blends of fly ash-slag and metakaolin-slag.

2.8 Effects of Seeding in Portland Cement, Alkali-activated Binders, and Geopolymer Binders

2.8.1 Portland Cement and Alkali-activated Binders

The addition of nucleation seeds, particularly synthesized C-S-H, to understand the reaction mechanism in hydrated cement and alite is well-studied \cite{53, 102, 105}. Thomas et al. showed that the addition of pure, laboratory synthesized C-S-H accelerates the hydration of C\textsubscript{3}S, OPC, and alkali-activated slag binders by providing additional nucleation sites for the growth of hydration products \cite{53, 104}. In the case of C\textsubscript{3}S or Portland cement hydration, the increased rate of reaction in the presence of seed proved that the hydration reaction is nucleation and growth limited. It is hypothesized by Thomas et al. that the presence of external C-S-H seed increases the amount of early hydration by causing a product to form in the capillary pore space away from the C\textsubscript{3}S surfaces (Figure 2.17), where it does not interfere with the dissolution of C\textsubscript{3}S. The microstructure of the seeded samples (shown in Figure 2.18) is characterized by less porosity, higher gel density, and an apparently finer fundamental particle size \cite{53, 104}. The hydration of Portland cement is an exothermic
reaction. Therefore, the hydration kinetics can be accurately measured by measuring the heat evolution using isothermal calorimetry \[53, 104\].

Figure 2.17: Normal unseeded Portland cement pastes a few minutes (a) and few hours (b) after mixing. Paste with C-S-H seed a few minutes (c) and few hours (d) after mixing. Seeded samples show significantly lower capillary porosity and greater extent of early hydration (adopted from \[104\]).

The presence of external C-S-H seed affects several aspects of cement hydration kinetics: (1) The induction period was reduced because of the presence of a large number of C-S-H nuclei available for growth; (2) The amount of heat evolved is higher due to a greater amount of reaction product growing at the same time; (3) The total amount of hydration during the early nucleation and growth period is greater because the seed material allowed regions of hydration product to nucleate in the pore space, thus preventing the accretion of hydration product on the reacting cement particle, which could act as a diffusion barrier and slow down the dissolution \[104\].

Simulations of mature hydrated paste made with and without C-S-H seed have been studied by Thomas et al. The work clearly showed that the seeded paste has a more uniform distribution of C-S-H hydration product throughout the pore space and much less capillary porosity \[53, 104\]. Beaudoin et al., observed through NMR measurements that the composi-
tion of seed influences the extent of the polymerization of C-S-H that grows on the surface of the seeds. It was proposed by Beaudoin et al. that the product mimics the nanos- tructural features of the nucleation site. Therefore, the addition of nucleation seeds provides opportunities to tweak the composition and nanostructure of the product to satisfy the needs of the construction industry.

If the reaction were dissolution controlled, the presence of seed would have little or no effect on the kinetics. Therefore, measuring reaction kinetics through the addition of reaction products as an external seeds give key insights to elucidate fundamentals about reaction mechanisms.

2.8.2 Geopolymer Binders

At present, research on the effect of seeding agents on the formation of the aluminosilicate gel is very limited, and most studies are confined to hydroxide activated fly ash binders. Rees et al. examined the effect of nano Al₂O₃ seeds on the kinetics of a hydroxide-activated
aluminosilicate binder using in-situ infrared spectroscopy. They observed significant changes in the reaction kinetics and the structure of the final binder (Figure 2.19a) [106]. Hajimohammadi et al. studied the effect of nanoscale Al$_2$O$_3$, ZnO, and ZrO$_2$ on geopolymers made from geothermal silica-sodium aluminate-water using time-resolved and spatially resolved synchrotron infrared spectroscopy [107]. The seeding enhanced the dissolution of geothermal silica by inducing nucleation of aluminosilicate gel in the initially Al-rich reaction mixture [107]. Seeding is reported to improve both the early strength development and the long-term strength in geopolymer binders, and the gel was more homogenous (Figure 2.19b).
2.9 Research Significance

The present study will provide insights into the reaction mechanism of geopolymer cements, where C-S-H/C-A-S-H coexist with (N,K)-A-S-H gels through the addition of synthesized reaction products as external seeds. It is important to understand the reaction mechanism to determine the specific rate controlling step. The knowledge of which will provide greater control over the length of the induction period, setting, and workability. In Portland cements, the length of the induction period and setting time is often adjusted by using accelerators and retarders. However, most of the conventional admixtures do not work in geopolymers because of high pH and limited knowledge of rate controlling mechanism which is hindering the development of suitable admixtures. Therefore, the research output from this study will offer an improved understanding of the reaction mechanism in geopolymer cements and suggests a suitable admixture to accelerate or retard the reaction in geopolymer cements enabling engineers to control the workability, induction period, and setting of geopolymer cements, realizing its full potential and use in field applications. Verification of the effect of seeds on the reaction mechanism and the structure of gel has the potential to inspire new ways of controlling the properties of geopolymer cements and encourage a wider use of this new sustainable cement.
CHAPTER 3

MATERIALS AND METHODS

3.1 Raw Materials

Fly ash-slag blends of different slag replacements have been chosen to study the effect of calcium on the reaction mechanism of fly ash - slag geopolymer cements. Class-F fly ash (supplied by Boral Material Technologies) and slag (from Lafarge Corporation) were used as aluminosilicate sources. Two different activators were used in this study, namely, potassium hydroxide (from Fisher Scientific) and potassium silicate solution (from Fisher Scientific). Commercially supplied potassium silicate solution had the $\text{SiO}_2/\text{K}_2\text{O}$ of 3.92 (molar ratio), therefore, 1.9 M potassium hydroxide solution was added to make $\text{SiO}_2/\text{K}_2\text{O} = 1.25$ (molar ratio) and the total water/solids = 0.32. Geopolymer cements were synthesized by mixing fly ash and slag with the activator solution made from potassium hydroxide and potassium silicate solutions. Keeping the concentration of activating solution constant (2.3 M), fly ash was partially replaced by slag (25% and 15% by weight). The mixing procedure was as follows: the solid precursors were weighed, and the dry powders were mixed for 30 seconds. The activator solution was then added and mixed for another 3.5 minutes at the same speed. It was observed that the geopolymer mixes were greatly influenced by the ambient temperature and the shear rate and cured at ambient temperature in a closed container. To minimize the effects of temperature, the activator and precursors were stored in a temperature-controlled room at $21\pm 2 ^\circ\text{C}$, 24 h prior to the mixing process. To minimize the effects of the shear rate, a constant amount of material was mixed. The oxide composition of raw materials as obtained from X-ray fluorescence (XRF) data is given in Table 3.1.
Table 3.1: Composition of raw materials (weight in %)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Fly ash (weight in %)</th>
<th>Slag (weight in %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ (Si)</td>
<td>60.17 (28.1)</td>
<td>35.7 (16.7)</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (Al)</td>
<td>21.91 (11.6)</td>
<td>11.21 (5.9)</td>
</tr>
<tr>
<td>CaO (Ca)</td>
<td>1.81 (1.3)</td>
<td>39.4 (28.2)</td>
</tr>
<tr>
<td>Na$_2$O (Na)</td>
<td>0.81 (0.6)</td>
<td>0.26 (0.2)</td>
</tr>
<tr>
<td>K$_2$O (K)</td>
<td>2.13 (1.8)</td>
<td>0.48 (0.4)</td>
</tr>
<tr>
<td>MgO (Mg)</td>
<td>1.28 (0.8)</td>
<td>10.74 (6.5)</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ (Fe)</td>
<td>7.57 (5.3)</td>
<td>0.42 (0.3)</td>
</tr>
<tr>
<td>SO$_3$ (S)</td>
<td>0.17 (0.1)</td>
<td>0.58 (0.2)</td>
</tr>
</tbody>
</table>

3.2 X-ray diffraction (XRD)

X-ray diffractograms were recorded on a Siemens-Bruker D 5000 using CuK$_\alpha$ radiation at a voltage of 40 kV and current of 30 mA. Specimens were scanned from 5° to 70° $2\theta$ at 0.02° $2\theta$ steps and stepped at the rate of 1° min$^{-1}$. The x-ray diffraction patterns of raw materials are presented in Figure 3.1. Fly ash spectrum shows the main peaks of quartz, mullite, magnetite, and hematite. The broad amorphous hump in the XRD pattern, which is characteristic of fly ash, is observed between 20° to 40° $2\theta$. Slag is an amorphous glass, as evident from its XRD pattern with a hump centered at 30° $2\theta$. The overall Si/Al ratio of fly ash is 2.33 (From Table 3.1). But, only the Si/Al ratio of amorphous aluminosilicate glass is of importance for the geopolymerization. So, Rietveld analysis was done on fly ash sample to estimate the phase abundance and calculate the Si/Al ratio of glass phase.

3.3 Rietveld

Rietveld refinement with XRD data was used to obtain quantitative phase abundance of fly ash. Rutile of 15% by weight (from Sigma-Aldrich) was used as an internal standard to enable the calculations of the mineral and amorphous phase content. Rutile obtained
Figure 3.1: XRD pattern of raw materials (fly ash and slag) where Q = Quartz, Mu = Mullite, Ma = Maghemite, and H = Hematite. Both raw materials show broad amorphous humps. The main crystalline phases observed in fly ash are quartz, mullite, maghemite, and hematite.

from the company had traces of anatase (7.84% by weight), a low-temperature polymorph of rutile. So, the rutile was heat-treated in an oven at 1000°C for 12h to convert the anatase back into rutile. Diffraction pattern of fly ash for Rietveld refinement was collected from 15° to 70° at a step size of 0.02°2θ steps with a scan rate of 0.25° per min. The diffraction pattern given in Figure 3.2 confirmed the absence of anatase from the internal standard. Jade automated phase identification software was used to analyze the diffraction patterns and Rietveld refinement was conducted using the JADE software with a psuedo-Voigt function. Rietveld refinement provided the wt% of the crystalline phases as well as the wt.% of
amorphous fraction as given in Table 3.2. The elemental composition of amorphous phase is given in Table 3.3. The amount of vitreous elements is calculated using Eqn. 3.1

\[
\begin{align*}
[S\text{i}]_{\text{amorphous}} &= [S\text{i}]_{\text{total}} - [S\text{i}]_{\text{Quartz}} - [S\text{i}]_{\text{Mullite}} \\
[Al]_{\text{amorphous}} &= [Al]_{\text{total}} - [Al]_{\text{Mullite}} \\
[Fe]_{\text{amorphous}} &= [Fe]_{\text{total}} - [Fe]_{\text{Maghemite}} - [Fe]_{\text{Hematite}}
\end{align*}
\] (3.1a, b, c)

Table 3.2: Quantitative mineral composition of fly ash by X-ray diffraction Rietveld refinement

<table>
<thead>
<tr>
<th>Phase</th>
<th>Weight%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>22.3</td>
</tr>
<tr>
<td>Mullite</td>
<td>15.1</td>
</tr>
<tr>
<td>Hematite</td>
<td>1.0</td>
</tr>
<tr>
<td>Maghemite</td>
<td>5.2</td>
</tr>
<tr>
<td>Amorphous</td>
<td>54.9</td>
</tr>
</tbody>
</table>
The total amorphous component as determined by quantitative analysis is 56.4%. Quantitative XRD does not include phases containing elements such as Mg, Na, K, Ca, and S which may be present as crystalline phases in quantities that are most likely below the detection limits of XRD. Comprehensive phase characterization of class F fly ash using multispectral image analysis has detected the presence of Mg in the form of crystalline compound periclase and elements like K, Na, and Ca in the amorphous aluminosilicates \[108\]. It has been assumed that the elements such as S, Mg are present in the form of minor crystalline compounds that are included are a part of the background pattern and Na, K, and Ca are a part of amorphous glass phase. Therefore, wt.% of MgO (1.28) and SO\(_3\) (0.17) are subtracted from the calculated amorphous content of 56.4 wt.% to obtain the true amorphous content of 54.9 wt.%.

Quantitative XRD along with XRF has determined that the amount of amorphous aluminosilicate material that is available for geopolymerization is approximately 54.9 wt.% and Si/Al ratio of amorphous glass to be 2.59 (higher than the bulk ratio).

Table 3.3: Elemental composition of amorphous phase as determined by quantitative XRD

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Element</th>
<th>Weight%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash</td>
<td>Si</td>
<td>15.7</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>Si/Al (weight)</td>
<td>2.69</td>
</tr>
<tr>
<td></td>
<td>Si/Al (molar)</td>
<td>2.59</td>
</tr>
<tr>
<td>Slag</td>
<td>Si</td>
<td>16.7</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>Si/Al (weight)</td>
<td>2.81</td>
</tr>
<tr>
<td></td>
<td>Si/Al (molar)</td>
<td>2.70</td>
</tr>
</tbody>
</table>
3.4 Fourier Transform Infrared Spectroscopy (FTIR)

IR spectra used in chapter 4 were collected using Thermo Nicolet Nexus 670 Fourier transform infrared spectrophotometer in absorption mode. Golden gate attenuated total reflectance accessory (ATR) with diamond crystal was used. The frequency range used was 2000 to 700 cm\(^{-1}\) at a resolution of 2 cm\(^{-1}\). Data obtained from this machine are always presented in absorption mode.

IR spectra used in chapter 6, chapter 5, chapter 7, chapter 8 were collected on Frontier Fourier transform infrared spectrophotometer from Perkin Elmer was used in absorption mode to acquire an infrared spectrum of samples at various ages. A golden gate attenuated total reflectance accessory (ATR) with diamond crystal was used. The frequency range was 2000 to 700 cm\(^{-1}\) at a resolution of 2 cm\(^{-1}\). Each spectrum was an average of 32 scans. FTIR spectra for raw materials are given in Figure 4.5. IR spectra of these blends are obtained by proportionally adding an individual spectrum of raw materials (Figure 4.5). Spectra are analyzed for an asymmetric stretching vibration of a Si-O-T bond, which lies between 1100-900 cm\(^{-1}\). Hereafter, the Si-O-T asymmetric stretching vibration band will be referred to as the main band.

The position of the main band in fly ash appears at 1037 cm\(^{-1}\). The main band of slag is broad and appears between 850 and 930 cm\(^{-1}\). The difference in the position of the main band in both materials is accounted for by the difference in the nature of aluminosilicate glass. The vibration spectra of vitreous or amorphous materials, unlike crystalline materials, are very broad and imprecisely defined as evident in Figure 4.5. In addition to the main band, fly ash spectrum also shows peaks at 795 cm\(^{-1}\) and 777 cm\(^{-1}\) which are attributed to quartz [81]. Slag spectrum has another peak at 1487 cm\(^{-1}\) which corresponds to an asymmetric C-O stretch. The position of main band in the spectrum is at 1020 cm\(^{-1}\) with remaining peaks very similar to that of the fly ash spectrum. Although slag spectrum shows carbonation, when fly ash and slag are added proportionally to obtain net spectra,
carbonation peaks are insignificant. This is believed to be due to the small intensity of carbonation peaks relative to the main band. All bands in fly ash and slag are summarized in Table 3.4.

Table 3.4: FTIR peak assignments in raw materials.

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Frequency (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash</td>
<td>777 &amp; 795</td>
<td>Quartz</td>
</tr>
<tr>
<td></td>
<td>1037</td>
<td>asymmetric Si-O</td>
</tr>
<tr>
<td>Slag</td>
<td>850-930</td>
<td>symmetric Si-O</td>
</tr>
<tr>
<td></td>
<td>1487</td>
<td>asymmetric C-O (CO(_3^{2-}))</td>
</tr>
</tbody>
</table>
3.5 Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS)

Microstructural development was monitored by using a JEOL JSM-6060 LV Scanning Electron Microscope, equipped with an energy dispersive X-ray spectroscopy (SEM-EDS). The fractured surface of different specimens at various ages was studied in a secondary electron mode (SE). Specimens were treated with 50/50 (by vol.) of methanol-acetone mixture to stop the reaction and then stored/dried in a vacuum desiccator until tested. The specimen surfaces were sputter coated with gold-palladium prior to imaging.

Quantitative EDS analysis was performed in order to study the chemical makeup of reaction products formed in the system. Microanalysis and quantitative EDS was performed in a backscattered mode (BSE). The samples were epoxy impregnated and polished prior to testing. After epoxy impregnation, the samples were ground using SiC papers of various grit sizes, 21.8 µm, 15.3 µm, 8.4 µm, and 5 µm. A glycol-based lubricant was used for polishing. For the final steps involving polishing, 3 µm and 1 µm diamond lapping films were used followed by polishing using a 0.25 µm diamond paste on a cloth until a glass-like finish was achieved. The samples were ultrasonically cleaned in isopropyl alcohol after each round of polishing to remove any debris. Microanalysis was performed at an accelerating voltage of 7 kV to minimize the interaction volume for X-ray generation, as prescribed by Lloyd et al. [66].

3.6 Calorimetry

The reaction progress of geopolymer cements was studied using Thermometric 3114/3236 TAM Air Isothermal Conduction Calorimeter (ICC) at 22 ºC. All the raw materials and the activator solution were stored at 22 ºC before mixing. Solids were mixed with the activator solution outside the instrument and the paste was then transferred to the instrument within
3-4 minutes after the mixing. Due to the heat generated from friction while placing the samples inside the instrument, first 45 minutes of data was ignored.

According to a previous study on fly ash-slag cements, it was observed that the rapid hardening occurs within 60 minutes of mixing, which is not captured by the calorimetric curves [26]. Unlike with Portland cements, isothermal calorimetry does not capture all the changes that are occurring in geopolymer cements. Thus, to accurately capture the reaction kinetics in these binders, this study employed two different methods: the Proctor penetration method and the ultrasonic wave reflection method. In previous studies, several researchers measured the setting times of metakaolin, fly ash- or slag-based geopolymers using a Vicat penetrating needle (ASTM C191) [19,109–114]. Although some useful information, such as the initial and final set times can be estimated, one serious drawback of using a Vicat needle is that it does not indicate any change in penetration prior to the initial set, and it does not provide any information about the hardening rate over time [115].

### 3.7 Proctor Penetration Method

As mentioned previously, the Vicat test provides only an estimate of the initial and final setting times. Setting times are estimated by measuring the penetration depth of a single needle while maintaining a constant load. In contrast, the Proctor test, initially developed for cement mortar, measures the resistance offered by the medium against a penetrating needle. Cement mortar does not provide any resistance to penetration immediately following the mixing. As hydration continues and the microstructure develops, resistance to the penetrating needle increases, and this helps in monitoring the rate of hardening/strength gain. ASTM C403 describes the Proctor penetration test method for cement mortars [116]. This method has been extended to study the hardening behavior of cement pastes with slight modifications. It has proven to be successful in determining the rate of hardening along with the determination of initial and final set values in Portland cements [115,117,118].
The method is based on measuring the resistance against a penetrating needle as the medium transforms from a liquid to a solid state. The same procedure is applied in order to study the hardening rate of geopolymeric binders, in spite of the differences in chemistry and underlying chemical reactions responsible for its hardening. Immediately after mixing, geopolymer paste was placed in a plastic container and covered with a moist towel to prevent water evaporation. The penetration resistance was measured by an Instron 4500 load frame. Six different needles of varying cross-sections (645 mm$^2$, 323 mm$^2$, 161 mm$^2$, 65 mm$^2$, 32 mm$^2$ and 16 mm$^2$) are used as needed. Measurements were initiated using the largest needle when the paste was liquid, and needles of progressively smaller cross sections were used as the paste hardens, so as to maintain a penetration depth of 25 mm (1-inch) in 10 ± 2 seconds (ASTM C 403) without exceeding the capacity of the load cell. The penetration resistance offered by the paste was calculated by dividing the resistance load with the area of the needle used for penetration.

3.8 Shear-wave Ultrasonic Wave Reflection Method

(S-wave UWR)

The inability of penetration-based methods to continuously monitor the hardening process has prompted researchers to study the use of acoustic methods. Non-destructive acoustic methods, including the ultrasonic wave reflection method (UWR), have been used extensively in the past in order to estimate the elastic properties of concrete. Recently, the process of monitoring the setting and hardening processes of cementitious materials using the UWR has become important [118][123].

These methods are based on the principle that shear waves cannot pass through fluids but can only transmit through solids. According to the wave theory, when a wave is incident at the boundary between two materials, some of it is reflected and some of it is transmitted. The amount of shear wave energy reflected at the boundary between a buffer material and
paste depends on the interconnectivity of the solid to transmit shear waves. When the paste is in a liquid state, the entire shear wave energy is reflected at the interface between the buffer material and the paste. Thus, the reflection coefficient is one. The transition of the paste from a liquid to a solid changes its acoustic impedance due to an increase in the interconnectivity of the solid within the paste. As more and more solids form, the ability of the paste to transmit shear waves increases, thus decreasing the reflection coefficient. Therefore, changes in the paste as a function of time can be monitored with S-wave UWR using a buffer material of constant acoustic impedance. Several buffer materials including steel and PMMA were used throughout the literature [121, 123]. However, the sensitivity of the measurements is maximized when the difference between the acoustic impedance of the buffer and the test material is small (High Impact Polystyrene in the case of cement paste) [122, 124].

Figure 3.4: Schematic diagram of UWR set up showing transducers, pulser and receiver units based on Chung et al. [124].

Initiation of the setting/hardening process in systems like cement pastes happens when the solid phases reach the percolation threshold. It has been established, in the case of cement
paste, that the reflection loss measured from UWR relates closely to the connectivity of the solid phases [123]. The amount of shear wave reflection decreases as the connectivity of solid increases [119]. A few studies of the wave-reflection method on cement mortars and cement pastes have concluded that the wave reflection method is very sensitive to the setting and hardening of cementitious materials and can be used in monitoring the hydration process during the early age of microstructural development [119,123]. Similar studies on cement pastes by Chung et al. have shown that the onset of early stiffening as measured from S-wave UWR, Proctor penetration resistance, and temperature rise from calorimetric experiment, correlate very well [118]. Numerical simulations have shown that the setting time calculated based on the reflection loss of shear waves match very well with the percolation threshold of the solid phase in the cement paste [119,125]. Chung et al. have also shown that the UWR is sensitive to study the sedimentation and flocculation of non-hydrating systems [126]. UWR was used to study the flocculation of cement particles immediately after mixing (before the initial setting). In the research presented here, the method of S-wave UWR is extended to monitor the hardening rate of geopolymer at an early age. In spite of the differences in the reaction kinetics that govern the formation of C-S-H (in cement paste) and aluminosilicate gel (in geopolymers), studies have shown that the physical process of setting may be regarded similarly and is governed by the percolation of solid phases [26].

In the current study, the reflection coefficient is measured by using a contact type 2.25 MHz S-wave transducer as shown schematically in Figure 3.4. Immediately after mixing, the geopolymer paste is poured into a high impact polystyrene (HIPS) container approximately sized, 50 mm x 60 mm x 50 mm (thickness 6.25 mm) and covered to prevent the evaporation of water. HIPS acts as a buffer between the transducer attached to the bottom of the container and the specimen. The transducer is connected to a pulser/receiver unit. Lab View is used to control, collect, and process the data. The rate of stiffening is monitored for the first 24 hours or until the specimen is completely debonded from the buffer material. Debonding creates an air pocket between the buffer and the specimen, which prevents the
further measurement and consequently, the acquisition of meaningful information. In order to avoid confusion, this part of the data is truncated from the UWR graphs presented in this chapter. Further details of this method can be found elsewhere [127].
CHAPTER 4

UNDERSTANDING STRUCTURAL EVOLUTION OF ALKALI ACTIVATED ALUMINOSILICATES

This chapter has already been published as “Co-existence of aluminosilicate and calcium silicate gel characterized through selective dissolution and FTIR spectral subtraction” in Cement and Concrete Research, Vol. 70, pg: 39-49, 2015

The primary goal of the present chapter is to verify the first hypothesis by quantifying the amount of C-S-H and K-A-S-H forming in the binder during early stages of hardening. A protocol will be developed to effectively characterize the evolution of reaction products with time when C-(A)-S-H and K-A-S-H co-exist in the binder by using selective dissolution techniques and Fourier transform infrared (FTIR) spectral subtraction corroborated through Scanning electron microscopy - Energy dispersive spectroscopy (SEM-EDS) results.

4.1 Background

FTIR is used extensively to characterize synthesized geopolymer gel as well as to monitor the reaction progress of alkali activated fly ash, fly ash-slag, metakaolin, and metakaolin-slag activated geopolymers [67,71,74,81,87]. However, characterization and interpretation of the results in the case of complicated phase assemblage is difficult as the Si-O-T (T =Al, Si) vibrations from the aluminosilicate raw material, geopolymer product, and calcium silicate hydrate yield an overlapping spectrum [81]. Similar issue has been faced by researchers while characterizing Portland cements and their reaction products using XRD technique [128,129]. Mineral phases in Portland cement and clinker have overlapping peaks in XRD that
makes the characterization difficult. So, cement and clinker samples have been traditionally subjected to various selective dissolution techniques to remove certain phases and amplify the response from the others for a better characterization. Salicylic acid-methanol (SAM) extraction initially developed by Takashima has gained much popularity in dissolving calcium silicate phases and is widely adopted for cement and clinker research [128–130]. Later, this method has been applied more extensively to other materials like cement-slag, cement-fly ash blends, alkali-activated slag binders, and synthesized C-S-H gels to determine reaction degree and the nature of the reaction products [131–134]. However, when SAM extraction was performed on a mixture of synthesized N-A-S-H and C-S-H, FTIR characterization failed to differentiate between them leading to inconclusive results [82].

Several researchers have also used 1:20 HCl to separate geopolymers and zeolites from unreacted fly ash to determine the reaction degree of fly ash, and 1:9 HCl solution followed by Na$_2$CO$_3$ to determine the reaction degree of metakaolin [81–83,135]. However, the presence of calcium complicates the response of alkali activated binders (due to a complex combination of products) to HCl extraction. Very few studies have used both SAM and HCl extractions on a complex geopolymer binder prepared from precursors with a soluble form of calcium to characterize reaction products [83]. As the development of geopolymers suitable for practical applications becomes important, there is an increasing need for rigorous characterization of binders often made from blends of fly ash-slag and metakaolin-slag. The present study elucidates the importance of using SAM and HCl extractions together to characterize geopolymers formed in a fly ash-slag bended binders through infrared spectroscopic studies. The method developed as a part of this research can be extended to other blended binders where geopolymer forms in the presence of a soluble calcium source.

Three mix compositions are selected to understand the structural evolution of geopolymer in the presence of external calcium, and hereafter, the mix with 25% slag-75% fly ash will be referred as high slag sample (HS), the mix with 15% slag-85% fly ash will be referred as low slag sample (LS), and the mix with 100% fly ash will be referred as zero slag sample (0S).
Geopolymer was synthesized by mixing fly ash and slag with the activator solution made from potassium hydroxide (Fisher Scientific) and potassium silicate (produced by Pfaltz and Bauer, and supplied by Fisher Scientific) of SiO$_2$/$K_2$O = 1.25 (water/solids = 0.32). Samples were mixed following the procedure described in chapter 3. Samples at various ages were collected and powdered by treating them with 50/50 (by vol.) of methanol-acetone mixture to stop the reaction and then stored/dried in a vacuum desiccator until tested. Selective dissolution extractions followed by characterization using FTIR, XRD, and SEM were all performed on dried-powdered samples within 24 hr after they were treated with methanol-acetone.

Physical, chemical and microstructural characterizations such as compressive strength test, calorimetry, SEM, XRD, selective dissolution treatments, and FTIR were performed on the high slag (HS) mixture to monitor reaction progress and evolution of reaction products. Samples were analyzed at three different ages, 1 hr, 24 hrs, and 7 days. Furthermore, compressive strength of 0S, LS, and HS samples at 7 days was measured and reported as an average and standard deviation of three measurements on 25.4 mm cubes. The strength of 0S, LS, and HS sample at 7 days are 1.1 MPa, 13.9±1.0 MPa and 28.8±3.3 MPa, respectively. The significant difference in the strength could be possibly due to differences in the extent of geopolymer product formation or the chemical make-up of the reaction products formed.

### 4.2 Selective Dissolution Techniques

Salicylic acid/methanol (SAM) extraction was performed on samples following the procedure described by Stutzman [128]. The attack dissolves calcium silicate hydrate but is not supposed to dissolve unreacted fly ash, slag or geopolymers [82, 136]. For SAM extraction, 1 g of powdered geopolymer sample was added to a solution containing 4 grams of salicylic acid mixed in 60 ml of methanol [128]. The mixture was stirred for 2 hrs and the suspension was vacuum filtered using a Buchner funnel and a Whatman filter (pore size of 0.2μm).
Insoluble residue was washed with methanol and stored in vacuum desiccator until analysis. IR spectra of these specimens were collected to observe changes after the extraction.

In another extraction method, finely ground powder samples were treated with 1:20 HCl (by volume). Acid attack provokes dissolution of the chief reaction products of alkali activated fly ash (aluminosilicate gel and zeolites) leaving behind the unreacted ash as insoluble residue \[81,135\]. However, the acid extraction also decomposes calcium silicate hydrate by removing \(\text{Ca}^{2+}\) and leaving silica gel behind \[129\]. As described elsewhere, the experimental procedure consists of adding 1g of activated fly ash (fly ash and slag in this case) to a beaker containing 250ml of HCl (1:20) \[81\]. The mixture was stirred for 3 hrs followed by filtration. Insoluble residue was washed with de-ionized water several times to a neutral pH, dried at 100°C for 24 hrs and then stored in a vacuum desiccator till the analysis is done. FTIR spectra before and after chemical extractions were analyzed and spectral manipulations including addition and subtraction were performed using OMNIC software. Selective dissolutions were repeated 3 times on all the samples. The effect of SAM and HCl extractions on raw materials like fly ash and slag has been verified before studying the effect of extraction on the activated fly ash-slag samples. FTIR characterization of 100% slag and fly ash before and after selective dissolutions is presented in Figure 4.1 and Figure 4.2 respectively.

Slag

The effect of SAM on slag is debatable \[132,133\]. This topic has been studied widely in the past. SAM is reported to partly dissolve slag and its reaction products such as hydrotalcite and calcium silicate hydrate \[132,133\]. In this study, a weight loss of approximately 1.85% was observed when slag was treated with SAM. The IR spectrum before (peak position: 850-930 cm\(^{-1}\)) and after (peak position: 850-926 cm\(^{-1}\)) treatment are very similar to each other as evident from Figure 4.1. Considering the small weight loss as well as the negligible shift in the peak position, the treatment is considered to be suitable for selectively dissolving certain phases and enriching the remaining phases for characterization. Similar treatments
Figure 4.1: IR spectrum of the raw material and the insoluble residue after SAM treatment on slag. The number in parentheses denotes the peak position in cm$^{-1}$.

using other chemicals such as EDTA has shown that such chemical treatments enrich the response of undissolved phases for characterization using methods like NMR \[133,134\].

Slag dissolves completely when treated with HCl (1:20) solution. The dissolution of slag is considered congruent in this study as seen in cement blends and alkali activated slag binders from other studies \[137,138\]. Therefore, unreacted slag at various ages in fly ash-slag geopolymer responds to SAM and HCl extractions in the same way as 100% slag would respond.
Fly ash

The effect of HCl and SAM on fly ash was studied by few researchers and is not quite as debatable as that of slag \cite{139,140}. In this study, fly ash has been subjected to SAM and HCl treatments and the weights dissolved in each of these treatments is presented in Table 4.1. The amount of fly ash dissolved in SAM treatment is less than 1% which matches with the existing literature \cite{140,141}. The amount of fly ash dissolved after HCl treatment is also very small (~ 3%). Insoluble residue of fly ash after SAM treatment was further treated with HCl (dissolved in HCl after SAM treatment). The amount of fly ash dissolved in both of these treatments combined is also very small (~ 3%).

Table 4.1: Analysis of selective dissolution treatments presented as dissolved % by the initial mass.

<table>
<thead>
<tr>
<th></th>
<th>Dissolved in SAM</th>
<th>Dissolved in HCl</th>
<th>% IR</th>
<th>Dissolved in HCl after SAM treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA</td>
<td>0.97</td>
<td>3.14</td>
<td>96.86</td>
<td>2.70</td>
</tr>
<tr>
<td>Slag</td>
<td>1.85</td>
<td>100.00</td>
<td>0.00</td>
<td>98.15</td>
</tr>
</tbody>
</table>

IR: Insoluble Residue

FTIR spectrum of fly ash before and after treatments (SAM, HCl) is given in Figure 4.2. The position of main band in fly ash remains at 1037 cm\(^{-1}\) after SAM treatment implying that the effect of this treatment is minimal. The fly ash residue obtained after SAM extraction was further treated with HCl (HCl residue after SAM) and it was observed that the effect is minimal as well (small weight loss and no change in the peak position). However, position of the main band (1037 cm\(^{-1}\)) changes to a higher wavenumber (1055 cm\(^{-1}\)) after HCl treatment. This implies dissolution of certain phases from fly ash which matches with the observations of Sarbak et al \cite{139}. Sarbak et al. have concluded that the treatment of fly ash with 2.5 M HCl solution changed its surface area and affected the microstructure sig-
nificantly due to dissolution of aluminum-rich components [139]. Owing to the small weight loss, the effect is considered minimal for fly ash.

The dissolution of fly ash is considered congruent in geopolymers after the early release of Al-rich species [106]. In fly ash-slag geopolymers, the dissolved Al species will most probably be consumed during the precipitation of C-A-S-H. This prevents Al species in the solution from retarding the further ash dissolution which accelerates the onset of congruent ash dissolution [106]. Also, at early ages when the solution has high pH (above 13) and the solution is under-saturated, dissolution of synthetic (calcium)aluminosilicate glasses (including compositions similar to fly ash and slag) is known to be congruent [138]. Thus, the response of both raw materials is assumed to be congruent to SAM/HCl attack at all ages.

4.3 Microstructural Characterization using SEM

Figure 4.3 shows SEM micrographs of fly ash-based geopolymers with and without slag replacement. HS and LS represent two extreme cases of microstructural development and are chosen for SEM characterization in an effort to understand the effects of slag and are also compared with LS sample. Figures 4.3a and 4.3b show the micrographs of 0S and HS, respectively, at 3 hours after mixing. As the figures indicate, the difference between the two microstructures is large. Within 3 hours, HS show clear evidence of reaction product formation on fly ash spheres whereas 0S does not show any sign of product formation. It appears, from Figure 4.3a, that there was minimal dissolution of the fly ash spheres in 0S by 3 hours. The microstructure seems to resemble a fractured sample of densely-packed fly ash spheres without any interconnectivity. This is not surprising based on the calorimetry and UWR results reported. In the case of HS (Figure 4.3b), the particle morphology of fly ash spheres did not change markedly, but they seemed to be connected by a gel-like network. The presence of slag enhances product formation, resulting in a gel-like network with increased interconnectivity. The difference in microstructures further explains the reason behind a
Figure 4.2: IR spectrum of the raw material and the insoluble residue of fly ash after the SAM treatment, HCl treatment, and HCl treatment on insoluble residue after SAM treatment. The number in parentheses denotes the peak position in cm⁻¹.
faster hardening rate of HS compared to 0S.

Figures 4.3c and 4.3d and Figures 4.3e and 4.3f show microstructure of 0S and HS at 24 hours and 7 days, respectively. In the case of Geo 15s, the microstructure developed continuously with age, and by 7 days, it seemed to be quite dense. As shown in Figure 4.3f, the fly ash spheres are densely covered with product, and there is no clear distinction between them. In the case of 0S, the microstructure development at 24 hours (Figure 4.3c), is comparable to that of HS at 3 hours (Figure 4.3b). However, compared to that of HS, the final microstructure shows less product formed on the fly ash surface even after 7 days. The amount of product formation clearly explains the difference in the strength of 0S and HS samples.

The SEM micrographs of HS sample at 1 hr shows fly ash spheres covered with small amount of products and very little connectivity (Figure 4.3). The nature of the microstructure could be described similarly at 24 hrs (Figure 4.3). As the reaction proceeds, at 7 days, a greater amount of product was seen that covered most of the fly ash particles completely. This implies greater connectivity between the fly ash spheres and hence greater load carrying capacity (compressive strength). Microstructure is seen to resemble the fly ash geopolymers made in the presence of Ca by other researchers [24, 26]. Microstructure of LS sample at 7 days is similar to that of the HS sample at 7 days. A slight difference can be observed, if the microstructure of LS sample is studied carefully. The reaction product in many places seemed to be almost transparent (possibly due to relatively thin layer of product formed) and the fly ash spheres underneath are visible. However, this difference between the two micrographs is qualitative and difference in 7 days compressive strength between these samples cannot be explained with confidence.
Figure 4.3: Secondary electron images of a: 0S 1hr, b: 0S 24 hr, c: 0S 7days, d: HS 1hr, e: HS 24hr, f: HS 7days, g: LS 24hr, h: LS 7days
4.4 Monitoring Reaction Progress using Calorimetry

Figure 4.4 presents the heat evolution of the 0S, LS, and HS samples at 22°C which compares well with the published literature on alkali activated slag binders, metakaolin-slag/CH blends, and fly ash blends [16, 19, 27, 100]. Calorimetric curves of HS and LS samples have similar patterns and 0S sample does not show any heat evolution corroborating the results found in previous sections. In LS and HS samples, there is an initial peak followed by an induction period and a prominent second peak. Apart from the heat generated from friction during placement of the ampoules into the instrument, the initial peak also corresponds to the particle wetting, initiation of slag dissolution, complexation of silicate units with calcium, sodium, and aluminum [16, 19, 27, 100]. From a previous study by the authors on a similar binder, it was noted that this peak also corresponds to the precipitation of initial reaction products which caused rapid hardening [26]. It has been hypothesized that the precipitation of C-S-H causes initiation and acceleration of hardening during first 60-80 minutes [17, 23, 26]. This hypothesis will be verified further through FTIR study. The second main peak (acceleration and deceleration) corresponds to the precipitation of the reaction products, which was hypothesized to be both geopolymer and C-S-H. A less prominent third peak is seen at a later age. These observations are common for both HS and LS mixes. The difference between LS and HS samples is the time at which the second peak and third peak appears, as well as, the area under the curves. The time at which the second peak appears depends heavily on the amount of slag in the binder [19, 26]. Early appearance of the second peak might indicate faster reaction in HS sample compared to LS sample. The area under the curve is greater in HS than LS sample indicating greater reaction degree in HS sample. This could explain the difference in 7 day compressive strength.
Figure 4.4: Heat released from HS and LS samples at 22°C.
4.5 Monitoring Reaction Progress using Infrared spectroscopy

Spectra of HS and LS blends are obtained by proportionally adding the individual spectra of raw materials (Figure 4.5). The position of the main band in LS spectra is at 1030 cm$^{-1}$ with positions of remaining peaks very similar to that of the fly ash spectrum. The position of main band in HS spectra is at 1020 cm$^{-1}$ with remaining peaks very similar to that of the fly ash spectrum. Although, slag spectrum shows carbonation, when fly ash and slag are added proportionally to obtain LS and HS spectrum, carbonation peaks are insignificant. This is believed to be only due to the small intensity of carbonation peaks relative to the main band.

The sample with 0% slag has shown a very low amount of reaction degree. So, LS and HS samples were chosen for further studies using FTIR to understand the structural evolution. Infrared spectroscopy has been used to monitor the evolution of reaction products with time in HS and LS samples and presented in Figure 4.6. The position of the main band (at 1020 cm$^{-1}$ and 1030 cm$^{-1}$ in HS and LS respectively) associated with Si-O-T asymmetric stretching vibration in the raw material moves to a lower frequency (to 969 cm$^{-1}$ and 965 cm$^{-1}$ respectively) in 7 days. The band shift to lower frequencies is known to be due to the precipitation of geopolymer with an increased substitution of Si with Al [81,135,142]. Si-O-T angle reduces when Al substitutes for Si and bond force constant of Si-O-Al bond is smaller than that of the Si-O-Si bond which shifts the main band to a lower frequency [81,142]. The exact position of this band depends on the Al/Si ratio of the product [81]. The peaks at 794 cm$^{-1}$ and 774 cm$^{-1}$ belong to quartz present in the remaining unreacted fly ash. The IR spectra of samples at various ages show bands corresponding to the asymmetric stretching of CO$_3^{2-}$ around 1380-1470 cm$^{-1}$ as an evidence of carbonation (also observed from XRD as shown in Figure 4.7). The scissoring bending mode of water also appears at 1638 cm$^{-1}$ in
Figure 4.5: FTIR spectra of raw materials. FA: Fly ash, slag, LS: 85% FA+ 15% slag, and HS: 75% FA+25% slag. The number in parentheses denotes the peak position in cm$^{-1}$. 

Figure 4.5: FTIR spectra of raw materials. FA: Fly ash, slag, LS: 85% FA+ 15% slag, and HS: 75% FA+25% slag. The number in parentheses denotes the peak position in cm$^{-1}$.
all IR spectra [143].

As mentioned above, the position of the main bands in both the HS and LS samples are comparable at 7 days. This does not explain the differences seen between the two types of samples from calorimetric curve and compressive strength results. Furthermore, it is evident from the SEM images presented earlier and elsewhere that the reaction of fly ash and slag is not complete even after 7 days [26]. Therefore, the main band of the sample at all ages is broad encompassing the response of unreacted fly ash, slag, aluminosilicate gel and C-S-H, and differentiating them from each other is not quite straightforward.

4.6 Phase Characterization using XRD

Figure 4.7 shows XRD pattern for HS sample at 1hr, 24 hrs, and 7 days. LS samples show similar response and it is not presented here. XRD patterns at various ages resemble that of the fly ash (Figure 3.1) and are very similar to each other. However, a very close and careful observation reveals that there are a few new peaks seen in the 27-35°2θ region highlighted in Figure 4.7 (inset panel). These XRD patterns were collected at a much slower rate of 0.15°min⁻¹ in order to increase signal to noise ratio.

The peak at 29.3°2θ becomes sharper and more defined with time. In addition to the sharp peak, a hump was also observed in 7 days sample at the same 2θ angle. The sharp peak might correspond to the presence of calcite and the hump could indicate existence of C-S-H, the amount of which is increasing with time. However, presence of geopolymer could not be confirmed from the XRD patterns. Since XRD results were not very conclusive, it was not performed on 7 days old LS sample.
Figure 4.6: Evolution of product with time using FTIR for a: HS, b: LS.
Figure 4.7: XRD patterns of HS sample at various ages (1hr, 24hr, 7days). Inset panel shows a close up of XRD patterns between 27-35°2θ angle. Q: Quartz, M: Mullite, H: Hematite
4.7 Quantitative Elemental Spot Analysis Using SEM-EDS

All of the ratios that are calculated from EDS microanalysis results are compared with the ratios set by Garcia-Lodeiro et al. in order to distinguish between C-A-S-H and (Ca,K)-A-S-H and are given below [98]:

\[
\text{C-A-S-H} : 0.72 < \frac{\text{CaO}}{\text{SiO}_2} < 1.94; 0 < \frac{\text{Al}_2\text{O}_3}{\text{SiO}_2} < 0.1
\]

\[
\text{(Ca,K)-A-S-H} : 0 < \frac{\text{K}_2\text{O}}{\text{Al}_2\text{O}_3} < 1.85; 0 < \frac{\text{CaO}}{\text{SiO}_2} < 0.3; 0.05 < \frac{\text{Al}_2\text{O}_3}{\text{SiO}_2} < 0.43
\]

EDS spot analysis on a 1 hour old sample indicates the presence of K-A-S-H geopolymer (average of 15 points) with an average of, \( \frac{\text{K}_2\text{O}}{\text{Al}_2\text{O}_3} = 0.47\pm0.44, \frac{\text{CaO}}{\text{SiO}_2} = 0.05\pm0.03, \frac{\text{Al}_2\text{O}_3}{\text{SiO}_2} = 0.23\pm0.09 \). Some points also indicated possible calcium substitution in the geopolymer. EDS analysis of a 1 hour old sample with a representative spectrum and an average atomic ratios of various elements is given in Figure 4.8a. A distinctive and segregated C-A-S-H phase is not found in the BSE images, which is similar to an earlier observation made on class F fly ash-slag geopolymers and Class C fly ash geopolymer [22, 23]. The interaction volume for X-ray generation is kept to minimum by working at a low voltage. However, the response from EDS spot analysis could still come from multiple phases whose size ranges from few nanometers to 1 \( \mu \)m, much smaller than the interaction volume (\( \sim 1 \mu \)m in diameter for the voltage of 7 kV as predicted by Lloyd et al. [66]). Early in the reaction, as calcium dissolves, C-A-S-H can form randomly throughout the microstructure and not necessarily around slag particles. This C-A-S-H can then possibly act as nucleation site for geopolymerization, developing an intermixed microstructure of C-A-S-H and K-A-S-H at an early age. The possible presence of calcium substituted geopolymer cannot be eliminated either. Early age samples could have a mixture of C-A-S-H and potassium geopolymer and/or calcium substituted potassium geopolymer.
Figure 4.8: BSE image of HS a: 1 hour b: 14 days showing a typical spectrum of the phase present along with average atomic ratios of various elements

The quantitative microanalysis of a 14 day-old sample, indicated the presence of two phases, C-A-S-H and (Ca,K)-A-S-H. The average composition of C-A-S-H (average of 5 points) is $K_2O/Al_2O_3 = 1.34\pm0.50$, $CaO/SiO_2 = 0.73\pm0.06$, $Al_2O_3/SiO_2 = 0.12\pm0.03$ and that of (Ca,K)-S-H (average of 15 points) is $K_2O/Al_2O_3 = 0.61\pm0.46$, $CaO/SiO_2 = 0.23\pm0.13$, $Al_2O_3/SiO_2 = 0.37\pm0.15$. The EDS analysis of a 14 day-old sample with a representative spectrum and an average atomic ratio of various elements is given in Figure 4.8b. Later age samples indicate a calcium substitution in the geopolymer as the EDS spot analysis shows the presence of (Ca,K)-A-S-H extensively. As the microstructure becomes denser with time, reaction becomes diffusion-controlled and an inward reaction of slag occurs. This explains the presence of a distinctive C-A-S-H phase in the later ages. The composition of C-A-S-H has $K_2O/Al_2O_3 = 1.34$, indicates an alkali binding as the C-A-S-H has higher tendency for alkali binding than C-S-H \[59\]. Assuming that Al substitutes Si in tetrahedral sites of C-S-H, alkalis are absorbed into C-S-H for charge balancing and for every one Al atom, one alkali atom will be substituted to balance the charge ($K/Al \sim 1$, $K_2O/Al_2O_3 \sim 1$). This is because the binding of alkali is predicted to occur by a valence compensation mechanism, where an imbalance in charge is created by the substitution of Al in Si tetrahedral sites and is compensated by the inclusion of alkali \[59\].

The coexistence of C-A-S-H and K-A-S-H (with partial Ca substitution) has been observed.
through EDS samples but differentiation between phases is difficult if they are smaller than interaction volume which is mostly the case in early age samples. Furthermore, EDS study involves time consuming sample preparation that can be avoided using Infrared spectroscopy method. Therefore, FTIR analysis was performed on samples by selectively dissolving the products by chemical methods to isolate the responses.

4.8 IR Spectra of Insoluble Residue After Selective Dissolution Treatment

The effect of selective dissolution treatments on slag and fly ash is given in Figure 4.1 and Figure 4.2 respectively and is considered to be minimal. Selective dissolution was performed on the HS samples at three different ages (1 hr, 24 hr, 7 days) to monitor the phase development, and compared with the LS sample at 7 days. Figure 4.9 shows the spectrum of the original sample along with the spectra of insoluble residues after SAM and HCl extractions at 1 hr, 24 hr, and 7 days. The insoluble residues after SAM and HCl treatments will be referred hereafter as ‘SAM residue’ and ‘HCl residue’, respectively. The insoluble residue after SAM extraction was also subjected to HCl treatment and will be denoted as ‘HCl residue after SAM’.

Figure 4.9a shows that HS at 1 hr has main band with peak centered at 999 cm\(^{-1}\) and after SAM extraction, the band moves to a higher frequency, 1024 cm\(^{-1}\) with a shoulder at 910 cm\(^{-1}\). The shoulder at 910 cm\(^{-1}\) indicates the presence of Si-OH groups [144]. Similar observations are made at 24 hrs and 7 days. Now, to determine what caused the shift in IR spectra, solubility of various phases in SAM was considered. SAM treatment is noted to dissolve calcium hydroxide, calcium oxides and calcium silicates but does not affect calcium carbonate [129]. From Table 4.1 it is clear that the amount of fly ash and slag that dissolves in SAM is less than 2% and the spectral shift due to SAM treatment on fly ash and slag is negligible. It is known that geopolymers (N/K-A-S-H) do not dissolve in
SAM \([82, 83, 131, 136, 145]\). In this paper, geopolymer formed in the presence of calcium ion is also considered to be insoluble in SAM as no evidence of its solubility in SAM is available in the literature \([82]\). Therefore, the shift observed in Figure 4.9 is concluded to be due to dissolution of calcium silicate hydrate \([82, 131, 136, 140]\).

As shown in Figure 4.9, HCl treatment at all ages shifts the main band to 1050 cm\(^{-1}\) which closely matches with the peak position in the fly ash spectrum after HCl treatment. When powdered samples are treated with 1:20 HCl solution, products like geopolymers and zeolites dissolve along with any unreacted slag. A negligible portion of unreacted fly ash dissolves during HCl treatment as well (\(\sim 3\%\)). HCl treatment also dissolves calcium carbonate and affects calcium silicate hydrate by removing calcium from the structure and leaves silica gel behind \([129]\). Due to dissolution of several products, it is concluded that the spectrum of insoluble residue after HCl treatment does not render any significant information.

To further simplify the issue of overlapping IR spectra, and avoid the response from the silica gel in the HCl recidue, the insoluble residue after the SAM treatment was subjected to HCl treatment. This spectrum is presented in Figure 4.9a as ‘HCl residue after SAM’ treatment for 1 hr sample. The position of the main band is now at 1054 cm\(^{-1}\) which is slightly different from the position of the main band after HCl treatment indicating differences in the nature of products dissolving. To gain further information on the products that have dissolved during various treatments, spectral subtraction was performed and presented in the later sections.

The weight \(\%\) of sample dissolved during SAM treatment (C-A-S-H), HCl treatment, HCl after SAM treatment and the amount (wt\%) of insoluble residue after HCl treatment (unreacted fly ash + silica gel) of HS sample (at 1hr, 24hr, 7 days) and LS sample (at 7 days) are presented in Figure 4.10. The amount of sample dissolved in SAM increases with time indicating an increase in the amount of C-A-S-H. At 7 days, HS sample showed higher weight loss during SAM treatment than the LS sample indicating greater amount of C-A-S-H formed in HS sample. This is reasonable as the HS sample had higher amount of calcium
available from higher slag replacement. The weight loss due to HCl treatment (dissolved in HCl) increases with time however it cannot be directly correlated with the amount of geopolymer formed due to other phases dissolving in HCl simultaneously. To eliminate the issue of partially dissolving C-A-S-H during HCl treatment, weight loss due to HCl treatment after SAM was considered. Weight loss due to HCl treatment after SAM actually decreased with time. This is counterintuitive at a first glance since the amount of geopolymer should not decrease with time, however not impossible as the amount of unreacted slag (that also dissolves in HCl) is decreasing with time. The weight of insoluble residue after HCl treatment provides general indication of fly ash reactivity as the insoluble residue is primarily unreacted fly ash and silica gel (left behind from C-A-S-H dissolution). It is clear that the amount of unreacted fly ash decreased with time. Comparing the weight of insoluble residue after HCl treatment at 7 days between the HS and the LS sample, it is clear that slag addition increases fly ash reactivity. This matches with similar conclusion made by other researchers and corroborates the microstructural and calorimetric study presented earlier [26,101].

4.9 Spectral Subtraction to Determine IR Spectrum of Dissolved Products in Selective Dissolution Treatments

Spectral subtraction has been performed to precisely understand the products dissolving with each treatment as well as to obtain their individual structural evolution. Subtraction is performed on spectra collected at various ages and is given in Figure 4.11 (1 hr), Figure 4.12 (24 hr), and Figure 4.13 (7 day).

Spectrum of components dissolved during the treatment is obtained by subtracting the IR spectrum obtained after attack from the original spectrum using OMNIC software. Similar to before, the spectrum collected before treatment is noted as ‘original’, after a specific treat-
Figure 4.9: IR spectrum of HS sample before and after different treatments, SAM, HCl, HCl on SAM at various ages a: 1 hr, b: 24 hr, and c: 7 day.
Figure 4.10: Analysis of selective dissolution treatments presented as dissolved % by the initial mass of HS sample (1 hr, 24 hr, and 7 days) and LS sample.
ment is noted as ‘(treatment) residue’. The resultant spectrum obtained through subtraction is referred as ‘dissolved in (treatment)’.

### 4.9.1 Spectral Subtraction After Selective Dissolution on 1 hr Sample

Figure 4.11a presents the following IR spectra for a 1 hr old sample: ‘original’, ‘SAM residue’ and the subtraction spectrum obtained for phases dissolved in SAM (dissolved in SAM spectrum). The spectrum after subtraction reveals a broad band at 978 cm$^{-1}$ and a shoulder at 860 cm$^{-1}$. The peak at 978 cm$^{-1}$ could be attributed to Si-O stretching vibrations in Q$^2$ tetrahedra of C-S-H gel whose position depends on Ca/Si ratio [89]. EDS analysis has shown the presence of C-A-S-H and K-A-S-H in 1 hr old sample and a combination of C-A-S-H, K-A-S-H, Ca(K)-A-S-H in the later ages [17,20,23,26]. Spectroscopy and spectral subtraction presented here also predicts the presence of C-S-H in the early ages.

The 1107 cm$^{-1}$ band is typical of Si-O asymmetric stretching vibrations generated by Q$^3$ silicon tetrahedra sites [82,89,94]. The presence of this peak in the subtracted spectrum indicates dissolution of a product which is rich in silica and may have taken up some amount of calcium and alkali [82]. As the intensity of this band is smaller than that at 978 cm$^{-1}$, the amount of such silica rich gel with calcium is predicted to be low. This peak is seen in all the samples at various ages. In few studies on acidic zeolites, bands present approximately at 1100 cm$^{-1}$ have been assigned to in-plane (plane defined as the triangle Si-O-Al) hydroxyl bending modes [146-149]. Subtraction spectrum also shows carbonate peaks at 1395 cm$^{-1}$, 1467 cm$^{-1}$ and 866 cm$^{-1}$ which are completely absent in the SAM residue spectrum. This may indicate the presence of soluble or low stability carbonate species in geopolymer that are removed during SAM extraction. Carbonation of geopolymers will be further discussed in later sections.

Figure 4.11b presents the IR subtraction spectrum after HCl treatment. Close observation
reveals that the ‘dissolved in HCl’ spectrum in Figure 4.11b and ‘dissolved in SAM’ spectrum in Figure 4.11a show very similar peaks in spite of the difference in the main band positions in their respective insoluble residues. Both treatments are not expected to dissolve same phases as HCl should dissolve geopolymer but SAM should not. The spectrum for the dissolved phases in HCl after SAM treatment is given in Figure 4.11c and is quite different from the other two. This indicates that indeed SAM and HCl do not dissolve the same phases.

The spectrum for dissolved phases in HCl after SAM has a very broad band ranging between 868 and 1011 cm\(^{-1}\) which resembles slag (whose main band is in the range of 870-940 cm\(^{-1}\) as seen in Figure 4.5). However, the subtraction spectrum is broader in the higher wave number region compared to the slag spectrum. The main band position of K-A-S-H is around 1200-950 cm\(^{-1}\) depending on the aluminum substitution \([67, 71, 74, 81, 85, 135, 142]\). Therefore, the broadness of the spectrum is attributed to the dissolution of a small amount of K-A-S-H geopolymer and complete dissolution of unreacted slag.

This implies that the spectral subtraction after selective dissolution is sensitive enough to identify not only the dominant phase in the microstructure at an early age (C-S-H/C-A-S-H) but also the small amount of K-A-S-H present as reported in an earlier study through EDS observation \([26]\). This confirms that the initial peak in calorimetry also corresponds to the initial precipitation of C-A-S-H and K-A-S-H besides wetting of raw materials. Furthermore, it proves the hypothesis 1. The broad band observed due to small amount of K-A-S-H geopolymer at 1 hr is seen to get sharper with time as presented in the later sections.

### 4.9.2 Spectral Subtraction After Selective Dissolution on 24 hr Sample

Figure 4.12 shows spectral subtraction results after similar treatments on 24 hr old sample. Peak positions of dissolved phases at 24 hrs is similar to 1 hr sample. Therefore, the following discussion will only highlight the differences observed. Peak related to Q\(^2\) tetrahedra of C-S-
Figure 4.11: Subtraction spectrum a: HS 1 hr after SAM extraction, b: HS 1 hr after HCl extraction, c: HS 1 hr after HCl extraction on the IR after SAM treatment.
H gel has shifted to a lower wavenumber compared to the 1 hr old sample. This implies either an increase in the aluminum substitution in the C-S-H structure or an increase in Ca/Si ratio with time [89]. Calcium silicate hydrate forming at an early age (at 1 hr) may have less aluminum due to the higher dissolution rate of calcium from slag than aluminum [29]. So, C-S-H is mostly formed from calcium dissolved from slag and silicon already present in the activator solution. As raw material dissolution continues providing more aluminum, calcium silicate hydrate with high aluminum content could be forming explaining the shift in the position of the main band. Aluminum substitution is also enhanced with decrease in pH of the pore solution [46, 55, 129, 150, 151]. The shift towards lower frequency could also be attributed to depolymerization of the silicate chains with an increase in Ca/Si ratio with time. Low Ca/Si ratio in C-S-H is often observed in early ages of slag activation due to the presence of little Ca from the dissolution of slag and significant amounts of Si present in the activator solution [151–154]. With increase in dissolution of slag, Ca/Si ratio of C-S-H could increase which can also explains the shift.

As in the case of 1 hr sample, even 24 hr sample has the IR spectra of phases dissolved in SAM and dissolved in HCl very similar except for the relative intensities of peaks. Presence of K-A-S-H is clearly identified from the subtraction spectrum of phases dissolved in HCl after SAM. This spectrum has a peak at 1000 cm\(^{-1}\) which resembles that of geopolymer, a shoulders at 1100 cm\(^{-1}\) and a broad band at 860-910 cm\(^{-1}\) resembling unreacted slag. It is clear that the method is sensitive enough to show an increase in the K-A-S-H content, decrease in the unreacted slag content and increase in Al content and/or Ca content in C-A-S-H with time. Therefore, the amount of K-A-S-H has increased by 24 hrs which corresponds to a time point after the appearance of reaction peak from calorimetry. The appearance of the reaction peak could be attributed to the gelation of K-A-S-H.
Figure 4.12: Subtraction spectrum a: HS 24 hr after SAM extraction, b: HS 24 hr after HCl extraction, c: HS 24 hr after HCL treatment on IR after SAM extraction.
4.9.3 Spectral Subtraction After Selective Dissolution on 7 day Sample

The main differences seen between 7 days sample and early age samples are discussed here. The peak positions corresponding to \( Q^2 \) tetrahedra of C-A-S-H gel shifted towards lower wavenumber compared to the 1 hr old sample and towards higher wavenumber compared to the 24 hr old sample. This implies increased aluminium substitution in C-A-S-H with time. As in the case of 1 hr and 24 hr samples, IR spectra of phases dissolved in SAM and dissolved in HCl are very similar except for the relative intensities of the peaks. The IR spectra of phases dissolved in HCl after SAM treatment is very different at 7 days compared to earlier ages. Sharper peaks in 7 days sample compared to early age samples indicates a greater amount of product which is also evident from the % weight dissolved. The peak corresponding to the main geopolymer product has shifted to a lower frequency compared to early age samples indicating continuing geopolymerization and increase in the Al/Si ratio of the geopolymer with time \[85, 155\]. Also, unlike 1hr or 24 hr sample, a shoulder appears at 1020 cm\(^{-1}\) indicating \( Q^4(nAl) \) units in a geopolymer whose Al content is lower than the one represented by a main band at 992 cm\(^{-1}\).

4.9.4 Evolution of Reaction Products in LS Sample

To check if selective dissolution treatment followed by FTIR spectral subtraction can identify the differences between two geopolymer mixes with different slag contents, experiments were performed on LS sample at 7 days. It has been observed that the spectrum of LS and HS sample at 7 days has similar peak positions (Figure \[4.6\]) which does not explain the differences in the compressive strength. Therefore, spectral subtraction was performed after SAM and HCl on SAM treatment. Direct HCl treatment was omitted because it proved to be less informative.

FTIR spectrum of sample before and after selective dissolution techniques along with sub-
Figure 4.13: Subtraction spectrum a: HS 7 day after SAM extraction, b: HS 7 day after HCl extraction, c: HS 7 day after HCl treatment on IR after SAM extraction.
traction spectrum is presented in Figure 4.14. Figure 4.14a shows the spectrum of phases dissolved in SAM with a main band at 960 cm\(^{-1}\) (Si-O stretching vibrations in Q\(^2\) tetrahedra of C-S-H gel), and shoulder at 1110 cm\(^{-1}\) which is similar to HS sample at 7 days. Figure 4.14b shows the spectrum of phases dissolved in HCl after SAM which has a broad peak (1066-1040 cm\(^{-1}\)) and another broad band corresponding to slag dissolved in HCl. The broad peak corresponds to a geopolymer of lower Al content compared to geopolymer in HS sample at 7 days. The relative peak intensities compared with the shoulder (1110 cm\(^{-1}\)) indicates that the LS sample has much lower amount of geopolymer compared to HS sample. Also, the amount of dissolved component in SAM treatment is greater in the case of HS compared to that of LS. The lower amount of reaction product and the low Al content of geopolymer explains the low strength seen in LS sample compared to HS sample. Selective dissolution treatments with FTIR spectral subtraction successfully explains the difference between two different geopolymer mixes.

It has been observed that the combined results from SAM treatment and HCl treatment on SAM residue followed by spectral subtraction render greater amount of information about calcium containing binders. FTIR characterization and spectral subtraction performed after SAM treatment and after successive chemical treatments using SAM and HCl clearly showed the co-existence of C-S-H and K-A-S-H in two different alkali activated fly ash-slag blends. The technique was shown to be very sensitive to the presence of small amounts of reaction products. The method successfully predicted the evolution of reaction products (C-A-S-H and K-A-S-H) with time. The greater amount of product as seen from SEM micrographs was also confirmed from selective dissolution and FTIR spectral subtraction. SEM micrographs and calorimetry further validate the selective dissolution followed by spectral subtraction method in determining the nature of products in a complex mix composition such as fly ash-slag.

Based on the selective dissolution techniques followed by FTIR spectral subtraction, the broad FTIR spectrum seen in geopolymer cements consisting of amorphous raw-materials
Figure 4.14: Subtraction spectrum of LS mix a: 7 day after SAM extraction, b: 7 day after HCl treatment on IR after SAM extraction.
and amorphous products, can be effectively deconvoluted. Figure 4.15 gives the final deconvoluted spectra from raw materials (fly ash and slag) and products (C-A-S-H and N-A-S-H).

4.10 Conclusions

The dominant phase in the microstructure during accelerated hardening phase was determined to be C-S-H/C-A-S-H thus proving the first hypothesis. Evidence of small amount of K-A-S-H at an early age was also observed.

Often it is difficult to determine the nature of the reaction products when calcium containing aluminosilicate precursors are activated using an alkali and/or alkali silicate combination. The present chapter presents a method to successfully characterize C-(A)-S-H and K-A-S-H phases forming in the binder through a combination of selective dissolution treatments and FTIR spectral subtraction. It was found that IR spectra collected on insoluble residue of sal-
icylic acid-methanol (SAM) and HCl treatment performed separately are still inconclusive. It was found to be crucial to perform both the chemical treatments successively i.e., HCl treatment on SAM residue. Furthermore, FTIR spectral manipulation such as subtraction of solid residue spectrum from the original provides valuable information. FTIR characterization and spectral subtraction performed after SAM treatment and after successive chemical treatment using SAM and HCl clearly demonstrated the co-existence of C(A)-SH and KASH in two different silicate-activated fly ash-slag blends. The technique was shown to be sensitive to the presence of small amounts of reaction products. The method successfully predicted the evolution of reaction products (C(A)SH and KASH) with time. The amount of K-A-S-H gel in the mix has increased considerably by 24 hrs compared to 5 hrs as indicated from the increased sharpness of peaks from IR spectra. The increase in K-A-S-H amount corresponds to the reaction peak seen in the calorimetry. Thus, the reaction peak is attributed to the formation of K-A-S-H in the mix.

FTIR analysis after selective dissolution treatments clearly shows a continued formation of C-S-H and continued geopolymerization as the respective peaks become sharper with time. The main IR which corresponds to Si-O-Si asymmetric stretching vibration in C-S-H tend to shift in general to a lower wavenumber with time due to possible increase in the aluminum substitution in the C-S-H structure or increase in the Ca/Si ratio.

The greater amount of product in the later age samples as seen from SEM micrographs was also confirmed from selective dissolution and FTIR spectral subtraction. SEM micrographs and calorimetry further validate selective dissolution followed by a spectral subtraction method in determining the nature of products in a complex mix composition such as fly ash-slag.
As a part of verifying the second hypothesis, precipitated C-S-H will act as a nucleation seed for geopolymer gel formation, we are proposing to add synthesized C-S-H as nucleation seeds to silicate-activated binders. Along with product-based seeds like C-S-H/C-A-S-H, we are also studying the effect of non-product based seeds such as nanoparticulate sized SiO$_2$ (nano-SiO$_2$), Al$_2$O$_3$ (nano-Al$_2$O$_3$), and ZnO (nano-ZnO) on the geopolymer gel formation.

### 5.1 Non-product Seeds

Non-product seeds used in this study with their surface area mentioned in parenthesis are nano-SiO$_2$ (55 m$^2$/g), nano-Al$_2$O$_3$ (80 m$^2$/g), and nano-ZnO (65 m$^2$/g). Nano-SiO$_2$ and nano-ZnO were purchased from US Research Nanomaterials Inc., and nano-Al$_2$O$_3$ was purchased from Alfa Aesar. The surface area measurements are provided by the supplier. The characteristic properties of purchased nano-seeds are given in Table 5.1. TEM micrographs of seeds as provided by manufacturers are given in Figure 5.1.

**Table 5.1: Characteristic properties of purchased seeds**

<table>
<thead>
<tr>
<th>Seed</th>
<th>Type</th>
<th>pH value</th>
<th>Particle size</th>
<th>Assay</th>
<th>Solvent</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>nano-SiO$_2$</td>
<td>Amorphous</td>
<td>8-11</td>
<td>5-35 nm</td>
<td>25%</td>
<td>75% water</td>
<td>99.99%</td>
</tr>
<tr>
<td>nano-Al$_2$O$_3$</td>
<td>γ form</td>
<td>10 nm</td>
<td>100%</td>
<td>dry powder</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nano-ZnO</td>
<td></td>
<td>8.9</td>
<td>30-40 nm</td>
<td>20 %</td>
<td>80 % water *</td>
<td>99.5%</td>
</tr>
</tbody>
</table>

*: poly N-vinyl-2-pyrrolidone ((C$_6$H$_9$NO)$_n$) surfactant also called PVP
Figure 5.2 shows FTIR spectra of nano-SiO$_2$, nano-Al$_2$O$_3$, and nano-ZnO seeds. IR spectra are presented in transmission mode which is the default data presentation obtained from Perkin Elmer machine. In the transmission mode IR peaks point in the downward direction and in the absorption mode IR peaks point in the upward direction. The position of main band in nano-SiO$_2$ is at 1116 cm$^{-1}$ which belongs to asymmetric stretching vibration of Si-O-Si in Q$^3$ tetrahedra [156]. FTIR spectrum of nano-ZnO resembles that of water (which constitutes 80% by weight). The amount of energy required to vibrate Zn-O bonds lies outside the detectability range for mid-infrared spectroscopy. Therefore, peaks corresponding to vibrational frequency of Zn-O bonds are missing. The FTIR spectrum of nano-Al$_2$O$_3$ shows a broad peak in the range of 500-900 cm$^{-1}$ assigned to Al-O stretching in AlO$_4$ or AlO$_6$ [157,158].

![Figure 5.1: TEM images of a: nano-SiO$_2$ and b: nano-ZnO](image)

Laboratory synthesized CaCO$_3$ was also used as a nucleation seed. CaCO$_3$ was synthesized following procedure from Sato et. al. which was originally proposed for synthesizing vaterite (a polymorph of CaCO$_3$) [159]. A 3M solution of CaCl$_2$ was prepared by dissolving 16.6 g of CaCl$_2$ in 50 ml of water and 1M solution of Na$_2$CO$_3$ by dissolving 47.7 g of Na$_2$CO$_3$ in 450 ml of water. These solutions were mixed simultaneously in a beaker and stirred for 30 minutes at 30 °C. Precipitated solution was then vacuum filtered using a Büchner funnel, washed rapidly with water and ethyl alcohol, and then dried in a desiccator with
Figure 5.2: FTIR spectra of purchased nano seeds. IR spectra is presented in transmission silica gel. Upon storage, the sample has converted to a more stable calcite form as evident from FTIR and XRD patterns shown in Figure 5.3. XRD pattern confirms that the vaterite has been converted into calcite upon storage. FTIR spectrum is characteristic of calcite with asymmetric stretching peak at 1385 cm$^{-1}$, out-of-plane bending peak at 875 cm$^{-1}$, and in-plane bending vibration at 711 cm$^{-1}$.

5.2 Product-based Seeds

Product based seeds, C-S-H and C-A-S-H, were synthesized in the lab using the reagent grade chemicals following the procedure described by Hunnicutt et. al. C-S-H gel was
synthesized by direct reaction of calcium oxide and fumed silica (SiO\textsubscript{2}) in water. Calcium oxide was obtained by calcining reagent grade CaCO\textsubscript{3} (Sigma-Aldrich) at 1000°C for 24 hrs and storing in a vacuum desiccator. Reagent grade fumed silica (Sigma-Aldrich) was heated in an oven at 105°C for at least 3 hrs to remove water. Required quantities of calcium oxide and fumed silica were dry mixed in HDPE bottles to synthesize C-S-H of Ca/Si ratios of 1.0 and 1.3. Then 100 mL of de-carbonated (boiled for ten minutes and cooled), de-ionized water was added to the mixture in a glove-box to reduce the extent of carbonation. The bottle was then tightly sealed and was shaken for one day using a multi vortex-genie shaker (Cole-Parmer). Precipitated solution was then vacuum filtered using a Büchner funnel, and the resulting wet C-S-H gel was stored in a sealed container in 100% RH. The mass fraction of solid C-S-H was determined by measuring the weight loss of small sample of C-S-H gel after drying at 160°C for 12 hrs \cite{53}. The amount of moisture or the amount of C-S-H solids in the wet gel was shown to have a larger effect than the seed composition on the reaction kinetics of cements \cite{104}. The effect is attributed to the sensitivity of C-S-H surface area to the amount of water to solids ratio. Therefore, for each batch of synthesized C-S-H, care was taken to ensure that the amount of C-S-H solids in the final filtered precipitate was always close to 10%. This was done by ensuring that the water/solid mass ratio of the initial
solutions was always constant, and the filtering was continued until no more liquid could be
removed.

The C-A-S-H seed was synthesized following the same procedure as that used for synthe-
sizing C-S-H except for a few modifications. Stoichiometric quantities of aluminum nitrate
were added to the dry mixture of calcium oxide and fumed silica before adding 100 ml of
water. The solution was then mixed for one-month to ensure a complete substitution of
aluminum.

Figure 5.4 gives FTIR spectra of laboratory synthesized C-S-H and C-A-S-H gels. The
position of the main band, an asymmetric stretching vibration of Si-O-Si in Q² tetrahedra,
is at 948 cm⁻¹ for C-S-H (Ca/Si - 1.0) and at 940 cm⁻¹ for C-S-H (Ca/Si - 1.3). The main
band position with C-A-S-H (Ca/Si - 0.95, Al/Si - 0.2) is at 959 cm⁻¹. The shift in the main
band position towards lower wave number with increasing Ca/Si ratio of C-S-H is attributed
to increasing depolymerization [89]. The position of the main band in C-A-S-H (Ca/Si -
0.95) is at higher wave number compared to C-S-H (Ca/Si - 1.0). Because Si-O-Al bond
energy is lower than Si-O-Si, band position is expected to move to lower numbers instead.
However, increasing cross-linking or increasing mean chain length increases the vibrational
energy and the band position moves to a higher wave number. Absence of any peaks in
1400-1500 cm⁻¹ implies lack of carbonation in the gels.

The effect of varying surface area of nucleation seed on the reaction mechanism was studied
through the addition of dry and wet seeds. Fonseca et. al. showed that the slow dried C-S-H
seed at lower humidity has much lower surface area compared to the wet seed (as shown in
Figure 5.5) [161]. Therefore, for seeds with a low surface, C-S-H gels were dried in vacuum
oven (with liquid nitrogen trap) at 40 °C at moderate vacuum conditions (~45cm of Hg from
atmospheric pressure) to constant mass (2-3 days) following the procedure and by using
an apparatus developed by William Hunnicutt [160]. The samples were then stored in a
desiccator under vacuum.
5.3 Seed Dispersion

SiO\textsubscript{2} and ZnO nanoparticles were supplied dispersed in water. Therefore, the amount of final mixing water was adjusted accordingly to maintain the effective water / binder (w/b) of 0.32. Dry nano-Al\textsubscript{2}O\textsubscript{3} seed was dispersed in the activator solution and probe sonicated for 10 mins at 30% energy using 1/8-inch diameter probe to ensure good dispersion.

The product based seeds were added to the pastes in the pre-determined weight percentages calculated as mass of wet solid C-S-H/C-A-S-H by mass of fly ash-slag/slag/cement. The water associated with the seed was accounted for, and w/b ratio of the activator so-
lution was adjusted to keep similar w/b ratios across mixes. An even and homogeneous distribution of seed within the paste was ensured by dispersing the seed in the activator solution and probe sonicating for 10 mins at 30% energy using 1/8-inch diameter probe. Activator solution with C-S-H/C-A-S-H seeds exhibited strong shear thickening behavior that persisted even when mixed with dry fly ash-slag.

Figure 5.6 shows the effect of probe sonication on the dispersion of wet C-S-H/C-A-S-H seed imaged using environmental scanning electron microscopy (ESEM) at 75% RH. Probe sonication on C-A-S-H for 10 mins at 30% energy has decreased the average particle size and significantly increased the surface area of the seed.

5.4 Mixing Procedure

Pastes were always mixed in small quantities (100 grams) using a hand held shear mixer to ensure that the seeds are uniformly and thoroughly mixed. Dry solids were always added to the wet probe sonicated seed solutions and then mixed for 2 minutes, mixing was paused
Figure 5.6: Environmental scanning electron micrographs of seed before (a, b) and after (c,d) probe sonication. Probe sonication on C-A-S-H for 10 mins at 30% energy has decreased the average particle size and significantly increased the surface area of seed. ESEM was done at 80% RH
for 30 seconds to scrape the sides and the bottom, and mixing was continued for another 2 minutes.

5.5 Effect of Nucleation Seeds on Fly ash-Slag Geopolymer Cements

Figure 5.7 shows the effect of the addition of 0.8% product based (C-S-H and C-A-S-H) and non-product (nano-\(\text{Al}_2\text{O}_3\), finely powdered \(\text{CaCO}_3\), nano-ZnO, nano-SiO\(_2\)) based seeds on the reaction kinetics of silicate-activated medium calcium binders. Irrespective of the seed composition, the initiation time for the main reaction peak and the time to reach maximum peak height were delayed. From inset, the total amount of heat is lowered in the presence of seeds. The result is contrary to the calorimetry results for Portland cements and silicate-activated slag pastes in the presence of nucleation seeds as seen from the literature \([53,104]\). Therefore, the delay in the reaction kinetics of silicate activated fly ash-slag mixes means one of the following:

- The delay in the appearance of the calorimetry peak in the presence of nucleation seeds implies that the C-S-H seed does not accelerate the formation of K-A-S-H. Thus, disproving the second hypothesis or

- The seeds are ineffective due to their insufficient dispersion or surface characteristics or both

5.6 Effectiveness of Seeds

To verify the effectiveness of seeds, product-based and non-product based seeds are added to Portland cement binders and alkali-activated slag binders. Portland cement binders were made by mixing cement with water keeping w/b as 0.44. Alkali-activated slag binder was
Figure 5.7: Rate of heat evolution at 22°C of silicate activated fly ash-slag pastes with 0.8% seed addition. a: C-S-H (Ca/Si - 1.0) and C-A-S-H (Ca/Si - 0.95, Al/Si - 0.12), b: nano-Al$_2$O$_3$, finely powdered CaCO$_3$, nano-ZnO, nano-SiO$_2$. Inset gives the total heat evolved with time.
made following the procedure followed by Hubler et al. [53]. The wet C-S-H seed was added to the activating solution (water in the case of Portland cement) and probe-sonicated following the procedure described in the previous section. The activator solution with dispersed seed was added to powders and mixed using a high shear mixer.

Figure 5.8 shows calorimetry curves for Portland cement binders and silicate-activated slag binders with and without 0.8% C-S-H seed. In the case of Portland cement binders, the effect of nano-Al$_2$O$_3$ and nano-ZnO are also given. In the presence of C-S-H seed, the induction period and the time to reach the maximum peak height are shortened for both binders. Thus, the added C-S-H gel acts as an effective nucleation seed promoting the faster reaction, proving that the synthesized C-S-H seeds have the required surface characteristic at least to act as nucleation site for further C-S-H formation.

Rees et al. examined the effect of nano Al$_2$O$_3$ seeds on the kinetics of a hydroxide-activated fly ash binders (low calcium) and observed significant improvement in the rate of geopolymer gel formation [106]. Therefore, we set out to see if the seeds prepared in this study will show results similar to that of Rees’s on hydroxide-activated fly ash-slag binders (medium-calcium). Fly ash - slag mix made with 75% fly ash and 25% slag was activated with potassium hydroxide (KOH) solution to prepare hydroxide-activated binders. The amount of K$_2$O in the activator solution and water to binder ratio were kept constant between the mixes. Figure 5.9 shows the effect of product based and non-product based seeds on hydroxide activated fly ash-slag binders.

The induction period and the time to reach the maximum peak height are shortened in the case of hydroxide-activated fly ash-slag binders in the presence of all seeds. Seeds, both product based and non-product based, accelerate the reaction in hydroxide-activated geopolymer cements. Seeds do not accelerate the reaction only in silicate activated geopolymer cements as shown in Figure 5.8. From the effect of synthesized seeds on Portland cement binders, alkali-activated slag binders, and hydroxide activated fly ash-slag binders, it has proved that the seeds are effective and they do not have any problem with insufficient dispersion or sur-
Figure 5.8: a: Rate of heat evolution at 22°C of cement hydration (w/c - 0.44) made with 0.8% of C-S-H, C-A-S-H, nano-Al$_2$O$_3$, and nano-ZnO seeds. b: Rate of heat evolution at 22°C of slag pastes activated with sodium silicate solution made with 0% and 1% by weight of wet C-S-H (Ca/Si - 1.0) seed. Inset shows total heat over time.
Figure 5.9: a: Rate of heat evolution at 22°C of fly ash-slag binders activated with potassium hydroxide solution and made with 0.8% (by wt. of fly ash + slag) of C-S-H (Ca/Si - 1.0) and C-A-S-H (Ca/Si - 0.95, Al/Si - 0.2) seed. Ca/Si ratio of C-S-H and Ca/Si, Al/Si ratio of C-A-S-H is given in the parentheses, b: Rate of heat evolution at 22°C of fly ash-slag binders activated with potassium hydroxide solution and made with 0.8% (by wt. of fly ash+slag) of nano-$\text{Al}_2\text{O}_3$, nano-$\text{ZnO}$, $\text{CaCO}_3$, and 0.8% and 3% of nano-$\text{SiO}_2$. Inset shows total heat over time.
face characteristics or both. Therefore, it is implied that the seeds act differently in silicate activated fly ash-slag binders and will be further explored in the later chapters.

The summary of the effect of seeds on binders of different calcium content is given in Figure 5.10. Seeds have an opposing effect on medium-calcium binders made with hydroxide and silicate activator solutions. To truly understand the effect of nucleation seeds on the reaction mechanism in silicate-activated binders, we should understand the differences between hydroxide- and silicate-activated fly ash-slag binders which forms the next chapter.

<table>
<thead>
<tr>
<th>Binder</th>
<th>Seeds</th>
<th>Effect</th>
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<tr>
<td>High-Ca: Silicate activated slag</td>
<td>C-S-H</td>
<td>Accelerate</td>
</tr>
<tr>
<td>Cement</td>
<td>C-S-H</td>
<td>Accelerate</td>
</tr>
<tr>
<td>Low-Ca: Hydroxide activated fly ash binders</td>
<td>Al₂O₃</td>
<td>Accelerate</td>
</tr>
<tr>
<td>Medium-Ca: Hydroxide activated fly ash slag binders</td>
<td>C-S-H, Al₂O₃, SiO₂</td>
<td>Accelerates</td>
</tr>
<tr>
<td>Medium-Ca: Silicate activated fly ash-slag binders</td>
<td>C-S-H, Al₂O₃, SiO₂</td>
<td>Decelerates</td>
</tr>
</tbody>
</table>

Figure 5.10: Summary of the effect of nucleation seed on the reaction kinetics of binders with varying calcium content

5.7 Conclusions

C-S-H and C-A-S-H gels have been successfully synthesized in the lab to be used as nucleation seeds in hydroxide and silicate activated fly ash-slag binders to test the hypothesis that the initial precipitation of C-S-H will nucleate the geopolymer gel formation. Probe-sonication of activator solutions containing synthesized gels for 10 mins at 30% pulse energy has proved to very effective in dispersing the gel.

Seeds, both product based and non-product based, accelerate the reaction in hydroxide-activated geopolymer cements. Seeds do not accelerate the reaction only in silicate-activated geopolymer cements.
6.1 Introduction

One of the major objectives of this research is to understand the early age reaction mechanism through the addition of nucleation seeds. Previous chapter reported how geopolymer cements can respond to seed additions differently depending on the activator solution. Therefore, it is important to carefully discuss the effect of activator solution (potassium hydroxide and potassium silicate) on the reaction kinetics, microstructure, hardening, and the extent of fly ash dissolution on medium-calcium (fly ash-slag) cements in this chapter.

Fly ash-slag mix made with 75% fly ash and 25% slag was activated with potassium hydroxide (KOH) and potassium silicate (KSil) solution. The amount of K$_2$O in activator solution and water to binder ratio were kept constant between the mixes. Potassium hydroxide solution of molarity 1.86 M was used for hydroxide activated binders, and potassium silicate solutions of SiO$_2$/K$_2$O - 1.25 was used for silicate activated binders. Mixes were prepared following the procedure described in chapter 3. Reaction kinetics was monitored using isothermal calorimeter and the hardening was measured using S-wave UWR. Microstructure of samples was analyzed using scanning electron microscopy (SEM). The extent of product formation and fly ash dissolution was determined through selective dissolution treatments. The nature of products was determined through FTIR spectral subtraction.
6.2 Hydroxide Activated Fly ash-Slag Cements

Figure 6.1 shows heat evolution of fly ash-slag pastes activated with solutions of two different KOH concentrations (1.6 M, 1.86 M) or two different w/b ratios (0.38, 0.32) with fixed amount of activator (KOH content). Calorimetry heat evolution curves show one initial peak before the induction period and one accelerated reaction peak after the induction period. The initial peak is attributed to the wetting and dissolution of slag and fly ash particles followed by an induction period. The main reaction peak appears after the induction period followed by a deceleration phase. As KOH concentration increased from 1.6 M to 1.86 M, there was a slight reduction in the induction period and significant increase in the height of the main reaction peak. From the total heat (given in inset), the rate of reaction is also slower in the case of diluted mixes (1.6 M). This is very similar to the effect of water to slag ratio on the heat evolution of hydroxide activated slag pastes and the effect of activator concentration on rate of geopolymer formation in sodium hydroxide activated fly ash pastes as reported in the literature \[29, 67\]. Rees et al. have seen an increase in the rate of geopolymer formation with increasing hydroxide concentration until 9 M \[67\]. Decrease in the rate of geopolymer formation at lower sodium hydroxide concentration was attributed to decreased rate of dissolution. Therefore, the time to reach supersaturation takes longer in lower activator concentration solutions. Moving forward, only samples made with 1.86 M KOH solution will be used unless otherwise mentioned.

Figure 6.2 shows the SEM micrographs of KOH activated fly ash-slag pastes at 24 hrs and 7 days. At 24 hrs during the deceleration stage, product is seen to have formed on the surface of the particles. Much like in the Portland cement hydration and hydroxide activated slag pastes, the product seems to grow densely on the surface of the grain and grow outward into the capillary pore space. The reaction product here seem to have a foil-like morphology (like C-S-H of low Ca/Si) similar to what is seen in alkali activated slag pastes \[29, 52\]. Therefore, the product could be the C-S-H/C-A-S-H (a product from
alkali-activated slag pastes) mixed with potassium aluminosilicate gel (a product of alkali-activated fly ash pastes), similar to what seen in the case of fly ash-slag geopolymers and alkali activated cement-fly ash blends [26,162,163].

The exact nature and the amount of reaction products will be determined by following the procedure described in Chapter 3 by sequentially treating the samples collected at various ages with salicylic acid-methanol (SAM) and hydrochloric acid (1:20 by volume) followed by infrared spectral subtraction [162]. Figure 6.3 shows the weight % of the sample that was dissolved during SAM treatment (C-S-H/C-A-S-H) and the unreacted fly ash that remained after HCl treatment on the residue after the SAM treatment (HCl on SAM). The presence of K-A-S-H could not be inferred directly from these sequential treatments because HCl treatment dissolves K-A-S-H as well as unreacted slag. Therefore, the amount of insoluble residue after HCl treatment gives the amount of unreacted fly ash. The amount of C-S-H/C-A-S-H (product dissolved in SAM treatment) increases with the time (from 5 hrs to 24 hrs...
Figure 6.2: SEM-SEI images of pastes activated with 1.86 M KOH solution at a, b: 24 hrs old; c,d: 7 days old
Figure 6.3: Analysis of selective dissolution treatments presented as dissolved % by the initial sample mass of hydroxide activated fly ash-slag paste at 5 hrs, 24 hrs, and 168 hrs (7 days). Also, the amount of fly ash decreases from 5 hrs to 24 hrs and remains almost constant from 24 hrs to 7 days. The large increase in C-S-H/C-A-S-H amount from 5 hrs to 24 hrs indicates that the reaction peak seen from isothermal calorimetry corresponds to a heavy precipitation of C-S-H/C-A-S-H.

Spectral subtraction was performed on samples collected at 5 hrs, 24 hrs, and 7 days to understand the nature of products dissolving in each of the treatments. The subtraction spectra obtained for phases dissolved in SAM treatment and HCl treatment on the residue after SAM treatment are given in Figure 6.4. The IR spectra of product dissolved in SAM treatment at various ages are given in Figure 7.10b. The spectrum of C-S-H/C-A-S-H at 5 hr reveals a broad band centered around 954 cm\(^{-1}\) which sharpens with age. The peak is positioned at much lower wave number than what is usually anticipated with K-A-S-H.
gel (lies closer to 1000 cm\(^{-1}\)) and therefore, it is believed that the product dissolved in SAM treatment is C-S-H/C-A-S-H \(^{82}\). The peak at 954 cm\(^{-1}\) may be attributed to Si-O stretching vibrations associated with Q\(^2\) tetrahedra of the C-S-H gel, whose position depends on Ca/Si ratio \(^{89}\). Sharpening of peak is indicative of increased amount of product as well as increased homogeneity in the composition of the product \(^{60}\). The spectrum of K-A-S-H and slag that dissolved after the HCl treatment at various ages is given in Figure 7.11b. The spectrum of dissolved phases is a broad band at all ages, ranging between 858 and 960 cm\(^{-1}\) at 5 hrs, 840 and 980 cm\(^{-1}\) at 24 hrs. The spectrum mostly resembles slag whose main band is in the range of 850–930 cm\(^{-1}\) indicating that the amount of K-A-S-H gel is quite small. The spectrum at 7 days is also broad ranging between 1003 and 930 cm\(^{-1}\) and has shifted to higher wave numbers (centered around 980 \(^{-1}\)). This band also resembles slag but is broader in the higher wave number region compared to the slag spectrum. The main band position of K-A-S-H is around 1200–950 cm\(^{-1}\) depending on the aluminum substitution \(^{71,81,135}\). Therefore, the broad peak at 7 days which is now centered at 980 \(^{-1}\) corresponds to dissolution of a small amount of K-A-S-H gel and the complete dissolution of unreacted slag. To conclude, the main reaction product of hydroxide activated fly ash-slag mixes is proved to be C-S-H/C-A-S-H.

### 6.3 Silicate Activated Fly ash-Slag Cements

Figure 6.5 shows the rate of heat evolution of fly ash-slag pastes activated with both potassium hydroxide (KOH) and potassium silicate solutions of the same K\(_2\)O content and w/b ratio. Figure 6.5 also shows that the calorimetry results of hydroxide and silicate activated binders are reproducible. Calorimetric measurements show that both the hydroxide and silicate activated fly ash-slag pastes show three stages, namely, high initial peak characterized by wetting of particles followed by induction period, and then main reaction peak due to heavy precipitation of products. Rate of heat evolution curves reveal that the main reaction
Figure 6.4: a: C-S-H/C-A-S-H, b: K-A-S-H + Slag at various ages 5 hrs, 24 hrs, 168 hrs (7 days) of hydroxide activated fly ash-slag pastes

peak in silicate activated binders starts later than hydroxide activated binders, although, time to reach maximum peak height seem to coincide when the activating solutions had the same amount of K$_2$O content and made with same w/b ratio. The peak height is smaller for silicate activated binders compared to hydroxide activated binders. However, the total amount of heat evolved is higher in the case of silicate activated binders compared to hydroxide activated binders indicating a higher extent of reaction in silicate binders. Also, there seems to be heat evolved during the initial peak of silicate activated binders (within first 5 hrs) that is more significant than that seen in hydroxide activated binders. This could be attributed to product formation apart from wetting of particles. Because calorimeter takes 45 minutes to stabilize the signal, much information about very early age reaction is lost. Therefore, UWR method was used to monitor very early age hardening behavior.

Figure 6.6a shows the change in the S-wave reflection coefficient over time for the KOH and KOH-KSil activated fly ash-slag pastes. For the fly ash-slag mixes activated with KOH, the rate of hardening is observed to be slow for the first 3 hours followed by a rapid drop in the S-wave reflection coefficient. In contrast, the rapid drop in the S-wave reflection coefficient of silicate activated binders is almost instantaneous which then slows down approximately after
Figure 6.5: Rate of heat evolution at 22°C. Inset shows the total heat evolved with time of fly ash-slag binders activated with potassium hydroxide (KOH) solution and potassium silicate (KOH-KSil) solution (SiO$_2$/K$_2$O = 1.25). Both hydroxide and silicate mixes are activated with solutions of same K$_2$O content and same w/b ratio.

the first one hour, characterized by change in the slope of the curve. The onset of hardening, defined as the point at which S-wave reflection curve deviates from the initial slope of a linear fit, is 10 mins for silicate activated binders compared to 3.2 hours for hydroxide activated binders [26]. Figure 6.6b reports Proctor penetration tests performed on silicate activated binders showing that the drop in S-wave reflection coefficient corresponds to the point of strength gain in the solid [26,164].

The proctor resistance of silicate activated fly ash slag pastes shows a rapid increase in resistance starting around 10 mins after mixing which matched with the onset time from S-wave UWR curve. Therefore, the initial rapid change in the curve seen from both proctor and UWR indeed corresponds to a microstructure that is hardening and rapidly gaining strength. The reaction products start forming as early as 10 mins in the case of silicate activated fly ash-slag pastes which explains the initial rapid heat gain as seen from calorimetry curve.
Figure 6.6: a: S-wave reflection coefficient vs. time plot of KOH and KOH-KSil activated fly ash-slag pastes, b: Proctor penetration curves of fly ash-slag mixes activated with potassium silicate (KOH-KSil) solution.
Also, the presence of reaction product on the fly ash surface is seen as early as 1 hr from SEM-SEI micrographs ([26]). Evidence of product on the fly ash surface at 5 hrs during the seemingly induction period from calorimetry curves is clear from SEM-SEI micrographs given in Figure 6.7. Figure 6.7 also shows SEM-SEI micrographs of silicate activated binders at 24 hrs which is right after the main heat peak from the calorimetry curve and also at 7 days.

At 24 hrs, after the rate peak, microstructure is characterized by a voluminous precipitation of gel like product within the interstitial space between the particles. Unlike what is seen in hydroxide activated binders, where at 24 hrs product seems to be growing out from the surface of particles into pore space, here the transparent gel like product seems to have formed everywhere. Same is true at 7 days although product seems to be less transparent than it was at 24 hrs. So, the main heat peak seen in calorimetry plot corresponds to heavy precipitation of a voluminous gel in the silicate-activated fly ash-slag pastes.

Qualitatively, calorimetry curves seem to have a similar heat peak in hydroxide and silicate activated binders but they correspond to the formation of different products following different reaction mechanisms. The reaction mechanism in hydroxide activated fly ash-slag pastes seems similar to dissolution-precipitation mechanism of a ‘topotactic’ growth of C-S-H in Portland cement mixes [104]. The reaction mechanism in silicate activated fly ash-slag pastes seems to be is similar to the ‘through solution’ precipitation/gelation of C-S-H in sodium meta silicate activated slag pastes [29, 53, 153]. The main reaction product in hydroxide activated binders was predominantly C-S-H/C-A-S-H at all ages. However, the literature suggests that in the case of silicate-activated binders, there could be a coexistence of C-S-H/C-A-S-H and (N,K)-A-S-H. To further understand the nature of the product that corresponds to the heat peak seen from calorimetry, selective dissolution treatments along with FTIR spectral subtraction were performed on samples collected at 1 hr, 24 hrs, and 7 days.

Figure 6.8 shows the analysis of selective dissolution treatments as % dissolved of initial
Figure 6.7: SEM-SEI images of potassium silicate activated fly ash-slag pastes at a, b: 5 hr; c, d: 24 hr; e, f: 7 days old.
mass of silicate activated pastes and compared with hydroxide activated pastes. It is evident from Figure 6.8 that the amount of C-S-H/C-A-S-H increases and the amount of unreacted fly ash decreases with time in both KOH and KOH-KSil pastes. The amount of C-S-H/C-A-S-H formed in binders activated with hydroxide and silicate solutions are similar in quantities at all ages. The critical difference between the binders using different activator solution is seen from the spectra of dissolved phases. Figure 6.9 shows the evolution of C-S-H/C-A-S-H and K-A-S-H product through time in silicate activated fly ash-slag pastes. The position of IR peaks of the dissolved phases at various ages is compared in Table 6.1.

![Figure 6.8: Analysis of selective dissolution treatments presented as % dissolved by the initial mass at 5 hrs, 24 hrs, and 168 hrs (7 days) of hydroxide activated pastes (KOH) and at 1 hr, 24 hrs, 168 hrs (7 days) of silicate activated (KOH-KSil) fly ash-slag pastes.](image)

From Table 6.1, it is clear that the position of C-S-H formed is always at 954 cm\(^{-1}\) at various ages in hydroxide binders. The peak at 954 cm\(^{-1}\) corresponds to asymmetric Si-O stretching vibrations associated with \(Q^2\) sites of C-(A)-S-H gel \[89\]. On the contrary, in silicate activated binders, position of the band moves from 978 to 952 cm\(^{-1}\) in 24 hours that could be attributed to the depolymerization of the silicate chains with an increase
Figure 6.9: a: C-S-H/C-A-S-H b: K-A-S-H + Slag at various ages (1h, 24h, 7days) of silicate activated fly ash-slag pastes

in the Ca/Si ratio over time. A low Ca/Si ratio in C-S-H is often observed at the early ages of slag activation due to the presence of small amount of Ca from the dissolution of slag and significant amounts of Si present in the activator solution. With an increase in the dissolution of slag, the Ca/Si ratio of C-S-H could increase which will account for the shift. At 7 days, the peak position corresponding to Q\(^2\) sites of C-S-H/C-A-S-H gel shifted towards a lower wavenumber compared to the 1 hr old sample and towards a higher wavenumber compared to the 24 hrs old sample. This implies an increased aluminum substitution in C-S-H/C-A-S-H with time causing an increased cross-linking in the gel.

In the case of silicate-activated pastes, the presence of K-A-S-H was identified from the subtraction spectrum of phases dissolved in HCl after SAM. At 1 hr, the subtraction spectrum of dissolved products is broader in the higher wavenumber region compared to the slag spectrum. The broadness of the spectrum is attributed to the dissolution of a small amount of K-A-S-H geopolymer and the complete dissolution of unreacted slag. By 24 hrs, peak corresponding to K-A-S-H gel (1000 cm\(^{-1}\)) becomes sharper implying an increased amount of K-A-S-H gel in the microstructure and an increased homogeneity in the gel composition. Therefore, the main heat peak seen in calorimetry curve corresponds to the formation of
Table 6.1: Position of main IR spectrum bands in wavenumber (cm\(^{-1}\)) of C-S-H/C-A-S-H, K-A-S-H, and slag obtained through FTIR spectral subtraction in hydroxide activated and silicate activated fly ash-slag pastes at various ages. The Si-O-T asymmetric stretching vibration band will be referred to as the main band.

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<tbody>
<tr>
<td>KOH</td>
<td>5 h</td>
<td>954 (b)</td>
<td>858-960 (b)</td>
</tr>
<tr>
<td>KOH</td>
<td>24 h</td>
<td>954</td>
<td>840-980 (b)</td>
</tr>
<tr>
<td>KOH</td>
<td>7 d</td>
<td>954</td>
<td>1003-930 (b), centered around 980</td>
</tr>
<tr>
<td>KOH-KSil</td>
<td>1 h</td>
<td>978</td>
<td>868-1011 (b)</td>
</tr>
<tr>
<td>KOH-KSil</td>
<td>24 h</td>
<td>952</td>
<td>1000, 860-910 (bs)</td>
</tr>
<tr>
<td>KOH-KSil</td>
<td>7 d</td>
<td>960</td>
<td>992, 1020 (s), 860-940 (bs)</td>
</tr>
</tbody>
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s: shoulder
b: broad

Both K-A-S-H and C-S-H/C-A-S-H gels from the solution. By 7 days, the peak shifts to lower wave numbers with an increasing substitution of Si with Al indicating continued polymerization or increasing mean chain length. The incorporation of Al atoms in the silicate chains is known to increase the silicate mean chain length of C-(A)-S-H gels when compared with Al-free samples \[58, 166\]. The presence of slag spectrum at 860-940 cm\(^{-1}\) even at 7 days shows that significant amounts of unreacted slag still remains in the mix.

In silicate activated binders, product seem to have precipitated in-between particles and within the interstitial pore space as a voluminous gel. In hydroxide activated binders, product was seen to grow from the surface of particles into the pore space. The formation of voluminous gel in silicate activated binders could be due to gelation where the activator solution gels once aluminosilicates oligomers in the solution reach a certain extent of polymerization. The longer it takes for aluminosilicate species to reach the polymerized state, the longer it takes for the gel formation to initiate. Therefore, the degree of polymerization of the predominant species in the activator solution will play an important role in the kinetics of gel formation in silicate activated binders. This will be further verified in later chapters.
6.4 Conclusions

The nature of activator solution has significant effect on the reaction kinetics, nature of reaction products, and the microstructure development of alkali activated binders with medium calcium content. The total heat evolved was higher in silicate activated binder compared to hydroxide activated binders indicating higher extent of early age reaction. S-wave reflection coefficient curves showed that the silicate activated binders harden faster than the hydroxide activated binders.

The C-S-H/C-A-S-H was seen to have formed in both binders. The C-S-H/C-A-S-H formed in silicate activated binders had higher Ca/Si ratio at 1 hr which seemed to have taken more Al with time. In hydroxide binders, C-S-H/C-A-S-H formed had same Ca/Si ratio at all ages.

At 1 hr, silicate activated binders had both C-S-H/C-A-S-H and K-A-S-H gels. From 5 hrs to 7 days, the amount of K-A-S-H gel increases with time indicated by an increase in the sharpness of peak from FTIR spectral subtraction. In the case hydroxide activated binders, C-S-H/C-A-S-H was the prominent product until 24 hrs. A very small amount of K-A-S-H like product with silica content characterized by broad peak from FTIR was seen at 7 days.

The main reaction product of hydroxide activated fly ash-slag mixes is proved to be C-S-H/C-A-S-H which corresponds to the reaction peak seen from the calorimetry. However, the main heat peak seen in calorimetry curve of silicate activated fly ash-slag mixes corresponds to the formation of both K-A-S-H and C-S-H/C-A-S-H gels from the solution. Therefore, the appearance of peak in silicate activated systems depend on the gelation of K-A-S-H.

In silicate activated binders, product seem to have precipitated in-between particles and within the interstitial pore space. In hydroxide activated binders, product was seen to grow from the surface of particles into the pore space.
CHAPTER 7

INFLUENCE OF NUCLEATION SEEDS IN HYDROXIDE ACTIVATED FLY ASH-SLAG BINDERS

7.1 Introduction

The primary goal of the present chapter is to verify the hypothesis 2 stated in chapter 1 that C-S-H/C-A-S-H seed can act as nucleation sites for geopolymer gel formation. From selective dissolution studies and FTIR spectral subtraction, the presence of C-S-H during the accelerated hardening phase (at 5 hrs) in hydroxide activated fly ash-slag geopolymer cements has already been established (hypothesis 1). The present chapter is set out to verify the hypothesis in hydroxide activated fly ash-slag medium calcium binders systematically by first understanding if the reaction mechanism is nucleation - growth controlled followed by the addition of synthesized C-S-H gel to monitor its effect on the formation of geopolymer gel.

To understand the nature of reaction mechanism in hydroxide activated fly ash-slag binder and to verify if the reaction is nucleation controlled, seeds of high surface area (both product based and non-product based) will be added to fly ash-slag binders. The addition of external seeds provides a valuable information about the early age reaction mechanism, which has important implications for controlling the rate of setting/hardening. If the reaction is nucleation and growth controlled, the addition of nucleation seeds are known to effect reaction kinetics, microstructure, amount of product formed, and the raw material dissolution as follows:

- Addition of seeds with high surface area increases the reaction rate. The rate is proportional to the surface area of the seed
• The total amount of product will be higher during the early reaction period due to nucleation in pore space

• Product formation away from particle surfaces increases the dissolution of raw materials

• The nucleation of hydration product in the pore space increases the amount of product between particles leading to a denser microstructure

If the reaction were dissolution controlled and not nucleation and growth controlled, then the seed would have little or no effect on the reaction kinetics. The effect of seed addition on reaction kinetics was monitored using isothermal calorimeter, and the hardening was measured using S-wave UWR. The extent of product formation and fly ash dissolution were determined through selective dissolution techniques. The microstructure of samples was analyzed using scanning electron microscopy (SEM). The effect of synthesized C-S-H gel on the formation of geopolymer gel will be studied by determining the nature of the reaction product at early age by performing selective dissolution treatments and FTIR spectral subtraction.

7.2 Reaction Mechanism in Hydroxide Activated Binders

Reaction mechanism in hydroxide activated fly ash-slag binders will be verified by adding nucleation seeds. If the reaction is nucleation controlled then the addition of nucleation seeds should accelerate the onset of reaction. The laboratory synthesized wet C-S-H (Ca/Si - 1.0), and C-A-S-H (Ca/Si - 0.95 and Al/Si - 0.12) seeds were used. The fly ash-slag pastes used in this chapter were activated with 1.86 M KOH concentration and w/b ratio of 0.32. At seed dosages >0.8% by weight of solids (fly ash + slag) or 1% by weight of fly ash, it
becomes harder to mix the paste without increasing w/b ratio because of shear thickening nature of the seed-activator solution. Therefore, 0.8% (by weight of solids) was chosen as seed dosage for the study. To understand the effect of surface area of seeds on the reaction kinetics, instead of increasing the dosage of the wet seed, we have used dry seed (of a lower surface area) of the same dosage.

The effect of non-reactive seeds on the reaction kinetics was also studied as a part of this study. The seeds like nanoparticulate SiO\(_2\) (nano-SiO\(_2\)), Al\(_2\)O\(_3\) (nano-Al\(_2\)O\(_3\)), ZnO (nano-ZnO), and finely powdered CaCO\(_3\) were added at 0.8% (by weight).

### 7.2.1 Effect of Nucleation Seeds on Early Age Reaction Kinetics

Figure 7.1 shows the effect of 0.8% (by total weight of solids or 1% by weight of fly ash) of C-S-H and C-A-S-H seeds addition on the reaction kinetics of hydroxide activated fly ash-slag pastes. The addition of seeds has effectively eliminated the induction period, increased the height of the main reaction peak, and shortened the time to reach the maximum peak height. The elimination of induction period in the presence of seeds could be due to the availability of a vast number of nuclei for the growth of the product starting from time zero \[104\]. The increase in the height of the reaction peak could be attributed to many regions of product growing at the same time \[104\]. The inset in Figure 7.1 shows the total amount of heat evolved from fly ash-slag pastes during the reaction with and without seed. Mixes with seeds show higher initial heat compared to the mix without any seed. The effect of the chemical composition of seed (C-S-H vs. C-A-S-H) on the reaction kinetics is negligible. Hereafter, the discussion will focus only on the effect of C-S-H (product based) seed.

Figure 7.2 shows the S-wave reflection coefficient of hydroxide activated fly ash-slag pastes with and without 0.8% C-S-H seed. In the presence of seed, the onset point is at 1.9 hrs compared to 3.2 hrs for the mix without any seed. The onset point occurs earlier in the presence of 0.8% C-S-H seed. Puligilla et al. proved that in geopolymer cement systems, the drop in s-wave reflection is related to the strength gain by the microstructure \[26\]. Therefore,
Figure 7.1: Rate of heat evolution at 22°C of fly ash-slag systems activated with potassium hydroxide solution and made with 0.8% (by wt. of fly ash + slag) of C-S-H (Ca/Si - 1.0) and C-A-S-H (Ca/Si - 0.95, Al/Si - 0.2) seed. Ca/Si ratio of C-S-H and Ca/Si, Al/Si ratio of C-A-S-H is given in the parentheses.
the earlier occurrence of onset point in samples with seed indicates a faster rate of product formation.

The reaction in hydroxide-activated fly ash-slag binders is further verified by using the diluted activator solution. Reaching supersaturation is expected to be delayed in dilute activator solution causing delay in the onset of nucleation. If nucleation is the rate limiting step in a reaction, addition of seeds should eliminate the time to reach supersaturation and for nucleation to initiate. Therefore, addition of seeds to diluted binders is an effective method for demonstrating if nucleation is the rate limiting step in hydroxide binders. Figure 7.3 shows the effect of 0.8% C-S-H seed addition on the heat evolution of diluted binders-high w/b ratio or a low-KOH concentration mix. From the calorimetry results, the addition of 0.8% C-S-H seed accelerates the onset of main reaction peak and eliminates the induction period even in the diluted systems (w/b - 0.38). Therefore, in hydroxide activated binders, the presence of seeds eliminates the time for nucleation which seems to be the rate limiting step.
Figure 7.3: Rate of heat evolution at 22°C of fly ash-slag systems activated with potassium hydroxide solution of two different concentrations (1.6 M, 1.86 M) or two different w/b ratios (0.32, 0.38) and made with 0.8% (by wt. of fly ash + slag) of C-S-H seed. Seed accelerates the reaction even in diluted systems.
Figure 7.4: Rate of heat evolution at 22°C of fly ash-slag systems activated with potassium hydroxide solution and made with 0.8% (by wt. of fly ash+slag) of nano-\( \text{Al}_2\text{O}_3 \), nano-ZnO, \( \text{CaCO}_3 \), and 0.8% and 3% of nano-\( \text{SiO}_2 \).

Figure 7.4 shows the isothermal calorimetry data of fly ash-slag pastes with 0.8% addition of nano-\( \text{SiO}_2 \), nano-\( \text{Al}_2\text{O}_3 \), nano-ZnO, and \( \text{CaCO}_3 \) seeds. In the case of nano-\( \text{SiO}_2 \), nano-\( \text{Al}_2\text{O}_3 \), and \( \text{CaCO}_3 \) addition, the effect on calorimetry reaction peak is similar to the addition of C-S-H seed. Non-product seeds (except ZnO) have an accelerating effect on the reaction peak to different degrees. The nano-ZnO seed decelerated the reaction and eliminated the reaction peak for at least 60 hours. Paste with added nano-ZnO seed remained soft even after 7 days. The retarding effect of nano-ZnO seed is discussed in detail later in the chapter.

7.2.2 Effect of Surface Area of the Seed on Early Age Reaction Kinetics

The effect of surface area on the reaction was studied by using C-S-H seed of same composition and dosage but different surface areas, namely, dry seed and wet seed. It has been
Figure 7.5: Rate of heat evolution at 22°C of fly ash-slag systems activated with potassium hydroxide solution made with 0.8% (by wt. of fly ash + slag) of C-S-H seed (Ca/Si = 1.0) of different surface areas (dry and wet)

presented in [Chapter 5](#) that dry C-S-H seed has considerably lower surface area than the wet seed at a similar Ca/Si ratio. The rate of heat evolution was monitored through isothermal calorimetry, and the data is presented in Figure 7.5. From the Figure 7.5, main reaction peak starts earlier in the case of wet seed compared to dry seed. Also, the time it takes for the peak to reach maximum height is shorter in the case of wet seed than the dry seed. The delay in the initiation reveals that fewer nucleation sites are available for a product to start growing in the case of dry seed. The increase in the surface area increases the early reaction by increasing the number of growth regions. However, because of the close proximity of growing regions, the product on adjacent areas starts impinging into each other, slowing down the rate of the growth. The mechanism becomes diffusion controlled sooner in the case of wet seed which explains the reduced total heat in wet seed sample compared to the dry seed mix. An optimum dosage of nucleation sites is needed for the growth to continue longer providing further proof that the hydroxide activated fly ash-slag is truly a nucleation-growth controlled reaction.
The effect of surface area can also be demonstrated through the addition of different dosages of non-product seeds. Figure 7.4 shows the effect of varying amounts (0.8% and 3%) of nano-SiO$_2$. For both the dosages, the induction period is essentially eliminated. As the amount of seed increases, the maximum reaction rate increases, as well as the total amount heat evolved at the end of main reaction period (inset to Figure 7.4). Results show that the reaction degree is proportional to the surface area of the seed. At both dosages, the time to reach the maximum peak height remains the same. This observation is similar to the effect of silica-containing additives on the hydration kinetics of C$_3$S by Thomas et al. [104]. It should, however, be noted that for the same dosage amounts, the wet C-S-H seed was more effective in accelerating the reaction than nano-SiO$_2$.

The nano-SiO$_2$ (55 m$^2$/g) seed has lower surface area than nano-Al$_2$O$_3$ (80 m$^2$/g) but it has a significantly larger accelerating effect on the reaction at similar dosages. Drawing similarities with the effect of silica fume on cements, the accelerating effect of nano-SiO$_2$ is attributed to nano-SiO$_2$ acting as a source of pure silica which reacts with calcium ions dissolving from slag to form C-S-H near its surface. The initial layer of C-S-H that forms on the surface of nano-SiO$_2$ could act as a nucleation seed for further precipitation of C-S-H. Nano-SiO$_2$ has a strong accelerating effect but still not as good as the C-S-H itself as the effectiveness of nano-SiO$_2$ seed must still depend on the rate of calcium release from slag. The acceleration of early age reaction is only modest in the presence of finely powdered CaCO$_3$ and nano-Al$_2$O$_3$, even though they do not react to form C-S-H, they provide a surface to promote heterogeneous nucleation within pore space away from the raw materials.

### 7.2.3 Effect of Nucleation Seed on the Extent of Product Formation

Selective dissolution treatments were performed on the pastes with and without 0.8% C-S-H (wet) at various ages to compare the amount of product formed and the amount of unreacted
Figure 7.6: Analysis of sequential selective dissolution treatments on hydroxide activated fly ash-slag paste with and without 0.8% C-S-H seed at 5 hrs, 24 hrs, and 7 days. Solid squares are for mixes without any seeds and open squares for mixes with added seeds. Y-axis on the left represents wt.% of C-S-H/C-A-S-H raw materials. Samples collected at different ages (5 hrs, 24 hrs, and 7 days) were treated with SAM solution and the amount of C-S-H product dissolved is shown in Figure 7.6. At 5 hrs, the amount of C-S-H is 12% in the seeded sample compared to 3% in the unseeded mix. In seeded samples, the amount of C-S-H/C-A-S-H keeps increasing until 24 hrs after which it pretty much remains constant. In unseeded samples, the amount of C-S-H/C-A-S-H was in lesser quantities than the seeded mix at all ages. However, the amount keeps increasing until 7 days. In the presence of seed, the amount of C-S-H is higher at early ages during accelerated hardening phase. The external C-S-H seed acts as a nucleation site for further C-S-H product precipitation.
7.2.4 Effect of Nucleation Seed on the Extent of Fly ash Dissolution

The insoluble residue after SAM treatment collected at different ages (5 hrs, 24 hrs, and 7 days) was further treated with HCl solution and the amount of unreacted fly ash left over was calculated and is shown in Figure 7.7.

At 5 hrs, the amount of unreacted fly ash is much smaller in seeded samples compared to unseeded samples, and it remains almost constant until 7 days. In the case of unseeded samples, the amount drops until 24 hrs and then remains constant after that for 7 days. The presence of seed increased the amount of reaction product and the extent of dissolution in raw materials during accelerated hardening phase. The total amount of reaction during early nucleation and growth period is higher in the case of seeds because the seed material will nucleate the product in the capillary pore space away from the particle surfaces thereby providing little to no interference to the dissolution of raw materials (fly ash and slag).

7.2.5 Effect of Nucleation Seed on the Microstructure

Figure 7.8 shows SEM-SEI micrographs of hydroxide activated systems with and without 0.8% C-S-H seed. At 5 hrs, the micrograph of the unseeded sample shows a very small amount of product around and in-between fly ash particles. On the contrary by 5 hrs, in the presence of seed, the sample has gained strength and shows the product on fly ash as well as in-between fly ash spheres. At 7 days, there does not seem to be a large difference between the micrographs of samples with and without seed.
Figure 7.7: Analysis of sequential selective dissolution treatments on hydroxide activated fly ash-slag paste with and without 0.8% C-S-H seed at 5 hrs, 24 hrs, and 7 days. Solid squares are for mixes without any seeds and open squares for mixes with added seeds. Y-axis on the left represents wt.% of unreacted fly ash.
Figure 7.8: SEM-SEI micrographs of KOH activated systems with and without 0.8% C-S-H seed at 5 hrs and 7 days. a: KOH at 5 hrs, b: KOH-0.8% C-S-H at 5 hrs, c: KOH at 7 days, d: KOH-0.8% C-S-H at 7 days.
7.2.6 Effect of Surface Area of Seed on C-S-H Formation and Fly ash Dissolution

Figure 7.9 shows the amount of C-S-H product and the amount of unreacted fly ash in hydroxide activated binders at various ages through selective chemical dissolution techniques. The graph shows that the amount of C-S-H is higher at all ages in the case of 0.8% C-S-H seed compared to 0.8% nano-SiO$_2$ seed and the mix without any seed. At 0.8% of seed quantity, wet C-S-H seed seems to have the most accelerating effect on the reaction rate of hydroxide activated fly ash-slag pastes because the wet C-S-H seed has the largest surface area compared to the other seeds.

In conclusion, the addition of both product based seeds and non-product based seeds in hydroxide activated binders had three important effects on the measured kinetics:

- The induction period was effectively eliminated
The total amount of reaction product was higher at early age

The higher amount of fly ash dissolution was observed at early ages

The effect of the addition of C-S-H/C-A-S-H seeds on the reaction of fly ash-slag pastes is similar to what is seen in the case of Portland cement hydration and alkali activated slag hydration \[53, 104\]. The addition of synthesized C-S-H/C-A-S-H seed accelerates the reaction of fly ash-slag by providing the additional nucleation sites for the growth of reaction products. In nucleation and growth controlled reactions, the reaction rate is proportional to the surface area of contact between the regions of the reaction product and the solution \[104\]. So, the effect of surface area on the rate of reaction was also verified. For Portland cement pastes, it is well known that the early hydration that corresponds to the characteristic rate peak in the calorimetry is nucleation and growth process. As fly ash-slag pastes activated with potassium hydroxide behave similarly, it indicates that the nucleation and growth are the rate-controlling steps in this case as well. If the reaction were dissolution controlled, then the seed would have had little or no effect on the reaction kinetics.

### 7.3 Effect of C-S-H on the Rate of Product Formation

The earlier section in the chapter has firmly established that the reaction in hydroxide activated fly ash-slag medium calcium binders is nucleation-growth controlled. The current section will study the effect of C-S-H/C-A-S-H on the geopolymer gel formation to verify hypothesis 2. From selective dissolution treatments, C-S-H seed promotes further C-S-H precipitation and increases raw material dissolution. However, selective dissolution treatments did not provide any information about the the nature of geopolymer gel that might be forming in the system. In this section, spectral subtraction of IR spectra before and after each of the selective dissolution treatments (SAM and HCl on SAM) was performed to study the effect of C-S-H on the nature of C-(A)-S-H product and any geopolymer gel forming in the microstructure.
7.3.1 Effect of Seed on the Nature of C-(A)-S-H

Samples collected at different ages (5 hrs, 24 hrs, and 7 days) were treated with SAM solution and the IR spectra of product dissolved in SAM treatment at various ages is given in Figure 7.10. The main band of product appears sharp and is positioned at 954 cm$^{-1}$ in seeded samples at all ages (5 hrs, 24 hrs, 7 days). The peak at 954 cm$^{-1}$ at 5 hrs is broader in the sample without any seed (refer to 7.10a) unlike seen in the sample with seed which becomes sharper by 24 hrs. As mentioned before, the peak at 954 cm$^{-1}$ is attributed to Si-O stretching vibrations associated with Q$^2$ tetrahedra of the C-S-H gel [89]. The peak for C-S-H product remains sharp until 7 days. The main band in FTIR spectrum of precipitated C-S-H in the presence of 0.8% C-S-H seed always appears at 954 cm$^{-1}$.
7.3.2 Effect of Seed on the Nature of the Phases Dissolved in HCl Treatment

The insoluble residue after SAM treatment collected at different ages (5 hrs, 24 hrs, and 7 days) was further treated with HCl solution and the amount of unreacted fly ash left over was calculated and is shown in Figure 7.7.

The subtraction spectra of products dissolved after the HCl treatment at various ages in the seeded mix is shown in Figure 7.11. The spectrum for dissolved phases has a broadband at all ages, ranging between 860 and 950 cm\(^{-1}\) at 5 hrs and 880 and 980 cm\(^{-1}\) at 24 hrs which resemble slag (whose main band is in the range of 850–930 cm\(^{-1}\)). Therefore, the only product in these systems until 24 hrs seems to be just C-S-H. At 7 days, the spectrum has two broad peaks, one centered around 1045 cm\(^{-1}\) and the other centered at 1106 cm\(^{-1}\) [81,167].

In the study done on hydroxide activated fly ash pastes, the peak position of aluminosilicate gel product formed varied from around 1000 cm\(^{-1}\) (Al-rich gel at 2 hrs) to 1020 cm\(^{-1}\) (at 7 days). Therefore, the peaks at 1045 cm\(^{-1}\) and 1106 cm\(^{-1}\) are characteristic of Q\(^3\) and Q\(^4\) silicon tetrahedra in silica gels and not aluminosilicate gel [82]. The lack of spectrum near 850-930 cm\(^{-1}\) indicates that the amount of high silica product dissolved in HCl treatment is relatively greater than the amount of undissolved slag.

The peak positions of C-S-H/C-A-S-H and K-A-S-H of hydroxide activated fly ash-slag systems with and without 0.8% C-S-H seed at various ages are summarized in Table 7.1 for easy comparison.

From subtraction spectra at various ages, it can be concluded that the C-S-H/C-A-S-H is the main product in hydroxide activated fly ash-slag systems when seeds are added. It is the only product at very early ages (5 hrs, 24 hrs) during the accelerated hardening phase. Combining the dissolution results and the FTIR results, synthesized C-S-H acts as a nucleation seed for the precipitation of C-S-H itself and doesn’t seem to have nucleated any K-A-S-H gel.
Figure 7.11: Subtracted spectra of products dissolved in HCl treatment (Unreacted slag and K-A-S-H) of hydroxide activated fly ash-slag pastes with 0.8% C-S-H seed (a) and without seed (b) at various ages (5 hrs, 24 hrs, 7 days)

7.3.3 Effect on Microstructural Development

Quantitative EDS analysis was performed on 7 day old KOH and KOH-0.8% C-S-H sample to study the chemical makeup of reaction products formed in the system. All the ratios that are calculated from EDS microanalysis results are compared with the ratios set by Garcia-Lodeiro et. al. to distinguish between C-A-S-H and (Ca, K)-A-S-H and are given below [98]:

\[
\text{C-A-S-H} : 0.72 < \frac{\text{CaO}}{\text{SiO}_2} < 1.94; 0 < \frac{\text{Al}_2\text{O}_3}{\text{SiO}_2} < 0.1
\]

\[
\text{(Ca,K)-A-S-H} : 0 < \frac{\text{K}_2\text{O}}{\text{Al}_2\text{O}_3} < 1.85; 0 < \frac{\text{CaO}}{\text{SiO}_2} < 0.3; 0.05 < \frac{\text{Al}_2\text{O}_3}{\text{SiO}_2} < 0.43
\]

EDS spot analysis on KOH sample indicates the presence of mixed phases (average of 15 points) with an average of, \( \frac{\text{K}_2\text{O}}{\text{Al}_2\text{O}_3} = 0.49\pm0.16, \frac{\text{CaO}}{\text{SiO}_2} = 0.40\pm0.09, \frac{\text{Al}_2\text{O}_3}{\text{SiO}_2} = 0.22\pm0.05. \) The compositional ratios of products do not fall into any of the ratios mentioned above. A distinctive and segregated C-A-S-H/C-S-H phase was not found in the BSE images, which is similar to an earlier observation made on class F fly ash-slag geopolymers and Class C fly ash geopolymers [22, 23]. It has been found that in geopolymers in the presence
Table 7.1: Position of main IR spectrum bands in wavenumber (cm$^{-1}$) of C-S-H/C-A-S-H, K-A-S-H, and slag obtained through FTIR spectral subtraction in hydroxide activated fly ash-slag pastes with and without 0.8% C-S-H seed at various ages. Slag spectrum is broad which ranges from 850-930 cm$^{-1}$. The Si-O-T asymmetric stretching vibration band will be referred to as the main band.

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<tr>
<td>KOH</td>
<td>5 h</td>
<td>954 (b)</td>
<td>858-960 (b)</td>
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<td></td>
<td>24 h</td>
<td>954</td>
<td>840-980 (b)</td>
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<td></td>
<td>7 d</td>
<td>954</td>
<td>1003-930 (b)</td>
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<tr>
<td>KOH-0.8% C-S-H seed</td>
<td>5 h</td>
<td>954</td>
<td>860-950(b), 1162</td>
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<td>880-980(b), 1106</td>
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<tr>
<td></td>
<td>7 d</td>
<td>954</td>
<td>1045(b), 1106(b)</td>
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s: shoulder
b: broad

of calcium, C-S-H/C-A-S-H phases to be always intermixed with (N, K)-A-S-H gels at a scale much smaller than the sensitivity of EDS leading to mixed phase response as seen here [22, 23, 26]. The EDS analysis of the sample with a representative spectrum and an average atomic ratio of various elements is given in 7.12a. At 7 days, the microstructure of KOH samples is a mixed phase which seems to match with FTIR of dissolved products after selective chemical dissolution tests.

The quantitative microanalysis of hydroxide activated sample with 0.08% C-S-H seed (KOH-0.08% C-S-H) sample, indicated the presence of (Ca, K)-A-S-H phase only. The average composition of (Ca,K)-A-S-H (average of 10 points) is $K_2O/Al_2O_3 = 0.33 \pm 0.11$, $CaO/SiO_2 = 0.13 \pm 0.06$, $Al_2O_3/SiO_2 = 0.22 \pm 0.07$. The EDS analysis of the sample with a representative spectrum and an average atomic ratio of various elements is given in 7.12b. At 7 days, the dominant phase that is present in the microstructure of KOH-0.8% C-S-H sample is (Ca, K)-A-S-H.

From FTIR subtraction results on 0.8% C-S-H seed samples, the product that dissolved in HCl after SAM treatment was predominantly slag at 5 hrs and 24 hrs. During the same
time, the analysis of weight loss during selective dissolution treatments showed a higher percentage of C-S-H/C-A-S-H product. Even at 7 days, there was no evidence of K-A-S-H gel but rather a silica gel. From EDS results, the dominant phase in the microstructure at 7 days seems to be (C, K)-A-S-H. Therefore, when an extra amount of C-S-H is supplied to the system as seed, it seems to nucleate more C-S-H but not K-A-S-H.

In seeded hydroxide systems, as Al and Si dissolve from slag and fly ash, they form silicate and aluminosilicate species. In the presence of Ca, very reactive silicate/aluminosilicate species precipitate as C-(A)-S-H owing to its low solubility. The precipitation of C-A-S-H continues until calcium ions are exhausted. When calcium ions become scarce, upon further dissolution of aluminate and silicate species from raw materials, aluminosilicate species can potentially reach supersaturation which could eventually result in the gelation of K-A-S-H. Especially with potassium based geopolymers, gelation does not initiate unless there is a sufficient supply of larger aluminosilicate anions because potassium cation can stabilize large aluminosilicate anions through cation-anion pairs. However, if a significant amount of C-(A)-S-H has already formed in the system, the probability of forming large aluminosilicate
species drops very sharply due to reduced movement of species. Even if K-A-S-H forms closer to the particle surface or in pore spaces, at high pH values, C-A-S-H is known to destabilize any K-A-S-H product to form (C, K)-A-S-H (high Al/Si and low Ca/Si ratio) \[98\]. Therefore, C-A-S-H gel is most probably the primary product in hydroxide activated fly ash-slag systems. In conclusion, C-(A)-S-H formed in hydroxide activated fly ash-slag binders does not provide nucleation sites for aluminosilicate gel formation. Thus, disproving hypothesis 2.

### 7.4 Combined Effects of Seeding and Retarder

Among all the nano seeds that were tested, nano-ZnO presented the most surprising results. The reaction peak in calorimetry was eliminated (for at least 80 hours), and it has a strong retarding effect at a dosage of just 0.8% (by weight). Hajimohammadi et. al. studied the effect of nanoscale ZnO on geopolymers made from geothermal silica-sodium aluminate-water using time-resolved and spatially resolved synchrotron infrared spectroscopy \[107\]. Hajimohammadi’s study showed that the nano-ZnO seeds enhanced the dissolution of geothermal silica by inducing nucleation of aluminosilicate gel in the initially Al-rich reaction mixture and thereby increasing the aluminosilicate gel formation in the microstructure at early stages of the reaction \[107\]. However, in the present study, nano-ZnO had an opposite effect retarding the silicate-activated fly ash-slag reaction.

The addition of ZnO is known to retard the hydration of cement (also shown in Figure \[5.8a\]) unlike the acceleration seen with the addition of C-S-H, C-A-S-H, and nano-Al\(_2\)O\(_3\) \[169,170\]. Gawlicki et al. noted that in an alkaline environment, ZnO turns into an amorphous zinc hydroxide effectively disturbing calcium hydroxide formation \[169\]. They hypothesized that during the early hydration, amorphous zinc hydroxide impregnates initially formed C-S-H layer forming a highly impermeable layer on C\(_3\)S surface effectively isolating cement particles from water and thus retarding the cement hydration \[169\]. They predicted that
the retardation ends with the transformation of amorphous zinc hydroxide into crystalline calcium hydrozincite. The difference in the density between amorphous and crystalline compounds causes porosity in the previously impermeable C-S-H layer. Increased porosity lets water access $C_3S$ surface again promoting further dissolution and hydration. Ataie et al. monitored the concentration of calcium in the pore solution of hydrating cement with added ZnO and concluded that the calcium ion concentration keeps increasing even during the prolonged induction phase [170]. Increasing calcium concentration contradicts Gawlick et al.'s hypothesis that ZnO inhibits dissolution of cement. Ataie et al. further proposed that the retardation may have been caused due to the dissolving zinc ions “poisoning” the hydration product (C-S-H) nuclei immediately after the precipitation. The process continues until all the zinc ions are consumed and the hydration resumes when there are no free Zn ions in the solution [170]. Studies by Tommaseo et al. and several others provide evidence that C-S-H gel uptakes Zn ions by getting incorporated into the interlayers of C-S-H gel which support the poisoning effect of Zn ions on C-S-H hypothesis proposed by Ataie et al. [171–175].

The retardation seen with ZnO solution in the present study could have been due to the poisoning of initial C-S-H nuclei by Zn ions or due to the adsorption of the surfactant (N-vinyl-2-pyrrolidone ($((C_6H_9NO)_n)$)) on the fly ash particles or due to the adsorption/absorption of ZnO on to the surface of fly ash [170]. PVP is added as a surfactant during the synthesis of ZnO particles to control their size during the synthesis. Retarder, namely PVP, could act by absorbing onto fly ash, slag particles, and reaction products preventing nucleation and growth much like how sucrose retards cement hydration by poisoning nucleation surfaces [104]. To confirm the action of ZnO on the retardation, 0.8% (by weight) of ZnO powder (without PVP coming from the solution) was added to the mix and the reaction kinetics were monitored. Both ZnO powder and ZnO solution had same amount of solids. ZnO nanopowder was procured from US Research nanomaterials and had an average particle size of 18 nm which was smaller than the particle size of nano-ZnO solution.
Figure 7.13: Rate of heat evolution at 22°C of fly ash-slag systems activated with potassium hydroxide solution and made with 0.8%, nano-ZnO solution and 0.8% ZnO powder (with PVP). Figure 7.13 shows that both ZnO powder and ZnO solution retard the reaction in hydroxide activated solutions. Therefore, it is not the surfactant on ZnO nano particle surfaces that is causing the retardation.

Figure 7.14 shows that the extent of retardation increases with the amount of ZnO seed (solution). The mix even with as small as 0.08% addition of ZnO exhibited no peak for the first 50 hrs and the total heat starts to increase very slowly only after 30 hrs. If ZnO is retarding the reaction by poisoning the initial C-S-H nuclei or by adsorbing on to solid precursors to prevent nucleation, then the addition of nucleation sites in the form of C-S-H seed should reduce or eliminate the retarding effect. Therefore, 0.8% C-S-H seed was added to the mixes with 0.4% and 0.08% nano-ZnO. When 0.8% C-S-H seed was added to 0.4% ZnO addition, reaction peak is small. The total heat evolution is shown to increase gradually. At 0.4% nano-ZnO with 0.8% C-S-H seed, ZnO must have been effectively adsorbed onto fly ash, slag, and C-S-H seed particles preventing nucleation on any surface leaving the system to rely on homogeneous nucleation in the solution which explains the slow and gradual reaction.
Figure 7.14: Rate of heat evolution at 22°C of fly ash-slag systems activated with potassium hydroxide solution and made with 0.8%, 0.4%, 0.08% (by wt. of fly ash+slag) of nano-ZnO. Rate of heat evolution of pastes with the 0.8% C-S-H seed was added to the mixes with 0.4% and 0.08% ZnO.

When 0.8% C-S-H was added to 0.08% ZnO mix, the reaction peak looked similar to the mix without any seeds. Thus, the retarding effect of ZnO has been completely eliminated.

Figure 7.14 shows the microstructure of 0.08% ZnO mix which looks quite different from microstructure of original mix (without any seeds) at 7 days (Figure 6.2c). In hydroxide activated fly ash-slag mixes, growth was seen originating from the surface into the pore space away from the particles. Whereas in 0.08% ZnO mix, product seems to have formed in the pore space instead of growing from the surface of any particle. The retardation was eliminated when 0.8% C-S-H seed was added to 0.08% ZnO mix. This is probably because the ZnO adsorbed completely onto C-S-H seed which has a much higher surface area than fly ash or slag particles nullifying C-S-H seed effect. Thus, nucleation happened on the surface of the fly ash and slag particles very much like mix without any seeds. The microstructure of 0.08% ZnO-0.8% C-S-H (Figure 7.15b) seed looks similar to the microstructure of original
Figure 7.15: SEM-SEI micrographs at 7 days of a: KOH-0.08% ZnO b: KOH-0.08% ZnO -0.8% C-S-H mix (without any seeds) at 7 days(Figure 6.2c). This shows that the retardation caused by ZnO is mostly caused by interference with the nucleation of C-S-H gel on the surface of the particle. Combined effect of retarder and seeding is a further proof that the reaction in hydroxide activated fly ash-slag is nucleation-growth controlled.

7.5 Conclusions

The work presented in this chapter seeks to verify the second hypothesis related to the accelerated hardening in the presence of calcium in hydroxide activated fly ash-slag binders. Product-based synthesized C-S-H gel was added as a nucleation seed. The reaction kinetics were monitored through calorimetry and the addition of relatively small amounts of synthesized C-S-H and C-A-S-H gels to hydroxide activated fly ash-slag pastes caused a significant acceleration of reaction kinetics. The induction period was completely eliminated, the main reaction rate peak occurred earlier, and the extent of reaction that occurred during the early ages was increased. Experiments with the addition of nucleation seeds has provided a proof that the reaction in hydroxide activated fly ash-slag binders is nucleation and growth
Selective chemical treatments at 1 hr showed an increase in the amount of C-S-H/C-A-S-H gel and the extent of fly ash dissolution in the presence of C-S-H seed. This is an evidence that the fly ash dissolution increases in the presence of calcium. Increased amount of C-S-H/C-A-S-H gel implied that added seed provided nucleation sites for the precipitation of more C-S-H/C-A-S-H gel out of the pore solution. The FTIR spectral subtraction did not reveal the presence of any K-A-S-H gel at early ages. In the presence of seeds, geopolymer formation was completely suppressed in early stages and C-S-H/C-A-S-H gel was preferred. Therefore, the precipitation of initial C-S-H product does not act as a nucleation surface for the formation of geopolymer product but instead acts as nucleation site for further precipitation of C-S-H. The second hypothesis that C-S-H gel acts as a nucleation site for K-A-S-H gel precipitation has been proved wrong. Accelerated hardening seen in hydroxide activated systems is only related to the accelerated precipitation of C-S-H.

Experiments were also conducted using ZnO nano particles which acts as a powerful retarder even at dosages as small as 0.08% (by weight of solids). The retardation of ZnO can be negated by adding C-S-H seed. ZnO seemingly retards the reaction by preventing the nucleation of C-S-H gel on the particle surfaces. In conclusion, nano-particles can either accelerate or retard the reaction. This is an important finding with possible practical implications for controlling the rate of early stage hardening in hydroxide activated fly ash-slag cements. Combined effect of retarder and seeding is a further proof that the reaction in hydroxide activated fly ash-slag is nucleation-growth controlled.
CHAPTER 8

EFFECT OF C-S-H NUCLEATION ON THE FORMATION OF K-A-S-H GEL

8.1 Introduction

The present chapter will verify hypothesis 2, precipitated C-S-H will act as a nucleation seed for geopolymer gel formation, in silicate activated fly ash-slag binders by adding synthesized C-S-H gel. The effect of addition of synthesized C-S-H gel on the reaction kinetics, microstructure, hardening, and the extent of fly ash dissolution will be studied. Silicate activated mix design used in chapter 4 will be used in this chapter unless otherwise mentioned. Reaction kinetics was monitored using isothermal calorimeter, and the hardening was measured using S-wave UWR. The microstructure of samples was analyzed using scanning electron microscopy (SEM). The extent of product formation and fly ash dissolution were determined through selective dissolution techniques. Reaction products namely C-S-H and C-A-S-H were added as external seeds at 0.8% by the weight of fly ash. Furthermore, the effect of nucleation seeds on the reaction mechanism was also studied by adding non-product based seeds (nano-Al₂O₃, nano-SiO₂, nano-ZnO, and finely powdered CaCO₃) and the reaction kinetics was monitored using isothermal calorimeter.

It has already been established in chapter 4 and chapter 7 that the precipitation of C-S-H gel is the main reason behind accelerated hardening in both hydroxide activated and silicate activated fly ash-slag binders proving hypothesis 1. In chapter 7, the addition of external C-S-H seed to hydroxide activated fly ash-slag binders did not precipitate any extra K-A-S-H gel while accelerating the reaction. Hypothesis 2 has been disproved in hydroxide activated binders. A brief glimpse into the effect of seeds on silicate activated binders in chapter 5
has shown results contradicting the hydroxide activated binders. Therefore, it would be important to study the effect of seeds in depth and to verify if the initial precipitation of C-S-H will act as nucleation sites for aluminosilicate gel precipitation in silicate based fly ash-slag binders.

The present chapter is set out to verify the hypothesis in silicate activated fly ash-slag medium calcium binders systematically by first understanding if the reaction mechanism is nucleation - growth controlled followed by the addition of synthesized C-S-H gel to monitor its effect on the formation of geopolymer gel similar to the chapter 7.

8.2 Reaction Mechanism in Silicate Activated Binders

The laboratory synthesized wet C-S-H (Ca/Si - 1.0), and C-A-S-H (Ca/Si - 0.95 and Al/Si - 0.12) seeds were used for the study. The fly ash-slag pastes used in this chapter were activated with potassium silicate solution of SiO$_2$/K$_2$O of 1.25 and w/b ratio of 0.32. The effect of non-reactive seeds on the reaction kinetics was also studied. The seeds like nanoparticulate SiO$_2$ (nano-SiO$_2$), Al$_2$O$_3$ (nano-Al$_2$O$_3$), ZnO (nano-ZnO), and finely powdered CaCO$_3$ were added at 0.8% (by weight).

8.2.1 Effect of Nucleation Seeds on Early Age Reaction Kinetics

Figure 8.1 shows the isothermal calorimetry data for silicate activated fly ash-slag pastes with 0.8% of wet C-S-H gel (Ca/Si - 1.0, 1.3), and wet C-A-S-H gel (Ca/Si - 0.95, Al/Si - 0.12). Reaction kinetics of fly ash-slag mixes are known to be very sensitive to the shear history and temperature [25]. Because the seeds were dispersed in the activator solution using probe-sonication, heat curve of fly ash-slag paste prepared from the probe sonicated activator solution was used as a control. From Figure 8.1 seeds do not accelerate the reaction and rather decelerate the reaction to different degrees. In the case of C-S-H and C-A-S-H seeds, there is a delay in the initiation of the main reaction peak and the time to
reach the maximum peak height. The addition of nucleation seeds has little or no effect on acceleration of the reaction kinetics. It implies that the reaction is not nucleation and growth controlled and could be dissolution controlled. The deceleration in the reaction could be because of lowered raw material dissolution or due to the reduced extent of silica polymerization or due to the slower rate of aluminosilicate condensation all factors known to influence the hydrolysis-condensation reaction in geopolymer binders \[4,32,33\]. The reasons for deceleration are explored in greater detail later in the chapter.

Figure 8.1: Rate of heat evolution at 22°C of silicate activated fly ash-slag pastes with the addition of 0.8% C-S-H (Ca/Si - 1.0, 1.3) and C-A-S-H (Ca/Si - 0.95, Al/Si - 0.12). Above mentioned seeds were added as wet gels.

Figure 8.2 shows the variation of S-wave reflection coefficient over time for silicate activated fly ash-slag pastes along with 0.8% of added C-S-H (1.0) binders. The S-wave reflection coefficient curve of the mix with 0.8% C-S-H seed look different from the mix without any seeds. In the mixes with C-S-H seed, the drop in S-wave reflection coefficient seem to start right from the point of pouring into the HIPS container, and the slope is maintained for an hour and changes slowly over time. The clear onset point is not seen unlike the mix
without any seeds. Reflection coefficient value at any point in time is higher for seeded mix compared to the mix without any seeds. This indicates the rate of hardening has slowed down in the presence of C-S-H/C-A-S-H seeds and progressed more gradually. The presence of synthesized C-S-H seed delays the early age hardening in silicate activated fly ash-slag pastes.

Figure 8.2: S-wave reflection coefficient change of KOH-KSil paste with and without 0.8% C-S-H (1.0) Inset gives a close-up of the onset point.

Figure 8.3 shows heat evolution of silicate activated fly ash-slag pastes with the addition of 0.8% nano-\(\text{Al}_2\text{O}_3\), 0.8% and 0.08% \(\text{ZnO}\), and 0.8% finely powdered \(\text{CaCO}_3\). The initiation time, time to reach maximum peak height were delayed and the total amount of heat is lowered in the presence of seeds. It should be reminded that the nano-\(\text{Al}_2\text{O}_3\) and finely powdered \(\text{CaCO}_3\) accelerate the reaction in hydroxide activated binders but have no effect in silicate activated binders.

Reaction kinetics of fly ash-slag mixes are known to be very sensitive to the shear history and temperature [25]. Seeds were dispersed in the activator solution and probe sonicated for 10 mins before adding the activator solution to fly ash-slag solids. Therefore, heat evolution
Figure 8.3: Rate of heat evolution at 22°C of silicate activated fly ash-slag pastes with the addition of 0.8% nano-Al₂O₃, 0.8% and 0.08% ZnO, and 0.8% finely powdered CaCO₃. Fly ash-slag paste made with probe sonicated activator solution is also included in the graph (KOH-KSil-probesonicated).

was monitored on fly ash-slag paste (KOH-KSil-probesonicated) made with probe sonicated activator solution. From the Figure 8.3, the use of probe sonicated activator solution slows down reaction kinetics. Therefore, the mixes with seeds from here on will be compared with fly ash-slag paste made from probe-sonicated activator solution (KOH-KSil-probesonicated).

From Figure 8.3, nano-Al₂O₃ and finely powdered calcium carbonate do not have any effect on the reaction kinetics of silicate activated fly ash-slag pastes. In hydroxide binders, nano-Al₂O₃ and CaCO₃ would nucleate C-S-H formation within the pore space away from the particle surfaces. This layer of C-S-H will act as nucleation site for further precipitation of C-S-H which leads to accelerated reaction. We have firmly established in the chapter 6 that the calorimetry peak in silicate-activated binders corresponds to the precipitation of C-S-H/C-A-S-H and gelation of K-A-S-H. Here, in silicate activated binders, nanoparticles are not influencing the reaction peak related to gelation of aluminosilicates. It is already known
from chapter 4 that C-S-H/C-A-S-H form in the early stages in silicate activated binders. Even if seeds are nucleating C-S-H, increased amount of C-S-H in the pore solution has no accelerating effect on gelation. This implies that reaction mechanism of silicate-activated fly ash-slag pastes is not nucleation and growth controlled.

The effect of nano-$\text{Al}_2\text{O}_3$, finely powdered CaCO$_3$ and nano-ZnO seed is quite different in the case of hydroxide-activated fly ash-slag binders and silicate-activated binders which further highlight the differences in the reaction mechanism between the two binders.

### 8.2.2 Effect of Nucleation Seeds on the Extent of Product Formation

The effect of wet C-S-H (1.0) seed on the amount of product formed at various ages of silicate activated fly ash-slag pastes was studied by selectively treating the samples to dissolve C-S-H/C-A-S-H and K-A-S-H. Figure 8.4 shows the % by weight of C-S-H/C-A-S-H formed in the samples at various ages with and without 0.8% C-S-H seed. The amount of C-S-H/C-A-S-H formed is higher in the mixes with seed addition compared to mix without the seed at all ages (1 hr, 24 hrs, and 7 days). It should be noted that no differentiation is being made between C-S-H formed in the binder and the K-A-S-H that got degraded to C-A-S-H at high pH. The SAM treatment dissolves all the C-S-H/C-A-S-H present in the binder.

### 8.2.3 Effect of Nucleation Seed on the Extent of Fly ash Dissolution

The insoluble residue after SAM treatment collected at different ages (5 hrs, 24 hrs, and 7 days) was further treated with HCl solution and the amount of unreacted fly ash left over was calculated and is shown in Figure 8.5. In the presence of seeds, the amount of unreacted fly ash is smaller at all ages even as early as 5 hrs (accelerated hardening period) compared to the unseeded mixes. From calorimetry and selective dissolution treatment

151
results, the presence of synthesized C-S-H seed decelerates the reaction kinetics, encourages the dissolution of raw materials, helps with the precipitation of more C-S-H but delays the gelation peak. This implies that reaction mechanism of silicate-activated fly ash-slag pastes is not nucleation and growth controlled but could be gelation controlled.

8.2.4 Effect of Nucleation Seed on the Microstructure

Quantitative EDS analysis is performed on 7 day old KSil and KSil-0.8% C-S-H sample to study the chemical makeup of reaction products formed in the binder. All the ratios that are calculated from EDS microanalysis results are compared with the ratios set by Garcia-Lodeiro et al. to distinguish between C-A-S-H and (Ca, K)-A-S-H and are given below [98]:

C-A-S-H : 0.72 < CaO/SiO$_2$ < 1.94; 0 < Al$_2$O$_3$/SiO$_2$ < 0.1
Figure 8.5: Analysis of selective dissolution treatments presented as dissolved % by the initial mass at 1 h, 24 h, 168 h (7 days) of silicate activated (KOH-KSil) fly ash-slag paste and 5 hrs, 24 hrs, 7 days with 0.8% C-S-H (Ca/Si - 1.0) substitution.

(Ca,K)-A-S-H : 0 < K₂O/Al₂O₃ < 1.85; 0 < CaO/SiO₂ < 0.3; 0.05 < Al₂O₃/SiO₂ < 0.43

EDS spot analysis on KOH-KSil sample (average of 9 points) indicates the presence of (C,K)-A-S-H at 7 days with an average of, K₂O/Al₂O₃ = 0.23±0.15, CaO/SiO₂ = 0.17±0.08, Al₂O₃/SiO₂ = 0.27±0.06. There was also an another phase with an average of K₂O/Al₂O₃ = 0.59±0.15, CaO/SiO₂ = 0.44±0.05, Al₂O₃/SiO₂ = 0.22±0.06, whose composition does not follow any of the above set compositional rules. The EDS analysis of the sample with a representative spectrum and an average atomic ratio of various elements is given in 8.6a. At 7 days, microstructure of KSil samples is seem to contain (C,K)-A-S-H phase and another phase possibly a mix of C-S-H, K-A-S-H, and (C,K)-A-S-H.

The quantitative microanalysis of KSil-0.08% C-S-H sample indicated the presence of mixed phase. The average composition of product is K₂O/Al₂O₃ = 0.64±0.25, CaO/SiO₂ = 0.45±0.18, Al₂O₃/SiO₂ = 0.18±0.12. The EDS analysis of the sample with a representative spectrum and an average atomic ratio of various elements is given in 8.6b. At 7 days, the
8.3 Effect of C-S-H on the Rate of Product Formation

The addition of synthesized C-S-H seed has not accelerated reaction kinetics in the silicate activated fly ash-slag binders implying that the reaction is not nucleation-growth controlled but could be gelation controlled. The current section will study the effect of C-S-H/C-A-S-H on the geopolymer gel formation (hypothesis 2). The effect of wet C-S-H (1.0) seed on the product composition formed at various ages of silicate activated fly ash-slag pastes was studied by selectively treating the samples to dissolve C-S-H/C-A-S-H and K-A-S-H. FTIR spectral subtraction was performed on samples before and after each selective dissolution treatments to understand the chemical nature of products and their evolution with time.
8.3.1 Effect of Seed on the Nature of C-(A)-S-H

The IR spectra of product dissolved in SAM treatment at various ages is given in Figure 8.7. The main band appears sharp and is positioned at 965 cm$^{-1}$ at all ages (5 hrs, 24 hrs, 7 days) in the seeded sample. The peak is attributed to Q$^2$ tetrahedra in C-S-H/C-A-S-H. The peak of C-S-H/C-A-S-H changes with time in the sample without any seed. From the Figure 8.7 in the presence of external C-S-H seed, the variation in the composition of C-S-H/C-A-S-H forming at various ages is minimal implying that the seed is regulating the composition of the product.

Figure 8.7: Subtracted spectra of products dissolved in SAM treatment (C-S-H) of silicate activated fly ash-slag pastes with 0.8% C-S-H seed (a) and without seed (b) at various ages (5 hrs, 24 hrs, 7 days)

8.3.2 Effect of Seed on the Nature of the Phases Dissolved in HCl Treatment

The subtraction spectra of products dissolved after the HCl treatment with and without external C-S-H seed at various ages is given in Figure 8.8. The IR spectral bands (in wavenumber) seen in the dissolved product spectra of samples with and without seed at
Figure 8.8: Subtracted spectra of products dissolved in HCl treatment (Unreacted slag and K-A-S-H) of silicate activated fly ash-slag pastes with 0.8% C-S-H seed (a) and without seed (b) at various ages (5 hrs, 24 hrs, 7 days)

various ages are summarized in the Table 8.1 for the ease of comparison.

At 5hrs, during accelerated hardening phase, the main band of K-A-S-H spectrum is at lower wavenumbers compared to the position of main band at 24 hrs and 7 days. By 24 hrs, the position of main band moves to higher wavenumber and remains at the same position until 7 days implying that the structural evolution might be minimal. It should be noted that the relative height difference between the main geopolymer gel peak and unreacted slag decreases with time which could be attributed to increasing K-A-S-H product formation or increasing slag dissolution or both. From the Figure 8.7, the amount of C-(A)-S-H increases with time implying an increased slag (only source of Ca) dissolution. Also, minimal change in the structure of K-A-S-H implies that the largest contributor to the height difference is the dissolution of slag.

From UWR curves (Figure 8.2), it has been shown that the drop in S-wave reflection curve is more gradual in the case of the binder with C-S-H seed compared to the unseeded binder. From FTIR spectra, the C-S-H forming in the binder has similar composition at various ages. The presence of C-S-H seed could be inhibiting the almost instantaneous precipitation
Table 8.1: Position of IR spectra bands in wavenumber (cm$^{-1}$) of C-S-H/C-A-S-H, K-A-S-H, and slag obtained through FTIR spectral subtraction in hydroxide activated and silicate activated fly ash-slag pastes at various ages. The Si-O-T asymmetric stretching vibration band will be referred to as the main band.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>1 h KOH-KSil</td>
<td>978</td>
<td>868-1011(b)</td>
</tr>
<tr>
<td>24 h KOH-KSil</td>
<td>952</td>
<td>1000, 860-910(bs)</td>
</tr>
<tr>
<td>7 d KOH-KSil</td>
<td>960</td>
<td>992, 1020(s), 860-940(bs)</td>
</tr>
<tr>
<td>5 h KOH-KSil-0.8% C-S-H</td>
<td>965</td>
<td>993, 868-930 (bs)</td>
</tr>
<tr>
<td>24 h KOH-KSil-0.8% C-S-H</td>
<td>965</td>
<td>1005, 868-930 (bs)</td>
</tr>
<tr>
<td>7 d KOH-KSil-0.8% C-S-H</td>
<td>965</td>
<td>1005, 868-930 (bs)</td>
</tr>
</tbody>
</table>

s: shoulder  
b: broad

of C-S-H (reason for accelerated hardening in the silicate activated fly ash-slag binders) by letting the binder reach supersaturation for C-S-H/C-A-S-H of a certain composition which explains the gradual change in the UWR curve in the presence of external seed instead of a rapid drop as seen in the mixes without any seed.

From calorimetry, the presence of synthesized C-S-H seed decelerates the reaction kinetics and delays the appearance of K-A-S-H gelation peak. The delay in the appearance of the gelation peak could be attributed to the lower amount of silicate/aluminosilicate species in the solution due to the formation of C-S-H. As more and more Si is taken up by C-S-H/C-A-S-H, net SiO$_2$/K$_2$O of the solution drops below 1.25 (starting ration) and decreases the amount of silicate species available for geopolymer gelation.

In conclusion, the addition of C-S-H seed does not accelerate the reaction and delays the K-A-S-H gelation in silicate activated binders implying that the reaction is not nucleation and growth controlled but gelation controlled. Addition of C-S-H seed increases the rate of fly ash dissolution. The effect of C-S-H precipitation and varying SiO$_2$/K$_2$O on gelation will be discussed in detail in the following sections to shed more light on the deceleration of...
main reaction peak in seeded binders. The effect of seeds on the rate of fly ash dissolution is studied by elucidating the differences in the reaction kinetics of mixes with nano-SiO$_2$ and C-S-H, which will also be discussed later in the chapter.

8.4 Factor that Effect the Reaction in Silicate Activated Binders

8.4.1 Effect of Silica Polymerization on Reaction Kinetics

In chapter 6, SEM micrographs of silicate activated fly ash-slag mixes showed voluminous gel in the microstructure between 1 hr and 24 hrs corresponding to the reaction peak seen from calorimetry. The reaction kinetics of silicate activated fly ash binders are known to depend on the degree of polymerization of silicate species in the activator solution [67, 77, 99]. The delay in the appearance of the peak in the presence of C-S-H seed has been predicted to be due to the lower amount of silicate/aluminosilicate species in the solution. Therefore, to understand the effect of silicate/aluminosilicate species on the appearance of main reaction peak, solutions of same alkalinity ([K$_2$O] content) but different silicate ion polymerization were used. State of silica polymerization in activator solutions was varied by changing the order and the amount of potassium hydroxide solution addition to the potassium silicate solution.

One solution was prepared by mixing 4 ml of commercially available potassium silicate solution of SiO$_2$/K$_2$O = 3.92 and 8.7 ml of 1.9 M KOH solution to achieve final SiO$_2$/K$_2$O = 1.25. This will be referred as 1.9 M KOH+KSil moving forward. Second solution was prepared by mixing 4 ml of commercially available potassium silicate of SiO$_2$/K$_2$O = 3.92 with 1.6 ml of 18 M KOH solution and was let to sit for a few hours before adding remaining 7.1 ml of water to achieve the final SiO$_2$/K$_2$O = 1.25 and same water content as the original activator solution. This solution will be referred as 18 M KOH+KSil.
Figure 8.9a shows FTIR spectra of two solutions along with the stock potassium silicate solution used for preparation. Potassium silicate solution (referred as KSil) of SiO$_2$/K$_2$O = 3.92 has a peak at 1015 cm$^{-1}$ and a shoulder at 1115 cm$^{-1}$. Bands in this range belong to asymmetric stretching vibration of Si-O-Si in $Q^3$ and $Q^4$ tetrahedra. The peak position of 1.9 M KOH+KSil solution is at 1005 cm$^{-1}$ and the peak position of 18 M KOH+KSil solution is at 990 cm$^{-1}$. Lower wave number in 18 M KOH+Ksil indicates that it takes less energy to vibrate the Si-O-Si bonds implying that silica network is more depolymerized and has higher non-bridging oxygen (NBO) atoms. Therefore, the 18M KOH+KSil solution has higher amount of silica species with low Q numbers (more monomers, dimers) compared to 1.9 M KOH+KSil solution and KSil solution. It should be noted that the final water, K$_2$O, and SiO$_2$ content are all the same in 18 M KOH +KSil and 1.9 M KOH+Ksil solutions. The order in which potassium hydroxide is added to potassium silicate has profound effect on the stability of silicate species in the solution long after addition. Alkali cations effect the state of stabilized silicate ions in the solution and as charge-balancers in the final geopolymer gel. Potassium ions are network modifying agents that effect the number of NBO atoms in the first coordination sphere of silicon atoms and thus the relative distribution of SiQ$^n$ ($n = 0$–4) structural units in the solution. Therefore, the concentration of KOH solution effects the distribution of SiQ$^n$ ($n = 0$–4) structures in the solution where higher concentration of KOH solution results in species with lower Q numbers. Therefore, H$_2$O/SiO$_2$ and OH$^-$/SiO$_2$ ratios have a considerable impact on the “molecular” or “polymeric” species of silica [84]. With increasing alkalinity, silica network gets progressively depolymerized.

From Figure 8.9b, for the paste activated with 18 M KOH+Ksil, initiation of the main reaction peak and time to reach maximum height are both delayed and the height of the main reaction peak is smaller compared to the main reaction peak in pastes activated with 1.9 M KOH+KSil solution. Two activator solutions have same amount of SiO$_2$/K$_2$O content as well as the total amount of water, but the appearance of the rate peak depends on the initial degree of silica polymerization in the solution. The solution with low degree of silica
Figure 8.9: a: FTIR spectra of silica solutions made with different KOH concentrations (1.9 M and 18 M). Both solutions have same amount of K₂O and SiO₂ contents. b: Rate of heat evolution at 22°C of silicate activated fly ash-slag pastes made with 18 M KOH+KSil and 1.9 M KOH+KSil solutions. All the pastes have same amount of K₂O content and same w/b ratio. Different concentrations of potassium hydroxide solutions were added to potassium silicate to change the silicate polymerization. Inset gives the total heat evolved with time.
polymerization (18 M KOH+KSil) shows delayed peak appearance.

For potassium based binders, gelation step is not initiated unless there is a sufficient supply of larger aluminosilicate anions [72]. As aluminum is dissolving from fly ash/slag into silicate solution, it is presented to several pre-existing silicate species (monomer, dimer, trimer etc.). The larger the silicate species, the smaller its average negative charge per silicon atoms, and it will be easily approached by aluminate ions. Therefore, when silicate solution with low Q numbers is used, it takes longer for larger stable aluminosilicates to form (condense) delaying the time for gelation. Highly charged species forming at elevated hydroxide concentrations repel each other and resist condensation reactions. From the calorimetry results, the heat peak is delayed for mixes activated with 18 M KOH+Ksil solution implying that the time to reach sufficient supply for larger aluminosilicates takes longer and therefore, the delay. Therefore, the time for the initiation of second calorimetry peak (main reaction peak) seem to depend on the state of silica polymerization in the activator solution.

The factor which also effects aluminosilicate polymerization is the SiO$_2$/K$_2$O ratio of the solution. To understand the effect of SiO$_2$/K$_2$O ratio of the activator solution on the reaction kinetics, fly ash-slag pastes were made with solutions of three different SiO$_2$/K$_2$O ratios (0, 0.45, 1.25) of the same K$_2$O and H$_2$O content but different SiO$_2$ content. The mix made with SiO$_2$/K$_2$O = 0 is hydroxide activated fly ash-slag binders, the mix made with SiO$_2$/K$_2$O = 1.25 is silicate activated fly ash-slag paste, and the mix made with SiO$_2$/K$_2$O = 0.45 is that of intermediary SiO$_2$ content.

Generally in the case of sodium silicate activator solution, low SiO$_2$/Na$_2$O molar ratios favor low Q numbers and high SiO$_2$/Na$_2$O molar ratios prefer high Q numbers. So, one would assume that the effect of intermediary SiO$_2$/K$_2$O ratio on the reaction kinetics would be intermediary to that of hydroxide activated (low SiO$_2$/Na$_2$O) and silicate activated binders (high SiO$_2$/Na$_2$O). However, the results seen from Figure 8.10 are quite the contrary. The rate peak of SiO$_2$/K$_2$O = 0.45 appears much later than the hydroxide and silicate activated binders. However, the comparison should be made with mix made with SiO$_2$/K$_2$O = 1.25
Figure 8.10: Effect of SiO$_2$/K$_2$O ratio of solutions on the rate of heat evolution of silicate activated fly ash-slag pastes at 22°C.

solution. This is because the main reaction peak in hydroxide activated binder corresponds to C-S-H formation whilst the main reaction peak in silicate activated binder corresponds to K-A-S-H formation.

The odd behavior of intermediary SiO$_2$/K$_2$O = 0.45 can be explained from literature based on the preferential [Al] ion complexation with Si units in the solution. Silicate solutions contain a mixture of species and the smaller species (lower molecular weight like monomers and dimers) are favored at higher alkalinity (low [Si] and high [K]). When aluminate solution containing Al(OH)$_4^-$ is added to highly alkaline silicate solutions, aluminosilicate (Al-O-Si) complexes are not formed. Glasser et al. have shown that the Al(OH)$_4^-$ does not readily complex with small, highly charged, silicate monomers (HSiO$_3^-$) [176]. On the other hand, at low alkalinity conditions (high [Si] and low [K]), all the Al might complex with silicates rendering aluminosilicate inert; thus, slowing down the condensation.

Glasser et al. have concluded that for the gel formation, the presence of a reasonable number of incomplete aluminate ions and small but not too highly charged silicate ions are
pre-requisites. When fly ash surface comes in contact with hydroxide ion, aluminate ion is released as Al(OH)$_4^-$ (the only form stable in the solution at pH >11), reacts with deprotonated monomeric Si(OH)$_4$ or preferably larger linear silicate anions (dimers). Linear silicate species can easily be depolymerized as the bulk conditions are changed, allowing polymerization to take place easily through the poly-condensation of silicate and aluminate monomers. On the other hand, the large cyclic structures, such as cage or ring silicate species, slow the kinetics and only serve as reservoirs for small, acyclic species that are more responsible for gel growth. Larger K$^+$ cation size contributes to the increase in number of Al-O-Si bonds because of its association with larger aluminosilicate anions (more effective ion pairing), which results in extended gel growth.

Therefore, in the case of SiO$_2$/K$_2$O = 0.45, silicate units were probably highly charged monomeric species slowing down the condensation rate which will also delay the gelation and therefore the delay in the peak. Smaller the silica species, longer it takes for condensation to start (same amount of K$_2$O and different amounts of SiO$_2$). SiO$_2$/K$_2$O ratio and state of silicate polymerization in the starting solution influence the reaction kinetics in silicate activated binders. The gelation of K-A-S-H seems to exclusively dependent on the extent and rate of aluminosilicate oligomers in the solution. Also, from the selective dissolution studies and IR spectral subtraction, it has been shown that the C-(A)-S-H does not nucleate the formation of K-A-S-H gel. Therefore, the gelation of K-A-S-H in the presence of calcium is influenced indirectly by the rapid precipitation of C-A-S-H which in turn influences aluminosilicate species polymerization in the solution.

### 8.4.2 Effect of C-S-H seed on Mixes with Varying SiO$_2$/K$_2$O Ratio

It has been shown in the Figure 8.10, the reaction kinetics depend on the SiO$_2$/K$_2$O ratio of the solution. The effect of C-S-H seed has already been verified on the SiO$_2$/K$_2$O = 0
Figure 8.11: Rate of heat evolution at 22°C of silicate activated fly ash-slag pastes of different SiO$_2$/K$_2$O ratios and the addition of 0.8% C-S-H seed on SiO$_2$/K$_2$O = 0.45. Activator solutions has same amount of K$_2$O content and same w/b ratio. (hydroxide binders) and SiO$_2$/K$_2$O = 1.25 (silicate activated binders). The presence of seeds accelerate the reaction in one case (hydroxide activated) and either decelerate or have no effect (silicate activated) in the other case. Since, SiO$_2$/K$_2$O = 0.45 behaves quite differently from the other two, the effect of seed was verified on these binders as well. Figure 8.11 shows the rate of heat evolution at 22°C of silicate activated fly ash-slag pastes of different SiO$_2$/K$_2$O ratios and the addition of 0.8% C-S-H seed on SiO$_2$/K$_2$O = 0.45.

The addition of 0.8% C-S-H seed to the mix made with activator solution of SiO$_2$/K$_2$O = 0.45 accelerates the reaction much like what is seen with SiO$_2$/K$_2$O = 0 (hydroxide) and therefore the reaction is nucleation-growth controlled. It is clear that there seems to be a minimum amount of Si concentration needed for the binder to gel within the interstitial void space away from the particle surface. This seems to match with the observation made by Lee et. al., where they have reported that there exists a threshold silica concentration in the solution (200mM in their study) below whereby precipitation onto the particles surfaces is
the dominant mechanism. Figure 8.12 shows SEM micrographs of samples made with SiO$_2$/K$_2$O = 0.45 along with and without 0.8% seed addition. At 5 hrs, without added seed, sample was just a fluid. With the addition of seed, at 5 hrs, there seems to be product forming in-between particles and on them. At 24 hrs, mix without seed addition still does not seem to have much product formed. However, by 24 hrs, in the presence of seed, the product has formed in large quantities and is now occupying interstitial space between particles. At low soluble silicate concentrations, the dissolution of fly ash could have been inhibited by secondary precipitates on the surface of the fly ash thus changing the reaction mechanism. Addition of nucleation seeds effectively captured the shift in the reaction mechanism from nucleation and growth controlled reaction to gelation with increasing amount of silica in activator solution.

### 8.4.3 Effect of Seed on Fly ash Dissolution in Silicate Activated Binders

Figure 8.13a shows the isothermal calorimetry data for silicate activated fly ash-slag pastes with 0.8% of nano-SiO$_2$ and wet C-S-H gel (Ca/Si - 1.0) along with unseeded binder. Seeded mixes (0.8% C-S-H and nano-SiO$_2$) show delay in the initiation of the main reaction peak compared to the unseeded mix. The S-wave reflection coefficient curve for nano-SiO$_2$ seed mix and 0.8% C-S-H seed, and unseeded mix are shown in Figure 8.13b. The S-wave reflection coefficient curve for nano-SiO$_2$ seed mix looks very similar to silicate activated fly ash-slag paste without any seed except for the onset point. The onset point in the case of nano-SiO$_2$ mix is 9 mins compared to 15 mins in the case of unseeded mix. The drop in S-wave reflection coefficient of mix with 0.8% C-S-H seem to start right from the point of pouring into the HIPS container and maintains the slope for an hour and changes slowly over time. The clear onset point is not seen unlike the mix without any seeds. Reflection coefficient value at any point in time is higher for C-S-H mix compared to the mix without
Figure 8.12: SEM of silicate activated fly ash-slag mixes at different ages made with K$_2$O/SiO$_2$ - 0.45 with and without 0.8% C-S-H added. a: No seed at 5 hrs, b: with 0.8% C-S-H seed at 5 hrs, c: no seed at 24 hrs, d: with 0.8% C-S-H seed at 24 hrs
any seeds. Results indicate that the rate of hardening as well as the initiation of the heat peak have slowed down in the presence of C-S-H/C-A-S-H seeds.

From UWR curves, nano-SiO$_2$ is accelerating the formation of initial C-S-H/C-A-S-H which is responsible for rapid hardening. The initial C-S-H formed would have consumed more silicon from the activator solution than the mix without seeds. Therefore, the reaction peak from calorimetry is delayed a bit because solution is now waiting for more Si to dissolve from the raw material and reach a level of super saturation and polymerization extent which explains the delay in the rate peak seen from calorimetry. The formation of initial C-S-H encourages fly ash dissolution. Therefore, the addition of seeds encourage fly ash dissolution without accelerating the reaction kinetics related to the gelation of K-A-S-H.

In conclusion, nano-SiO$_2$ accelerates initial hardening but delays the gelation. Accelerated hardening is attributed to C-S-H precipitation. Precipitated C-S-H will preferentially uptake Si from the solution and more Si should dissolve from raw materials to form K-A-S-H. The gelation peak seen from calorimetry is delayed while the system awaits for more Si to dissolve from the raw materials.

### 8.4.4 Effect of Retarder and Insights into Reaction Mechanism

Mixes with ZnO seeds offer interesting insights into the reaction mechanism of silicate-activated pastes. At 0.8% ZnO addition, the reaction peak is completely eliminated similar to hydroxide activated pastes. However, comparing the total heat (inset), 0.8% ZnO shows some amount of heat early-on which then levels off. Figure 8.14a shows SEM-SEI micrographs of silicate activated pastes with 0.8% nano-ZnO seeds. At 7 days, there seems to be some amount of product on the particles similar to early age samples of silicate activated pastes without any seeds. It should be noted that samples were too soft even at 7 days. If the retardation by ZnO is caused by poisoning of C-S-H nuclei with Zn to prevent further growth, the initial heat seen in 0.8% nano-ZnO solution of silicate activated binders due to the formation of C-S-H product, should not have happened [170].
Figure 8.13: Effect of nano-SiO$_2$ and C-S-H seed on the initial age hardening a: rate of heat evolution from calorimetry, b: shear-wave ultrasonic wave reflection
The calorimetry peak is only slightly delayed at 0.08% ZnO addition in silicate activated binders (refer to Figure 8.3) contrast to complete peak elimination seen in hydroxide activated binders at similar dosages. Microstructure (Figure 8.14c Figure 8.14d) of 0.08% ZnO mixes at 7 days look very similar to the microstructure of paste without any seed with gel like product in the interstitial space between particles. Nano-ZnO seeds are dispersed in the solution using Poly-vinyl-pyrrolidone surfactant commonly called PVP. The nitrogen and/or oxygen atoms (of -N-C=O (electron donor atoms)) in the side groups of PVP could form hydrogen bonds with silanol groups in the activator solution and prevent the polymerization of aluminosilicates and thus retard the gelation in silicate activated binders [177–179]. Goncharuk et al. have shown that the PVP can also effect the agglomeration and flocculation of silica units through electrostatic repulsions [179]. At low concentrations, flocculation and agglomeration of silica is not inhibited. However, at higher PVP concentrations, the interaction between PVP and silica particles is stronger than the interaction between silica agglomerates due to electrostatic repulsion between similarly charged silica particles [179]. Thus, PVP can inhibit condensation through physical separation of aluminosilicate agglomerates that form in the solution. The detailed study of the effect of ZnO seeds on the silicate activated fly ash-slag systems is out of the scope of the present work and will be a part of the future study.

8.5 Conclusions

The work presented in this chapter seeks to verify the second hypothesis related to the accelerated hardening in the presence of calcium in silicate activated fly ash-slag binders. Product-based synthesized C-S-H gel was added as a nucleation seed. The reaction kinetics were monitored through calorimetry and the addition of relatively small amounts of synthesized C-S-H and C-A-S-H gels to silicate activated fly ash-slag pastes had a deceleration effect of early reaction kinetics. The addition of non-product based seeds had similar effect.
Addition of non-product seeds has no effect on the reaction kinetics of the paste. However, the factors that had decelerating or accelerating effect on the reaction kinetics were SiO$_2$/K$_2$O ratio of the solution, state of silicate polymerization in the solution, and the order of mixing potassium hydroxide to potassium silicate solution. Addition of product-based seeds has consistently decelerated the reaction which is attributed to the preferential
consumption of silicate species in the solution by C-S-H. Therefore, it has been determined that the rate controlling step in silicate activated binders is gelation.

 Preferential uptake of silicate species by C-S-H product does indirectly increase the dissolution of fly ash particles but the precipitation of C-S-H does not act as a nucleation site for K-A-S-H formation but rather delays its formation. Thus, the second hypothesis that C-S-H gel acts as a nucleation site for K-A-S-H gel precipitation has been proved wrong.

 Addition of nucleation seeds effectively captures the shift in the reaction mechanism from nucleation and growth controlled reaction to gelation with increasing amount of silica in the activator solution.
The main objective of this study was to understand the role of calcium on the low-workability and rapid hardening seen in user-friendly geopolymer cements. The present study also provided insights into the reaction mechanism of geopolymer cements, where C-S-H/C-A-S-H coexist with (N,K)-A-S-H gels through the addition of synthesized reaction products as external seeds. It has been hypothesized that the accelerated hardening seen in the presence of calcium was due to:

1. The precipitation of calcium silicate hydrate initiates rapid hardening

2. The precipitation of calcium silicate hydrate or Ca(OH)$_2$ from the solution provides nucleation sites which triggers rapid aluminosilicate gel formation and accelerated hardening

To prove the first hypothesis, it was necessary to develop a protocol to effectively characterize and quantify C-S-H and K-A-S-H forming at various ages and monitor their structural evolution through time by using selective dissolution techniques and FTIR spectral subtraction.

Often it is difficult to determine the nature of the reaction products when calcium containing aluminosilicate precursors are activated using an alkali and/or alkali silicate combination. Chapter 4 elucidates the importance of using SAM and HCl extractions together to characterize geopolymers formed in a silicate activated fly ash-slag bended systems through spectroscopic studies. The specific conclusions are listed below.

- FTIR characterization and spectral subtraction performed after successive chemical
treatment using SAM and HCl clearly showed the dominant phase in the microstructure during accelerated hardening phase was C-S-H/C-A-S-H thus proving the first hypothesis. Evidence of small amount of K-A-S-H at an early age was also observed

- It was found that IR spectra collected on insoluble residue of salicylic acid-methanol (SAM) and HCl treatment performed separately were still inconclusive as the IR spectra for phases dissolved in SAM and dissolved in HCl were very similar. It is found to be crucial to perform both the chemical treatments successively i.e., HCl treatment on SAM residue. Furthermore, FTIR spectral manipulation such as subtraction of solid residue spectrum from the original provides valuable information

- The main band due to the presence of C-S-H tend to shift in general to a lower wavenumber with time due to possible increase in the aluminum substitution in the C-S-H structure or increase in the Ca/Si ratio. Furthermore, FTIR analysis clearly indicates continued formation of C-S-H and continued geopolymerization as the respective peaks become sharper with time

- The co-existence of C-S-H gel and the K-A-S-H gels was confirmed from the FTIR spectral subtraction. The difference in the reaction degree as proved from calorimetry and selective dissolution was also seen from the secondary electron images of HS sample at 1 hr and 24 hr. The initial heat released in the calorimetry also corresponds to the formation of C-A-S-H and geopolymer as seen from the selective dissolution experiments

- The increase in K-A-S-H amount corresponds to the reaction peak seen in the calorimetry. Thus, the reaction peak is attributed to the formation of K-A-S-H in the mix

- SEM micrographs and calorimetry further validated the selective dissolution followed by spectral subtraction method in determining the nature of products in a complex mix composition such as fly ash-slag
The nature of activator solution has significant effect on the reaction kinetics, nature of reaction products, and the microstructure development of alkali activated medium-calcium systems.

- The total heat evolved was higher in silicate activated systems compared to hydroxide activated systems indicating higher extent of early age reaction. S-wave reflection coefficient curves showed that silicate activated systems harden faster than hydroxide systems.

- C-S-H/C-A-S-H was seen to have formed in both systems and the amount of C-S-H/C-A-S-H in early ages was higher in silicate activated systems compared to hydroxide activated systems. But the predominant phase during the accelerated hardening phase in both cases was C-S-H providing further proof for hypothesis 1.

- C-S-H/C-A-S-H formed in silicate activated system had higher Ca/Si ratio at 1 hr which seemed to have taken more Al with time. In hydroxide systems, C-S-H/C-A-S-H formed had same Ca/Si ratio at all ages At 1 hr, silicate activated systems had both C-S-H gel and K-A-S-H gel. From 5 hrs to 7 days, the amount of K-A-S-H gel increases with time indicated by the increase in the sharpness of peak from FTIR spectral subtraction. In the case hydroxide activated systems, C-S-H/C-A-S-H was the prominent product until 24 hrs. A very small of K-A-S-H like product with silica content characterized by broad peak from FTIR is seen at 7 days.

- In hydroxide activated systems, product was seen to grow from the surface of particles into the pore space. In silicate activated systems, product seem to have precipitated in-between particles and within the interstitial pore space.

- The main reaction product of hydroxide activated fly ash-slag mixes is proved to be C-S-H/C-A-S-H which corresponds to the reaction peak seen from the calorimetry. However, the main heat peak seen in calorimetry curve of silicate activated fly ash
-slag mixes corresponds to the formation of both K-A-S-H and C-S-H/C-A-S-H gels from the solution. Therefore, the appearance of peak in silicate activated systems depend on the gelation of K-A-S-H

The second hypothesis was verified in both hydroxide and silicate activated systems by adding synthesized C-S-H gel as a nucleation seed and by monitoring its effect on the reaction kinetics, microstructure, hardening, and the extent of fly ash dissolution in hydroxide activated fly ash-slag cements.

In hydroxide activated systems:

- Precipitation of C-S-H gel was proven to be the reason for accelerated hardening in hydroxide fly ash systems in the presence of external calcium

- Addition of product-based seeds and non-product based seeds has accelerated the reaction with increased amount of product formation and raw material dissolution. This has firmly established that the hydroxide activated fly ash-slag was a nucleation-growth controlled reaction

- Addition of product based seeds such as C-S-H/C-A-S-H gel increased the amount of C-S-H product formation at the expense of K-A-S-H gel. Therefore, the precipitation of initial C-S-H does not act as a nucleation surface for the formation of geopolymer product but instead acts as nucleation site for further precipitation of C-S-H

- Accelerated hardening seen in hydroxide activated systems was only related to precipitation of C-S-H and improved dissolution of fly ash but not related to the geopolymer formation

- C-S-H gel was the main binding phase in the microstructure at all ages

- Experiments conducted using ZnO nano particles proved them as a powerful reaction retarder even at dosages as small as 0.08% (by weight of solids). The retardation of
ZnO can be negated by adding relatively large amounts of C-S-H seed. ZnO retards the reaction by preventing the nucleation of C-S-H gel on the particle surfaces.

In silicate activated systems:

- Performing selective chemical dissolution treatments on the sample at 1 hr during the accelerated hardening phase and FTIR spectral subtraction proved the existence of C-S-H gel along with small amounts of K-A-S-H gel

- Addition of non-product based seeds has no effect on the reaction kinetics of the paste. However, the factors that had decelerating or accelerating effect on the reaction kinetics were SiO$_2$/K$_2$O ratio of the solution, state of silicate polymerization in the solution, curing temperature, and the order of mixing potassium hydroxide to potassium silicate solution

- Addition of product-based seeds has consistently decelerated the reaction attributed to the preferential consumption of silicate species in the solution by C-S-H. Therefore, it has been determined that the rate controlling step in silicate activated systems was gelation

- Preferential uptake of silicate species by C-S-H indirectly increases the dissolution of fly ash particles but the precipitation of C-S-H does not act as a nucleation site for K-A-S-H formation but rather delays its formation. Thus, the second hypothesis that C-S-H gel acts as a nucleation site for K-A-S-H gel precipitation has been proved wrong

- Addition of nucleation seeds effectively captures the shift in the reaction mechanism from nucleation and growth controlled reaction to gelation with increasing amount of silica in the activator solution

The research output from this study offered an improved understanding of the reaction mechanism in fly ash-slag geopolymer cements. The reaction mechanism depends on the
nature of the activator solution. In hydroxide activated fly ash-slag geopolymers, the rate controlling step is the nucleation-growth controlled reaction, early age hardening behavior in these systems can be controlled via mechanisms that increases or decreases the rate of nucleation and growth of C-S-H. The reaction can be accelerated by adding synthesized C-S-H seed or a small percentage of nanoparticles which will promote nucleation of the product in the pore space. In silicate activated systems, the rate determining step is gelation which depends exclusively on the extent and the rate of aluminosilicate oligomers formation in the solution. Any factor that will affect the availability of silicate species or the rate of aluminosilicate oligomer formation will affect the reaction mechanism. Retarders that will selectively polymerize with silicate species in the pore solution can be used to develop retardation in these cements. Addition of nucleation seeds to study reaction kinetics was shown to effectively capture the shift in the reaction mechanism from nucleation-growth controlled to the gelation with varying silica concentration in the solution. The protocol developed in the study to separate the responses of two amorphous gels (C-A-S-H and (Na,K)-A-S-H) from the amorphous precursors can be extended to understand the structural evolution of phases in other alkali activated blends of complex chemistry. The fundamental understanding gained through this research can pave a way for large-scale adaptation of alkaline cement technology.
REFERENCES


