Admixtures for Use in Geopolymers

By

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Abstract

This study examined two novel approaches for the geopolymerisation of fly ash produced at thermoelectric power stations by combustion of coal. The first approach involved the use of cullet, a post-consumer glass waste, to supplement dissolved aqueous silicon for the geopolymerisation of fly ash, thereby reducing the sodium silicate requirement in the activating solution and the overall cost of geopolymer manufacture. The second approach consisted of adding xylitol, a sugar alcohol known to enhance the strength of cement-based concrete, to the geopolymer activating solution.

Substituting up to 34% of a high-calcium fly ash by cullet while decreasing sodium silicate addition by up to 20% caused the 3- and 7-day compressive strengths to decrease by up to 58% and 48% when geopolymer mortars were cured at 40 °C and 70 °C, respectively. Hydrothermal pre-treatment of the cullet with a 5M sodium hydroxide solution at 175 °C for 4 hours increased the 3-day strength by 25% compared to geopolymer mortar containing untreated cullet but required additional sodium hydroxide. Overall, the results show that cullet is not effective as partial replacement for sodium silicate activator. Micromineralogical analyses revealed that cullet reacted only slightly in the geopolymer matrix cured at 70 °C, causing the formation of a thin boundary layer containing higher concentrations of Si and Ca and lower concentrations of Al and Fe around cullet particles. This boundary layer was physically weaker than the surrounding sodium aluminosilicate hydrate phase. The sharp corners of cullet particles acted as crack initiation locations during compressive strength testing, thus contributing to the lower strength. Substituting 20% of the sand by cullet reduced the 3-day compressive strength by

14% when curing the geopolymer at 40 °C, indicating that cullet is not effective either as partial replacement for fine aggregate.

The second part of the study investigated the effect of xylitol on the strength development, setting time, isothermal calorimetry, and microminerology of geopolymer mortars based on Type C fly ash (FA-C), Type F fly ash (FA-F), and a slag/Type C fly ash blend activated by sodium silicate solution. Geopolymer mortars containing concentrations of xylitol up to 2% of fly ash mass were cured for up to 90 days at 23 °C, 40 °C, and 70 °C. Xylitol did not generally improve the compressive strength of geopolymer mortars, except for FA-C geopolymer mortars where 0.3% xylitol addition by mass of fly ash consistently improved the 56-day compressive strength at all three temperatures. The initial and final setting times of FA-C geopolymer mortars were not affected by the addition of xylitol at a concentration of 0.3 wt% but were retarded by xylitol concentrations of 0.7 wt% and 2.0 wt%. By contrast, the setting times of FA-F and slag/FA-C geopolymer mortars were not significantly changed by the addition of 0.7 wt% xylitol. Isothermal calorimetry studies revealed that geopolymerisation reactions at 23 °C caused an exothermic peak in the first hour after contact of the solid with the activating solution. The peak intensity was not affected by xylitol dosage; however, it was positively correlated with the calcium content of the solid and negatively correlated with the mortar setting times. Xylitol did not cause any appreciable changes in either the microstructure or the elemental composition of the geopolymer gel phase in mortars cured for 90 days at 40 °C.

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Chapter 1

Introduction

1.1 Introduction

Geopolymerisation is a process in which aluminosilicate-rich solids are activated by a highly alkaline solution to form an alkaline aluminosilicate hydrate gel.The solid reactant can be any aluminosilicate-containing material, including coal combustion fly ash, kaolin, metallurgical blast furnace slag, natural minerals, and mixtures of them. The activating solution often consists of sodium or potassium hydroxide with dissolved silicon in the form of water glass or sodium silicate solution. Alkaline minerals such as calcite, dolomite, or sodium orthophosphate have also been used as part of alkaline activators [1-3]. Since the solid reactants utilised for making geopolymers differ in their physico-chemical properties, optimum synthesis conditions are only applicable to individual systems. The mechanical properties of the final products depend on many different parameters such as initial dissolved silicon concentration, curing temperature, age of curing, physico-chemical properties of the solid reactant, and Si/Al molar ratio of the activating solution [4-19].

Amongst many aluminosilicates studied for geopolymerisation, coal combustion fly ash has attracted much attention. Fly ash is a by-product of coal combustion and classified according to its calcium content into low-calcium (<10 wt%) and high-calcium (>10 wt%) fly ashes (ASTM Class F and Class C fly ashes, respectively). The properties of fly ash, which play a significant role in the geopolymerisation process, depend on the sources of coal and the combustion process.

Development of geopolymers has been largely motivated by the utilisation of industrial solid waste materials, primarily to address the increasing environmental and economic challenges facing industry on how to deal with these materials. Coal combustion fly ash and blast furnace slag are the two main solid aluminosilicate sources that have been extensively studied to develop geopolymers. These are industrial waste materials produced in massive quantities around the world due to ever increasing global energy consumption and industrial activity. They are usually dumped into landfills, which is not a viable long-term solution, especially when more stringent environmental regulations are put in place. Landfilling is not only costly due to regulatory and logistical issues, but it also has long-term environmental impacts. Such industrial wastes usually contain heavy metals that may leach and penetrate into subsurface water causing contamination. Geopolymerisation provides the opportunity to turn waste hazardous materials into commercially-viable products with similar or even superior properties compared to cement-based products for some applications [17-19]. Geopolymerisation is also a successful technique to treat such waste materials to immobilise heavy metals [20-24].

Glass is one the oldest man-made materials that is still produced and consumed in massive quantities globally. It is made from natural minerals through intensive energy-consuming heating and melting processes with applications in building materials, food and beverages, and consumer products. Despite the fact that plastics are used for many such applications, glass is still produced in huge quantities around the world. The unique physical and chemical properties of glass make it possible to recycle it several times. However, large-scale recycling of glass requires collection networks and recycling facilities that are not available everywhere, which leaves no option other than dumping it into landfills. Due to the sheer volume of non-recyclable waste glass and the environmental and economic implications, much attention has been focused on finding industrial applications for glass cullet. The major area of interest has been the construction industry where massive quantities of concrete are produced. Glass cullet exhibits beneficial properties in concrete if used as either cement replacement or aggregate [25-37].However, its use in concrete is limited as increased levels of cullet can have deleterious effects such as reduced mechanical strength and durability, poor workability, excessive bleeding and segregation of phases, etc. [26, 28, 30].

Concrete, which is a mixture of water, cement, and aggregates in its basic form, may not be suitable for all applications and it is almost always necessary to adjust and improve its properties by addition of admixtures. Admixtures are chemical ingredients other than water, cement, and aggregates that are added to the concrete batch immediately before or during the mixing process. Admixtures are used in cementitious systems to confer specific and beneficial properties such as strength, workability and flow, setting time acceleration, setting time retardation, resistance to freeze-thaw cycles, plasticity, etc. [38]. These effects are results of interaction of admixtures with cement. Organic admixtures are widely used in cementitious systems to impart specific properties and make them suitable for different applications. They are used as plasticisers, water reducers, set retarders, etc. amongst other applications. One group of organic compounds used as admixtures are sugar alcohols or polyols. Polyols have been studied in cementitious systems as set retarders, and it is believed that the set retardation is caused by the formation of a barrier layer around either reacting cement particles or the reaction products, thus hindering the hydration reactions [39]. It has also been recently found that addition of a group of polyols could improve the unconfined compressive strength of concrete, resulting in less cement consumption to achieve the same compressive strength [40].

This thesis examines two novel opportunities for the synthesis of fly ash-based geopolymer mortars. The first part of the project was devoted to the utilisation of cullet as partial replacement for sodium silicate solution and sand. Cullet has been widely studied in cementitious systems owing to its pozzolanic reactivity in highly alkaline media [41, 42]. It has been reported that cullet can impart beneficial properties to the cementitious systems such as reducing alkali-silica reaction (ASR) related expansion, improving compressive strength, improving the pozzolanic activity of the mixture, and improving the durability of concrete, provided that sufficient time (>90 days) is given for the reactions to occur and that the cullet particle size is small enough (<40 μm) [41-43]. To our knowledge, cullet has not been previously considered in the synthesis of geopolymers.

The second part of the study is focused on using polyols in geopolymeric mixtures. Compared to concrete where chemical admixtures are very often used, no report has been found on the use of admixtures in geopolymeric systems to improve the physical or mechanical properties of geopolymers. Based upon the recent findings on the effectiveness of polyols in cementitious systems, the effects of polyols on geopolymeric systems were investigated in this study.

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Chapter 2

Literature Review

2.1 Admixtures in Cementitious Systems

2.1.1Overview

Ordinary Portland cement (OPC) is a widely used construction material and is produced in huge quantities in many parts of the world. Concrete, a composite made with cement, water, and aggregates is by far the most abundant man-made material. Although it comprises only one-third of the volume of concrete, the final properties and performance of concrete are determined by the cement paste. Concrete in its basic form may not be suitable for some applications and, depending on the application, it is often necessary to adjust and improve its properties by addition of admixtures. Admixtures are chemical ingredients other than water, cement, and aggregates that are added to the concrete batch immediately before or during the mixing process. Admixtures are used in cementitious systems to confer specific and beneficial properties such as strength, workability and flow, setting time acceleration or retardation, resistance to freeze-thaw cycles, plasticity, etc. [1]. These effects are the results of interaction of admixtures with cement. Admixtures should not be confused with those chemicals that are added to the clinker during the cement manufacturing process to aid in the manufacture and handling of the final product. The mode of action and mechanisms by which they function can be classified as follows [2]:

- Dispersing cement particles in the aqueous phase
- Changing the normal rate of hydration of cement
- Reaction with by-products of cement hydration
- No interaction with either cement particles or hydration products

Water reducing chemical admixtures are widely used in concrete. They are chemicals that permit less water to be consumed to achieve the same slump (a measure of workability) as the control concrete. They can improve the properties of concrete and increase the strength of hardened concrete. They can be used to attain higher slumps at a given water to cement ratio. Lignosulfonic alkali metal or alkaline earth salts are by far the most widely used commercial water reducing admixtures for cementitious systems. Others include carbohydrates, such as glucose and sucrose, and also alkali metal or alkaline earth salts of hydroxylated carboxylic acids such as gluconic or heptogluconic acid. [1,2]

Accelerators, also known as set accelerating admixtures, are defined as chemicals added to the cementitious system to shorten the time of setting and increase the rate of early strength development. This property is very important when concrete is made at low-temperature conditions and it is necessary to reduce the curing and protection periods to achieve the specified strength in concrete. Calcium chloride is a well- known accelerator, which has been the subject of extensive research for many years. Non-chloride concrete accelerating admixtures include calcium formate, calcium nitrate, calcium thiousulphate, and potassium carbonate and organic compounds such as triethanolamine (TEA). [1]

Set retarding chemical admixtures are added to the cementitious system to delay the time of setting and consequently the early strength development. The most commonly used set retarders are water soluble inorganic salts such as sodium metaborate ($Na_2B_2O_4$) or tetraborate ($Na_2B_4O_7$), stannous sulphate ($SnSO_4$), lead acetate ($Pb(C_2H_3O_2)_2$), and monobasic calcium phosphate ($Ca(H_2PO_4)_2$) [1]. The main application of set retarding admixtures is the prevention of slump loss in concrete under hot weather conditions. Hot, dry weather accelerates setting and increases the rate of slump loss. Additional water can be added to retain slump, but this will cause a loss in strength. Thus, addition of set retarders to concrete can retain slump at specified levels without adding more water.

Air entraining admixtures are another group of chemicals widely used in concrete technology. They create air bubbles that become part of the matrix of concrete and binding aggregates in the hardened concrete. The most important effect of air entraining agents is that they increase the durability of concrete and increase its resistance to frost attacks or freeze-and-thaw conditions. Air entraining can also improve the consistency and workability of concrete, plus reduce bleeding and segregation. Air entraining admixtures belong to a class of chemicals called surface active agents or surfactant. A surfactant molecule is comprised of one or more polar (hydrophilic) groups bound to a non-polar (hydrophobic) chain. Depending on the charge of the polar head of the molecule, surfactants are classified as anionic (negatively-charged head), cationic (positively-charged head), and nonionic (uncharged head). The non-polar part of the surfactant is typically a straight or branched hydrocarbon of eight to fifteen carbons. [1]

Mineral admixtures are finely ground materials that are added in large proportions on the order of 20 to 100 percent of the weight of cement in concrete. Raw or calcined minerals called pozzolans constitute a major part of mineral admixtures. Pozzolans are aluminosilicate minerals which do not possess any cementitious value by themselves; however, in the presence of moisture at ordinary temperatures they react with calcium hydroxide to produce material with cementitious properties. This chemical reaction in alkaline conditions is called the pozzolanic reaction. Natural pozzolans are of volcanic origin and are still used in the manufacturing of cement. However, industrial by-products such as fly ash, the by-product of coal combustion in power plants, exhibit pozzolanic properties and are now used in large quantities as mineral admixtures. Another example is blast furnace slag a non-metallic compound of silicates and aluminosilicates which is produced in huge quantities in metallurgical furnaces.

Superplasticisers also known as super water reducers are water reducing agents that are chemically different from the ordinary water reducing admixtures and capable of decreasing the water requirements by up to 30%. [1] By comparison, normal water reducing admixtures reduce water requirements by up to 15%. Water reduction gives higher strength and improved workability, or ease of placement of concrete. Concrete strength is inversely proportional to water:cement ratio for a given air content, therefore the addition of water reducers to achieve the same workability and slump will result in higher strength by reducing the water:cement ratio [1]. Superplasticisers are broadly classified in four groups: sulphonated melamine-formaldehyde condensate (SMF); sulphonated naphthalene-formaldehyde condensate (SNF); modified lignosulphonates (MLS); and others which include sulphonic-acid esters. [1] The effect of on workability is attributed to their ability to disperse cementitious materials into smaller particles, hence improving the flow of the mixture. The dispersive function of superplasticisers is related to their interactions with cement particles. The workability of fresh concrete is measured by the slump test [1]. The effectiveness of plasticisers for improving the workability of fresh concrete depends on the type, dosage, time of addition, water/cement ratio, type of cement, temperature, aggregate, etc. The chemical composition of plasticizers determines their effectiveness to increase the slump value of fresh concrete. [1]

There are a large number of chemicals other than those mentioned earlier, that are used in cementitious systems to impart different properties in either the fresh concrete or hardened one. They include anti-freezing admixtures, colouring admixtures, pumping aids, corrosion inhibitors, bacteriocidal and fungicidal admixtures, etc.

2.1.2 Glass Cullet

Glass is one of the oldest man-made materials and has been known for centuries. Due to the unique properties of glass such as transparency, chemical resistance, scratch resistance, chemical inertness, and the ability to be formed in different shapes, glass is still an indispensable part of modern life. Despite the fact that alternative materials such as plastics have been introduced to substitute glass, especially in the packaging industry, glass is still increasingly and widely used.

Glass is a noncrystalline and X-ray amorphous material that is made by melting a mixture of minerals such as silica and calcium carbonate at high temperatures followed by a cooling process during which solidification occurs. Minor quantities of other chemicals and inorganic pigments are usually added to the raw mixture to impart some special properties to the final product, aid in the manufacturing process, and to make glasses of different colours. Depending on the chemical composition of raw materials used, glasses can be classified as vitreous silica, alkali silicates, soda-lime glasses, borosilicate glasses, lead glasses, barium glasses, and aluminosilicate glasses [3]. Postconsumer glass should either be recycled and reused, or disposed of in landfills. Glass can be recycled several times without changes in its chemical or mechanical properties. In other words, postconsumer glass such as bottles can be crushed and melted again to make new bottles. Using scrap glass as part of raw materials is practised in glass making facilities where glass recycling can reduce consumption of energy and raw materials, and improve the equipment productivity. [10, 18] However, it is not always possible to recycle glass because of the cost or quality of collected glass. The efficiency of the recycling process depends on how bottles are collected and sorted. Bottles of the same colour can be crushed together and used to make new bottles. However, if bottles of different colours are crushed together, they are no longer suitable for bottle-making. Having few other applications, the cullet is generally disposed of in landfill. However, in the long run this creates a waste management problem.

Improved utilisation of waste glass cullet has been the focus of extensive research in order to reduce the solid waste disposal costs, extend the life of landfill sites, and reduce raw materials extraction [3-16]. Glass cullet can be utilised for many applications including concrete aggregates, building materials (glass tiles and bricks), abrasives, landscaping, agricultural fertilisers, and road construction [17].

Utilisation of non-recyclable glass in concrete is perhaps amongst the most viable options and has attracted the attention of many researchers. That is because of the huge quantities of concrete produced globally, the low quality requirements of the construction industry, and the pozzolanic properties of glass. Glass cullet has been considered for three major applications in concrete including: fine aggregate [7, 10, 13], partial replacement of cement [8, 9, 11, 12], and coarse aggregate [6].

Early attempts to utilise glass cullet as concrete aggregate date back to the 1960s and were unsuccessful due to crack development in hardened concrete [3]. However, due to disposal problems and increasing amounts of non-recyclable glass, research has regained momentum in recent years.

Top□u and Canbaz used green soda glass crushed to 4-16 mm in proportions of 0-60% of calcareous crushed stone aggregates to make concrete [6]. Taha and Nounu found no significant changes in the compressive strength of concrete in which natural sand was replaced by 50 and 100% mixed colour recycled glass of particle size less than 5 mm [14].

Park *et al*. concluded that up to 30% of the fine aggregate in concrete can be replaced with waste glass, but with a concomitant loss in slump (up to 27%) studied the mechanical properties of concrete containing glass cullet as fine aggregate which they believed is caused by the grain shape and fineness modulus of the waste glass aggregates [7]. In addition, the air content increased by up to 22%. Therefore, it is necessary to use appropriate chemical admixtures in order to secure fluidity when adding waste glass aggregates. Chen *et al.* investigated the properties of concrete containing various waste E-glass particle contents [18]. The size distribution of cylindrical glass particles was from 38 to 300µm, and 40% of particle sizes were less than 150µm. E-glass mainly consists of SiO_2, Al_2O_3, CaO, and MgO and is amorphous by X-ray diffraction. They found that the compressive strength and resistance to sulphate attack and chlorine ion penetration improved significantly in concrete with 40wt% E-glass content with particles not larger than 75µm. Chen *et al.* found that substitution of 40 wt% concrete fine aggregates by E-glass improved the compressive strength of 28-, 91-, and 365-day concrete specimens by 17, 27, and 43%, respectively [18]. They also found that E-glass can be used as supplementary binding material in addition to partial replacement for fine aggregates. They experimentally found that E-glass particles with sizes less than 75 µm could exhibit cementitious properties due to hydration or pozzolanic reactions. Their investigation showed a decrease in slump as the glass content increased and also the necessity of addition of high-range water reducers to obtain a uniform mixture. Top□u *et al.* used three different colour glass cullets in four quantities (25, 50, 75, and 100 wt%) as fine aggregate in mortar bars [10]. They concluded that glass aggregates could be added up to 25% provided that other admixtures such as fly ash were added to prevent deleterious reactions such as alkali-silica reactions, expansion, and internal crack formation in the cementitious system. Top□u and Canbaz showed that the utilisation of waste glass as aggregate did not have a significant effect on the workability of concrete, while they observed drops in slump, air content, and fresh unit weight. With addition of waste glass, the flow behaviour improved [6]. They also found that in hardened concrete specimens, compressive, flextural, and tensile strength values decreased in proportion to an increase in glass content.

One of the major concerns about the feasibility of utilisation of waste glass as aggregate is the expansion and cracking of concrete containing glass particles. In cementitious systems, certain types of silica present in the aggregate react with hydroxide ions in the pore solution, resulting in internal stresses that can cause expansion and cracking [19]. This reaction is known as the alkali-silica reaction (ASR). Park *et al.* found that mortar bars containing waste glass displayed a relatively higher expansion rate compared to control ones [7]. It was also found that the increase in expansion rate is proportionate to waste glass content. It has been shown that glass aggregates of different colours do not display the same expansion effects, with white colour glass aggregates resulting in the greatest expansion [10]. Park *et al.* concluded that ASR is suppressed by green glass aggregate due to the presence of Cr_2O_3. This is further supported by the studies of Park *et al.*, who studied the effect of green and brown colour waste glass on ASR expansion in mortar bars [7]. They found that the expansion rate of mortar bars containing brown glass was 2.5-10.3 times higher than that of mortar bars having no waste glass. The bars containing green glass displayed an expansion rate of 1.8-3.9 times that of plain mortar bars, which is less than that of mortar bars containing brown glass. They supported the ASR-repressing mechanism of Cr_2O_3 present in the green glass by the hypothesis that the expansive pressure resulting from electrical double-layer repulsion is inversely proportional to the ionic valence. Thus, the gel containing Cr^{3+}appears to be less expansive. Topçu *et al.* also investigated the effect of addition of Class F fly ash as mineral admixture in order to reduce the expansion of mortars containing waste glass aggregates [10]. Although the effect of fly ash on

ASR was seen to be different for different replacement ratios of glass cullet and fly ash, they concluded that the addition of fly ash reduces expansion and provides ASR resistance. They argued that the pozzolanic reaction between fly ash and $Ca(OH)_2$ decreases the pH of pore solution, which in turn reduces the reactivity between silica content of the aggregate and the alkalis of cement. In another study using waste E-glass particles as coarse aggregates in cementitious systems, Chen *et al.* [18] found that the coarse cylindrical glass particles acted as crack-arresters and inhibited internal crack propagation, which ultimately increased concrete strength.

Utilisation of ground glass as partial cement replacement has been the subject of several investigations [4, 8, 9, 11, 12, 14, 17]. Shao *et al*. used a finely-ground soda-lime glass obtained from recycled fluorescent lamps as partial replacement of cement in concrete to measure the pozzolanic activity of ground glass, compressive strength development of concrete having 30% cement replaced by ground glass, and to study the potential expansion [4].They used six different ground glass particle size ranges: 150µm glass; 150-75 µm; 75 µm; 75-38 µm; 38 µm; and<38 µm. The cement replacement by ground glass was targeted at 30% by volume in the concrete. Compressive strength tests were done to study the strength development at early and late stages. The control concrete with no mineral additives was based on a cement content of 300 kg/m^3 with target strength of 25 MPa at 28 days. The compressive strengths of lime-glass mixtures indicated that 38 µm glass satisfied the minimum strength requirements at 7 days and attained further strength after additional 21 days of curing in water. The 150 µm glass mixture displayed strength far below the limit because the size of glass was too coarse to act as a pozzolan. The 75 µm glass mixture performed marginally, as its 7-day strength was slightly lower than the minimum strength requirement of 4.1 MPa, while its additional 21-day curing in water enhanced the strength to a satisfactory level. The strength activity indexes of the concrete with 30% cement replaced by 38 µm glass were 91, 84, 96, and 108% at 3, 7, 28, and 90 days, respectively, exceeding the 75% recommended by ASTM C618. The strength activity index is defined by ASTM C 311 as the ratio (in %) of the average compressive strength of mortar containing substituting materials to that of the control mortar having the same age. The expansion of mortar bar containing 30% cement replaced by the 38 µm glass was reduced to half that of control. They concluded that the observed strength development, reduction in expansion, and lime activity was indicative of pozzolanic activity of soda-lime glass in the cementitious system.

Shayan and Xu utilised fine glass powder as pozzolanic material in cementitious systems [17]. The results of 28-day compressive strength tests showed a steady reduction in strength proportionate to the extent of cement replacement. They argued that for up to 30% cement replacement, it could be a short-term effect because in such short periods, pozzolanic effects would not become evident. This is supported by 90- and 270-day compressive strength results that showed that mortar specimens containing 20% fine glass powder as cement replacement continued to develop further strength with time, indicating pozzolanic activity. Incorporation of fine glass powder in the cementitious system did not appear to cause detrimental ASR expansion. Microstructural analysis of 270-day mortar specimens revealed that fine glass powder produced a dense matrix and improved the durability of the concrete.

Shi *et al.* studied the pozzolanic activity of four glass powders: one from the screening of crushed glasses (GP-fine), one from a dust collector (GP-dust), and the other two, GP-4000 and GP-6000, from the grinding of GP-dust in a ball mill [8]. All four glass powders had the same chemical composition and, according to ASTM C618, they could be classified as Class N natural pozzolans if Na_2O content was not a concern. In the test mixtures, 20% of the mass of cement was replaced by glass powder. The GP-fine from the screening process is very coarse and contained particles with sizes ranging from 40-700 μm. The GP-dust from the dust collector was finer than the GP-fine, but still coarser than the Portland cement. Portland cement contained about 40% of particles smaller than 10 μm, while the GP-dust contained only about 20% particles smaller than 10 μm. The particle size distribution of GP-4000 was almost the same as that of Portland cement when particles were smaller than 30 μm. GP-4000 shows a coarser distribution than Portland cement in sizes smaller than 30 μm. One obvious factor is that GP-4000 still contained some particles larger than 100 μm, whereas Portland cement did not. GP-6000 had a finer particle size distribution than GP-4000. Compared to Portland cement, GP-6000 showed a finer particle size distribution in the portion of particles smaller than 50 μm, but a slightly higher portion of particles larger than 60 μm compared to Portland cement. They showed that GP-fine exhibited the lowest strength and the lowest pozzolanic strength activity index amongst the materials tested due to its coarse particles. Its pozzolanic strength activity index values were around 70 to 74% at 7 and 28 days, respectively, which are slightly lower than the minimum 75% as specified in ASTM C618 for pozzolanic materials. Although GP-6000 was finer than GP-4000, there was only a marginal difference in pozzolanic strength activity index between them. At 28 days, the pozzolanic strength activity index of GP-4000 and GP-6000 rose to around 110%. This indicates that these two glass powders had very high pozzolanic reactivity. Shi *et al.* also examined the effect of curing temperature on the pozzolanic strength activity index and strength development [8]. They found that when the curing temperature was elevated to 35 or 65 °C, the pozzolanic strength activity index of GP-4000 increased significantly from 1 to 28 days, as shown in Figures 2.7 and 2. 8. The strength of cement containing 20% fine glass powder was higher than that of 100% Portland cement at 7 days at both temperatures. Compared with the results at 23 °C, this means that elevating temperature is very beneficial for increasing the early strength of the cementitious system containing glass powder.

Shayan and Xu performed a field trial on concrete slabs $(15 \times 2.5 \times 0.25 \text{ m})$ to investigate the performance of glass powder in concrete under field conditions [9]. They used mixed colour waste packaging glass comprising soda-lime glass. The glass powder consisted of particles which were 88% <10 μm and 12% >15 μm. The surface area of the glass powder was around 800m^2/kg, which was much higher than that of the cement (350m^2/kg). A concrete mix, commonly used in the locality as structural concrete of 40 MPa strength, was chosen as the reference mix, having a cement:aggregate:sand ratio of 1:2.68:2.02 with a water/cement ratio of 0.49. This composition was used for any further adjustment in the formulation. The purpose of the trial was to determine the effect of glass powder as a cement replacement material at 20-30% dosage rates. The experiments showed that only one concrete mix containing 20% glass powder met the strength requirement for 40 MPa concrete at 28 days. However, at 40 days all the other mixes containing 30% glass powder approached 55 MPa, despite 30% reduction in cement content, indicating further strength development over time due to pozzolanic reaction between glass powder and cement.

2.1.3 Polyols

As mentioned earlier, organic admixtures are widely used in cementitious systems to impart specific properties and make them suitable for different applications. Organic admixtures are used as placticisers, water reducers, set retarders, etc. One group of organic compounds used as admixtures are sugar alcohols or polyols. They are carbohydrates and belong to a larger family of chemicals called saccharides. [20].

Although the mechanism of interaction between sugars and cement is poorly understood, it is generally accepted that retardation occurs because sugars adsorb to (1) surfaces of hydrating cement particles, or (2) surfaces of hydration products, thereby forming a temporary barrier to further hydration [21].

Garci Juenger and Jennings studied the effects of sugars on the hydration and microstructure of cement pastes [21]. They added 1% table sugar to ASTM Type I Portland cement pastes having a water/cement ratio of 0.45. They studied the cement hydration at 20 °C, 30 °C, and 40 °C to assess the effect of curing temperature on the degree of hydration of pastes containing 1% sugar and found that sugar retards cement hydration at each temperature examined.

Bishop and Barron proposed a dissolution-precipitation mechanism with the use of organic phosphonic acid. The dissolution of calcium exposes the aluminum-rich surface to catalyse hydration followed by precipitation of a layered calcium phosphate that binds to the surface of the cement grains. This inhibits further hydration by acting as a diffusion barrier to water as well as nucleation inhibitor [22]. Based upon these results, they investigated the analogous reactions of sucrose as an inhibitor to determine if the new mechanism is prevalent in that system. They studied the reactions of sucrose with tricalcium silicate ($3CaO.SiO_2$, C_3S), tricalcium aluminate ($3CaO.Al_2O_3$, C_3A) in both the absence and presence of gypsum. The results showed that when C_3S is hydrated in the presence of sucrose, the resulting paste is much more watery than the paste hydrated in the absence of retarder, indicating a significant inhibition of hydration. C_3A pastes hydrated in the presence of sucrose were initially runny; however, the pastes set and became hard after ca. 1 minute. The results showed that sucrose accelerated ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$) formation and retarded C_3S hydration. They proposed that the mechanism by which sucrose retarded cement hydration involved surface adsorption and nucleation poisoning initiated by calcium-sucrose complexes.

Peschard *et al.* found it difficult to establish a mechanism of interaction between cement and polysaccharides [20]. Their results revealed the importance of the chemical structure of polysaccharides and that higher polysaccharide-to-cement weight ratios lead to an extended delay in hydration.

Zhang *et al.* studied the effect of aliphatic sugar alcohols on the hydration of C3S and ordinary Portland cement and compared them with those of sucrose [23]. Results demonstrated the ability of sugar alcohols to retard C_3S hydration and increase setting time. Xylitol and sorbitol exhibited the highest retarding effect amongst the sugar alcohols studied; pastes containing 1.3 wt% xylitol or 0.8 wt% sorbitol remained unset even after 56 days. Addition of as little as 0.15wt% sucrose resulted in an inhibiting effect surpassing that of all sugar alcohols. Dose-dependency of the setting time of OPC in the presence of sugar alcohols was examined and results showed that, similar to C_3S, both initial and final setting times increased exponentially with saccharide content. The effect of sorbitol addition on the unconfined compressive strength of cement pastes at 21±1 °C was studied. It was found that at 56 days the cement paste containing 0.40 wt% sorbitol showed ca. 15% higher strength than the additive-free cement paste.

2.2 Geopolymers

2.2.1 Introduction

Geopolymers are synthetic materials formed by the aqueous alkali-activation ofaluminosilicate solid particles. Geopolymer activating solutions are based on alkali hydroxide solutions, generally containing variable amounts of dissolved silicon. The presence of large amounts of silicon and aluminium in minerals, clays and industrial wastes and ashes makes these materials common for use as feedstock in geopolymerisation. Geopolymers are principally known for their high compressive strength, acid resistance and waste encapsulation capability, though the inorganic framework structure renders these materials intrinsically fire-resistant [24, 35].

The term ‘Geopolymer’ was first applied to X-ray amorphous aluminosilicate bindersformed through hydrothermal synthesis of aluminosilicates in the presence ofconcentrated alkaline or alkaline silicate solutions by Joseph Davidovits [24].Davidovits’ aim was to create an inorganic analogue of composite organic constructionmaterials and take advantage of the intrinsic heat-resistant and non-combustiblenature of inorganic materials after numerous plastic-related catastrophicfires in France between 1970 and 1973. The first geopolymers were synthesised frommixtures of kaolinite, quartz and sodium hydroxide solution of varied concentrations,which were cured at 150 °Cto form a solid material with appreciable mechanicalproperties. Currently, geopolymersmaybesynthesisedatambientorelevatedtemperaturebyalkaline activationof alarge variety ofaluminosilicate materialsobtainedfromindustrialwastes [25-30],calcinedclays[31, 32],naturalminerals[33],ormixturesoftwoormoreofthesematerials[28, 34].Activation is achieved by addition of highly concentrated alkali metal hydroxide solution now more broadly describedas the alkaline activating solution, which is composed of any alkali cation andpredominantly contains pre-dissolved silicon. The range of common synthesistemperatures in the literature varies from ambient to mildly hydrothermal.Davidovitscoined the word ‘Geopolymer’ in order to emphasise what he thought were the keyaspects to the technology; ‘Geo’ referring to the inorganic nature of the material, and‘polymer’ to infer a structure analogous to that of organic polymers.

Although the cost for manufacturing Portland cement is relatively low, the massive environmental impact alone is incentive enough to trigger the search for new construction materials such as geopolymers, which can equal, or improve the existing properties of Portland cement-based materials, including durability, chemical resistance, fire resistance and waste encapsulation capability, and eliminate the environmentally unfriendly Portland cement manufacturing processes. Since the desired market for geopolymers is predominantly a replacement for OPC, geopolymer research programs were initially focused onaligning the science of geopolymers with traditional cement technology and relatedforums. OPC binders are based mainly on hydration reactions of calcium oxide andsilicon dioxide to form calcium silicate hydrates. Therefore, the chemistry of OPCbinders is of an intrinsically different nature to that of geopolymers, which is moreclosely aligned with zeolites and aluminosilicate gel formation [33].

2.2.2 Chemical and Structural Characters

Davidovits initially defined the structure of geopolymers to be a three-dimensional matrix of silicon and aluminium in tetrahedral geometry linked by oxygen atoms [35]. Alkali cations are associated with the aluminium to provide a single positive charge to balance the negative charge on the AlO_4^- group. The Davidovits model describes the matrix as being comprised of three structural units, polysialate (PS) (-Si-O-Al), polysialate-siloxo (PSS) (-Si-O-Al-Si-), and polysialate-disiloxo (PSDS) (-Si-O-Al-O-Si-O-Si-) based on the presence of only Si-O-Si and Si-

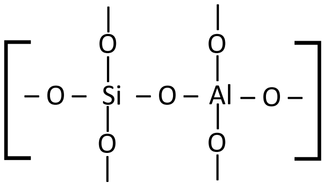
O-Al linkages. It excludes Al-O-Al linkages. The Davidovits model is fundamentally simplistic and does not incorporate or predict the effects of variation in Si/Al ratio or the alkali cation type.

When Davidovits was first working on geopolymers, he felt therewas no appropriate or equivalent nomenclature capable of describing the structure ofgeopolymers. Therefore, Davidovits defined geopolymers to have a backbone structure analogous to organic polymers,and created a nomenclature to describe the connectivity of the three-dimensionalframework structure of linked SiO_4 and $MAlO_4$ tetrahedra (where M is a monovalentcation, e.g. Na^+, K^+) [35]. This nomenclature was determined based on the observation thatgeopolymers were amorphous to X-rays and contained exclusively tetrahedrallycoordinated silicon and aluminium by observation withnuclear magnetic resonance (NMR). The nomenclature calls forthree linear oligomeric building units, called ‘polysialates’. The term‘sialate’ is an abbreviation for silicon-oxo-aluminate and is used here to describe thebonding of silicon and aluminium by bridging oxygen. Poly(sialates) are said to havean empirical formula of [24, 35]:

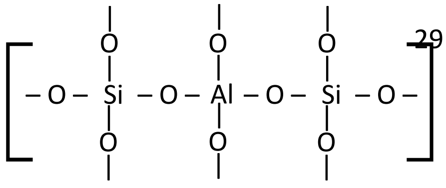
$$M_p\{(SiO_2)_z\ AlO_2\}_p\ ._wH_2O$$

where p is the degree of polycondensation, z is either 1, 2 or 3, and w describes thewater content of the composite. The poly(sialate) oligomers are described as chainand ring polymers with Si^{4+} and Al^{3+} in IV-fold coordination with oxygen and range fromamorphous to semi-crystalline [35]. The oligomeric building units aredepicted below:

z = 1: Poly(sialate) (PS)



$$\left[-O-\underset{|}{\underset{O}{\underset{|}{Si}}}\overset{|}{\overset{O}{\overset{|}{\ }}}-O-\underset{|}{\underset{O}{\underset{|}{Al}}}\overset{|}{\overset{O}{\overset{|}{\ }}}-O-\right]$$



$$\left[-O-\underset{|}{\underset{O}{\underset{|}{Si}}}\overset{|}{\overset{O}{\overset{|}{\ }}}-O-\underset{|}{\underset{O}{\underset{|}{Al}}}\overset{|}{\overset{O}{\overset{|}{\ }}}-O-\underset{|}{\underset{O}{\underset{|}{Si}}}\overset{|}{\overset{O}{\overset{|}{\ }}}-O-\right]$$

z = 2: Poly(sialate-siloxo) (PSS)

z = 3: Poly(sialate-disiloxo) (PSDS)

Davidovits describes the geopolymeric binder as having a three-dimensionalnetwork structure [35], yet the polysialate oligomers are two-dimensional and theirdescription as ring and chain polymers has not been experimentally verified in theliterature. Furthermore, the three polysialate oligomers do not provide for thepossibility of Al-O-Al linkages.Hence, the polysialate oligomers under-specify theconnectivity of each SiO_4 and AlO_4 centre in three-dimensional space, and fail to allow forthe possibility of Al-O-Al linkages.

Geopolymers are X-ray amorphous, and as such, characterisation utilising NMR and Fourier transform infra-red (FTIR) spectroscopy has been carried out by many researchers [28, 36-40]. NMR studies have shown that the silicon and aluminum present in geopolymers are tetrahedrally coordinated to oxygen. Barbosa *et al.* used NMR, XRD, and FTIR spectroscopy to study the polymerisation and structure of geopolymers synthesised by the sodium silicate activation of dehydroxylated aluminosilicate clay (metakaolinite) [36]. Based on their NMR results, they proposed a basic structural model of geopolymers. The structure contains Si and Al tetrahedra distributed randomly along the polymeric chains joined by an oxygen bridge with hydrated sodium ions in the framework cavities.

Yunsheng *et al.* synthesised a fully-reacted sodium-PSDS geopolymeric matrix by alkaline activation of metakaolin at room temperature [41]. They proposed a three-dimensional molecular model of the geopolymer based on results obtained by Environmental Scanning ElectronMicroscope equipped with Energy Dispersion X-rayAnalysis (ESEM-EDXA), and highly sensitive Magic AngleSpinning-Nuclear Magnetic Resonance Spectroscopy(MAS-NMR) techniques. The structure shows chains of Si atoms partially replaced by 4-coordinated Al tetrahedral.

2.2.3 Synthesis

Geopolymers are synthesised by the dissolution of aluminosilicate particles in highly-alkaline solutions with predissolved silicon. Several aluminosilicates have been used as precursors for geopolymer synthesis. These include: metakaolin [31, 32], kaolin [29, 32, 34], fly ash [28, 29, 32, 34, 37, 40, 42, 43, 44, 45], blast furnace slag [25, 26, 28, 32, 46], natural pozzolans and zeolite [32], other aluminosilicate minerals [33], as well as mixtures of different minerals [28, 34]. The majority of research has been focused on the utilisation of low-calcium fly ash; however there seems no reason why high-calcium fly ash could not be used for geopolymer synthesis [46].

Metakaolin has been used as a model aluminosilicate mineral to study geopolymerisation [47]. It is produced by the dehydroxylation of kaolinite ($Al_2O_3.2SiO_2.2H_2O$) when heating the kaolinite to 500-900 °C [48].

Fly ash is another aluminosilicate that is produced as the by-product of coal combustion processes. The chemical composition and physical properties of fly ash depends on factors such as the source of coal, particle size of coal, and the combustion process. Fly ashes reported in the literature have varying amounts of CaO, Fe_2O_3, and other metal oxides such as TiO_2, and NiO. According to ASTM C618-08a designation, fly ash can be categorised based on its chemical composition. The criteria for different categories are given in Table 1. Class F fly ash is normally produced from burning of anthracite or bituminous coal, and Class C fly ash from the burning of lignite or sub-bituminous coal. Class F and C fly ashes are also known as low-and high-calcium content fly ashes, respectively. Class C fly ash contains a total calcium content, expressed as CaO, higher than 10% (mass).

Blast furnace slag is a by-product of ferrous and non-ferrous metallurgical processes and composed mainly of calcium magnesium aluminosilicate. The slags used for geopolymer synthesis show variations in composition; particularly the amounts of Ca, Mg, and Fe are variable amongst different raw materials [25-28].

Table 2.1: Chemical composition requirements for the classification of fly ash (ASTM C618)

	Fly Ash Class	
	F	**C**
$SiO_2 + Al_2O_3 + Fe_2O_3$, min wt%	70.0	50.0
SO_3, max wt%	5.0	5.0
Moisture content, max wt%	3.0	3.0
Loss on ignition, max wt%	6.0	6.0

Geopolymerisation is a complex multiphase process, involving a series of dissolution-reorientation-solidification reactions analogous to those observed in zeolite synthesis by hydrothermal treatment of solid precursors [49]. van Deventer *et al.* presented a basic conceptual model for reaction processes involved in geopolymerisation [47] . This model was originally developed to show the reaction mechanisms involved in the geopolymerisation of metakaolin. Since the geopolymerisation of metakaolin and fly ash are believed to be similar this model can be extended to fly ash as well.

The alkaline solution, also called the alkaline activator that is added to the solid aluminosilicate precursor consists of an alkaline hydroxide (NaOH or KOH) and liquid sodium silicate, usually dissolved in deionised water. Other alkali-containing activators have been used for geopolymer synthesis including sodium carbonate and sodium orthophosphate [25]. A wide range of synthesis and post-synthesis temperatures have been reported in the literature ranging from room temperature to 80 °C, at different time intervals.

The properties of the final product very much depend on the raw materials and the synthesis conditions including: chemical composition and morphology of solid reactant [29, 43, 47], SiO_2/Na_2O molar ratio [50], curing temperature [34, 37, 44, 51], Na/Al ratio [37, 43], water content and soluble silicon in the aqueous phase [39], and alkali metal in the activation liquid [42, 43].

High strength geopolymer mortars up to 70.0 MPa have been produced using high-calcium lignite fly ash [46]. The geopolymer synthesis was carried out at 65 °C for 48h, and sodium hydroxide and sodium silicate solution were used as activation. Provis *et al.* studied different activating solution compositions and liquid/solid ratios to synthesise sodium silicate-fly ash geopolymers [45]. They achieved strength up to 60 MPa and correlated the mechanical strength with activator SiO_2/Na_2O mole ratio and liquid/ash mass ratio.

2.2.4 Admixtures

There is not any published work in the literature on the use of chemical admixtures in geopolymeric systems. Chemical admixtures have been extensively researched and are widely used in cementitious systems to impart different properties. However, the majority of research carried out so far on geopolymers centre around the synthesis of geopolymers using different precursors and understanding the relationship between composition and synthesis parameters on various aspects of the final materials.

There are some reports on using mineral admixtures in geopolymer synthesis [52-54]. Yip *et al.* investigated the mechanical strength of metakaolin-based geopolymers where 0-100% of metakaolin was replaced by two calcium carbonate minerals, that is calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). They found that moderate amounts (20% by mass) of calcite and dolomite could be beneficial to the strength development of geopolymers. Excessive amounts of those minerals had a detrimental effect on the compressive strength of the geopolymers [52].

The effect of calcium compounds (CaO and $Ca(OH)_2$) as fly ash substitutes was studied by Temuujin *et al.* [53]. They added 1-3 % (mass) of calcium compounds and cured the fly ash-based geopolymers at ambient temperature and 70 °C. Their results showed the beneficial effect of adding calcium compounds on the mechanical properties of geopolymers cured at ambient temperature, and that calcium hydroxide proved to be superior to calcium oxide.

Hu *et al.* utilised Class F fly ash for geopolymer synthesis where zeolite or bentonite (two aluminosilicate minerals) were used as supplementary materials and sodium hydroxide together with calcium oxide wereused as the alkali-activators [54]. They replaced 5-15% of fly ash with zeolite or bentonite and cured the specimens at 20 °C. The results indicated the importance of CaO as part of the alkali-activator and are consistent with previous studies in which higher CaO content may be beneficial to geopolymerisation and the dissolution phase. The authors suggest using both NaOH and CaO as alkali-activators to accelerate the synthesis of fly ash-based geopolymer synthesis. In those batches where zeolite was used as fly ash substitution, the highest strength and the best sulphate resistance was observed. Bentonite appeared to act simply asa mineral filler without improving the properties and microstructure of the final products.

2.3 Summary

Geopolymers have been shown to be a promising alternative to ordinary cement as construction materials amongst other applications. Major sources of aluminosilicate materials needed for the synthesis of geopolymers are industrial by-products that normally would be disposed of in landfill. Consequently, geopolymerisation provides the opportunity to convert massive quantities of waste materials into value-added products and, if used in construction industry, they can reduce CO_2 emission associated with cement manufacturing. However, due to variation in the chemical composition and other properties of raw materials at different locations, there should be specific investigations to ascertain the feasibility of using aluminosilicate-containing raw materials for geopolymer synthesis. Using nonrecyclable glass particles as cement replacement has shown to be beneficial in strength development in the cementitious systems. Glass, mainly an aluminosilicate mineral, is thought to display pozzolanic reactivity as finely-ground particles at the highly-alkaline conditions present in the cementitious system.

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Chapter 3

Utilisation of Glass Cullet in Geopolymer Mortars

3.1 Abstract

This study investigated the possibility of using cullet to supplement dissolved aqueous silicon for the geopolymerisation of a high-calcium fly ash, thereby reducing the sodium silicate requirements in the activating solution and the overall cost of geopolymer manufacture. Substituting up to 34% of the fly ash by cullet while decreasing sodium silicate addition by up to 20% caused the 3- and 7-day compressive strengths to decrease by up to 58% when geopolymer mortar was cured at 40 °Cand by up to 48% when geopolymer mortar was cured at 70 °C. Hydrothermal pre-treatment of the cullet with a 5 M sodium hydroxide solution at 175 °C for 4 hours increased the 3-day strength by 25% compared to geopolymer mortar containing untreated cullet, but required additional sodium hydroxide. Substituting 20% of the sand by cullet reduced the 3-day compressive strength by 14% when curing at40 °C. Micromineralogical analyses

revealed that cullet reacted only slightly in the geopolymer matrix cured at 70 °C, causing the formation of a thin boundary layer containing higher concentrations of Si and Ca and lower concentrations of Al and Fe around cullet particles. This boundary layer was physically weaker than the surrounding alkali-silica-aluminate phase. The sharp corners of cullet particles acted as crack initiation locations during compressive strength testing, thus contributing to the lower strength.

3.2 Introduction

Geopolymers are synthetic materials formed by the aqueous alkali-activation of aluminosilicate solid particles [1, 2]. Geopolymers may be synthesized at ambient or elevated temperatures by alkaline activation of a large variety of aluminosilicate materials obtained from industrial wastes [3-8], calcined clays [9,10], natural minerals [11], or mixtures of two or more of these materials [12,13]. The presence of large amounts of silicon and aluminium in clays, metallurgical slags, and fly ashes makes these materials common for use as feedstock in geopolymerisation. The alkaline activating solution added to the solid aluminosilicate precursor usually consists of an alkaline hydroxide (NaOH or KOH) and liquid sodium silicate in water. Other alkali-containing activators have been used for geopolymer synthesis, including sodium carbonate and sodium orthophosphate [3], calcite and dolomite [14], and calcium oxide [15].

Fly ash is an aluminosilicate-containing by-product of coal combustion which has been widely studied as a viable precursor for geopolymerisation [6-8, 13, 15-27]. The composition and physical properties of fly ash depend on the source of coal, combustion process, and particle size. Fly ashes reported in the literature have varying amounts of CaO and metal oxides, and the majority of research has focused on the utilisation of low-calcium fly ash for geopolymer synthesis. Much less work has been carried out with high-calcium fly ash, where the total calcium content expressed as CaO is higher than 10% by mass [16].

Geopolymerisation is a complex process, and the properties of the final product depend on the raw materials and on the synthesis and post synthesis conditions including chemical composition and morphology of the solid reactant [7, 17, 18], SiO_2/Na_2O molar ratio [16, 19, 20], curing temperature [13, 21-23], Na/Al ratio [17, 24], water content and soluble silicon in the aqueous phase [25], and alkali metal in the activation liquid [17, 26]. High strength geopolymer mortars up to 70.0 MPa have been produced using high-calcium lignite fly ash cured at 65 °C for 48 h, using sodium hydroxide/sodium silicate activating solution [16]. Provis *et al.* [20] studied different activating solution compositions and liquid/solid ratios to synthesize sodium silicate-fly ash geopolymers. They achieved strengths up to 60 MPa and correlated the mechanical strength with the activator SiO_2/Na_2O mole ratio and the liquid/ash mass ratio.

Extensive research has been conducted on the utilisation of cullet in cementitious systems for applications as fine aggregate [28-30], coarse aggregate [31], and partial replacement of cement [32-35]. Cullet, an aluminosiliceous material itself, exhibits pozzolanic reactivity at specific conditions. These include particle size usually less than 40 µm [32, 36-37], highly alkaline aqueous medium [36], extended contact time (90 to 404 days) [33, 35-38], and moderately elevated temperature (35 °C-65 °C) [36-39].Shao *et al.* [38] studied cement replacement by finely-ground soda-lime glass particles and found higher strength development and reduced expansion in mortar bars containing 30% cement replacement by 38 µm cullet particles. They attributed these results to the pozzolanic reactivity of cullet, which is further supported by other studies [39, 40]. The majority of the previous research on cullet has focused on cementitious systems. Our study is the first to report on the effect of cullet utilisation in geopolymeric systems.

The hypothesis for this research is that the incorporation of reactive cullet powder in geopolymer mortar may allow a reduction in the amount of sodium silicate solution used as activator during geopolymer synthesis. Because the activator solution represents a significant cost in the production of geopolymer materials, this research has important economic implications. This hypothesis is tested by comparing the strength of geopolymers containing cullet and a reduced amount of sodium silicate activator to that of control samples containing a larger amount of sodium silicate activatorand no cullet. The effects of curing time and curing temperature on strength are also investigated. The reactivity of cullet particles in geopolymer matrices is further investigated by micromineralogical observations.

In some tests, cullet was hydrothermally treated to increase its reactivity. Hydrothermal treatment of glass is a process in which glass particles react with water at elevated temperature and pressure. This leads to enhanced ion mobility which causes a high rate of alkali ion and hydronium ion exchange along with an increased solubility of the alkali components [41, 42]. Corigliano and Mavilia [36] studied extractive treatment of glass powder using sodium hydroxide solution as the extracting phase under moderate temperature and pressure conditions, i.e., 60-105 °C and 101.3-460.4kPa, in order to solubilise significant amounts of amorphous silica. They found that the main product of extraction was alkaline sodium silicate, while the unextracted phase contained calcium and sodium monosilicates as well as untreated glass particles. Hydrothermal treatment has also been used to change the specific surface area and size of the particles being treated [42].

One of the major drawbacks of using cullet as aggregate in concrete is the alkali-silica reaction between glass aggregate and cement [31, 38, 43-44] which can cause expansion and cracking. On the other hand, cullet may have beneficial applications as a partial aggregate replacement in fly ash-based geopolymer concretes because these concretes have been shown to be much less prone to the alkali-silica reaction [45]. In the present study, cullet has also been tested as partial fine aggregate replacement in geopolymer mortars.

3.3 Materials and methods

3.3.1 Materials

High-calcium fly ash was obtained from the Atikokan Generating Station in Ontario, Canada. This is a Type C fly ash according to ASTM C618. The cullet was obtained by crushing and grinding colourless soda glass jars (Classico Sauce, Heinz, Toronto). The chemical compositions of fly ash and cullet, determined by XRF (major elements and chloride), and LECO (sulfur), are shown in Table 1. Detailed characterisation of the fly ash was reported elsewhere [46]. It is predominantly (~75%) X-ray amorphous, the main crystalline phase is quartz. Some periclase and possible trace amounts of other phases are also present. The fly ash specific gravity is 2.404 ± 0.048g/cm3.

The particle size distributions of fly ash and cullet determined by laser diffraction (Mastersizer 2000, Malvern Instruments Ltd, UK) are compared in Figure 3.1. The d_{50} and d_{95} of the fly ash are around 14µm and 110µm, respectively. The cullet is somewhat finer than the fly ash, having d_{50} and d_{95} values around 10.9µm and 36µm, respectively.

3.3.2 Preparation of geopolymer mortars

Geopolymer mortar samples were prepared by mixing fly ash and sand (ASTM 20/30 Graded Sand, US Silica Company) with sodium silicate solution (Technical Grade, Fisher Scientific, USA, SiO_2: 29.2 mass%, Na_2O: 9.1 mass%, H_20: 61.7 mass%), sodium hydroxide pellets (Technical Grade, Fisher Scientific, USA; 95% purity), and deionised water. The liquid activator was made by dissolving sodium hydroxide pellets in deionised water and subsequently adding sodium silicate solution to achieve the desired SiO_2/Na_2O mole ratio. When cullet was used in the recipe, it was weighed and added to the activator solution followed by mixing to allow the particles to disperse throughout the entire solution. The activating solution was then added to fly ash/sand mixture to achieve the desired number of moles of Na_2O per 100g of fly ash and activator liquid-to-fly ash mass ratio. Mixing was conducted according to ASTM C 305-06 using a 4.73 liter bench mixer (Hobart Mortar Mixer, Hobart Corporation, USA). The geopolymer mortar was then transferred into six 2-in polypropylene cube moulds held in a brass mould frame (ELE International, USA). The moulds were placed in an environmental chamber (ESL-3CA, ESPEC Corp., USA) for 24 hours at 39.5 ± 0.5 °C and relative humidity of 99 ± 1%. Samples were demoulded after 24 hours of curing and were put back in the environment chamber for the rest of the curing time prior to strength testing. For samples cured at 70 °C, the cube moulds were first placed in a sealed box in a thin layer of deionised water to provide a humid atmosphere and then in a convection oven (Isotemp Oven, Fisher Scientific, USA).

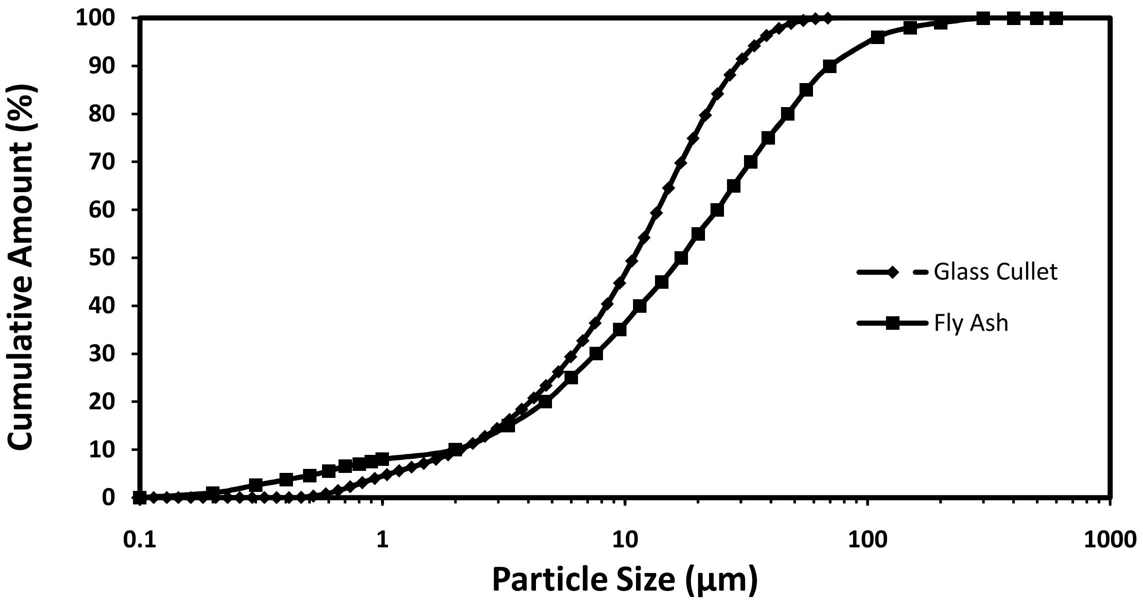


Figure 3.1: Particle size distribution of fly ash and cullet

Table 3.1: Chemical composition of fly ash and cullet

Oxide	Mass%

	Fly ash	Cullet
SiO_2	43	72.7
Al_2O_3	21	1.67
Fe_2O_3	4.2	0.60
MgO	2.6	0.25
CaO	14.5	10.8
Na_2O	7.5	14.0
K_2O	0.6	0.26
TiO_2	0.9	0.05
P_2O_5	0.6	0.02
MnO	0.02	< 0.01
Cr_2O_3	0	< 0.01
V_2O_5	0.02	< 0.01
S	0.62	0
LOI[a]	0.78	0.36
Total	96.34	100.8

[a] Loss on ignition

3.3.3 Compressive strength testing

Compressive strength tests were conducted on 2-in cubes according to ASTM C109-08 to assess the strength development of geopolymer mortars at the age of 3 and 7 days cured at 39.5±0.5 °C and 69±1 °C. For each geopolymer batch composition, six cubes were tested using a compressive strength machine (Model Super L60; Tinius Olsen Testing Machine Co., USA), and the average compressive strength and standard deviations were reported.

3.3.4 Hydrothermal pre-treatment of cullet

The hydrothermal pre-treatment process was carried out by placing 30g of finely ground cullet into a pressure vessel containing 50g of 5.0M sodium hydroxide solution. The pressure vessel was sealed and placed in an oven at 175 °C for 4 hours. The pressure vessel was shaken every 5 minutes for the first hour. After 4 hours, it was allowed to cool down before collecting the treated cullet as a flowing paste. No sodium hydroxide solution remained in the vessel. Because the pressure vessel could not take more than 30 g of cullet at a time, several batches of pre-treated cullet needed to be made to prepare one batch of geopolymer.

3.3.5 Micromineralogical analysis

Micromineralogical analyses were carried out to investigate the reactivity of cullet in the geopolymer matrix. Polished sections of crushed geopolymer mortars were prepared after strength tests. While preparing a polished specimen, the porous space was first filled with epoxy resin to stabilize the microstructure and prevent further damage during polishing. Filling the pores with epoxy was achieved using vacuum impregnation, in which the dried specimen is immersed in epoxy solution while under a vacuum and then is brought to atmospheric pressure while still immersed. The sections were lapped and polished using kerosene so as not to alter the water-soluble minerals. After carbon-coating, the sections were imaged by scanning electron microscopy (SEM) and quantitative elemental analysis of the samples was carried out by energy dispersive spectrometry (EDS) with an Oxford Link ISIS system. The following calibration standards were used: corundum for Al; jadeite for Na; and pyroxene for Si, and Ca. An accelerating voltage of 20kV, beam current of 0.475mA, working distance of 10mm, and a vacuum pressure of 5×10^{-5} torr were consistently used for viewing all samples.

3.4 Results and discussion

3.4.1 Compressive strength results for geopolymer mortars containing no cullet

Several geopolymer batches were made to approach the optimum composition of reacting phases with respect to strength. Provis *et al.* [20] correlated the compressive strength of sodium silicate-fly ash geopolymer mortars cured at 40 °C for 3 days with respect to the activator liquid/fly ash mass ratio (m) and the activator SiO_2/Na_2O molar ratio (r). The highest compressive strength values (50-60 MPa) were achieved in the region defined by $0.5\leq m \leq0.8$ and $0.7\leq r \leq 1.7$ when the number of moles of Na_2O added per 100g of fly ash (u) was in the range of $0.075 \leq u \leq 0.225$. The fly ash/sand mass ratio was held constant at 0.47 in their study. These ranges were used as a starting point in our experiments.

Table3.2 shows the composition of geopolymer samples containing no cullet where the compositional parameters m, r, and u range from 1.400 to 1.666, 0.533 to 0.581, and 0.129 to 0.137, respectively. The fly ash/sand mass ratio was kept constant at 0.47, similar to Provis *et al.* [20]. The 3-day compressive strength of the geopolymer samples cured at 40 °C was the highest (33.9±0.7 MPa) for $m = 1.510$, $r = 0.588$, and $u = 0.137$ (Mix A3). The strength results were quite reproducible; Mix A5, which had almost the same composition as Mix A3, gave a similar strength (32.6±0.4 MPa).

The positive effect of dissolved silicon content in the activating solution on strength development can be seen by comparing Mixes A1 and A3, which only differed by the amount of sodium silicate solution. A reduction of 13% in the mass of sodium silicate solution from Mix A3 to Mix A1 resulted in a strength loss of 27%. Sodium hydroxide also had a positive effect on strength, as can be seen by comparing Mixes A6 and A3, which only differed by the amount of sodium hydroxide. Reducing the amount of sodium hydroxide by 10% by mass from Mix A3 to Mix A6 resulted in 9% decrease in strength.

Water content also played a significant role in strength development. Mixes A2 to A4 correspond to a decrease in water content while keeping constant the amount of the other components. Decreasing the water content by 10.7% (Mix A2 to Mix A3) caused the strength to increase by 50.7%. However, further decreasing the water content by 7.5% (Mix A3 to Mix A4) decreased the strength by 23.4%. Hence, there is an optimum water content (and consequently a liquid/solid ratio) for which strength is maximised when all the other components in the mixture are held constant.

Table3.2: Effect of liquid activating solution composition on compressive strength of geopolymer mortars cured at 40 °C for 3 days

Mix	**Sodium Silicate Solution (g)**	**Sodium Hydroxide (g)**	**Deionised Water (g)**	**Fly Ash (g)**	**Cullet (g)**	**Sand (g)**	**Activator SiO_2/Na_2O mole ratio (m)**	**Activator liquid/Fly Ash mass ratio (r)**	**Mole Na_2O/ 1oo g Fly Ash (u)**	**Average compressive strength (MPa)**
A1	185.68	31.40	49.67	500.1	0	1063.9	1.400	0.533	0.129	24.86 ± 3.44
A2	212.97	31.47	55.64	500.1	0	1064.0	1.510	0.600	0.137	22.48 ± 1.42
A3	213.22	31.50	49.69	500.3	0	1063.8	1.510	0.588	0.137	33.89 ± 0.72
A4	213.22	31.47	45.97	500.5	0	1063.1	1.511	0.581	0.137	25.95 ± 2.21
A5	213.50	31.42	48.26	500.0	0	1064.1	1.514	0.586	0.137	32.57 ± 0.36
A6	213.26	28.31	49.10	500.2	0	1063.9	1.599	0.581	0.130	30.93 ± 2.61
A7	234.72	28.74	27.10	500.1	0	1063.8	1.666	0.581	0.137	31.16 ± 1.83

3.4.2 Compressive strength results for geopolymer mortars containing cullet

The next stage of the study was to investigate whether cullet can be used to provide dissolved silicon and hence reduce the sodium silicate solution requirements for making geopolymer mortars. The effectiveness of cullet addition was assessed based upon the compressive strengths of the mortars (Table 3.3). Geopolymer Mix B1 was prepared by replacing 17% of the fly ash mass by cullet while decreasing the amount of sodium silicate solution by 10% by mass compared to Mix A3, which was found to provide the highest strength among the mixes containing no cullet. The amount of deionised water was adjusted so that the total mass of water (i.e., that contributed by the sodium silicate solution plus the deionised water) remained the same as in Mix A3. The amount of sodium hydroxide was also kept unchanged from Mix A3. Mix B2 corresponds to 34% replacement of fly ash by glass cullet and 20% decrease in the sodium silicate solution content in the activating solution. Mixes B3, B4 and B5 were prepared by increasing the sodium hydroxide content by 16%, 32%, and 68% compared to Mix B2 while keeping the amounts of other components unchanged.

As can be seen in Table 3.3, addition of cullet to the geopolymer in Mixes B1 and B2 decreased the 3-day compressive strength of geopolymer mortars cured at 40 °C by 19% and 50%, respectively, compared to the control mortar (Mix A3). Increasing sodium hydroxide by 32% (Mix B2 to Mix B4) improved strength by 22% from 16.9 ±0.9 MPa to 20.6 ±0.7 MPa, but further addition of sodium hydroxide (Mix B4 to Mix B5) did not change strength significantly. These results are in agreement with the findings of Mavilia and Corigliano on the dependency of the silica yield on sodium hydroxide concentration during extractive treatment of glass in an alkaline aqueous medium[36]. The authors found that the amount of extracted silica initially increased with increasing NaOH concentration but then decreased at higher NaOH concentrations. They attributed this effect to the lower solubility of monosilicates compared with that of condensed silicates at higher alkaline concentrations.

3.4.3 Effect of curing time

The effect of increasing the curing time from 3 to 7 days at 40 °C on geopolymer mortar strength is shown in Table 3.4. Mix C1 contained no cullet and was similar to Mix A3 (control mortar), except that curing time was extended. Mix C2 and Mix B2 both had 34% of the fly ash replaced by glass cullet and contained 20% less sodium silicate solution in the activating solution), and therefore different only in their curing time. Extending the curing time improved the strength of the cullet-free and cullet-containing geopolymers by 38% and 16%, respectively. After 7 days of curing, the difference in strength between cullet-free and cullet-containing geopolymer mortars was 58%, which was higher than the difference of 50% determined after 3 days of curing. These results indicate that the reactivity of cullet did not significantly benefit from an increase in curing time.

Table 3.3: Effect of cullet addition on the compressive strength of geopolymer mortars cured at 40 °C for 3 days

Mix	Sodium silicate solution (g)	Sodium hydroxide (g)	Deionised water (g)	Fly Ash (g)	Cullet (g)	Sand (g)	Compressive strength (MPa)
B1	192.00	31.45	61.46	414.70	85.50	1063.80	27.42 ±2.28
B2	170.82	31.46	74.58	328.9	171.30	1063.80	16.86 ±0.92
B3	170.90	36.59	74.55	328.70	170.90	1063.80	19.28 ±0.57
B4	170.52	41.50	74.55	328.80	171.20	1063.80	20.59 ±0.73
B5	170.21	52.83	74.59	328.80	170.21	1063.80	20.39 ±1.68

Table 3.4: Effect of cullet addition on the compressive strength of geopolymers cured at 40 °C for 7 days

Mix	Sodium Silicate Solution (g)	Sodium Hydroxide (g)	Deionised Water (g)	Fly Ash (g)	Cullet (g)	Sand (g)	Compressive Strength (MPa)
C1	213.80	31.48	48.60	500.10	0.00	1063.80	46.86±2.04
C2	170.85	31.45	75.67	330.71	170.02	1064.04	19.49±1.24

3.4.4 Effect of curing temperature

An attempt was made to increase the reactivity of cullet by increasing the curing temperature of the geopolymer to 70 °C. Compressive strengths of control and cullet-containing geopolymer mortars after 3 and 7 days of curing at 70 °C are reported in Tables 3.5 and 3.6, respectively. Mixes D1 and E1 (control mixes) had the same composition as Mix A3 (the strongest geopolymer containing no cullet). Mixes D2 and E2 had the same composition as Mix B2, i.e., 34% fly ash replacement by cullet and 20% reduction in sodium silicate solution. The results show that the higher curing temperature increased the 3-day strengths of both control and cullet-containing geopolymers by 88% (Mix D1 versus Mix A3) and 95% (Mix D2 versus Mix B2), respectively. Similarly, the higher curing temperature increased the 7-day strengths of both control and cullet-containing geopolymers by 40% (Mix E1 versus Mix C1) and 124% (Mix E2 versus Mix C2), respectively. However, the 3-day and 7-day strengths of geopolymers containing cullet cured at 70 °C (Mixes D2 and E2) were lower by 48% and 34% compared with control geopolymer mortar cured at 70 °C (Mixes D1 and E1). Comparing these differences in strength to those observed at a curing temperature of 40 °C (50% and 58% after 3 and 7 days of curing, respectively) suggests little or no beneficial effect of increasing the curing temperature on the reactivity of cullet in the geopolymer matrix.

Table 3.5: Compressive strength of geopolymers mixtures cured at 70 °C for 3 days

Mix	Sodium silicate solution (g)	Sodium hydroxide (g)	Deionised water (g)	Fly Ash (g)	Cullet (g)	Sand (g)	Compressive strength (MPa)
D1	213.82	31.45	48.50	500.0	0.00	1063.8	63.59±4.49
D2	170.37	31.53	74.68	330.29	170.15	1064.40	32.94±1.41

Table 3.6: Compressive strength of geopolymers mixtures cured at 70 °C for 7 days

Mix	Sodium silicate solution (g)	Sodium hydroxide (g)	Deionised water (g)	Fly Ash (g)	Cullet (g)	Sand (g)	Compressive strength (MPa)
E1	213.83	31.40	48.37	500.0	0.00	1063.8	65.80±3.89
E2	171.49	31.58	74.83	330.19	170.29	1064.18	43.70±3.64

3.4.5 Effect of hydrothermal treatment of cullet

Table 3.7 compares the 3-day strength of a geopolymer mortar containing hydrothermally treated cullet (Mix F1) to that of a geopolymer having the same composition but containing untreated cullet (Mix B2). Both geopolymer mortars were cured at 40 °C. The amount of sodium hydroxide reported for Mix F1 accounts for the sodium hydroxide solution used to treat the cullet. The results show that hydrothermal treatment of the cullet increased the 3-day strength by 25% compared to non-treated mix. This indicates that hydrothermal treatment is effective in increasing cullet reactivity. However, this came at the cost of using an additional amount of sodium hydroxide (0.333g NaOH per g of cullet) to hydrothermally treat the cullet. Further investigation through XRD analysis suggested the formation of analcime ($NaAlSi_2O_6.H_2O$) as a result of the hydrothermal treatment process.

3.4.6 Aggregate replacement by cullet

The effect of partially replacing aggregate by cullet, while keeping constant the amount other geopolymer components, is shown in Table 3.8 where the 3-day strength of the control mortar containing no cullet (Mix A3) is compared with that of a geopolymer mortar having 20% of its sand replaced by cullet (Mix G1). The curing temperature was 40 °C for both mixes. The results show that the 3-day strength was reduced by 14% as a result of sand replacement by cullet. This indicates that cullet is less effective than sand as aggregate.

Given that cullet particles were considerably smaller than sand particles (d_{95} = 36 µm for cullet versus 850µm for sand), the above result seems to conflict with previous reports that finely ground particles improve the strength of hardened concrete due to the ability of fine particles to decrease air voids [47, 48]. When cullet is used as sand replacement in concrete, however, the shape of the glass particles plays an important role in strength development. Chen *et al.* found that cylindrical glass particles obtained from electronic grade glass fiber scraps acted as crack-arresters and inhibited crack propagation in a cementitious matrix, ultimately leading to increased strength [49]. As will be shown in the next section, the sharp corners of the cullet particles used in the present study likely account for their detrimental effect on strength.

Table 3.7: Effect of using hydrothermally pre-treated cullet on the compressive strength of geopolymer mortars cured at 40 °C for 3 days

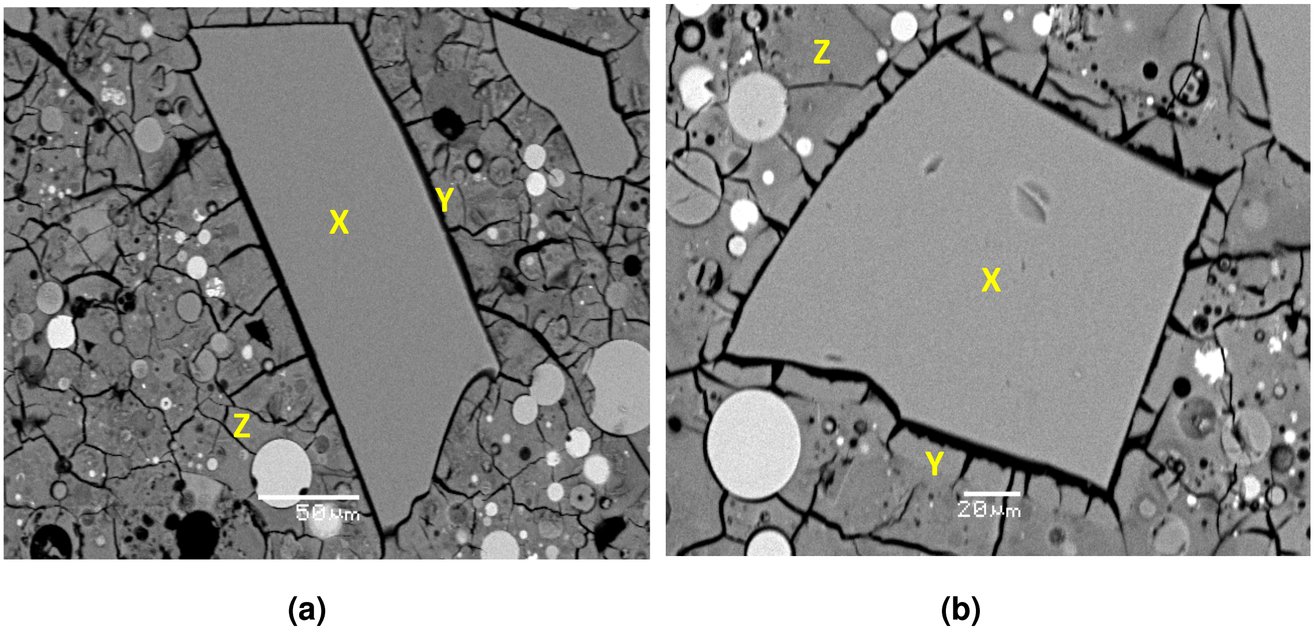
Mix	Sodium silicate solution (g)	Sodium hydroxide (g)	Deionised water (g)	Fly Ash (g)	Cullet (g)	Sand (g)	Compressive strength (MPa)
B2	170.82	31.46	74.58	328.90	171.30	1063.80	16.86±0.92
F1	170.63	88.50	74.92	328.80	171.90	1063.50	21.12±1.32

Table 3.8: Effect of partial replacement of aggregate by cullet in geopolymer mortars cured at 40 °C for 3 days

Mix	Sodium silicate solution (g)	Sodium hydroxide (g)	Deionised water (g)	Fly Ash (g)	Cullet (g)	Sand (g)	Compressive strength (MPa)
A3	213.22	31.50	49.69	500.3	0	1063.8	33.89±0.72
G1	213.50	31.50	48.20	500.00	212.76	851.10	29.06±1.62

3.4.7 Micromineralogical study of geopolymers

Figure 3.2a and 3.2b show backscattered electron images of geopolymer mortar matrix containing untreated cullet cured at 70 °C for 3 and 7 days, respectively. Cullet particles are dispersed in the geopolymer binding phase consisting of sodium aluminosilicate hydrate (NASH). The presence of multiple cracks in the geopolymer is explained by the fact that the material was crushed during compressive strength testing. Many of the cracks originate at the sharp corners of cullet particles, thus suggesting that these corners may be a major factor in the lower compressive strength values obtained with geopolymer mortars containing cullet. This corroborates the critical role played by cullet particle shapes on determining their effect on compressive strength.



(a) (b)

Figure 3.2: Backscattered SEM image of cullet particles and surrounding geopolymer matrix cured at 70 °C for (a) 3 days, and (b) 7 days, where X,Y, and Z represent cullet, boundary layer, and NASH, respectively.

A brighter (i.e., denser) boundary layer measuring approximately between 10 and 15μm in thickness surrounds the cullet particles. This layer is more readily apparent in the sample cured for 7 days (Figure 3.2b). Tables 3.9 and 3.10 report the weight percentages of various elements in the boundary layer and in the bulk NASH phase outside the boundary layer for curing times of 3 and 7 days, respectively. The bulk NASH composition did not significantly change between 3 and 7 days, although the geopolymer compressive strength increased from 32.9±1.4 MPa (Batch D2, Table 3.5) to 43.7±3.6 MPa (Batch E2, Table 3.6). This shows that the increase in geopolymer strength with curing time was not associated with a change in elemental composition of the bulk NASH phase. By contrast, the elemental composition of the boundary layer was different from that of the bulk NASH and was dependent on curing time. After 3 days of curing, the boundary layer contained a significantly higher concentration of Ca and lower concentrations of Al and Fe (t-test confidence level greater than 97%) by comparison with the bulk NASH phase (Table 3.9). After 7 days of curing, these trends were more accentuated and the concentration of Si became significantly higher in the boundary layer compared to the bulk NASH phase (t-test confidence level greater than 99.99%). These results demonstrate the reaction of cullet in the geopolymer matrix cured at 70 °C. The higher Si and lower Al and Fe in the boundary layer are consistent with the higher concentration of SiO_2 and lower concentrations of Al_2O_3 and Fe_2O_3 in the cullet than in the fly ash (Table 3.1). On the other hand, the higher Ca concentration in the boundary layer seems at odds with the lower concentration of CaO in the cullet than in the fly ash. This indicates that Ca may be more soluble in cullet than in fly ash under the conditions present in the geopolymer matrix.

The NASH phase in the boundary layer appear to be physically weaker than in the bulk phase, as evidenced by the larger number of cracks formed in the boundary layer during the compression test (Figures 3.2a and 3.2b). This is consistent with the lack of observed beneficial effect of cullet on compressive strength.

Table 3.9: Elemental composition of alkali-silica-aluminate phase cured at 70 °C for 3 days

Element	Boundary layer (wt%)[a]	Bulk NASH (wt%)[b]	t-test Confidence level (%)
Na	9.2 ± 2.9	8.1 ± 1.6	83.5
Al	3.6 ± 1.3	5.4 ± 2.1	99.3
Si	23.5 ± 1.9	23.5 ± 1.2	94.1
Ca	9.0 ± 1.2	7.6 ± 2.1	97.2
Fe	0.74 ± 0.45	1.17 ± 0.36	99.6

[a] Average and standard deviation of EDS analyses at 18 different locations within the boundary layer (3 – 15 μm from the cullet particle surface)

[b] Average and standard deviation of EDS analyses at 16 different locations in the bulk alkali-silica-aluminate phase (31 – 161 μm from the cullet particle surface).

Table 3.10: Elemental composition of alkali-silica-aluminate phase cured at 70 °C for 7 days

Element	Boundary layer (wt%)[a]	Bulk NASH (wt%)[b]	t-test Confidence level (%)
Na	7.33 ± 0.65	7.67 ± 0.80	81.2
Al	1.85 ± 0.89	5.10 ± 0.98	100.000
Si	26.5 ± 1.5	24.3 ± 1.3	99.996
Ca	10.71 ± 0.99	7.47 ± 1.06	100.000
Fe	0.25 ± 0.25	1.22 ± 0.22	100.000

[a] Average and standard deviation of EDS analyses at 24 different locations within the boundary layer (3 – 13 μm from the cullet particle surface).

[b] Average and standard deviation of EDS analyses at 15 different locations in the bulk alkali-silica-aluminate phase (36 – 125 μm from the cullet particle surface).

3.5 Conclusions

This study investigated the use of cullet as a partial substitute for fly ash or sand aggregate in the preparation of geopolymer mortars. The following conclusions were drawn:

1. Substituting 17% to 34% of the fly ash by cullet, while decreasing sodium silicate addition by 10% to 20%, caused the 3-day compressive strength to decrease by 19% to 58% when the geopolymer mortar was cured at 40 °C.
2. Micromineralogical studies suggest that the poor strength results obtained with cullet are attributable to the lack of reactivity of cullet particles in the geopolymer matrix and the initiation of cracks on the sharp corners of cullet particles during compressive strength testing.
3. Extending the curing time from 3 to 7 days at 40 °C increased the strength of geopolymer mortars but did not improve the reactivity of cullet.
4. Increasing the curing temperature to 70 °C also increased the geopolymer mortar strength. Cullet reactivity was not improved during the first 3 days of curing, although extending the age of curing to 7 days resulted in 33% increase in mechanical strength. SEM/EDS analysis of the boundary layer formed around cullet particles can be considered as evidence of cullet reactivity in the high alkaline medium, which is more evident in the mix cured at 70 °C for 7 days. The distinctive chemical composition of the boundary layer further supports that the layer formation was a consequence of cullet dissolution in the geopolymer matrix, albeit insufficient to increasea compressive strength beyond that of equivalent cullet-free geopolymer mixes.

5. Hydrothermal treatment was effective in increasing cullet reactivity and the strength of geopolymer mortar. However, the treatment required an additional amount of sodium hydroxide (0.333 g NaOH per g of cullet).

6. Replacement of 20% of the sand by cullet reduced the 3-day compressive strength of geopolymer mortar by 14%, thereby indicating that cullet is less effective than sand as aggregate. This is likely attributable to the presence of sharp corners on cullet particles which favours the initiation of cracks during compressive strength tests.

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Chapter 4

Effect of Xylitol on Strength Development and Setting of Geopolymer Mortars

4.1 Abstract

This study investigates the effect of xylitol on the strength development, setting time, isothermal calorimetry, and microminerology of geopolymer mortars based on Type C fly ash (FA-C), Type F fly ash (FA-F), and a slag/Type C fly ash blend activated by sodium silicate solution. Geopolymer mortars containing concentrations of xylitol up to 2% of fly ash mass were cured for up to 90 days at 23 °C, 40 °C, and 70 °C. Xylitol did not generally improve the compressive strength of geopolymer mortars, except for FA-C geopolymer mortars where 0.3% xylitol addition by mass of fly ash consistently improved the 56-day compressive strength at all three temperatures. The initial and final setting times of FA-C geopolymer mortars were not affected by the addition of xylitol at a concentration of 0.3 wt% but were retarded by xylitol concentrations of 0.7 wt% and 2 wt%. By contrast, the setting times of FA-F and slag/FA-C geopolymer mortars were not significantly changed by the addition of 0.7 wt% xylitol. Isothermal calorimetry studies revealed that geopolymerisation reactions at 23 °C caused an exothermic peak in the first hour after contact of the solid with the activating solution. The peak intensity was not affected by xylitol dosage; however, it was positively correlated with the calcium content of the solid and negatively correlated with the mortar setting times. Xylitol did not cause any appreciable changes in either the microstructure or the elemental composition of the geopolymer gel phase in mortars cured for 90 days at 40 °C.

4.2 Introduction

Geopolymers are synthetic materials made by aqueous alkaline activation of aluminosilicate solid particles [1-4]. A broad range of aluminosiliceous materials can be used for making geopolymers. These include industrial wastes [5-10], calcined clays [11, 12], natural minerals [13], or mixtures of two or more of these materials [8, 14]. Alkaline activating solution normally consists of sodium silicate and a strong alkaline hydroxide, all dissolved in water. However, there are some reports in the literature on the use of supplementary alkaline components such as sodium carbonate and sodium orthophosphate [5], calcite and dolomite [15], and calcium oxide [16]. Amongst many natural minerals and industrial solid waste products, fly ash has been most extensively researched for making geopolymers [8-10, 14, 16-28]. Fly ash is an aluminosilicate solid material produced as a coal-combustion side product. It has been used as pozzolan for making blended ordinary Portland cement (OPC) [29-36]. The composition and physico-chemical properties of fly ash depend on the source of the coal, the combustion process, and the particle size. The majority of the previous research has focused on using low-calcium content fly ash for geopolymer synthesis, where the calcium content expressed as CaO is lower than 10% (mass). However, there are reports that high-compressive strength geopolymers can be made using high-calcium content fly ash [17].

Blast furnace slag (BFS) is a non-metallic product, mainly consisting of silicates and aluminosilicates of calcium and of other bases, which is developed in a molten condition simultaneously with iron in a blast furnace. Granulated blast furnace slag (GGBFS) is a glassy material formed by quenching BFS in water [37]. Partial replacement of OPC by GGBFS in concrete mixtures is reported to improve the workability of concrete and extend the initial setting time. BFS cements have also been found to display high resistance to sulphate attack and lower the heat of hydration [5, 37]. BFS from different metallurgical activities have been studied as a potential precursor for geopolymerisation, either as the only solid reactant [5, 38-40] or in combination with fly ash [8]. Bakharev *et al.* [5] studied the alkaline activation of slag using sodium silicate, sodium hydroxide, sodium carbonate, and sodium orthophosphate solutions.They obtained 28-day compressive strengths in the range of 20 to 40 MPa, with sodium silicate being the most effective alkaline activator. Incorporation of low-calcium content fly ash in alkali-activated slag reduced the compressive strength of the mortar, which was attributed to insufficient Na concentration in the activating solution to adequately activate the fly ash.

Geopolymerisation is a complex process and the properties of the final product depend on the raw materials and on the synthesis and post-synthesis conditions, including chemical composition and morphology of the solid reactant [9, 18, 19], SiO_2/Na_2O molar ratio [16, 20, 21, 38], curing temperature [14, 22-24, 38, 39], Na/Al ratio [18, 25], water content, soluble silicon in the aqueous phase [26], alkali metal in the activation liquid [18, 27, 38], curing time [38, 39], and humidity during curing [40]. High strength geopolymer mortars up to 70.0 MPa have been produced using high-calcium lignite fly ash cured at 65 °C for 48h with sodium hydroxide/sodium silicate activating solution [17]. Provis *et al.* [22] correlated the geopolymer mechanical strength with the activator SiO2/Na2O mole ratio and the liquid/ash mass ratio.

It has recently been reported that some sugar alcohols, which are primarily known as set retarders in cementitious systems, are also capable of improving the compressive strength of ordinary Portland cement at a given water/cement ratio [41]. Cement paste containing 0.40wt% sorbitol has been found to have ca. 15% higher 56-day strength compared to the sorbitol-free paste. The mechanism by which sorbitol improves cement strength has not been elucidated. Collepardi *et al.* [44] studied D-sorbitol as a chemical admixture to improve the workability of a fresh OPC-free binder based on GGBFS, Class F fly ash, and hydrated lime activated by an NaOH aqueous solution. The addition of D-sorbitol to the mixture not only improved the workability of the fresh mixture but also surprisingly increased the compressive strength of the binder at a given water/binder ratio.

Although the mechanism of interaction between sugars and cement is poorly understood, it is generally accepted that sugars adsorbs to either the surfaces of the hydrating cement particles or the surfaces of hydration products, thereby forming a temporary boundary layer that hinders hydration [42] and retards setting. Bishop and Barron [43] studied the reactions of sucrose with tricalcium silicate (C_3S) and tricalcium aluminate (C_3A) both in the absence and presence of gypsum. Their results showed that when C_3S is hydrated in the presence of sucrose, the resulting paste is much more watery than in the absence of the retarder, indicating a significant inhibition of C_3S hydration. C_3A pastes hydrated in the presence of sucrose were initially runny; however, the pastes set and became hard after ca. 1 minute, thus showing that sucrose accelerated ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$) formation. They proposed that the mechanism by which sucrose retarded cement hydration was via surface adsorption and nucleation poisoning initiated by calcium-sucrose complexes. Zhang *et al.* [41] studied the effects of aliphatic sugar alcohols on the hydration of C_3S and ordinary Portland cement and compared them with those of sucrose. Xylitol and sorbitol exhibited the highest retarding effect amongst other sugar alcohols studied. Both initial and final setting times increased exponentially as saccharide content increased.

The main purpose of this study is to investigate the effect of xylitol on strength development and setting times of geopolymer mortars. Experiments were carried out using high-calcium and low-calcium fly ashes, as well as metallurgical slag. Isothermal calorimetry was used to gain insight on the effects of xylitol on the kinetics of the geopolymerisation reactions. Scanning electron microscopy and energy dispersive X-ray spectroscopy were used to assess microstructual and micromineralogical changes associated with the addition of xylitol to the geopolymer mortars.

4.3 Materials and Methods

4.3.1 Materials

The chemical compositions of FA-C, FA-F and slag determined by XRF (major oxides and chloride) and LECO (sulfur) are shown in Table 4.1. Type C (high-calcium) fly ash (FA-C) was obtained from Atikokan Generating Station in Ontario, Canada. Detailed characterisation of FA-C was presented by Johnson [46]. The d_{50} and d_{95} of this fly ash are around 14µm and 110µm, respectively. Its specific gravity is 2.404±0.048g/cm^3. Type F (low-calcium) fly ash (FA-F) was obtained from Gladstone Power Station in Queensland, Australia. Detailed characterisation of FA-F is reported elsewhere [21]. FA-F contains small quantities of crystalline quartz, mullite, and iron oxides (hematite/maghemite/magnetite), and is predominantly (~75%) X-ray amorphous. The d_{50} of Gladstone fly ash is around 10µm, and 5 vol. % of the ash particles are retained on a 45µm sieve. Granulated blast furnace slag was obtained from Independent Cement and Lime (ICL), New South Wales, Australia. Slag consisted of amorphous material having a d_{50} and d_{95} of around 11µm and 36µm, respectively.

Pure xylitol (Qingdao Oriental Yongde Trading Co.,Qingdao, China; > 98% pure) was used in the study. ASTM sand (ASTM 20/30 Graded Sand, US Silica Company) was used as aggregate. Sodium silicate solution (Technical Grade, Fisher Scientific, USA; containing 29.2 wt% SiO_2, 9.1 wt% Na_2O and 61.7 wt% H_2O), and sodium hydroxide pellets (Technical Grade, Fisher Scientific, USA; 95% purity) were used as alkaline reagents. Deionised water was used throughout all experiments.

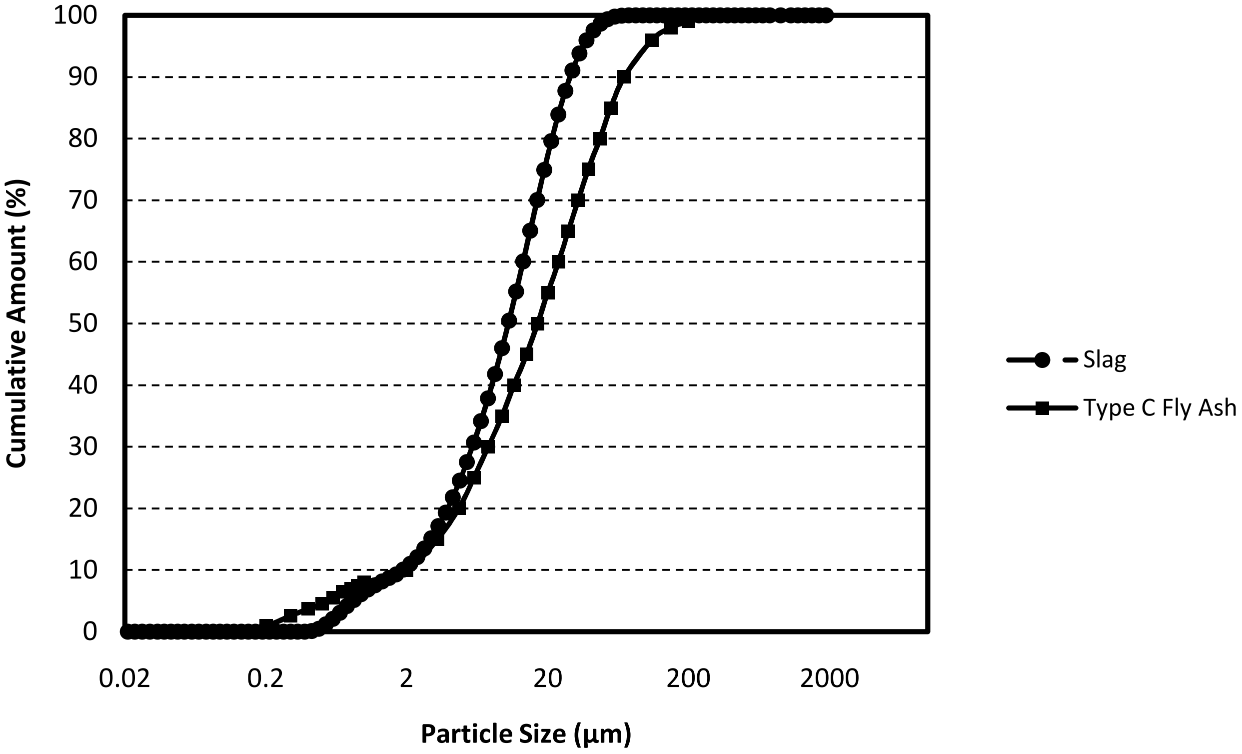

Figure 4.1: Particle size distribution of FA-C and slag

Table 4.1: Chemical composition of fly ashes and slag

Oxide	Mass%		
	FA-C	FA-F	Slag
SiO_2	43.0	46.4	33.8
Al_2O_3	21.0	28.3	13.68
Fe_2O_3	4.2	11.7	0.40
MgO	2.6	1.4	5.34
CaO	14.5	5.1	42.56
Na_2O	7.5	0.3	0.06
K_2O	0.6	0.6	0.36
TiO_2	0.9	1.4	0.54
P_2O_5	0.6	1.0	0.02
MnO	0.02	0.2	0.15
Cr_2O_3	0	0	0.01
V_2O_5	0.02	0	0
S	0.62	0.3	0.83
LOI[a]	0.78	3.3	1.81
Total	96.34	100.0	99.56

[a] LOI: Loss on ignition

4.3.2 Preparation of geopolymer mortars

The composition of the geopolymer mortar used in all experiments is reported in Table 4.2. This composition was adjusted to achieve a high compressive strength (as described in

Chapter 3). The liquid activator was made by dissolving sodium hydroxide pellets in deionised water and subsequently adding sodium silicate solution. When xylitol was added to the mixture, it was weighed and mixed into the activator solution. Fly ash and sand were mixed manually in the mixing bowl to achieve homogeneity. Next, the activator solution was added to the solid and mixing was conducted according to ASTM C 305-06 using a 4.73 litre bench mixer (Hobart Mortar Mixer, Hobart Corporation, USA). The geopolymer mortar was then transferred into 2-in polypropylene cube moulds held in a brass mould frame (ELE International, USA) and stored at the desired curing temperature. The moulds were initially cured for 24 hours under 99 ± 1% RH either in a) a sealed box, b) an environmental chamber (ESL-3CA, ESPEC Corp., USA) at 39.5±0.5 °C or c) at 69±1 °C in a convection oven (Isotemp Oven, Fisher Scientific, USA). Samples were then demoulded and returned to their curing environment for the rest of the curing time prior to strength testing.

Table 4.2: Geopolymer composition

Component		Mass % of sand
Fly ash or slag/fly ash mixture		47.0
Sand		100
Activator:	H_2O	17.7
	SiO_2	5.9
	Na_2O	4.1

4.3.3 Compressive strength measurements

Compressive strength tests were conducted on the 2-in cubes according to ASTM C109-08 using an MTS compressive strength testing machine (Model 311.21 Load Frame 100/50 KIP;MTS Systems Corporation, USA) after 3, 7, 14, 28, 56 and 90 days of curing at each temperature. The loading was displacement-controlled at a constant rate of 0.001in/sec for all compression tests. Strength measurements were carried out in sextuplicate.

4.3.4 Setting time measurements

Setting time measurements of geopolymer mortars were carried out at 22 ± 1 °Caccording to ASTM C 403 using a Humboldt ACME penetrometer (Model H-4133; Humboldt Mfg Co, USA). For each concentration of xylitol, three geopolymer mortar mixtures were made, and the average and standard deviation of three measurements were reported.

4.3.5 Isothermal calorimetry

Isothermal calorimetry of FA-C, FA-F, and slag/FA-C geopolymer mortars was carried out according to ASTM C1679-09 using an I-CAL 8000 isothermal calorimeter (CALMETRIX INC., USA). A total of 8 samples could be tested concurrently during each calorimetry run. One of the eight samples was a blank sample consisting of sand and deionised water with the same liquid/solid mass ratio as the geopolymer mortars. Two were control mortar samples containing no xylitol. The remaining five mortar samples contained 0.3%, 0.5%, 0.7%, 1.0%, or 2.0% xylitol per mass of fly ash or slag/fly ash mix. The xylitol was dissolved in the liquid activator and then left to equilibrate at room temperature for four hours. Geopolymer mortars were made as previously described and loaded into the calorimeter, which had already been set at 23 °C for several hours prior to testing.

4.3.6 Microstructure and geopolymer gel composition

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were used to investigate potential microstructural and mineralogical change in geopolymer mortars due to xylitol addition. Geopolymer mortar samples were collected after compressive strength tests to prepare polished sections. The porous space was filled with epoxy resin to stabilize the microstructure and prevent damage during polishing. Filling the pores with epoxy was achieved using vacuum impregnation, in which the dried specimen is first immersed in epoxy solution under a vacuum and then brought to atmospheric pressure while still immersed. Thin sections were lapped and polished using kerosene so as not to alter the water-soluble minerals. Micrographs of geopolymer samples were obtained using an Oxford Link ISIS scanning electron microscope operated at 20kV, beam current of 0.475mA, and working distance of 10mm. The following calibration standards were used for quantitative EDS: corundum for Al; jadeite for Na; pyroxene for Si, Mg, and Ca; orthoclase for K; and Mn-Hort for Fe. Fifteen EDS spot measurements were taken across each geopolymer matrix to obtain a representative geopolymer gel composition.

4.4 Results and discussion

4.4.1 Effect of xylitol on strength development of geopolymer mortars

4.4.1.1 High-calcium content fly ash-based geopolymer mortars

The effect of xylitol addition on the strength development of FA-C geopolymer mortars at different curing temperatures is shown in Figures 4.2-4.4.

At 23 °C, the control mortar initially gained strength until Day 14. Between 14 and 56 days, its strength remained constant or slightly decreased before resuming an increasing trend after Day 56. The effect of xylitol addition was to allow a continuous strength increase during the first 56 days. As a result, the strength of geopolymer mortars containing xylitol was significantly higher than that of the control mortar at Day 56. However, the increase in strength was much slower after 56 days, such that the strength of the control mortar slightly surpassed that of the mortars containing xylitol at Day 90. The data do not indicate a consistent effect of xylitol dosage on strength.

At 40 °C, the strength of the control geopolymer mortar behaved similarly as at 23 °C, increasing during the first 14 days, remaining almost stable between 14 and 56 days, and increasing again, albeit at a smaller rate, between 56 and 90 days. The 90-day strength at 40 °C (72.7 MPa) was larger than at 23 °C (55.1 MPa), demonstrating the favourable effect of temperature on strength, as reported by previous studies [14, 24, 38, 47, 48]. Higher temperature is believed to enhance the rate and extent of dissolution of precursors (primarily Si and Al), which lead to higher nucleation and polycondensation rates [24, 47]. The 0.3wt% xylitol dosage provided the highest benefits in terms of strength development, as it resulted in significantly higher strength compared the control mortar at 56 and 90 days. However, this same xylitol dosage resulted in lower strengths compared to the control mortar at 7 and 14 days. Overall, the data do not show compelling evidence for an overall substantive benefit of xylitol addition on compressive strength at any dosage.

At 70 °C, the control mortar strength increased during the first 28 days and then remained constant or slightly decreased. The 90-day strength at 70 °C (106.6 MPa) waslarger than at 40 °C (72.7 MPa), showing that increasing the curing temperature beyond 40 °C had a positive effect on mortar strength. As observed at the other two temperatures, the 0.3 wt% xylitol dosage provided the largest strength gain compared to the control mortar between 14 and 56 days. At

Day 90, however, all mortars had similar strengths irrespective of xylitol dosage.

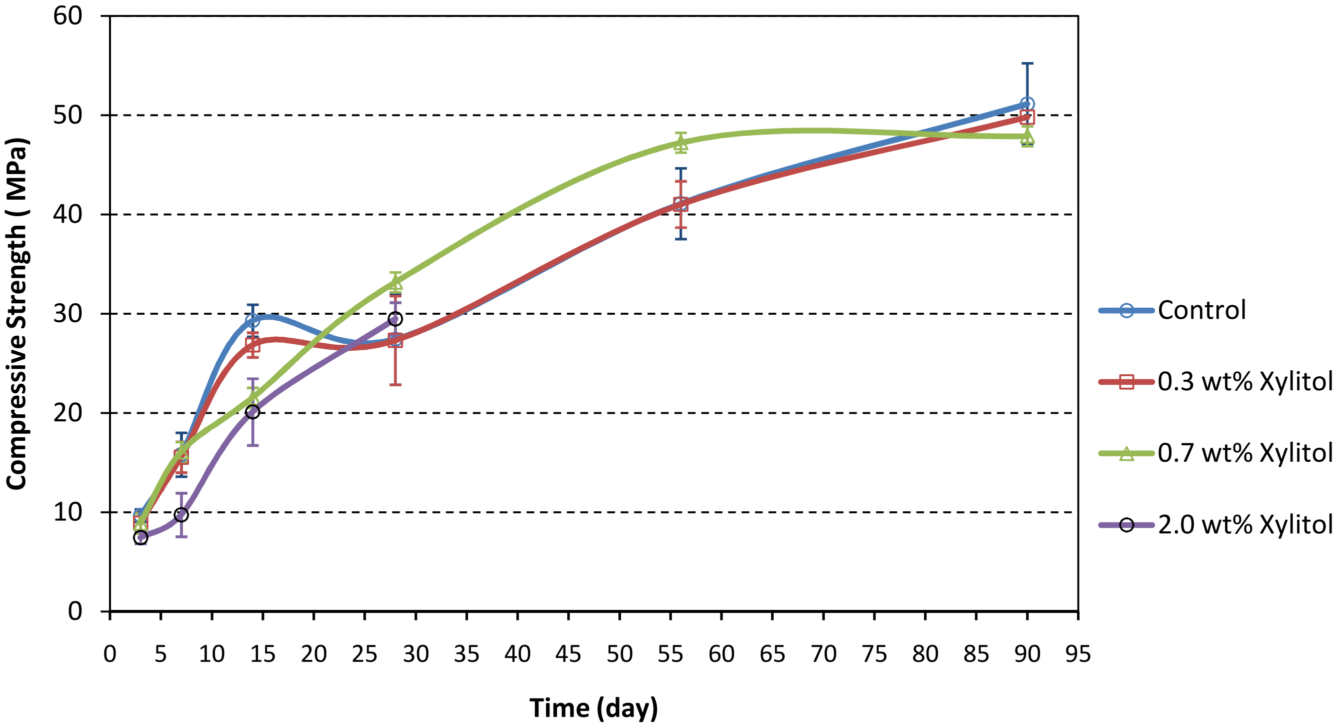

Figure 4.2: Effect of xylitol on strength development of FA-C geopolymer mortars cured at 23 °C. Error bars correspond to ±1 standard deviation.

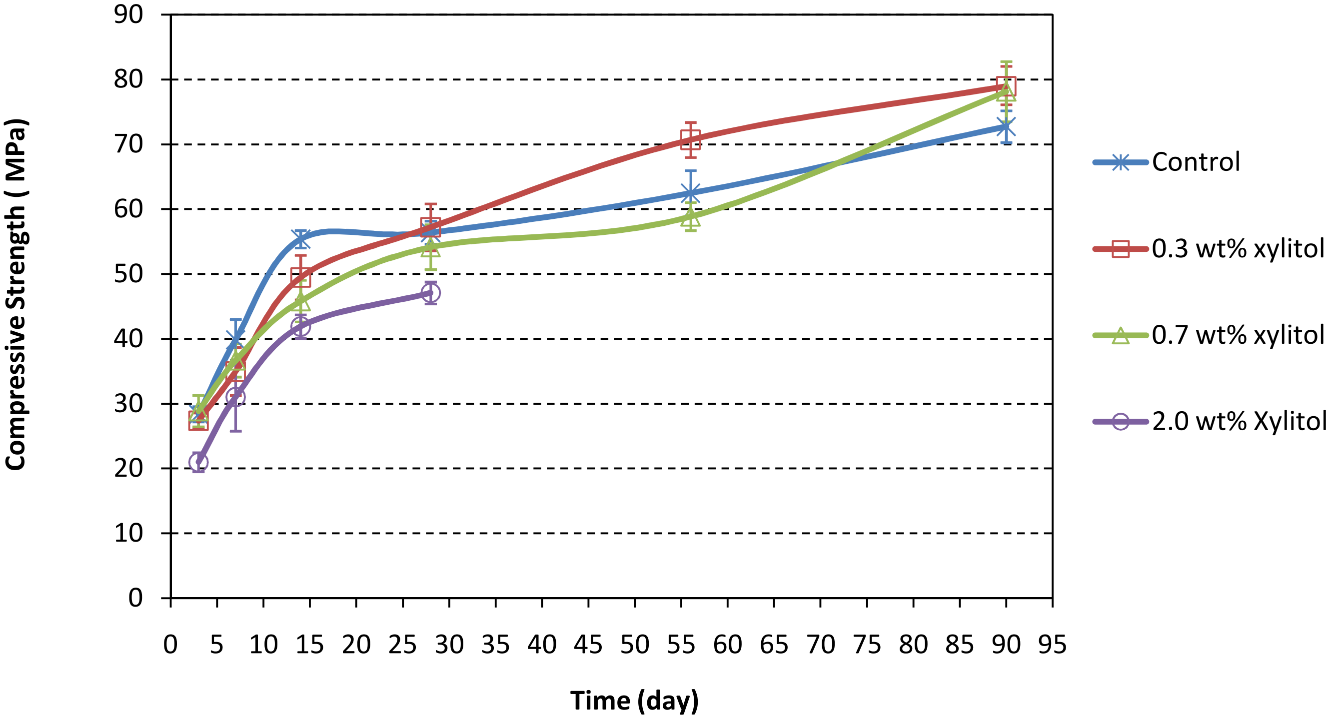

Figure 4.3: Effect of xylitol on strength development of FA-C geopolymer mortars cured at 40 °C. Error bars correspond to ±1 standard deviation.

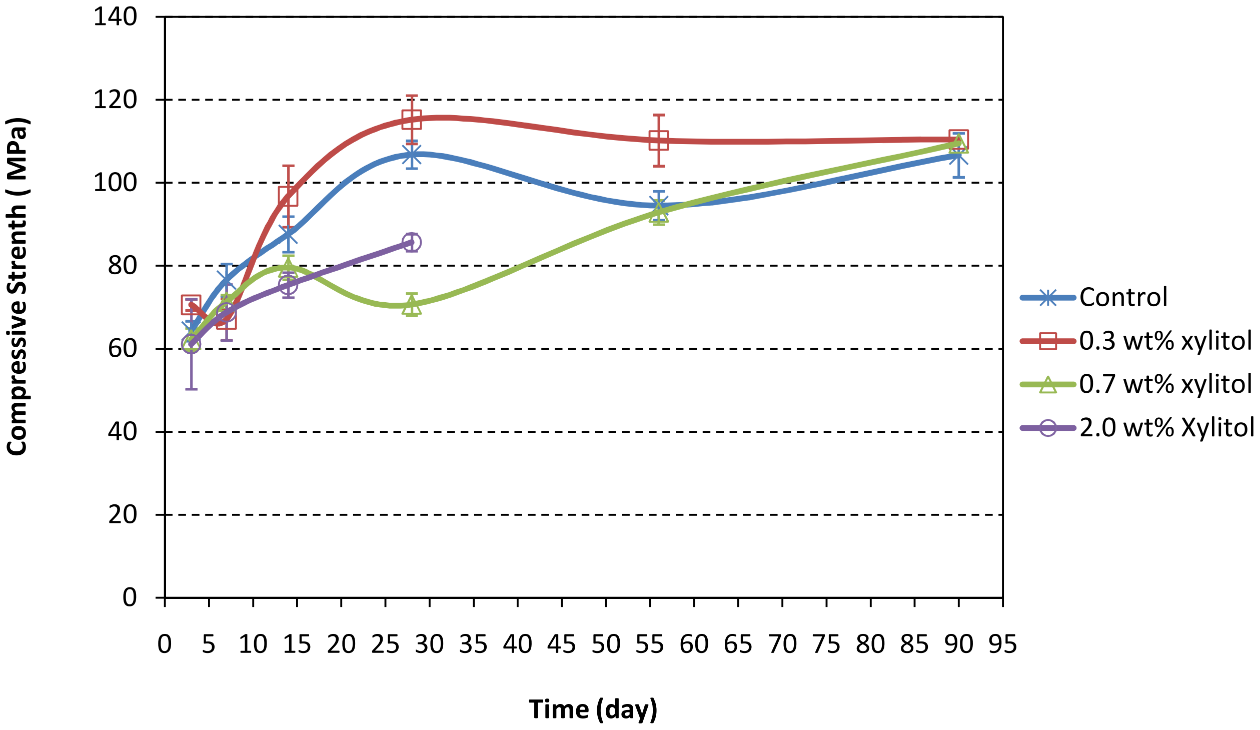

Figure 4.4: Effect of xylitol on strength development of FA-C geopolymer mortars cured at 70 °C. Error bars correspond to ±1 standard deviation.

4.4.1.2 Low-calcium content fly ash-based geopolymer mortars

Figure 4.5 shows that adding 0.7wt% xylitol to FA-F geopolymer mortar had a negative effect on strength from Day 7 onward when curing took place at 40 °C. The negative effect of this xylitol dosage is more pronounced than for FA-C geopolymer cured at the same temperature (Figure 4.3).

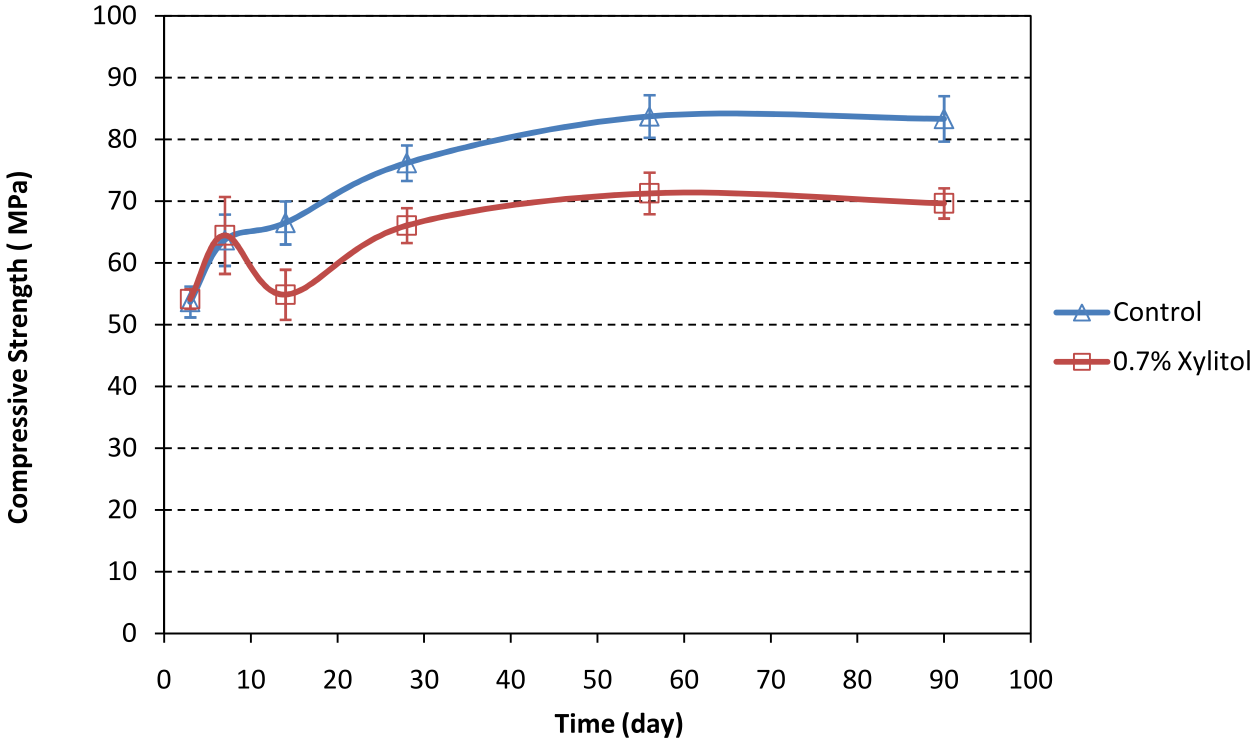

Figure 4.5: Effect of xylitol on strength development of FA-F geopolymer mortars cured at 40 °C. Error bars correspond to ±1 standard deviation.

4.4.1.3 Slag and high-calcium content fly ash-based geopolymer mortars

Figure 4.6 and 4.7 show the effects of 0.7wt% xylitol on the strength of geopolymer mortar based on a mixture of slag and FA-C cured at 23 °C and 40 °C, respectively. The effect was negligible at 23 °C and negative at 40 °C before Day 56. The short and medium term strengths (0 to 28 days) of the control mortar were enhanced at 40 °C compared to 23 °C. However, the 90-day strength of the control mortar at 40 °C (118.7 MPa) was only slightly larger than that at 23 °C (112.8 MPa). This shows that thecuring temperature had a much lower effect on the long-term strength of slag/FA-C geopolymer mortars compared to FA-C geopolymer mortars.

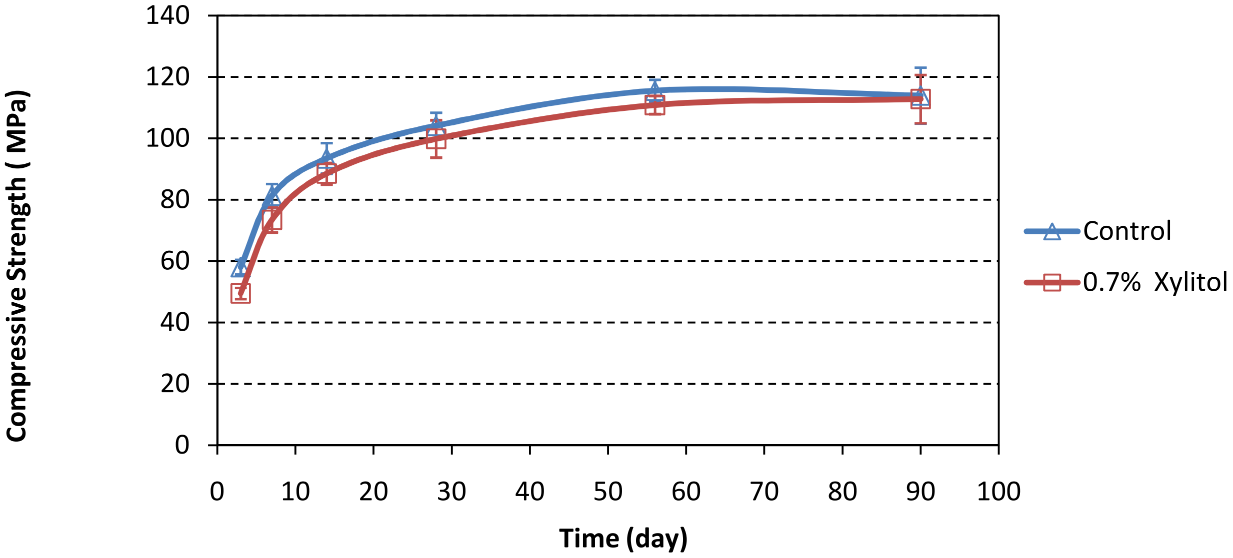

Figure 4.6: Effect of xylitol on strength development of slag/FA-C geopolymer mortars cured at 23 °C. Error bars correspond to ±1 standard deviation.

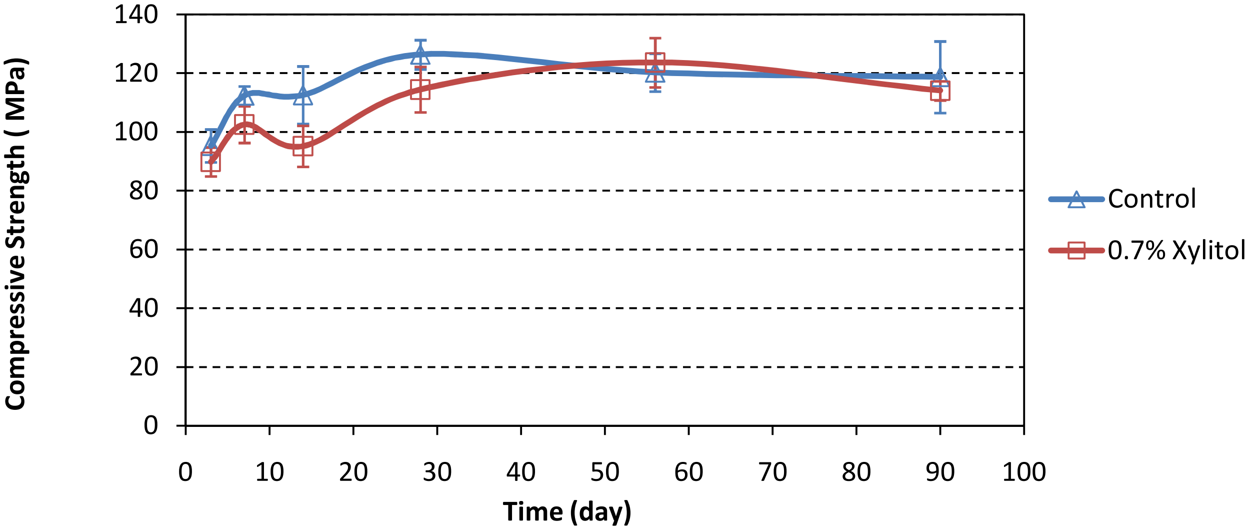

Figure 4.7: Effect of xylitol on strength development of slag/FA-C geopolymer mortars cured at 40 °C. Error bars correspond to ±1 standard deviation.

4.4.2 Effect of xylitol on setting time of geopolymer mortars

Figures 4.8-4.10 show the effect of different xylitol concentrations on the initial and final setting times of FA-C, FA/F, and slag/FA-C geopolymer mortars. Setting times were shortest for the slag/FA-C geopolymer (< 25 min), intermediate for the FA-C geopolymers (30 – 90 min) and longest for the FA-F geopolymers (> 2000 min). Xylitol had a significant retarding effect on the FA-C geopolymer mortar at concentrations greater than 0.7 wt% (Figure 4.8). However, there was no significant effect of xylitol on the setting times of FA-F, and slag/FA-C geopolymer mortars (Figures 4.9-4.10).

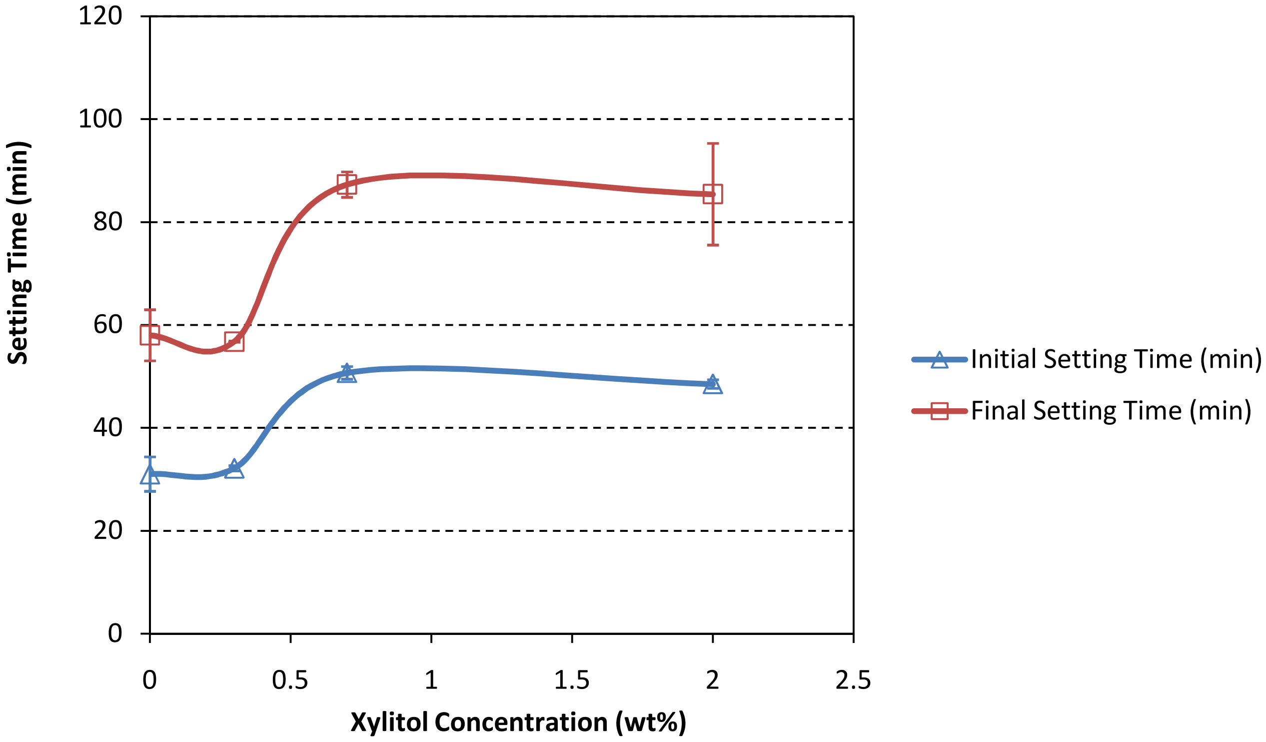

Figure 4.8 Effect of xylitol on setting time of FA-C geopolymer mortars at 22 ± 1 °C. Error bars correspond to ±1 standard deviation.

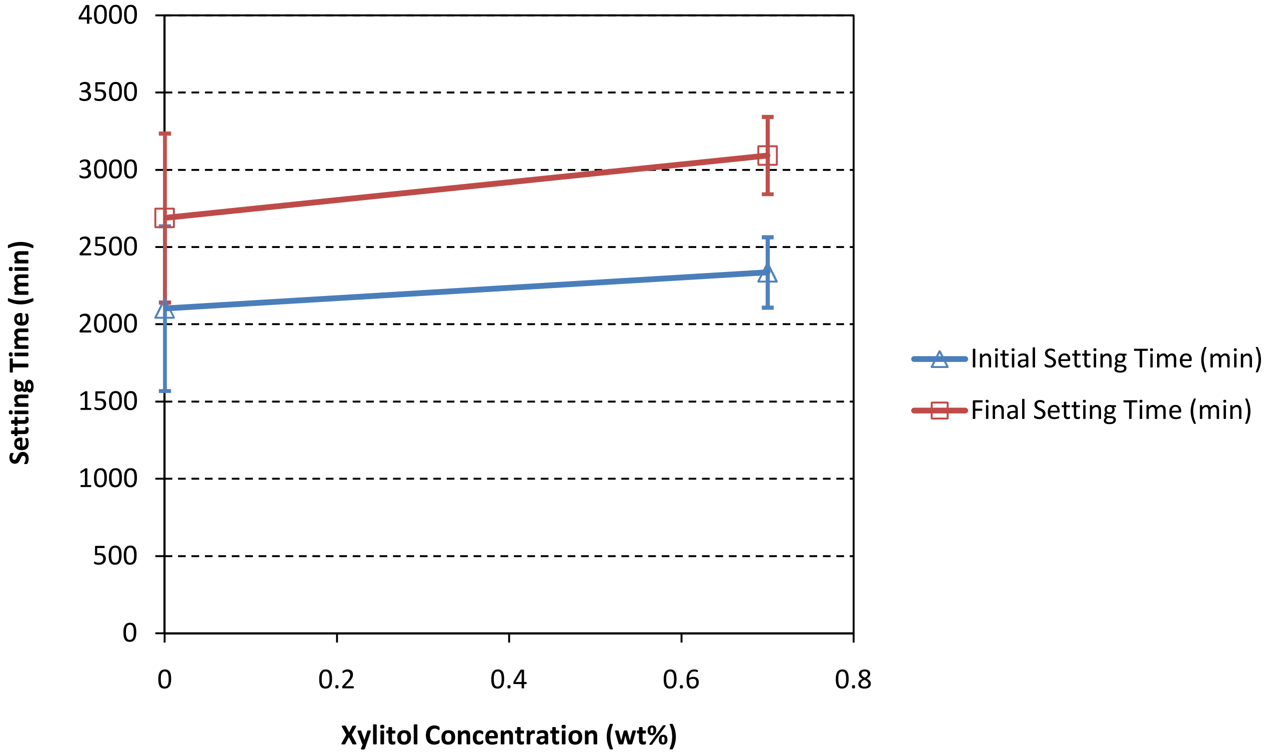

Figure 4.9: Effect of xylitol on setting time of FA-F geopolymer mortarsat 22 ± 1 °C. Error bars correspond to ±1 standard deviation.

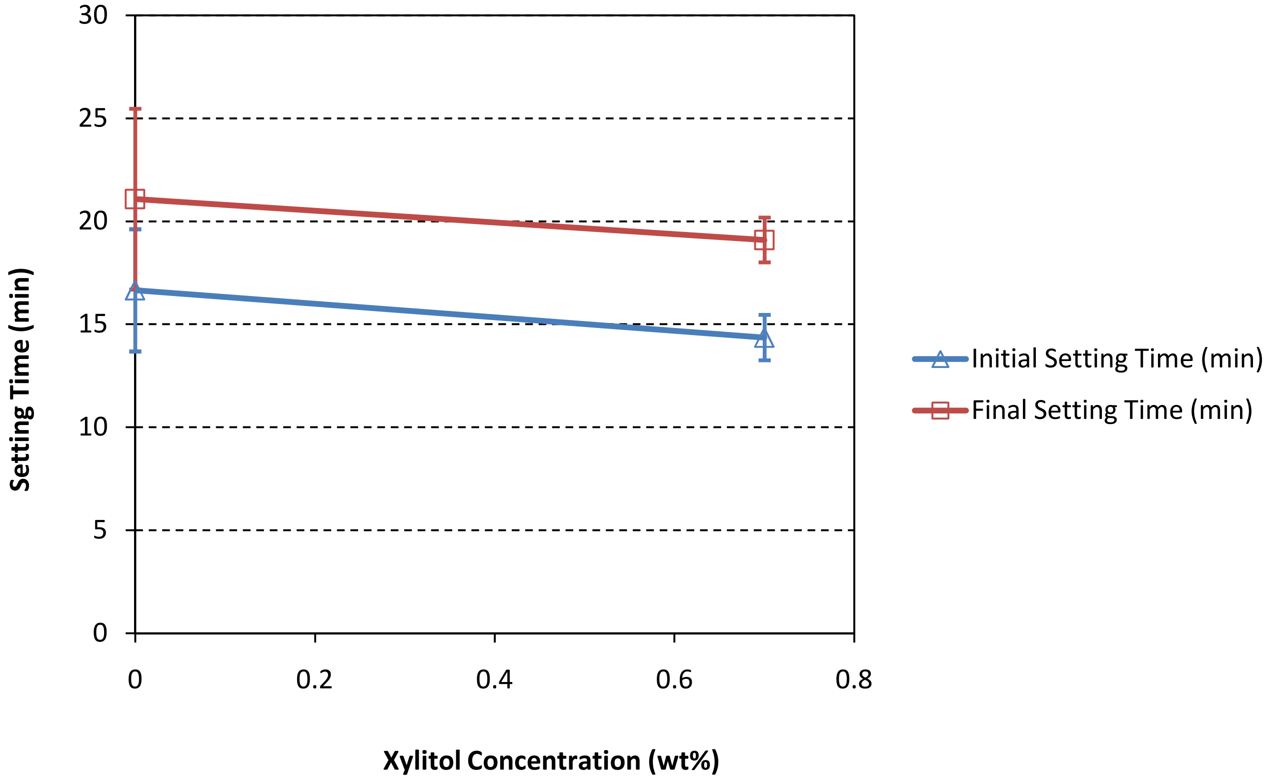

Figure 4.10: Effect of xylitol on setting time of slag/FA-C geopolymer mortars at 22 ± 1 °C. Error bars correspond to ±1 standard deviation.

4.4.3 Isothermal calorimetry results

Figures 4.11-4.13 show the results of isothermal calorimetry measurements for geopolymer mortars containing up to 2 wt% xylitol at 23 °C. The produced heat normalised by mass of geopolymer mortar is plotted as a function of time after contact of the solid with the activating solution. To our knowledge, no calorimetric analysis of geopolymeric systems has been previously reported.

The endothermic (negative) peak that occurred within the first few minutes was caused by of the mortars warming from room temperature to the calorimeter temperature. This was followed by an exothermic (positive) peak that is attributable to the formation of the sodium aluminosilicate hydrate (NASH) gel. The height of the exothermic peak was highest for slag/FA-C (7.34mW/g), intermediate for FA-C (6.54mW/g), and lowest for FA-F geopolymer mortars (0.66mW/g). Thus, exothermic peak heights correlate with the CaO contents of the solids which are 42.6 wt% in slag, 14.5 wt% in FA-C, and 5.1 wt% for FA-F (Table 4.1). Higher calcium content leads to faster reactivity of the solid with the activating solution, which in turn leads to a larger liberation of heat in the first 2 hours of reaction and shorter setting times.

The effect of xylitol on the formation of the NASH gel was examined by comparing the time and height of the maximum of the exothermic peak at different xylitol concentrations. This comparison can be only approximate because the magnitude of the first endothermic peak affects both the height and time of the maximum of the exothermic peak. In spite of this uncertainty, the heat curves were remarkably similar at all xylitol dosages for a given type of geopolymer mortar. Hence, calorimetry measurements did not show a significant effect of xylitol on the kinetics of the geopolymerisation reactions.

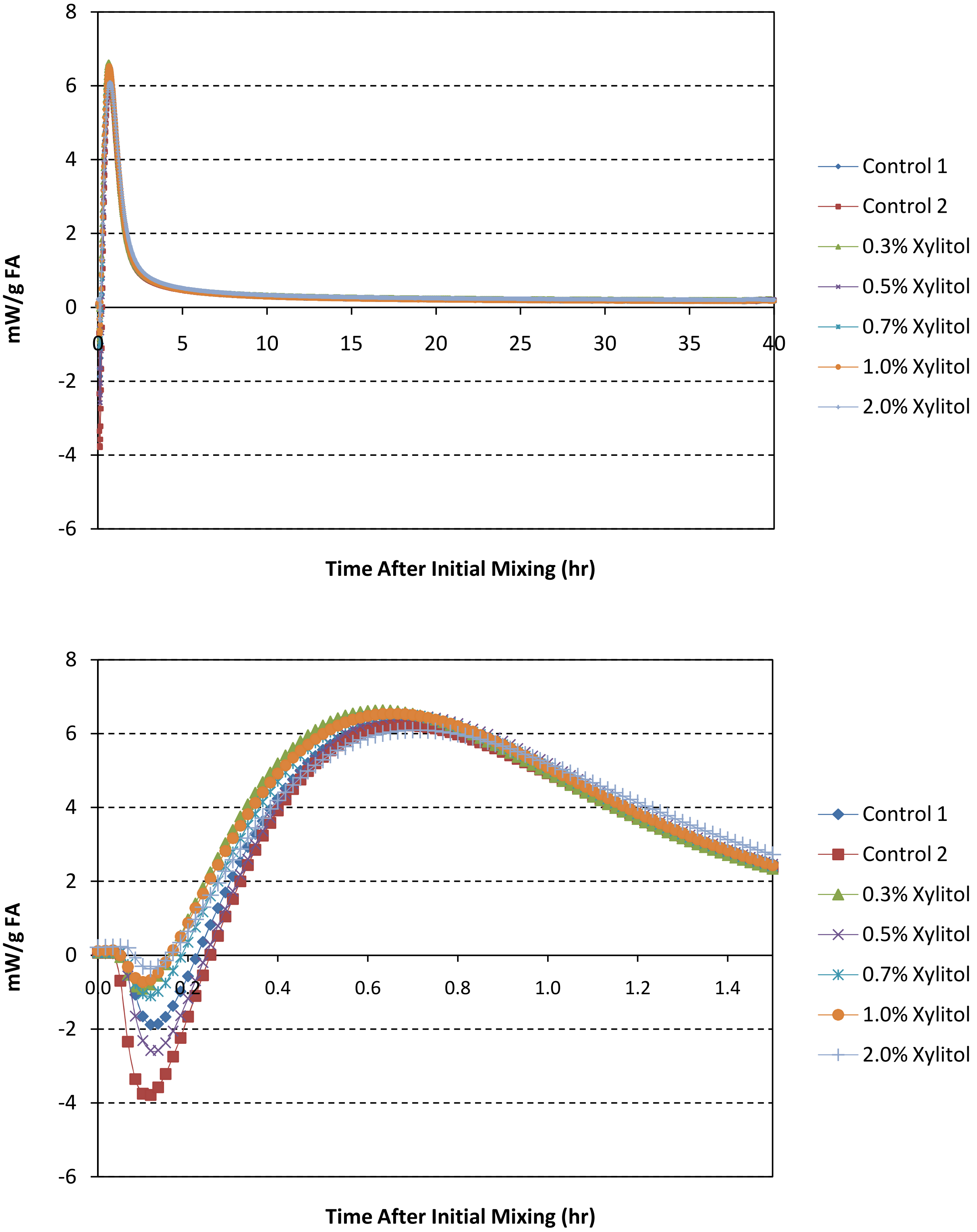

Figure 4.11: Calorimetric analysis of FA-C geopolymer mortars at 23 °C

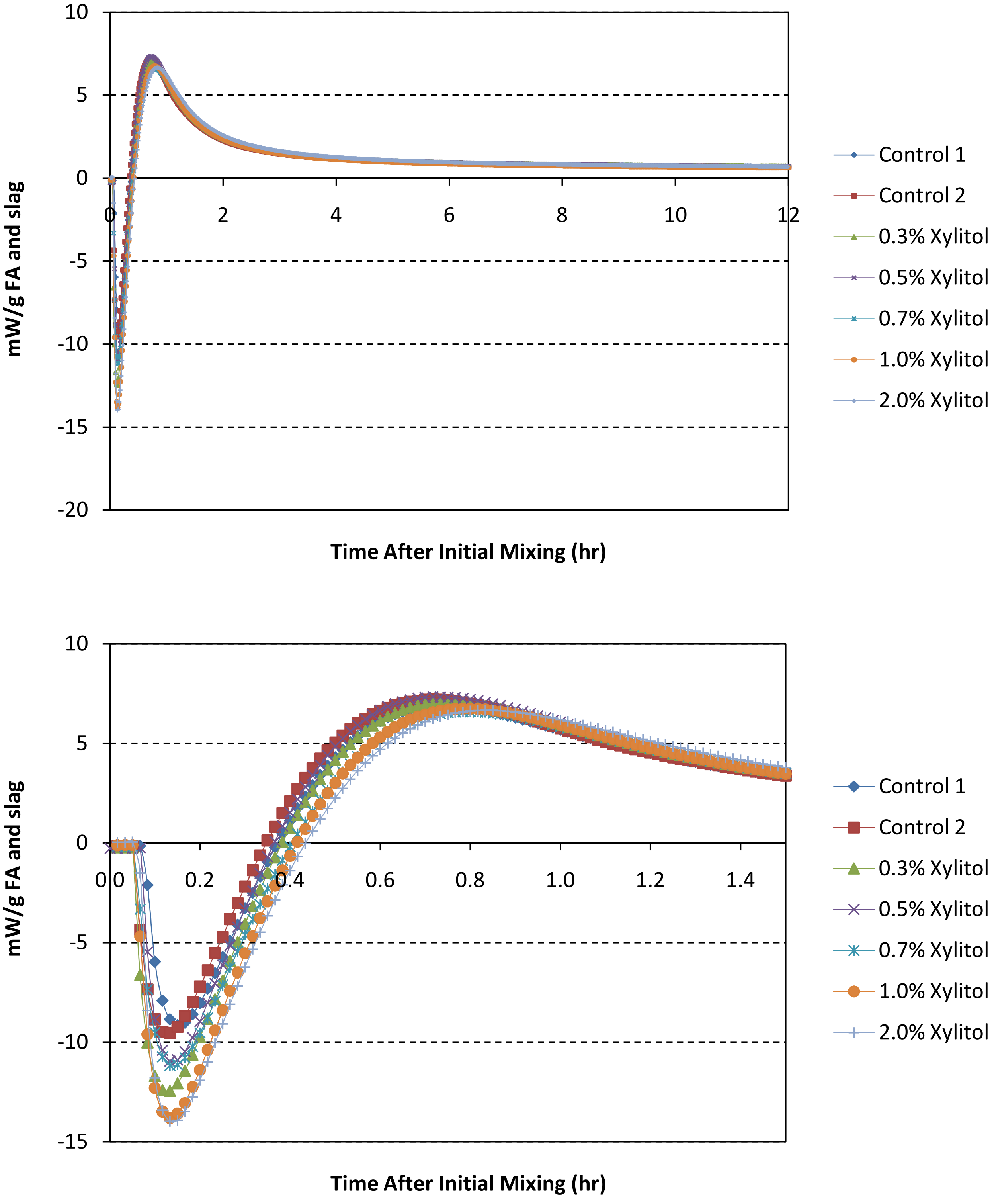

Figure 4.12: Calorimetric analysis of slag/FA-C geopolymer mortars at 23 °C

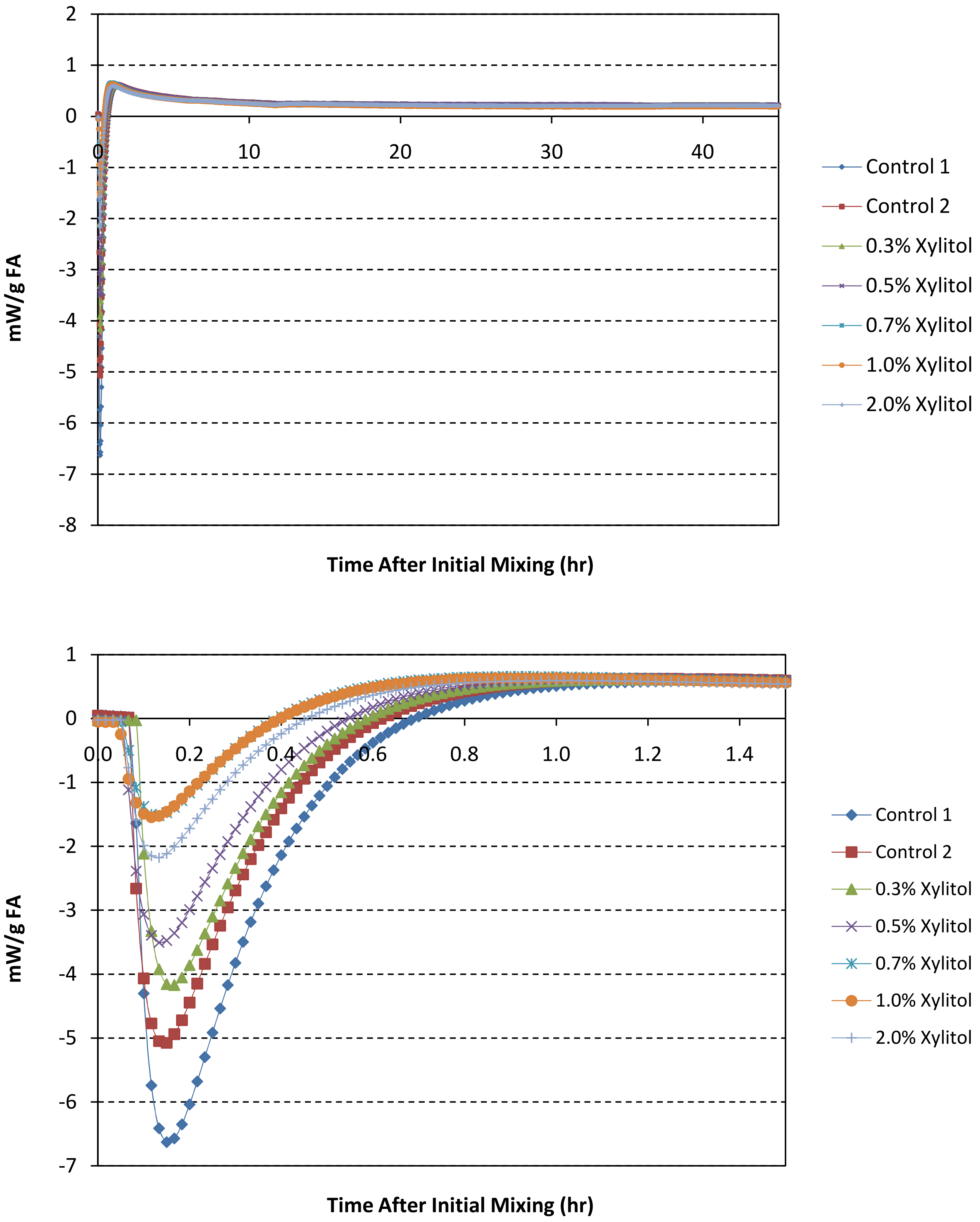

Figure 4.13: Calorimetric analysis of FA-F geopolymer mortars at 23 °C

4.4.4 Micromineraology and microstructure analysis

Figures4.14 (a-f) compare the microstructure of FA-C, FA-F and slag/FA-C geopolymer mortars containing no xylitol or 0.7 wt% xylitol, after curing for 90 days at 40 °C. They show partially dissolved fly ash and slag particles (Figures 4.14e and 4.14f) scattered in the geopolymer gel phase. The slag/FA-C combination led to a denser, less porous gel compared to geopolymers based on fly ash alone, consistent with the observed higher strengths. The addition of xylitol to the geopolymer mortars did not change the appearance of their microstructures.

Table 4.3 compares the compositions of the sodium aluminosilicate hydrate (NASH) gel in geopolymer mortars containing 0.0 wt% and 0.7 wt% xylitol. The reported compositions were obtained by averaging 15 individual EDS measurements taken in the gel. The addition of xylitol did not significantly affect the composition of the NASH gel in either the FA-C, FA-F or slag/FA-C geopolymer mortars. The differences in composition are consistent with differences in elemental concentrations in the raw aluminosilicate materials (Table 4.1), except for sodium which was mostly contributed by the activating solution.

Table 4.3: Composition of the NASH gel in the FA-C, FA-F, and slag/FA-C geopolymer mortars cured for 90 days at 40 °C

Element	**FA-C**		**FA-F**		**Slag/FA-C**	
	0.0wt% Xylitol	0.7wt% Xylitol	0.0wt% Xylitol	0.7wt% Xylitol	0.0wt% Xylitol	0.7wt% Xylitol
	(mass %)	(mass %)	(mass %)	(mass %)	(mass %)	(mass %)
Na	7.6±0.9	7.5±0.7	7.6±1.7	7.4±0.6	5.2±0.6	5.5±0.8
Al	6.1±0.08	7.1±1.9	9.7±1.2	9.4±1.1	4.9±0.2	5.4±1.2
Si	18.1±1.2	19.2±0.7	22.1±1.7	21.0±1.1	16.3±0.6	16.8±1.8
K	0.43±0.06	0.39±0.04	0.24±0.08	0.28±0.06	0.26±0.03	0.35±0.16
Ca	5.8±1.1	5.5±0.5	1.2±0.3	1.3±0.1	14.7±0.5	14.5±2.2
Fe	1.4±0.3	1.4±0.2	2.9±0.3	3.5±0.5	0.48±0.20	0.61±0.20

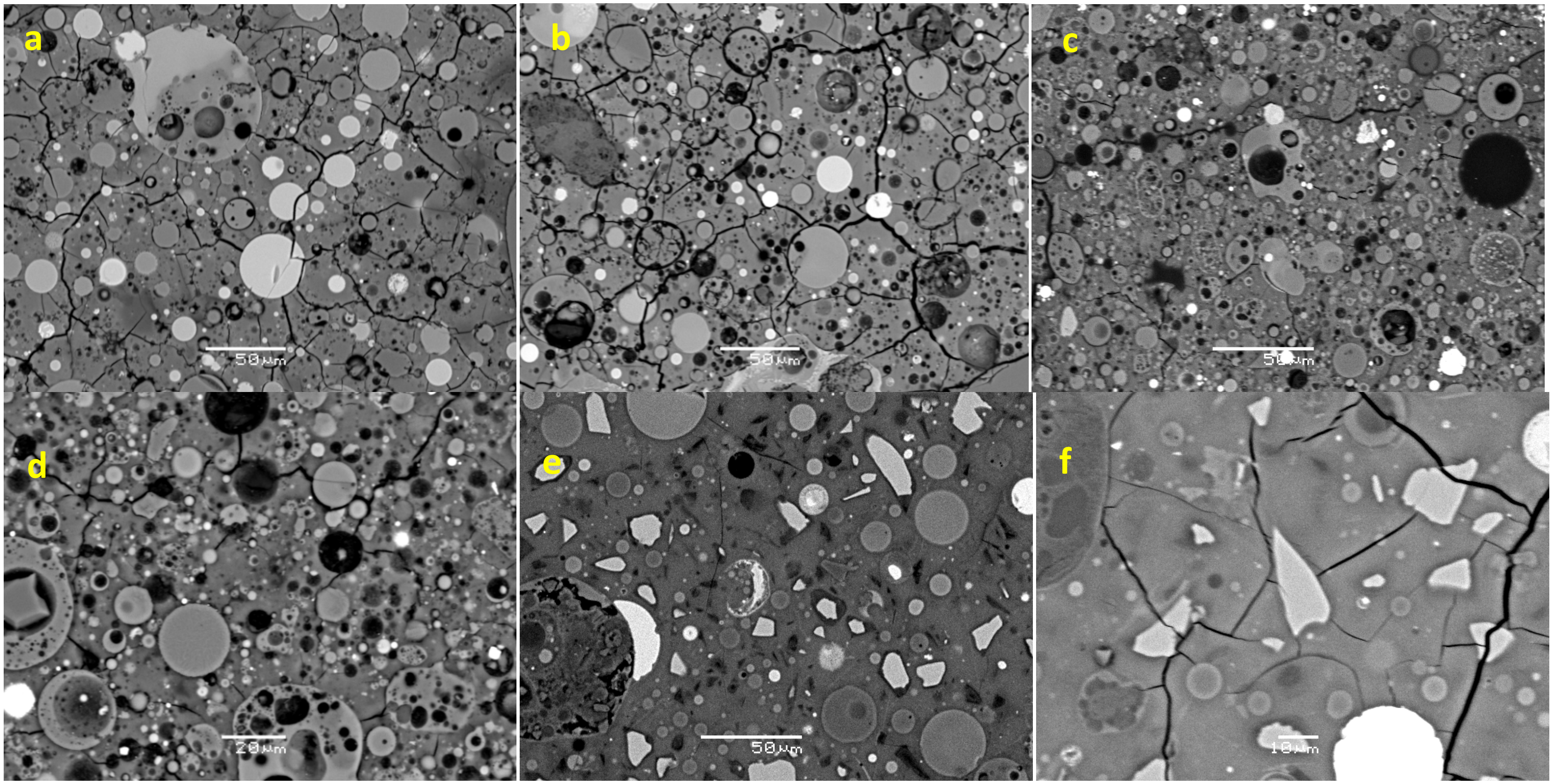

Figure 4.14: Backscattered SEM image of geopolymer mortars cured at 40 °C for 90 days. (a) FA-C+0.0% xylitol, (b) FA-C+0.7% xylitol, (c) FA-F+0.0% xylitol, (d) FA-F+0.7% xylitol, (e) slag/FA-C+0.0% xylitol, and (f) slag/FA-C+0.7% xylitol.

4.5 Conclusions

- The addition of xylitol to FA-C, FA-F or slag/FA-C geopolymer mortars did not improve their short-term (< 14 days) or long term (90 days) compressive strength. However, a dosage of 0.3 wt% xylitol consistently increased the 56-day compressive strength of FA-C geopolymer mortars at all tested curing temperatures (23 °C, 40 °C, and 70 °C).
- The initial and final setting times of FA-C geopolymer mortars were not affected by the addition of xylitol at a concentration of 0.3 wt% but were retarded by xylitol concentrations of 0.7 wt% and 2 wt%. By contrast, the setting times of FA-F and slag/FA-C geopolymer mortars were not significantly changed by the addition of 0.7 wt% xylitol.
- The heat released by the geopolymerisation reactions at 23 °C was not significantly affected by the addition of xylitol. The intensity of the exothermic peak occurring in the first hour after contact of the aluminosilicate solid with the activating solution was positively correlated with the CaO content of the solid and negatively correlated with the mortar setting times.
- Xylitol did not appreciably affect the microstructure of the geopolymer mortars nor the elemental composition of the NASH gel in 90-day geopolymer mortars cured at 40 °C.

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Chapter 5

Conclusions and Recommended Future Work

5.1Use of cullet in geopolymer mortars

The following conclusions were drawnwith regards to the use of cullet as a partial substitute for fly ash or sand aggregate in the preparation of geopolymer mortars:

- Cullet was not effective as a partial replacement for sodium silicate activator. Substituting 17% to 34% of the fly ash by cullet, while decreasing sodium silicate addition by 10% to 20%, caused the 3-day and 7-day compressive strengths to decrease significantly when compared to control geopolymer devoid of cullet. The negative impact of cullet was observed at curing temperatures of 40 °C and 70 °C.

- Cullet was not effective as a partial substitute for fine aggregate. Replacing 20% of the sand by cullet significantly reduced the 3-day compressive strength of geopolymer mortar.

- Cullet reacted only slightly in the geopolymer matrix, as evidenced by the presence of a thin boundary layer containing higher concentrations of Si and Ca and lower concentrations of Al and Fe around cullet particles. However, this boundary layer was physically weaker than the surrounding sodium aluminosilicate hydrate phase.

- The sharp corners of cullet particles acted as crack initiation locations and thuscontributed to the decrease in geopolymer strength.

- Hydrothermal treatment was effective in increasing cullet reactivity and the strength of geopolymer mortar. However, the treatment required an additional amount of sodium hydroxide.

5.2 Use of xylitol as a chemical admixture in geopolymer mortars

With regards to the use of xylitol as a chemical admixture in geopolymer systems, the following conclusions were drawn:

- The addition of xylitol to FA-C, FA-F,and slag/FA-C geopolymer mortars did not improve their short-term (< 14 days) or long term (90 days) compressive strength. However, a dosage of 0.3 wt% xylitol consistently increased the 56-day compressive strength of FA-C geopolymer mortars at all tested curing temperatures (23 °C, 40 °C, and 70 °C).
- The initial and final setting times of FA-C geopolymer mortars were not affected by the addition of xylitol at a concentration of 0.3 wt% but were retarded by xylitol concentrations of 0.7 wt% and 2 wt%. By contrast, the setting times of FA-F and slag/FA-C geopolymer mortars were not significantly changed by the addition of 0.7 wt% xylitol.
- The heat released by the geopolymerisation reactions at 23 °C was not significantly affected by the addition of xylitol. The intensity of the exothermic peak occurring in the first hour after contact of the aluminosilicate solid with the activating solution was positively correlated with the CaO content of the solid and negatively correlated with the mortar setting times.
- Xylitol did not appreciably affect the microstructure of the geopolymer mortars nor the elemental composition of the NASH gel in 90-day geopolymer mortars cured at 40 °C.

In order to obtain more conclusive results on the effectiveness of cullet in geopolymer mortars, it is recommended to extend the age of curing up to at least 90 days. In this study, cullet-containing geopolymer mortars were cured at temperatures of 40 °C and 70 °C, which may be uneconomical for long curing times. Hence, it is also recommended to test curing at room temperature.

Class F fly ash-based geopolymer mortars showed promising compressive strength results. However, the initial and final setting times were excessively long, making room temperature applications impractical. Reducing the water content of the activating solution or adding accelerators to the mixture could be tested as means to reduce setting times.

Appendix A

Compressive Strength and Setting Time Raw Data

A1: Compressive Strength Development

Following is the raw data for sextuplicate analysis of compressive strength development of geopolymer mortars. A constant displacement rate of 0.001in/sec was consistently appliedto fracture a 2-in cubic geopolymer specimen, and then the applied force to fracture was recorded in lb_f. Tables A1 to A4 show the raw data for FA-C geopolymer mortars. Tables A5-A6 and A7-A8 represent raw data for FA-F, and slag/FA-C geopolymer mortars, respectively.

Table A1: Compressive strength results for xylitol-free FA-C geopolymer mortars.

Curing Temperature (*°C*)	**Curing Time (*day*)**	**Force to Fracture(lb_f)**						**Average Compressive Strength (±1 standard deviation) (*MPa*)**
		1	**2**	**3**	**4**	**5**	**6**	
23±2	3	4804	3118	6466	6380	5974	6976	9.68±2.46
	7	8386	7718	8864	10487	9892	9722	15.82±1.79
	14	*10712*	*9774*	16349	*12156*	17492	17184	29.31±1.02
	28	14396	16271	14603	16705	16747	16831	27.44±1.94
	56	-	22352	25004	-	24768	23258	41.09±2.17
	90	-	29219	29589	30235	29165	30164	51.14±0.87
39.5±0.5	3	16000	15500	16600	16300	17200	17200	28.38±1.16
	7	24800	21200	23400	24200	*13500*	*11500*	39.86±3.13
	14	31600	31500	33200	*19000*	*24000*	32200	55.36±1.34
	28	31539	32708	32534	32501	32353	34661	56.38±1.79
	56	33542	36653	35494	34965	37514	39278	62.45±3.49
	90	43253	43043	39703	41651	41983	43542	72.71±2.46
69±1	3	35000	37500	37800	39000	38000	36500	64.28±2.39
	7	40027	45290	44073	45037	45965	46096	76.54±3.91
	14	47800	53000	50000	49000	54400	50700	87.57±4.27
	28	59921	60889	65443	62457	60924	62118	106.77±3.34
	56	54550	57924	54655	51697	54366	55715	94.46±3.49
	90	60470	63372	61656	60614	58045	67071	106.62±5.31

- Note, “-“indicates a result was not available due to testing failure. Values shown in *italics* indicate that the data were not taken into account and not used in calculation of average and standard deviation due to the large difference with the rest of the results.

Table A2: Compressive strength results for FA-C geopolymer mortars containing 0.3% xylitol.

Curing Temperature (°*C*)	**Curing Time (*day*)**	**Force to Fracture(lb_f)**						**Average Compressive Strength (±1 standard deviation) (*MPa*)**
		1	**2**	**3**	**4**	**5**	**6**	
23±2	3	4500	4700	4700	5700	5700	5700	8.90±1.01
	7	7800	8400	9700	10300	8780	9200	15.56±1.55
	14	16400	15600	16300	15600	14500	15100	26.85±1.24
	28	*11199*	14354	17106	17306	17717	17458	27.32±4.47
	56	-	25648	22835	23024	24836	22661	41.01±2.33
	90	25979	27766	29040	29457	30838	30356	49.81±3.08
39.5±0.5	3	15300	15800	15900	17200	15200	15900	27.37±1.23
	7	16500	21000	19400	20500	21700	22600	34.95±3.70
	14	25300	28500	30500	30900	28500	28500	49.46±3.43
	28	30444	31320	33050	35195	33373	35788	57.20±3.60
	56	42980	42154	40290	39134	41948	39549	70.67±2.70
	90	45406	44551	44958	44804	46131	48937	78.92±2.82
69±1	3	41000	40500	42500	40500	40600	40600	70.57±1.35
	7	38000	34200	41600	37600	41600	40500	67.06±4.98
	14	58600	52800	60000	60000	56000	49400	96.73±7.41
	28	61202	67455	68712	69406	64490	69885	115.21±5.82
	56	63831	66624	61639	69691	60516	61342	110.18±6.17
	90	-	61769	64220	66690	59470	68359	110.46±6.20

- Note, “-“indicates a result was not available due to testing failure. Values shown in italics indicate that the data were not taken into account and not used in calculation of average and standard deviation due to the large difference with the rest of the results.

Table A3: Compressive strength results for FA-C geopolymer mortars containing 0.7% xylitol.

Curing Temperature (*°C*)	**Curing Time (*day*)**	**Force to Fracture(*lb_f*)**						**Average Compressive Strength (±1 standard deviation) (*MPa*)**
		1	**2**	**3**	**4**	**5**	**6**	
23±2	3	4400	4800	5400	5400	5400	5600	8.90±0.80
	7	7700	8460	9840	10120	10200	9700	16.09±1.76
	14	-	12660	12667	10998	12540	13663	21.55±1.65
	28	20397	18092	18832	20074	18867	19238	33.17±1.47
	56	28173	28589	27095	26822	28252	25510	47.23±2.00
	90	28186	26664	29914	28336	26399	27231	47.89±2.24
39.5±0.5	3	15000	15000	18000	18000	17500	17000	28.86±2.42
	7	20500	19700	23600	22000	21900	20000	36.68±2.56
	14	23408	26045	25995	27890	27802	28418	45.83±3.20
	28	31449	28079	30460	32314	33981	32234	54.14±3.46
	56	-	35793	34135	34225	32278	34332	58.85±2.15
	90	44629	42775	43547	48750	43601	48686	78.12±4.63
69±1	3	36500	34000	35000	35500	37000	38500	62.18±2.75
	7	41300	39600	42200	42200	41700	41200	71.28±1.66
	14	46638	44408	48408	44967	44803	47790	79.56±2.91
	28	42090	40949	40800	43063	38514	40552	70.64±2.65
	56	52380	53429	54690	51618	55339	55849	92.85±2.91
	90	63485	67194	61882	64082	64118	60456	109.48±3.95

- Note, “-“indicates a result was not available due to testing failure.

Table A4: Compressive strength results for FA-C geopolymer mortars containing 2.0% xylitol.

Curing Temperature (°*C*)	Curing Time (*day*)	Force to Fracture(*lb$_f$*)						Average Compressive Strength (±1 standard deviation) (*MPa*)
		1	2	3	4	5	6	
23±2	3	3960	4701	4122	4600	4616	3936	7.45±0.61
	7	4512	4453	5063	7461	6958	5485	9.75±2.19
	14	9354	10617	11392	15158	11380	12107	20.11±3.36
	28	16514	15431	17719	17938	17670	17361	29.48±1.65
39.5±0.5	3	12158	11644	11430	13125	13330	11392	20.99±1.48
	7	18178	18092	-	20151	20051	19452	33.06±1.72
	14	23320	25322	23056	25603	23942	24611	41.89±1.80
	28	28488	26622	28126	26969	27760	25914	47.07±1.69
69±1	3	-	35599	36597	40709	37150	39489	65.32±3.65
	7	39931	-	42013	42415	40650	42211	71.42±1.88
	14	43284	41461	43622	43161	46788	44056	75.35±3.00
	28	50847	47618	49401	50042	50772	49416	85.61±2.05

- Note, “-“indicates a result was not available due to testing failure.

Table A5: Compressive strength results for xylitol-free FA-F geopolymer mortars.

Curing Temperature (*°C*)	**Curing Time (*day*)**	**Force to Fracture(lb_f)**						**Average Compressive Strength (±1 standard deviation) (*MPa*)**
		1	**2**	**3**	**4**	**5**	**6**	
39.5±0.5	3	28942	30672	32046	33280	31011	30934	53.67±2.50
	7	33272	37136	37756	35074	38594	39880	83.68±4.15
	14	36323	36184	40957	40374	39342	38278	66.48±3.48
	28	46226	44321	44787	41165	44653	44044	76.16±2.87
	56	46773	47078	48916	47004	51764	49927	83.71±3.45
	90	47042	46429	46331	49977	51603	48699	83.31±3.68

Table A6: Compressive strength results for FA-F geopolymer mortars containing 0.7% xylitol.

Curing Temperature (*°C*)	**Curing Time (*day*)**	**Force to Fracture(lb_f)**						**Average Compressive Strength (±1 standard deviation)(*MPa*)**
		1	**2**	**3**	**4**	**5**	**6**	
39.5±0.5	3	32553	31096	29915	32230	31351	31367	54.14±1.60
	7	35215	31160	38673	39386	41126	38860	64.45±6.23
	14	29957	31443	36231	29837	32297	31204	54.85±4.05
	28	35779	36900	39818	39674	38614	39173	66.04±2.82
	56	39847	39339	44868	41917	41191	40927	71.25±3.38
	90	39815	40240	39163	41005	39259	42946	69.63±2.44

- Note, “-“indicates a result was not available due to testing failure.

Table A7: Compressive strength results for xylitol-free slag/FA-C geopolymer mortars.

Curing Temperature (°*C*)	**Curing Time (*day*)**	**Force to Fracture(*lb_f*)**						**Average Compressive Strength (±1 standard deviation)(*MPa*)**
		1	**2**	**3**	**4**	**5**	**6**	
23±2	3	34942	31480	35217	33365	32811	34311	58.05±2.44
	7	48268	49230	46747	48635	47139	43007	81.29±3.86
	14	52290	53099	50095	56652	55896	57493	93.49±4.96
	28	64933	57865	59053	60246	59308	61168	104.13±4.26
	56	65068	65133	66082	70514	68134	67325	115.53±3.60
	90	62464	61401	61344	71165	73592	66849	113.97±9.13
39.5±0.5	3	60484	52446	56228	56894	51673	54192	95.33±5.60
	7	67275	67027	64309	62755	63887	66193	112.42±3.19
	14	59108	75672	64998	61324	`65294	65653	112.60±9.81
	28	72672	77394	70426	72027	71124	76418	126.39±4.96
	56	69562	77077	66579	67423	69052	69175	120.30±6.45
	90	75758	77874	71524	61658	63566	63025	118.73±12.18

- Note, “-“indicates a result was not available due to testing failure.

Table A8: Compressive strength results for slag/FA-C geopolymer mortars containing 0.7% xylitol.

Curing Temperature (*°C*)	**Curing Time (*day*)**	**Force to Fracture(*lb_f*)**						**Average Compressive Strength (±1 standar deviation) (*MPa*)**
		1	**2**	**3**	**4**	**5**	**6**	
23±2	3	29966	28022	28712	29712	27014	29382	49.47±1.82
	7	40665	46501	41617	41059	41299	44582	73.44±4.07
	14	49898	52484	48652	51582	54499	51092	88.52±3.51
	28	53752	55366	59016	57725	64042	57721	99.84±6.10
	56	66399	62417	64062	64120	62692	66363	110.88±2.97
	90	66355	73848	65806	63466	61563	61748	112.81±7.87
39.5±0.5	3	52004	49247	52202	50496	56810	-	89.87±4.94
	7	53186	52305	54760	60511	51829	58829	95.18±6.23
	14	56357	56658	60453	66906	56560	60169	102.56±7.10
	28	62229	73377	68200	66652	67217	60851	114.46±7.74
	56	68410	69851	77422	68364	67966	78546	123.66±8.40
	90	63922	65003	66839	65550	66546	69385	114.09±3.24

- Note, “-“indicates a result was not available due to testing failure.

A2: Setting Time

Following are the setting time raw data for geopolymer mortars measured in accordance with ASTM C 403 procedure. Triplicate data were used for the analysis of initial and final setting times of geopolymer mortars and to determine if there is any dependency on xylitol concentration. All experiments were carried out at room temperature, and the average of three values is reported in the thesis. For each measurement, the applied force for needle penetration in $lb_f$was recorded and together with the needle area in in^2 was used to calculate the penetration resistance expressed in lb_f/in^2 (psi). The calculated penetration resistance data were subsequently used to calculate the initial and final setting times, which correspond to 500 and 4000 psi, respectively.

Table A9: Setting time data for xylitol-free FA-C geopolymer mortars.

Batch(I)

Elapsed Time (*min*)	**Load (*lb*$_f$)**	**Needle Area (*in*^{2})**	**Penetration Resistance (*psi*)**
30	157	¼	628
35	170	¼	680
40	122	1/10	1220
45	120	1/20	2400
50	74	1/40	2960
55	99	1/40	3960
60	113	1/40	4520
65	130	1/40	5200

Batch(II)

Elapsed Time (*min*)	**Load (*lb*$_f$)**	**Needle Area (*in*^{2})**	**Penetration Resistance (*psi*)**
25	50	½	100
30	166	½	332
35	154	¼	616
40	113	1/10	1130
45	85	1/20	1700
50	112	1/20	2240
55	129	1/20	2580
60	92	1/40	3680
65	98	1/40	3920
70	110	1/40	4400
75	150	1/40	6000

Batch(III)			
Elapsed Time (*min*)	**Load (lb_f)**	**Needle Area(in^2)**	**Penetration Resistance (*psi*)**
20	81	1	81
25	137	½	274
30	159	¼	636
35	135	1/10	1350
40	108	1/20	2160
45	133	1/20	2660
50	150	1/20	3000
55	113	1/40	4520
60	122	1/40	4880

Table A10: Setting time data for FA-C geopolymer mortars containing 0.3% xylitol.

Elapsed Time (*min*)	**Load (lb_f)**	**Needle Area(in^2)**	**Penetration Resistance (*psi*)**
20	60	1	60
25	142	½	284
30	164	¼	656
35	120	1/10	1200
40	97	1/20	1940
45	124	1/20	2480
50	154	1/20	3080
55	108	1/40	4320
60	135	1/40	5400

Table A11: Setting time data for FA-C geopolymer mortars containing 0.7% xylitol.

Elapsed Time (*min*)	**Load (*lbf*)**	**Needle (in^2)**	**Penetration Resistance (*psi*)**
20	80	1	80
25	130	½	260
30	153	¼	612
35	120	1/10	1200
40	192	1/10	1920
45	115	1/20	2300
50	135	1/20	2700
55	93	1/40	3720
60	115	1/40	4600

Table A12: Setting time data for FA-C geopolymer mortars containing 2.0% xylitol.

Elapsed Time (*min*)	**Load (*lb*$_f$)**	**Needle Area(*in*^{2})**	**Penetration Resistance (*psi*)**
25	126	1	126
30	156	½	312
35	152	¼	608
40	122	1/10	1220
45	93	1/20	1860
50	117	1/20	2340
55	130	1/20	2600
60	143	1/20	2860
65	96	1/40	3840
70	113	1/40	4520
75	133	1/40	5320

Table A13: Setting time data for xylitol-free FA-F geopolymer mortars.

Batch(I)			
Elapsed Time (*min*)	**Load (lb_f)**	**Needle Area(in^2)**	**Penetration Resistance (*psi*)**
1301	78	1	78
1422	138	½	276
1447	168	½	336
1477	98	¼	392
1502	102	¼	408
1537	142	¼	568
1577	75	1/10	750
1757	84	1/20	1680
2011	100	1/40	4000

Batch(II)			
Elapsed Time (*min*)	**Load (lb_f)**	**Needle Area(in^2)**	**Penetration Resistance (*psi*)**
2335	71	1/10	710
2395	105	1/10	1050
2575	146	1/10	1460
2645	158	1/10	1580
2695	124	1/20	2480
2765	122	1/20	2440
2825	124	1/20	2480
2940	130	1/20	2600
3220	145	1/40	5800

Batch(III)			
Elapsed Time (*min*)	**Load (*lb$_f$*)**	**Needle Area(*in^2*)**	**Penetration Resistance (*psi*)**
2315	62	1/10	620
2375	74	1/10	740
2555	110	1/10	1100
2625	152	1/10	1520
2675	92	1/20	1840
2745	117	1/20	2340
2805	133	1/20	2660
2920	134	1/20	2680
3200	142	1/40	5680

Table A14: Setting time data for FA-F geopolymer mortars containing 0.7% xylitol.

Batch (I)

Elapsed Time (*min*)	**Load (lb_f)**	**Needle Area(in^2)**	**Penetration Resistance (*psi*)**
1925	134	½	268
1954	134	½	268
1982	72	¼	288
2050	115	¼	460
2123	63	1/10	630
2195	91	1/10	910
2310	62	1/20	1240
2432	88	1/20	1760
2554	114	1/20	2280
2673	83	1/40	3320
2790	112	1/40	4480

Batch (II)

Elapsed Time (*min*)	**Load (lb_f)**	**Needle Area(in^2)**	**Penetration Resistance (*psi*)**
2310	146	1	146
2550	77	1/10	770
2915	145	1/10	1450
3195	119	1/20	2380
3665	164	1/40	6560

Batch (III)			
Elapsed Time (*min*)	**Load (lb_f)**	**Needle Area(in^2)**	**Penetration Resistance (*psi*)**
2310	138	1	138
2550	86	1/10	860
2915	149	1/10	1490
3195	151	1/20	3020
3665	176	1/40	7040

Table A15: Setting time data for xylitol-free slag/FA-C geopolymer mortars.

Batch (I)

Elapsed Time (*min*)	Load (lb_f)	Needle Area(in^2)	Penetration Resistance (*psi*)
18	105	½	210
23	157	1/10	1570
25	134	1/20	2680
27	115	1/40	4600
29	152	1/40	6080

Batch (II)

Elapsed Time (*min*)	Load (lb_f)	Needle Area(in^2)	Penetration Resistance (*psi*)
16	104	1/10	1040
17	100	1/20	2000
18	136	1/20	2720
19	183	1/20	3660
20	126	1/40	5040
21	140	1/40	5600
22	152	1/40	6080
23	190	1/40	7600

Batch (III)			
Elapsed Time (*min*)	**Load (*lb$_f$*)**	**Needle Area(*in^2*)**	**Penetration Resistance (*psi*)**
14	122	½	244
15	143	1/10	1430
16	179	1/10	1790
17	145	1/20	2900
18	186	1/20	3720
19	125	1/40	5000
20	164	1/40	6560

Table A16: Setting time data for slag/FA-C geopolymer mortars containing 0.7% xylitol.

Batch (I)

Elapsed Time (*min*)	**Load (lb_f)**	**Needle Area(in^2)**	**Penetration Resistance (*psi*)**
15	173	¼	692
17	129	1/10	1290
19	122	1/20	2440
21	117	1/40	4680
23	154	1/40	6160

Batch (II)

Elapsed Time (*min*)	**Load (lb_f)**	**Needle Area(in^2)**	**Penetration Resistance (*psi*)**
12	65	½	130
13	86	1/10	860
14	138	1/10	1380
15	115	1/20	2300
16	146	1/20	2920
17	93	1/40	3720
18	112	1/40	4480
19	130	1/40	5200
21	162	1/40	6480
22	178	1/40	7120

Batch (III)

Elapsed Time (*min*)	**Load (lb_f)**	**Needle Area(in^2)**	**Penetration Resistance (*psi*)**
12	33	¼	132
13	65	¼	260
14	106	¼	424
15	92	1/10	920
16	117	1/10	1170
17	84	1/20	1680
18	143	1/20	2860
19	122	1/40	4880
21	138	1/40	520

Appendix B

Results of SEM/EDS Analysis of Geopolymer Specimens

B1: EDS Data

Following are the results of SEM/EDS analyses of FA-C, FA-F, and slag/FA-C 90-day geopolymer samples containing 0.0% and 0.7% xylitol. For each specimen, three different areas of gel phase were considered. Within each area, five different points were selected to determine the percentage of Na, Al, Si, K, Ca, and Fe. The average of a total of fifteen readings is reported.

Table B1: Elemental analysis result of xylitol-free FA-C geopolymer mortars cured for 90 days.

Element	**Gel Phase Area**															**Average (%)**
	I					**II**					**III**					
	Point 1	Point 2	Point 3	Point 4	Point 5	Point 1	Point 2	Point 3	Point 4	Point 5	Point 1	Point 2	Point 3	Point 4	Point 5	
Na	8.12	7.53	8.07	7.48	6.65	7.07	6.90	7.68	7.70	5.81	6.56	9.88	8.03	8.73	7.26	7.56
Al	6.18	6.22	6.47	8.18	6.44	5.97	5.29	5.54	5.92	4.99	6.19	4.93	6.07	5.86	6.49	6.05
Si	19.41	18.39	19.52	17.94	19.36	17.28	17.29	17.49	18.05	16.95	18.95	15.18	18.12	18.13	19.03	18.07
K	0.53	0.43	0.47	0.39	0.50	0.45	0.40	0.44	0.46	0.33	0.39	0.36	0.33	0.49	0.44	0.43
Ca	6.21	5.86	6.12	2.15	6.03	4.95	5.65	5.66	6.24	6.39	6.54	5.63	6.45	6.75	5.96	5.77
Fe	1.20	1.57	1.65	0.64	1.61	1.42	1.43	1.70	1.28	1.16	1.51	1.19	1.27	1.33	1.44	1.36

Table B2: Elemental analysis result of FA-C geopolymer mortars containing 0.7% xylitol cured for 90 days.

Element	**Gel Phase Area**															Average (%)
	I					**II**					**III**					
	Point 1	Point 2	Point 3	Point 4	Point 5	Point 1	Point 2	Point 3	Point 4	Point 5	Point 1	Point 2	Point 3	Point 4	Point 5	
Na	5.69	8.05	8.24	6.81	7.43	7.39	7.36	7.41	7.83	8.25	8.42	6.88	8.30	7.96	7.08	7.54
Al	7.46	6.69	6..65	7.09	7.87	7.07	6.36	7.19	6.62	6.70	6.82	8.09	7.27	7.31	7.33	7.13
Si	18.74	19.10	17.90	19.69	19.49	19.43	18.06	19.69	18.77	19.40	19.10	20.35	18.91	19.48	20.33	19.23
K	0.37	0.42	0.33	0.40	0.41	0.44	0.32	0.35	0.37	0.40	0.43	0.41	0.39	0.48	0.39	0.39
Ca	6.84	5.67	5.25	5.49	5.94	5.14	5.97	5.72	5.48	5.38	4.91	5.35	4.88	5.11	5.14	5.48
Fe	1.45	1.21	1.23	1.56	2.05	1.50	1.25	1.38	1.44	1.33	1.37	1.05	1.30	1.40	1.61	1.41

Table B3: Elemental analysis result of xylitol-free FA-F geopolymer mortars cured for 90 days.

Element	Gel Phase Area															Average (%)
	I					II					III					
	Point 1	Point 2	Point 3	Point 4	Point 5	Point 1	Point 2	Point 3	Point 4	Point 5	Point 1	Point 2	Point 3	Point 4	Point 5	
Na	7.72	7.86	7.85	7.82	6.56	7.11	3.61	8.57	7.60	7.86	8.29	5.98	8.33	11.93	7.19	7.62
Al	8.78	9.29	9.89	9.61	9.22	9.23	8.73	8.42	8.59	9.61	9.41	13.23	9.47	11.52	10.08	9.67
Si	21.16	22.66	21.90	21.55	21.60	20.84	24.26	21.46	21.17	21.99	22.78	20.79	22.26	27.06	20.38	22.12
K	0.20	0.32	0.20	0.22	0.29	0.19	0.25	0.08	0.12	0.34	0.31	0.33	0.30	0.28	0.24	0.24
Ca	1.30	1.18	1.79	1.30	1.05	1.19	1.00	1.04	1.01	1.15	1.42	0.94	1.42	1.69	1.18	1.24
Fe	3.18	2.63	2.98	3.02	3.08	3.24	2.40	2.76	2.96	3.46	3.14	2.79	3.04	2.89	2.61	2.95

Table B4: Elemental analysis result of FA-F geopolymer mortars containing 0.7% xylitol cured for 90 days.

Element	**Gel Phase Area**															**Average (%)**
	I					**II**					**III**					
	Point 1	Point 2	Point 3	Point 4	Point 5	Point 1	Point 2	Point 3	Point 4	Point 5	Point 1	Point 2	Point 3	Point 4	Point 5	
Na	7.03	7.91	7.40	7.81	8.23	8.42	6.88	7.61	7.32	7.86	7.18	7.55	6.51	6.20	6.93	7.39
Al	9.91	8.75	8.75	10.39	10.73	9.05	8.35	9.26	10.27	9.39	9.58	9.50	8.22	7.23	11.78	9.41
Si	20.89	20.60	20.82	21.58	22.28	22.01	19.99	21.30	21.64	21.87	21.11	21.20	21.25	17.47	20.96	21.00
K	0.35	0.30	0.27	0.39	0.29	0.20	0.25	0.24	0.34	0.27	0.34	0.24	0.31	0.20	0.24	0.28
Ca	1.25	1.39	1.50	1.28	1.19	1.27	1.25	1.29	1.35	1.27	1.56	1.33	1.33	1.31	1.30	1.32
Fe	3.24	3.36	4.95	3.47	3.18	2.85	3.84	3.49	3.69	3.50	3.39	3.94	3.39	3.11	2.96	3.49

Table B5: Elemental analysis result of xylitol-free slag/FA-C geopolymer mortars cured for 90 days.

Element	**Gel Phase Area**															**Average (%)**
	I					**II**					**III**					
	Point 1	Point 2	Point 3	Point 4	Point 5	Point 1	Point 2	Point 3	Point 4	Point 5	Point 1	Point 2	Point 3	Point 4	Point 5	
Na	4.46	4.39	4.58	4.38	4.37	3.99	3.99	4.48	4.21	5.01	4.44	4.38	4.13	3.96	4.13	4.33
Al	5.65	5.21	5.06	4.98	5.29	5.06	4.91	6.09	4.66	4.78	5.19	5.24	5.19	4.94	5.30	5.17
Si	16.44	16.33	16.60	16.14	16.18	16.65	16.59	17.15	16.21	14.21	16.29	16.36	16.42	16.84	15.99	16.29
K	0.28	0.29	0.22	0.18	0.26	0.19	0.22	0.37	0.16	0.19	0.21	0.21	0.19	0.22	0.21	0.23
Ca	13.49	13.60	13.30	13.64	13.34	14.00	14.82	13.34	14.58	12.06	13.44	13.38	13.85	14.54	14.20	13.71
Fe	0.48	0.59	0.72	0.74	0.48	0.33	0.38	0.40	0.36	0.57	0.51	0.22	0.52	0.52	0.52	0.49

Table B6: Elemental analysis result of slag/FA-C geopolymer mortars containing 0.7% xylitol cured for 90 days.

Element	Gel Phase Area															Average (%)
	I					II					III					
	Point 1	Point 2	Point 3	Point 4	Point 5	Point 1	Point 2	Point 3	Point 4	Point 5	Point 1	Point 2	Point 3	Point 4	Point 5	
Na	4.90	4.57	4.87	4.72	5.01	5.59	5.46	5.19	5.21	5.32	4.75	4.76	4.73	5.19	7.16	5.16
Al	4.94	4.81	4.93	4.83	4.96	4.85	5.03	5.01	4.92	5.04	5.27	4.87	4.65	5.34	4.62	4.94
Si	16.85	16.39	16.71	16.45	16.58	16.63	16.54	16.60	16.08	16.35	16.39	16.07	16.21	16.30	14.29	16.30
K	0.33	0.28	0.28	0.22	0.23	0.24	0.27	0.26	0.24	0.22	0.29	0.28	0.25	0.31	0.26	0.26
Ca	15.07	15.07	14.66	14.67	15.03	15.44	14.86	14.81	14.47	14.48	14.87	14.65	14.48	14.40	13.16	14.67
Fe	0.38	0.24	0.34	0.55	0.24	0.32	0.50	0.51	0.34	0.67	0.45	1.02	0.52	0.70	0.46	0.48