



Trinity College Dublin

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DESIGN AND EVALUATION OF LOW-CARBON CONSTRUCTION MATERIALS MADE WITH WASTE

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Declaration

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Keywords

Industrial waste; Agricultural waste; Reactivity; Low-carbon cement; Alkali fusion; Geopolymer; Durability; Environmental impact; Life cycle assessment.

Abstract

Energy, food and water sustain modern human life. Oil refineries, power plants, food factories, and water purification plants run non-stop throughout the year providing the essential goods and commodities upon which modern society relies. These facilities, operating around the clock, generate various wastes while offering convenience to humans. These wastes are often disposed of in passive stockpiles or landfills, occupying extensive land and posing threats to the environment.

Portland cement (PC)-based concrete ranks as the world's second most utilized commodity, surpassed only by water, and forms the backbone of most of the infrastructure and housing. However, in the eco-conscious 21st century, cement and concrete are continuously blamed for their contribution to carbon emissions and overexploitation of resources. The construction industry must embrace green development practices to fulfil the imperative of carbon neutrality.

This research designs and evaluates geopolymers made with waste. It also measures the reactivity of wastes that can be used as PC clinker replacements to produce low-carbon cements. Geopolymer is an exemplary model of circular economy as it is primarily derived from industrial waste and transforms waste into a cementing material with a considerably lower carbon footprint than Portland cement.

In this study, four types of solid waste--spent fluid catalytic cracking catalyst (FCC), alum sludge (AS) crops biomass ash (CBA) and olive pit ash (OBA) --collected from oil refineries, drinking water purification plants, biomass power plants and olive oil producers were utilized to produce geopolymers. Their properties, including chemical and mineral composition, particle size distribution, specific surface area, morphology, and reactivity were investigated. The mechanical performance, microstructure and durability of geopolymers resulting from these wastes were studied after component optimisation. Additionally, a life cycle assessment was conducted on selected geopolymers to compare their environmental impact to that of Portland cement.

All wastes are reactive and can be used to produce low-carbon cement either as supplementary cementitious materials (SCMs) or in geopolymer technology. FCC is semi-crystalline and mainly composed of faujasite, a reactive zeolite. SiO₂ and Al₂O₃ account for over 90% of the FCC's chemical composition. Chemical and mechanical methods confirmed its high reactivity. AS is an amorphous waste consisting mainly of organic matter and Al₂O₃, hence it is potentially active. However, it requires treatment as its high organic content may hinder pozzolanic and geopolymerisation reactions. CBA is highly crystalline as it is produced under controlled, high-temperature calcination. Although it mainly consists of SiO₂ and Al₂O₃, the crystalline structure of its main components (quartz and albite) limits reactivity. The OBA is a unique waste consisting mainly of K₂O and CaO. The low SiO₂ and Al₂O₃ suggest low reactivity. However, its high alkali content allowed us to use it as a novel, low-carbon activator to produce low-carbon cement.

Following the results of waste characterization, some wastes were treated to enhance their reactivity. High-temperature calcination, oxidation and acid etching did not significantly

improve the reactivity of FCC. However, alkali fusion with 15% NaOH converted FCC into an amorphous substance, enhancing its reactivity but significantly increasing its carbon footprint. AS, was pyroprocessed at 800°C to remove organic matter and moderate its reactivity, preventing flash setting due to the high content of reactive aluminium. High-crystallinity CBA, treated with alkali fusion and 25% NaOH, showed increased reactivity due to the decomposition of quartz and albite into soluble silicates.

Building on this foundation, the wastes were used as precursors and blended with ground granulated blast-furnace slag (GGBS) and fly ash (FA) to develop two-part and one-part geopolymers. In two-part systems, FCC and CBA were mixed with GGBS or FA and activated with sodium silicate solutions to produce geopolymers. FCC-based geopolymers exhibited excellent compressive strengths of 45-57 MPa. Alkali-fused CBA-based geopolymers showed improved mechanical properties compared to raw CBA-based geopolymers from 29.83 MPa to 46.47 MPa. Furthermore, high calcium systems including GGBS demonstrated superior performance, including robustness and shorter setting times. The mechanical properties of FA-mixed geopolymers were found to be highly sensitive to mixing ratios and activator composition which emphasized the importance of optimizing the design.

One-part geopolymer systems were studied using AS, CBA and OBA blended with GGBS. Optimal AS geopolymer mix ratios ($\text{SiO}_2/\text{Al}_2\text{O}_3=2.5$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3=1.0$) achieved a compressive strength of 66.50 MPa. Additionally, a reliable binder can be produced with 30% raw CBA and 70% GGBS, activated by sodium carbonate and sodium silicate featuring a compressive strength of 46.09 MPa and a quick setting pattern. Alkali-fusing CBA allowed to increase in CBA content to 50%; the resulting geopolymer achieved a compressive strength of 45 MPa. OBA, due to its high alkali content, was effectively used as an activator, reaching 15.43 MPa alone and 43.94 MPa when optimized with sodium carbonate. All the geopolymers showed a dense and compact matrix.

The durability of the geopolymers was estimated by measuring their resistance to wet-dry cycles, sulphate attack and high-temperature resistance. Geopolymers prepared with high activator dosage and alkali-fused precursors showed poor performance in cycling tests. This evidenced that Na^+ content significantly undermines durability. X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) analyses revealed that repeated salt dissolution and crystallization were key factors in mechanical loss rather than matrix composition changes. Moreover, high temperatures significantly reduced strength due to thermal expansion disparities. The amorphous and dense microstructure was maintained when calcined below 450-600 °C.

Finally, the environmental impacts of geopolymers were evaluated through a life cycle assessment (LCA). The results indicate that the production method of activators and carbon allocation in GGBS significantly influence the environmental impact. Environmentally friendly activator production methods can substantially reduce carbon emissions. When GGBS carbon allocation is based on its economic value, as a by-product rather than waste, geopolymer shows 38-78% lower carbon emissions compared to CEM I and CEM II, except for the AS geopolymer. The higher carbon emissions of the AS geopolymer are due to the high carbon content of the AS waste. This comprehensive analysis underscores the potential of optimized geopolymers as sustainable construction materials.

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On this autumn night in Dublin, I have completed my doctoral thesis, bringing to a close 22 years of education. I still recall the conversations of my kindergarten classmates, a group of children imagining their future as scientists. More than two decades later, I am proud to say that I have fulfilled the dreams of that young kid.

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In my master's thesis, I wrote that the journey of study is like a train passing through a dark tunnel. Today, that train has emerged from the darkness and is now heading towards the open expanse of my life.

Zehao Lei
The Cement Doctor

6th Oct 2024
Dublin

致谢

This is a Chinese version of acknowledgement.

今天是我抵达爱尔兰的第 1446 天，也是我 28 岁的最后一天。

在都柏林的秋夜里，我终于完成了博士毕业论文，为我二十二年的求学之路画下了句点。还记得在幼儿园，一群字都不识的小朋友说着将来要成为科学家天真愿望，而二十多年后的我，也终于没有辜负那个咿咿呀呀的小朋友的童年梦想。

四年的求学生涯是一段充满起伏与挑战的征途，是同一场冲向未知的长途跋涉。如果没有许多人的支持、指导和鼓励，我不可能走到今天。此时此刻，我满怀感激，愿以最深的敬意，向所有帮助我、陪伴我走过这段旅途的人致以衷心的感谢。

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虽然我的名字被印在这篇论文的封面上，但它的每一行字、每一分成果，皆承载着无数人的心血与贡献。这份成就，不仅属于我，更属于所有曾经帮助过我的人。

在我硕士毕业论文的最后，我曾写道，求学的旅程就像一列穿越隧道的火车。而如今，这列火车终于冲破黑暗，驶向人生广阔的旷野。

此致。

类泽灏
水泥博士

2024 年 10 月 6 日
于都柏林。

Chapter 1: Introduction

1.1 BACKGROUND

Portland cement (PC) is the material most used in construction today, to make concrete, pre-cast elements, mortars and renders. PC concrete ranks as the world's second most-used substance, trailing only water, and is the primary material in construction. It surpasses all other building materials combined in usage (Van Damme, 2018; Gagg, 2014). Joseph Aspdin, an English mason, is often credited with inventing PC in 1824 (Hall, 1976). However, its industrial production did not commence until the mid-19th century, involving the transit from vertical to rotary kilns which remains the global standard (Schneider et al., 2011).

The manufacturing of Portland cement involves three principal stages: preparation of raw materials, pyro-processing, and final cement preparation. The preparation stage encompasses limestone mining, crushing, drying, pre-homogenization, and grinding. The production methods diverge into the dry process, where raw materials are ground and heated before entering the kiln, and the wet process, involving the creation of a slurry from crushed, ground, and mixed raw materials. High-temperature processing includes preheating, pre-calcining, clinker production in rotary kilns, cooling, and storage in silos. This stage is notably energy-intensive, featuring the critical transformation of limestone during pre-calcining and clinker production from raw materials. The final preparation stage involves grinding clinker and combining it with additives like gypsum, fly ash, and slag to produce the finished cement product, stored in silos.

Since World War II, PC production has significantly increased. In 2019, the EU28 produced 182.1 million tonnes, accounting for 5.9% of global output and making it the third-largest producer after India (320 million tonnes) and China (2.30 billion tonnes), which alone constituted 56.2% of the world's production (The European Cement Association, 2019). While BRIC countries (Brazil, Russia, India, and China) demonstrated substantial growth through 2020, a plateau is expected between 2020 and 2030. Notably, the "SETIVIM" group (Saudi Arabia, Egypt, Turkey, Iran, Vietnam, Indonesia, and Mexico) and the "Future Seven" (Algeria, Morocco, Nigeria, Pakistan, Malaysia, Thailand, and the Philippines) are projected to drive significant growth by 2030 (Harder, 2013; Schneider, 2015).

In the eco-sensitive 21st century, PC production is continuously criticized for its significant contribution to greenhouse gas emissions and resource consumption. PC production is an energy-intensive process requiring the burning of limestone with shale, clay, and iron ore in a kiln at approximately 1450 °C (Hewlett & Liska, 2019). Fuelling the kilns for clinker production and grinding the raw materials and clinkers consumes substantial energy and emits significant CO₂. Approximately 40% of CO₂ emissions in cement manufacturing (dry process) result from the combustion of fossil fuels in the kiln process, while 50% arises from the calcination of limestone (Arachchige et al., 2019). The wet process consumes additional energy as 30% of the slurry water must evaporate before the raw materials reach the required temperature for calcination. Additionally, the modern cement industry requires 110-120 kWh of electricity to produce one ton of cement for the grinding process, accounting for the remaining 10% of CO₂

emissions (Mejeoumov, 2007). Cement manufacturing accounts for 83% of the energy consumption and 94% of the CO₂ emissions in non-metallic mineral production (Srivastava et al., 2011). The cement industry emitted 5-7% of global greenhouse gases (GHGs) in 2009, with recent estimates increasing this range to 8-10% (Rocha et al., 2022). Furthermore, the cement industry is considered one of the most polluting industries, consuming large amounts of energy and producing harmful gases such as carbon monoxide (CO), sulfur dioxide (SO₂), nitrogen oxides (NO_x) and dust particles. Within a 3-kilometer radius of cement plants, concentrations of PM₁₀, PM_{2.5}, total suspended particles, SO₂, NO₂, and CO often exceed air quality standards (Ekinici et al., 2020). In 2010, the cement industry also emitted 136 tons of nitrogen oxides, 4,833 tons of sulfur dioxide, 183 tons of volatile organic compounds (including toxic dioxins, furans, and polychlorinated biphenyls), and 320 kg of mercury (Mohamad et al., 2022).

The greenhouse gases emitted directly or indirectly in the manufacture of Portland cement place a significant burden on the environment. The European Climate Law commits to carbon neutrality by 2050. The transport, agriculture, building, and waste management sectors accounted for approximately 60% of the EU's greenhouse gas emissions in 2014 (EU Press Corner, 2021). To meet the 2050 carbon neutrality target, the EU aims to reduce net greenhouse gas emissions by at least 55% by 2030, compared to 1990 levels.

Currently, PC producers are reducing CO₂ emissions in several ways: (1) by replacing PC clinker with supplementary cementitious materials (SCMs), (2) by using alternative fuels in clinker production, (3) by using secondary raw materials, and (4) by improving the production process (Farooq et al., 2021). The efficiency of kilns and grinding mills and the use of alternative fuels for PC production have been investigated for decades to economize energy and costs. However, due to the combustion of fuels and the unavoidable decarbonization of limestone ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ at ~800-900 °C), even the most efficient plant will release at least 60% of the total mass of the raw material as carbon dioxide during PC production. Therefore, there is a need for high-performance materials that can replace PC products with a lower environmental impact.

Additionally, billions of tonnes of industrial and agricultural waste are generated worldwide each year. Approximately 500 million and 476 million tonnes of fly ash and biomass ash are produced annually for power generation (Mathapati et al., 2022; Vassilev et al., 2010). The vast amount of landfilled waste consumes substantial land resources and contaminates the surrounding soil and groundwater. Due to the lack of storage and safe disposal, waste has become an environmental liability. Landfilling waste is expensive, and increasingly stringent environmental regulations pressure producers to find alternative waste disposal routes.

This thesis investigates the properties, composition and reactivity of industrial and agricultural wastes and uses them to produce new cements of low-carbon emissions and low environmental impact. The wastes are used as precursors or novel activators in geopolymer technology, to produce geopolymer cement. Geopolymer is a more sustainable alternative to PC. Geopolymers can be fabricated from aluminosilicate minerals such as kaolinite, feldspar, and industrial solid residues such as fly ash, slag and calcined sludge. The raw materials for geopolymer production are diverse and can complement each other, thereby reducing the consumption of natural resources and recycling waste into the circular economy. Large-scale production of geopolymers would not only save substantial energy (consumed during the calcination of raw materials and grinding of PC clinker) but it would also reduce CO₂ emissions and decrease the use of landfills as well as soil and water contamination. In addition, it would

lessen the exploitation of non-renewable natural resources such as shale and limestone and provide a functional route to convert waste into new construction materials.

1.2 OBJECTIVE AND RESEARCH SCOPE

The lack of clinker and the inclusion of recycled waste as the main component, make geopolymer more sustainable than PC. Geopolymer, as an alternative construction material, has outstanding environmental potential: it reduces CO₂ emissions and energy use, minimizes the use of non-renewable resources, and recycles waste, thereby contributing to the circular economy.

The overall aim of this research is to provide sound and viable alternatives for producing reliable, low-carbon, sustainable cements. The specific objectives are as follows:

1. Explore the potential of novel industrial and agricultural wastes as geopolymer precursors/activators and SCMs.

Identify and characterise new wastes with activation potential to serve as precursors or activators to produce geopolymer. To expand the list of potential raw materials to produce blended PCs and diminish the dependence on the existing commercial SCMs.

The properties of wastes, such as specific surface area (SSA), particle size distribution, chemical composition, mineral composition and morphology are characterised, and possible heavy metal elements in the waste are determined for safety.

2. Design and produce geopolymers in the laboratory and optimise their design by modifying variables that govern polymerisation reactions.

The composition and reactivities of the wastes differ. Stable and efficient routes for the synthesis of geopolymer cements are determined based on the different properties of the wastes. The effect of designed waste/reactive agent combinations on the properties of the resulting geopolymer, including setting, rheology, strength development and durability, are investigated.

3. Assess the environmental impact and economic potential of the optimal geopolymers.

A life cycle assessment of the geopolymers developed in this research is conducted and compared with traditional construction materials. The study measures global warming potentials and other environmental factors of geopolymer production and makes sound suggestions for carbon reduction in the building sector.

1.3 LAYOUT OF THIS THESIS

This thesis consists of ten chapters. A brief outline of each chapter is presented below.

Chapter 1, the current chapter presents the background, objective, research scope and layout of this thesis.

Chapter 2 covers the literature on the history and development of geopolymers and alkali-activated materials, along with the research progress of several novel precursors and activators.

Chapter 3 details the materials and methods used in the research.

Chapter 4 characterizes the wastes used in this research, including their chemical composition, mineral composition, particle size distribution, specific surface area and morphology.

Chapter 5 presents various treatments applied to wastes to enhance their reactivity. The reactivity of the wastes, an essential indicator for their potential recycling as precursors and SCMs, is determined using chemical and mechanical methods.

Chapter 6 focuses on the design and optimization of two-part geopolymers made with spent fluid cracking catalyst (FCC) and crop biomass ash (CBA). It studies the influence of activators ($\text{SiO}_2/\text{Na}_2\text{O}$ ratio, Na^+ concentration) and blended ratios (with GGBS and FA) on mechanical strength.

Chapter 7 presents the design and optimization of one-part geopolymers made with alum sludge (AS), crop biomass ash (CBA), and olive pit bottom ash (OBA). It examines the type and usage of activators and the blended ratio with GGBS on mechanical strength in one-part geopolymer systems. OBA is explored as a novel activator, either alone or with sodium carbonate, blended with GGBS to produce one-part geopolymer.

Chapter 8 studies the durability of geopolymers, including resistance to wet-dry cycles, sulphate attack and high temperatures. The mechanical strength and microstructural changes caused by these durability tests are investigated.

Chapter 9 investigates the environmental impact of the geopolymers using life cycle assessment (LCA) methodology. It examines the influence of allocation methods and the production process of precursors and activators on the environmental impacts of geopolymers and presents a comparison of the environmental impacts between geopolymers and PC.

Chapter 10 presents the conclusions drawn from the research conducted in this thesis.

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Chapter 2: Literature Review

2.1 WASTE AND ITS POTENTIAL RECOVERY IN THE CONSTRUCTION SECTOR

According to the definition from the European Union on waste and repealing certain directives (Directive 2008/98/EC), waste means *any substance or object which the holder discards or intends or is required to discard*.

The significant increase in waste generation began in the sixteenth century with urban migration spurred by the Industrial Revolution. By the nineteenth century, public officials started managing waste disposal to safeguard public health (Tchobanoglous et al., 1993; Wilson, 2007). Waste generation, particularly in the industrial and agricultural sectors, is inevitable; however, it represents a loss of vital resources and places a burden on the environment. Landfill disposal is expensive and unsustainable, as it consumes substantial land resources and contaminates the surrounding soil and groundwater.

Reusing and recycling waste align better with the concepts of a circular economy and sustainable development compared to landfilling (Geissdoerfer et al., 2017). The industrial production process generates large amounts of waste, while the construction industry has a high demand for materials. Notably, the composition of industrial waste often shares physical and chemical properties with traditional building materials, as elements like O, Si, Al, Fe, and Ca are abundant in the earth's crust and essential for construction. Thus, recycling industrial waste in construction materials is a promising approach for better waste management.

Concrete prepared with PC is the most widely used building material globally. Producing one tonne of PC clinker consumes approximately 1.5 to 1.7 tonnes of natural resources, including limestone and other materials like clay, silica sand, and bauxite. Additionally, it requires 0.11 to 0.15 tonnes of coal or alternative fuels, generating 0.7 to 1.0 tonnes of CO₂. The rising urban population, improved living standards, and economic growth are expected to increase the demand for construction materials. However, the focus on carbon neutrality places pressure on the construction industry to enhance sustainability. The high carbon emissions and resource consumption associated with cement production are particularly concerning. Measures to reduce emissions and resource consumption include improved energy efficiency, increased reuse and recycling practices, adoption of circular economy models, potential carbon dioxide capture and storage (CCS) technologies, and the development of new low-carbon building materials. However, over 60% of CO₂ emissions from modern cement plants originate from the calcination of natural stone which alternative energy sources or improved energy efficiency cannot mitigate. Decarbonized feedstocks are currently in use, however, they are expected to reduce emissions by only 8%, in Europe, by 2050 (Guo et al., 2024). In addition, while CCS is considered a promising method to counteract carbon emissions from construction material production, it is not currently cost-competitive or marketable (Moya et al., 2011; Gür, 2022; Krishnan et al., 2023).

In contrast, replacing the natural materials in PC production with waste would lower the depletion of non-renewable resources and avoid the energy consumption and carbon

emissions associated with grinding and calcination. Recycling waste in construction as partial PC clinker replacement (such as SCM) and developing new low-carbon building materials are currently the most feasible and promising measures to lower the carbon impact of construction. SCMs are materials that, when used in conjunction with Portland cement, contribute to the properties of the hardened concrete. The application of SCMs in PC has a long history and it is now common practice.

SCMs include pozzolans, latent hydraulic material and inert fillers. Pozzolans are materials composed of reactive silica and/or alumina that react with lime (calcium hydroxide, portlandite, CH) in the presence of water forming cementing hydrates. The term 'pozzolan' originally originated from Pozzuoli (Naples) where natural volcanic ash is found (Hewlett & Liska, 2019). Pozzolans can be natural, such as radiolarite, volcanic tuffs, ash and pumice, or artificial such as ceramics or waste, derived from industrial and agricultural processes (Figueiredo & Pavia, 2018). The first use of pozzolans in mortars and concretes is often attributed to the Romans. However, the earliest evidence of application of pozzolanic material may be a terrazzo floor made with burnt limestone and clay found in a religious structure at Gobekli Tepe in Anatolia, erected 12,000–10,000BC (Hewlett & Liska, 2019). The first use of natural pozzolan (volcanic tuff) to enhance the water resistance and durability of Greek mortars dates from around 500 BC (Hewlett & Liska, 2019). Subsequently, the Romans used mainly pure calcium limes mixed with volcanic pumices tuffs and crushed ceramics to build floor slabs, mass concrete walls, mortars and renders in many structures that have survived to this day (Pavía & Caro, 2008) (Pavia & Caro, 2008).

In the last decades, the initial development of SCMs was driven by the limited availability of raw materials for PC clinker production. The idea of incorporating alkali refuse into PC dates back to the 1850s (Quietmeyer, 1912). However, the significant rise of SCMs was attributed to the study of blast-furnace slag. In 1865, the first Portland blast-furnace slag cement was produced in Germany, and used in Paris in construction by 1869. The earliest standard for blast-furnace cement was issued in Germany in 1917, followed by the British Standard in 1923 (Barnes & Bensted, 2002; Newman & Choo, 2003). The incorporation of SCMs has been one of the major advancements in cement technology over the past 40 years. The increased acceptance of SCMs has necessitated a redefinition of Portland cement and allowed for a variety of approved composites (Voglis et al., 2005; Douglas Hooton, 2015). After numerous efforts, European cement standards were harmonized in 1999 with the publication of EN 197-1. According to this standard, cements may contain up to 5% minor additional constituents and still be classified as Portland cement (CEM I). Other minerals, including blast-furnace slag, silica fume, natural and calcined pozzolana, siliceous and calcareous fly ash, burnt shale, and limestone, can be mixed with PC clinker to produce CEM II to CEM V cements (EN 197-1, 2011).

The reaction kinetics of SCMs depend on the chemical composition and fineness of the SCM, the amount of reactive phase (e.g. glass or zeolite), and the composition of the interacting solution (Lothenbach et al., 2011). SCMs influence the chemistry of composites in two primary ways. For fine-grained materials, the additional surface area provided by the SCM can serve as a nucleation site for the hydration products of the clinker phase (Lothenbach et al., 2011). This "filler effect" is often mistaken for the own reactivity of SCM. Second, SCMs participate in chemical reactions to form hydration products. The pozzolanic reaction or hydration of SCM follows a dissolution-precipitation mechanism, wherein the SCM dissolves in the pore solution, forms a supersaturation with other reactants, and allows the reaction products to

precipitate (Scrivener et al., 2015). Thus the solubility of SCM in pore solution determines its reactivity.

Typically, SCMs have comparable chemical composition to the clinker phases in PC, although the proportions and combinations of the main chemical elements in the constituent phases differ. As a result, SCM reactions produce hydration products like those formed upon PC hydration. For silica-rich SCMs, the reaction produces calcium silicate hydrate (C-S-H); for aluminate-rich SCMs, calcium alumina silicate hydrate (C-A-S-H) forms. Additionally, when SCMs contain magnesium and calcium, hydrotalcite forms as an additional reaction product (Skibsted & Snellings, 2019).

However, the chemical reaction of SCM is slow (Massazza, 2002), and several variables influence the extent and rate of the reaction. The reaction rate is influenced by the specific surface area of the pozzolans, the Si/Al ratio, temperature, and amorphous content (Massazza, 1998). The reaction rate of pozzolanic materials is proportional to the square of their specific surface area (Takemoto & Uchikawa, 1980). Additionally, as SCM particle size decreases, the number of nucleation sites for hydrate precipitation and growth increases, potentially accelerating the hydration process of both the SCM and clinker phases at an early stage.

Walker & Pavía (2011) found that, for SCMs including recycled ceramics, GGBS, FA, silica fume and metakaolin, the amorphousness (or vitreousness) determines reactivity to a greater extent than any other pozzolan property. The glass phase usually consists of acid silicate (SiO_4) and aluminates (AlO_4) tetrahedra, which are held together in a polymeric network by covalently bonded bridging oxygens. Ca^{2+} and other alkali or alkaline metal ions can act either as charge-compensating ions or as network-modifying ions. Network-modifying ions disrupt the aluminosilicate network and produce non-bridging oxygen, which forms ionic bonds with the modified cations. It is well known that amorphous atomic structures have weak atomic links and release species under suitable conditions easily, contributing Si and Al early, which become available for polymerization/hydration or pozzolanic reactions that produce cements. Based on previous work and current results (on alum sludge and fluid cracking catalyst), it appears that the early reactivity of an SCM is likely controlled by the amount of amorphous (available) Si/Al, while the amount of silica (or Si/Al ratio) controls long-term reactions and determines the material's strength development (Fernández-Jiménez et al., 2006; Lei & Pavia, 2023, 2024).

A key element in the evaluation of the potential of SCMs is the assessment of their reactivity. SCMs combine Ca^{2+} in pozzolanic reactions. Therefore, hydrated lime is critical to the pozzolanic reaction of SCMs. In PC systems, the SCM reacts with the portlandite formed upon PC clinker hydration. Hence, almost all test methods for pozzolanic reactivity involve the chemical reaction of SCM with $\text{Ca}(\text{OH})_2$. Although the degree of SCM reaction under simplified test conditions may differ from actual, more complex reactions in PC blends, SCM-lime tests allow to rate SCMs according to their initial reactivity, providing valuable information for initial screening of materials, independent of cement type.

Except for inert fillers, almost all SCMs can be used as precursors to develop geopolymer, making the assessment of waste activity a valuable indicator of their potential as precursors. Test methods to determine pozzolanic activity are categorised as direct or indirect. Direct methods monitor the amount of calcium hydroxide (portlandite, $\text{Ca}(\text{OH})_2$, CH) and the subsequent decrease over time as pozzolanic reaction proceeds. The Frattini test is a standardised test using chemical titrations to determine the concentration of dissolved Ca^{2+}

and OH^- in solutions containing CEM-I and pozzolanic materials. Largen (1978) criticized the “Frattini test” because the system did not reach equilibrium and was performed in a static environment. He introduced modifications, namely the continuous stirring during testing, and renamed the method “modified Chapelle test”. The modified Chapelle test monitors the consumption of Ca^{2+} in a saturated $\text{Ca}(\text{OH})_2$ solution and it is used in this research (Ferraz et al., 2015; Quarcioni et al., 2015).

Indirect test methods use physical properties to measure the amount of pozzolanic activity. The most common method is the mechanical activity index (MI). Based on EN450-1, it measures reactivity by monitoring the compressive strength development of a lime: pozzolan mix in relation to a standard lime mix at constant water content over 28 days. Other indirect test methods are based on electrical conductivity (De Luxan et al., 1989) and heat evolution (Mostafa et al., 2001).

Sometimes the results from mechanical and chemical methods to evaluate reactivity do not agree. For example, pozzolanic materials with clay minerals can fix significant lime but the resultant hydrates develop little strength, hence, lime consumption does not cause measurable hardening /strength. In general, strength increases as the amount of combined lime increases. However, there isn't always a direct relationship between the amount of combined CH and the compressive strength. As noted by Walker and Pavia (2011), the mechanical index measures strength, which is influenced not only by the early evolution of the pozzolanic reaction (amount of combined lime) but also by physical factors that densify the structure, such as grain packing and the composition and microstructure of the cementing hydrates formed. Despite this complexity, a good correlation is often found between the chemical and physical activity indices (Walker & Pavía, 2011).

As conventional supplementary cementitious materials (SCMs) such as fly ash (FA), ground granulated blast furnace slag (GGBS), and silica fume (SF) are consumed in large quantities, and their production is reduced due to the shift towards renewable energy sources, there is concern that the current supply will not meet future demand. Consequently, researchers have been exploring alternative SCMs. A circular economy can be achieved by reusing non-hazardous construction and demolition materials, industrial wastes, and other by-products as SCMs. However, the chemical, physical and mineralogical properties of wastes can pose challenges for direct utilization, and some require additional treatments to enhance their reactivity.

Aluminosilicate wastes and other materials with potential activity can be activated to increase the amount of reactive phase that participates in chemical reactions leading to cement formation such as pozzolanic reactions and geopolymerisation. Activation can improve the performance of the resultant materials and geopolymers.

Mechanical activation is one common method used to enhance the reactivity of SCMs. This process increases the reactivity of a solid by imparting mechanical energy without altering its chemical composition (Xu et al., 2022). The primary effect of mechanical activation is the reduction of particle size, which leads to changes in physical properties such as particle size distribution and specific surface area. Mechanical treatment may also induce compositional or structural changes, such as crystal disorder and defects, thereby decreasing the activation energy barrier of the process (Boldyrev & Tkáčová, 2000). Mechanical activation is usually carried out using mills, and grinding efficiency is influenced by several factors including mill type, grinding media type and material, grinding atmosphere, filling level of the grinding

chamber, ball-to-powder ratio, grinding temperature, mill speed, and grinding time (Tchadjie & Ekolu, 2018).

For instance, Li et al. (2022) used a wet grinding process to activate blast furnace ferronickel slag and found that after 20 minutes of grinding, the activity index increased by 24.7%. Andersson et al. (2023) also reported that due to the amorphous nature of BFFS, no evident mineral change was found after a long time of grinding. However, in the semi-crystalline wastes such as copper slag (Feng et al., 2019), and siliceous gold ore tailings (Yao et al., 2019), after a long time of grinding, some crystal phases such as fayalite, magnetite and muscovite were totally or partially converted into amorphous content due to the amorphization caused by grinding. Prolonged grinding affects the mineral structure and reaction properties of waste by causing localized amorphization, structural stability disturbances, and defect introduction.

Although mechanical activation has many advantages as mentioned above, it also has unavoidable drawbacks. Wilińska et al. (2023) noted that there is a limit to the size reduction effect of grinding, beyond which further size reduction is not achieved. This limitation may restrict the activation of certain highly crystalline wastes. Additionally, when mechanical activation was applied to fly ash, it increased the reactivity but also caused agglomeration and increased water demand (Temuujin & Williams, et al., 2009).

There are several chemical activation methods that are applicable to silicoaluminate wastes. A typical chemical activation method is alkali fusion. In this method, raw material and sodium hydroxide are mixed and calcined at a temperature above the melting point of NaOH. Alkali fusion can transform quartz into soluble aluminosilicate and increase the dissolution of Al and Si (Xu et al., 2010). Increasing the amount of Na₂O significantly enhances the production of the reactive phase (Tchadjie et al., 2016). However, excessive alkali can negatively affect the properties of the geopolymer (Ke et al., 2015).

Mao et al. (2022) found that, when the amount of sodium hydroxide increased from 20% to 50%, the reactive aluminium content in basalt increased from 3.73% to 12.4%. This raised the reaction from approximately 8% to 37.96%, and the 7-day compressive strength from 2.4 MPa to 12.1 MPa. Chen et al. (2023) found an optimal compressive strength of 26.52 MPa for a geopolymer made with coal gasification slag when the alkali: slag ratio was 1.2. Luo et al. (2024) increased the amorphous content of lithium slag from 15.9% to 53.1% by fusing it with 10% NaOH at 700 °C. Moukannaa et al. (2019) fused phosphate sludge with 10% NaOH at 550 °C which attained a compressive strength 40 MPa in the resulting geopolymer. The optimal amount of alkali and calcination temperature varies for different wastes and needs further research.

Thermal activation is another commonly used activation method to regulate the reactivity of SCMs. Thermal treatment can induce phase transitions in materials due to the loss of volatile components or atomic structure reorganization, increasing potential reactivity. One of the most obvious examples is the activation of metakaolin. Kaolinite is converted to metakaolin by calcination at temperatures between 600 and 900°C. Increasing the firing temperature and/or time beyond the optimum conditions results in a reduced tendency for disorder within the structure of the metakaolin, thus reducing the reactivity of the metakaolin (Elimbi et al., 2011; Khaled et al., 2023). Furthermore, thermal treatment can remove the organic matter from the waste which may hinder the pozzolanic reaction and geopolymerisation (Cordeiro et al., 2009; Tantawy, 2015; Cordeiro et al., 2018).

Thermal activation is not effective for all SCMs. For some amorphous or semi-crystalline wastes, thermal activation may decrease their activity. Temuujin & van Riessen (2009) found that calcining FA at 500 and 800°C removed unburnt carbon but also crystallized mullite and hematite, inhibiting FA dissolution.

2.2 ALKALI-ACTIVATED MATERIALS AND GEOPOLYMERS: HISTORY AND DEVELOPMENT

Victor Dmytrovych Glukhovsky (Глуховський Віктор Дмитрович) is recognized as the pioneering researcher who modelled the geological process of zeolite formation in the 1950s. He proposed that the transformation of volcanic rocks into zeolites, which occurs during the formation of sedimentary rocks at low temperatures and pressures, could be replicated and achieved within cementitious systems (Krivenko & Kovalchuk, 2007). A key pioneer in this field, Glukhovsky, along with his colleagues at the Kyiv National University of Construction and Architecture (informally referred to as KNUCA), studied the alkali activation of various natural soils and industrial wastes post-World War II. In 1952, they published a seminal work entitled *Soil Silicates (Грунтосилікати)* which focused on the production of building materials through the reaction of sodium silicate ($\text{Na}_2\text{O}-\text{SiO}_2$) with local precursors including natural soils (e.g. loess or river sand) and industrial by-products like blast furnace slag and coal fly ash. Glukhovsky introduced a novel binder termed "soil-cement," derived from mixing ground aluminosilicates with alkaline-rich industrial waste. The term "soil" was used because the material resembled ground rock and "cement" was used due to its binding properties.

Since the 1960s, the department now named in honour of Glukhovsky as the V.D. Glukhovsky Scientific Research Institute for Binders and Materials, has been using alkali-activated blast-furnace slag for various construction applications. These include flat blocks, railway sleepers, road segments, pipelines, drainage and irrigation canals, dairy farm floors, prefabricated panels, and blocks (P. Krivenko, 2017). Subsequent studies of the building materials extracted from these original structures have shown high durability and a dense microstructure (Xu et al., 2008).

Glukhovsky's early research, starting in the 1950s, aimed to reduce the cost and cycle time of concrete production by using local materials as aggregates and sodium silicate solutions as liquid binders. He demonstrated that many natural materials and industrial by-products could react with alkaline solutions to harden into cement binders (Ponomar et al., 2023). This approach differs from current alkali-activated material (AAM) research, which is largely driven by the overwhelming environmental problems which we are currently facing.

In the 1970s, French scientist Joseph Davidovits developed a series of binders derived from metakaolin and alkaline solutions which he named "geopolymers" (Davidovits, 1991). These are new types of aluminosilicate inorganic polymer with an amorphous three-dimensional network structure of silica-oxygen tetrahedra and aluminium-oxygen tetrahedra connected by bridging oxygens. Since then, research in the field of alkali activation has grown exponentially.

Thanks to the development of various characterisation techniques, the understanding of AAMs and geopolymers has been promoted (Duxson et al., 2007). In the 1980s, Davidovits first utilized NMR to investigate the structure of metakaolin-based geopolymers (Davidovits & Orlinski, 1988). It was discovered that both Al(IV) and Al(VI) (i.e., Al in tetrahedral and octahedral coordination) were presented in the metakaolin geopolymer, with Al(V) and Al(VI)

in metakaolin being converted to tetrahedral sites Al(IV), accompanied by an alkali cation to maintain electroneutrality during the geopolymerisation process (Davidovits, 1991). ^{29}Si MAS-NMR spectroscopy of cured geopolymers revealed a broad resonance (Davidovits & Orlinski, 1988). At the time, understanding the structure of amorphous silicate materials was limited due to the poor resolution of these individual sites in geopolymers. The chemical shift of ^{29}Si was found to be primarily dependent on the degree of condensation of the SiO_4 units, increasing with the degree of polymerization (Lippmaa et al., 1980). Consequently, it is possible to reliably deconvolve silicon resonances into the Gaussian peak components of the $\text{Q}^4(\text{mAl})$ centres that form the aluminosilicate framework. In a low-Ca geopolymer system, silicon and aluminium form a three-dimensional aluminosilicate network structure in the form of tetrahedra, dominated by SiQ^4 and AlQ^4 . Increasing the Si/Al ratio converts $\text{SiQ}^4(4\text{Al})$ and $\text{SiQ}^4(3\text{Al})$ to $\text{SiQ}^4(2\text{Al})$ (Prasanphan et al., 2023). The incorporation of Ca^{2+} leads to depolymerization of silicate chains (García-Lodeiro et al., 2012); therefore, the high-Ca system primarily consisted of calcium-aluminium-silicate hydrate (C-A-S-H) gels with mainly SiQ^2 , some SiQ^1 , and SiQ^3 (a structure similar to tobermorite) (Provis et al., 2015).

Fourier Transform Infrared Spectroscopy (FTIR) has been used to analyse the microstructure and enhance the understanding of alkali-activated materials (AAMs) and geopolymers. At the initial stage of the reaction, the alkali dissolves the precursors, releasing Si and Al species and forming N-A-S-H gels in low Ca systems. A pendular movement of the Si-O-Si(Al) stretching band (centered at $999\text{--}1026\text{ cm}^{-1}$) was observed in the early reaction period (Fernández-Jiménez & Palomo, 2005). This indicates the formation of two different gels: an Al-rich gel (Gel 1), which initially forms and evolves into Si-rich gels (Gel 2) responsible for developing mechanical strength (Criado et al., 2007). In high Ca systems, such as alkali-activated slag, a shift towards a higher wavenumber of the Si-O-Si(Al) stretching band (centered at $978\text{--}989\text{ cm}^{-1}$) was observed in the early stage of the reaction (Cao et al., 2020). This shift is due to the increase in Si/Al in C-A-S-H gels. Later, the band was observed to move to a slightly lower wavenumber due to the continuous participation of Ca^{2+} in the reaction. Ca^{2+} tends to replace Na^+ , triggering the degradation of sodium aluminosilicate gels and resulting in a decrease in the polymerization degree of hydration products (Garcia-Lodeiro et al., 2011).

The development of one-part geopolymers was driven by the user-unfriendly nature of traditional “two-part” geopolymers. In a one-part geopolymer system, this material behaves more like Portland cement, requiring only the addition of water to create a homogeneous and reliable binder (Duxson & Provis, 2008). In 1940, Purdon proposed a method of pre-mixing slag and solid sodium hydroxide, subsequently adding water to produce binders, marking the first attempt at a one-part geopolymer (Purdon, 1940). Duxson & Provis (2008) suggested three potentially viable approaches for developing green precursors for “just add water” geopolymer systems. Over the subsequent 16 years, significant research has been conducted on one-part geopolymers. Among the mixtures obtained by the one-part mixing method, GGBS was most frequently used in conjunction with aluminosilicate materials. Additionally, metakaolin and both low-calcium and high-calcium fly ash are prominent sources of aluminosilicates. The most commonly used alkali activator is anhydrous sodium metasilicate (Gökçe et al., 2021). Generally, the compressive and flexural strength of a one-part geopolymer was lower than that of a two-part geopolymer with the same composition (Zhang et al., 2021). However, the flowability and setting time of a one-part geopolymer were debatable and largely depended on the properties and usage of the activator compared to a two-part geopolymer (Luukkonen et al., 2020; Zhang et al., 2021). The one-part geopolymerization technique facilitates on-site production of concrete compared to

conventional two-component mixing methods, paving the way for wider application of geopolymers in the construction industry.

Although these binders have been created and investigated for decades, there is still controversy over terminology. To avoid confusion between alkali-activated materials (AAMs) and alkali-aggregate reactions, Davidovits introduced terms such as geopolymer cement, inorganic polymers, geopolymeric cementitious compounds, geocements, or poly(sialates) (Duxson et al., 2007; Pacheco-Torgal et al., 2008). The terms AAMs and geopolymer have been used interchangeably or even in conjunction without distinction for a long time (Khater & Abd el Gawaad, 2016; Lv et al., 2018; Xie et al., 2019), despite Davidovits publishing several articles highlighting the significant differences between them (Davidovits, 2018).

In general, geopolymer is used to describe low-calcium systems, while AAMs are used to describe high-calcium systems (Davidovits, 1991; Duxson et al., 2007; Provis et al., 2015). However, with the recent development of one-part geopolymer, a preparation method similar to Portland cement that only requires the addition of water, the term "one-part geopolymer" has become conventional (Luukkonen et al., 2018). The term "one-part alkali-activated materials" is rarely used, even though many one-part geopolymers are based on GGBS, a high-calcium system.

The debate over the terminology of AAMs and geopolymers is beyond the scope of this thesis. When quoting, the same terminology as in the literature is used herein. When discussing the findings of this thesis, the term "geopolymer" is used for simplicity and in conjunction with the "one-part geopolymer" expression under study.

AAMs and geopolymers consist of a precursor (usually an aluminosilicate) and an activator, typically an alkaline solution in two-part systems and solid powder in one-part geopolymers. Although aluminosilicate precursors are available from a wide range of sources, their reactivity, accessibility, and cost vary significantly worldwide. Additionally, except for fly ash (FA) and ground granulated blast furnace slag (GGBS), these materials are not standardized. This diversity and lack of standardization necessitate the investigation and characterization of individual precursors on a global scale, which is one objective of this study.

The mechanism of coagulation and hardening of AAMs and geopolymers is complex, varying depending on the precursor and activator used. The basic alkaline activation mechanism involves a series of reactions, such as disruption-condensation, including the disruption of raw materials into low-stability structural units, their interaction with condensed structures, and the generation of new condensed structures. The first step involves breaking the covalent Si-O-Si and Al-O-Si bonds, which occurs when the pH of the alkaline solution increases, transforming these groups into a colloidal phase. The broken products then begin to accumulate and interact with each other to form a condensed structure, completing the condensation phase (Glukhovskiy et al., 1980). These stages occur almost simultaneously and cannot be analysed in separate models.

The specific mechanisms can be classified into high-calcium and low-calcium systems. In high-calcium systems, Ca^{2+} acts as the main network modifier, reacting with Si and Al to form calcium silicate-aluminate hydrate (C-A-S-H) (Li et al., 2010). It was confirmed by NMR that SiQ^2 and $\text{SiQ}^2(1\text{Al})$ links predominate in the high-calcium system, and thus C-A-S-H gels with longer chains are formed (Lecomte et al., 2006). The high calcium content leads to faster setting and hardening, as well as higher early strength (Temuujin, van Riessen, et al., 2009;

Kim & Lee, 2020). Calcium is therefore thought to have a positive effect on the strength development of geopolymer binders.

In contrast, the final hydration product in low-calcium systems is a sodium silicate-aluminate hydrate (N-A-S-H) gel. N-A-S-H is believed to have a three-dimensional polymer structure, consisting of alternating SiO_4 and AlO_4 tetrahedra connected by shared oxygen atoms (Granizo et al., 2002). This process requires high alkalinity or external heat input to be triggered which results in longer hardening times for low-calcium systems. Additionally, low-calcium systems are highly dependent on the correct proportioning and activator composition. If the Si/Al ratio is not appropriate, the geopolymer will not develop satisfactory strength (Duxson et al., 2005; He et al., 2016).

2.3 THE APPLICATION OF WASTE IN GEOPOLYMERIZATION

2.3.1 Ground Granulated Blast-furnace Slag (GGBS)

Ground granulated blast furnace slag (GGBS) is a by-product of blast furnaces used in metal production. In pig iron production, the melt primarily consists of a mixture of limestone and magnesia olivine, or occasionally dolomite. In blast furnaces, slag floats on top of the iron and is poured out to separate it. Slow cooling of the slag melt produces a non-reactive crystalline material composed of calcium aluminium magnesium silicates. To achieve good slag reactivity, the slag melt needs to be rapidly cooled or quenched below 800 °C to prevent the crystallization of magnesia, zeolite, and magnesite. Its composition is essentially an overcharge-balanced calcium-aluminosilicate skeleton. The chemistry of GGBFS consists mainly of the $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3$ system, described as a phase mixture with compositions similar to those of gehlenite ($2\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$) and akermanite (2CaO-MgO-2SiO_2) compositions, and depolymerised calcium-aluminium silicate glasses (Li et al., 2010). Like PC, GGBS typically consists of approximately 30-40% silica and 40% calcium oxide. The decrease in iron and steel production has led to the GGBS shortage since 2016 in the UK (BEIS, 2017). Furthermore, some of the original blast furnaces for ironmaking are being replaced by more efficient electric arc furnaces which do not produce GGBS (Lee et al., 2019). The paradoxical facts of the high demand for SCMs versus the shortening availability, have led some countries to seek imports to meet their construction needs (BEIS, 2017). Long-distance transport piles up the price of SCMs and overshadows their low-carbon nature.

Generally, GGBS is ground to achieve a fine particle size distribution and a large specific surface area. Despite being ultra-fine, GGBS-based cement pastes and alkali-activated slag pastes exhibit feasible flowability (Alelweet & Pavia, 2021b). The dense particle morphology of GGBS contributes to this property (Alelweet & Pavia, 2019). GGBS is a common supplementary cementitious material (SCM) in Portland cement systems, with a Si/Al ratio ranging from 1.71 to 3.67. Due to its low hydraulic activity, GGBS reacts relatively quickly compared to other common SCMs such as fly ash, natural pozzolan, and silica fume. Even at low temperatures, GGBS helps to shorten the setting time and increase early strength development (Cong & Cheng, 2021).

GGBS has been extensively used to produce geopolymers. Wang et al. (1994) investigated the factors affecting the strength of alkali-activated slags. They found in comparison to sodium hydroxide, waterglass was the best activator for slags and adding the best alkali dosage was within the range of 3.0-5.5% Na_2O . Aliabdo et al. (2019) investigated the influence of various

factors on the compressive strength of GGBS-based geopolymers, including NaOH activator concentration (10M, 12M, and 14M), alkali solution/slag ratio (0.40, 0.45, and 0.50), curing temperature (30, 60, and 90°C), curing time (1, 2, and 3 days), and NaOH/Na₂SiO₃ ratio (1:1.75, 1:2.50, and 1:3.25). The results showed that increasing the NaOH concentration enhanced compressive strength. However, thermal curing was not recommended for slag-based geopolymers as it negatively affected the formation of calcium silicate hydrate (C-S-H). The optimal curing temperature for slag-based geopolymers was found to be 30°C. The main hydration product of alkali-activated slag was C-S-H with a low Ca/Si ratio. The slag activated by NaOH was semi-crystalline, while the slag activated by waterglass was completely amorphous (Wang & Scrivener, 1995). Alelweet & Pavia (2021) investigated the durability of alkali-activated slag, including accelerated weathering tests and freeze-thaw cycles. Sodium silicate-activated slag demonstrated robust resistance to both the weathering test and cycling test, exhibiting minimal strength loss and microstructure damage.

GGBS has also been blended with other precursors such as FA to develop geopolymers. The addition of GGBS to FA-based geopolymers decreased setting time and improved early-age performance. Nath & Sarker (2014) found that incorporating GGBS into FA-based geopolymers could eliminate the need for heat curing, favouring the production of low to moderate strength concrete. Yang et al. (2008) and Phoo-ngernkham et al. (2015) found that increasing GGBS content enhanced the compressive strength and microstructure of the geopolymer due to the formation of additional C-S-H. Xie et al. (2019) reported that combining GGBS and FA provided good synergy for the workability and mechanical properties of recycled aggregate geopolymer concrete, with GGBS contributing to higher mechanical performance and flowability. They also claimed that a sucrose solution could effectively prolong the setting time in the GGBS geopolymer system.

Alexander & Shashikala (2022) reported that geopolymers made with GGBS and FA showed excellent resistance to acid, sulphate and seawater attack, with no weight loss after six months of exposure. Alam et al. (2019) found that alkali-activated, GGBS-stabilized red mud is durable and exhibits higher compressive strength after 12 wet and dry cycles. However, Al-Otaibi (2008) reported that GGBS-based AAMs were more easily carbonated than Portland cement materials but were less sensitive to expansion caused by alkali-silica reactions.

2.3.2 Fly Ash (FA)

Fly ash (FA) is produced from burning coal to generate electricity in power plants. It is generated when finely ground coal is burned in a boiler and is captured in the chimneys of power plants using particle control devices such as electrostatic precipitators or fabric filters. FA is nearly spherical, enhancing the rheology of pastes, resulting in high flowability and easy mixing. There are two types of fly ash, Class C (high calcium content) and Class F (low calcium content), depending on the type and source of coal being burned (Hewlett & Liska, 2019). The FA used in this study is pozzolanic and was characterized by Alelweet & Pavia (2020) as a high silica and alumina FA of low calcium content (c.3%) and $\sum \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 70\%$ by mass, and classified as Class F in the ASTM C618 standard. The authors also identified the FA as partly amorphous with some crystalline phases, including quartz and mullite.

FA is one of the most common SCMs. Since the first report on the economic potential of FA in the 1930s, it has become an indispensable part of the cement industry. However, coal, the most carbon-intensive fossil fuel, is being replaced by more sustainable fuels in response to

climate change mitigation. For instance, the U.S. saw its coal-fired power generation share drop from 50.1% in 2002 to 19.3% in 2020 (US Energy Information Administration, 2022). China, the largest producer of coal-generated electricity, reached its peak coal consumption in 2014, and many coal-burning plants have closed since then (Qi et al., 2016; Reuters, 2021). Portugal, Belgium, and Austria closed their last coal power plants in 2016, 2020, and 2021, respectively (CAN Europe, 2016, 2020; The Portugal News, 2021), and other European countries such as France, Germany, the Netherlands, and the UK plan to close their remaining coal power plants by 2024, 2030, 2030, and 2024, respectively (BEIS, 2021; France-Presse, 2017; Reuters, 2022a, 2022b). the UK has experienced a shortage of fly ash since 2016, and the continued phase-out of coal will exacerbate this scarcity (BEIS, 2017).

FAs have been successfully used to produce geopolymers. Somna et al. (2011) used NaOH at concentrations ranging from 4.5 to 16.5 M as the activator to prepare FA-based geopolymers. They obtained reasonable compressive strengths of 20.0-23.0 MPa at NaOH concentrations between 9.5 and 14.0 M at 28 days. However, increasing the NaOH concentration beyond this range resulted in a strength reduction due to early precipitation of silica-aluminate products.

Curing temperature significantly affects the strengths of FA geopolymers. Somna et al. (2011) found that FA-based geopolymers required longer time to develop strength at room temperature. Heat acts as a catalyst for many chemical reactions, so thermal curing likely speeds up the dissolution of the precursors and the condensation of the resultant anions into polymeric structures. Andini et al. (2008) report that the kinetics of polycondensation reactions in FA geopolymers at 40 and 60°C were poor but significantly enhanced at 85°C. Rattanasak & Chindaprasirt (2009) cured FA geopolymers at 65°C for 48 hours achieving ultimate strengths of 60-70 MPa when using sodium silicate activator (10M NaOH; Ms=1.0).

Wang et al. (2020) investigated the influence of the Si/Al ratio on the properties of FA-based geopolymers and found that, when the Si/Al ratio was 1.5, the content of $[AlO_4]^-$ reached its maximum value, and the pore size and pore volume were relatively low. Lu et al. (2022) used sodium tert-butanol, an organic strong alkali, as an activator to prepare FA geopolymers. The results showed that an alkali activator prepared with 5% sodium tert-butoxide and 10% sodium silicate improved the density and mechanical properties of the FA geopolymer. The authors proposed that organic bases enhance activation and the properties of FA geopolymers, supporting the development of organic bases as activators.

Izquierdo et al. (2009) reported that FA-based geopolymers could inhibit the mobility of heavy metals, although the high pH increased the mobility of oxyanions such as Ba, Be, Bi, Cd, Co, Cr, Cu, Nb, Ni, Pb, REE, Sr, Sn, Th, U, Y and Zr. The main immobilization mechanism of FA-based geopolymers may be physical encapsulation rather than chemical stabilization. Furthermore, FA-based geopolymers have been used as photocatalysts for dye degradation in wastewater (Zhang & Liu, 2013) and removed Pb from an aqueous solution (Al-Zboon et al., 2011).

2.3.3 Alum Sludge (AS)

Water is essential to sustain all life forms, and the provision of clean water is of paramount significance for human health and the broader societal fabric. In 2015, coinciding with the 70th anniversary of the establishment of the United Nations, the objective of "Ensuring availability

and sustainable management of water and sanitation for all" was incorporated into the UN 2030 Agenda for Sustainable Development. Against the backdrop of expanding global populations, aging infrastructure, compromised source water quality and other factors, the task of guaranteeing a secure and dependable water supply to communities constitutes an increasingly formidable challenge.

Water treatment plants draw in raw water from surface resources such as lakes or reservoirs. In surface water, insoluble impurities and microorganisms either settle at a sluggish pace or remain suspended due to their inherent repelling surface charges. To separate these impurities, coagulants containing opposite charges (typically metal salts) are introduced into the water. The coagulants help counteract repulsive forces allowing the particles to aggregate, a phenomenon referred to as "coagulation" (Jiang, 2015). Following coagulation, unstable charged particles, alongside insoluble products, organic matter and impurities adsorbed on the coagulant's surface form larger agglomerates or flocs. This facilitates their removal from the water, a process termed "flocculation" (Cui et al., 2020).

Coagulation and flocculation were first proposed by Mer & Healy (1963). Now these techniques have become integral to drinking water treatment facilities and have garnered substantial recognition within the field of water treatment. Their popularity is rooted in their salient attributes, including minimal energy consumption, uncomplicated design, user-friendly operation, high efficiency, non-toxic properties and cost-effectiveness. After the coagulation and flocculation process, a considerable amount of sludge is filtered out (referred to as water treatment sludge or drinking water treatment sludge).

Salts of aluminium are the most commonly used coagulant in drinking water treatment plants due to low cost, wide availability and high efficiency (Matilainen et al., 2010). When aluminium salts are used as coagulants, the sludge produced is known as alum sludge (AS). AS is an underrated waste which may contain soil particles, organic matter and aluminium. The crystalline phases in AS can include quartz, albite, calcite, and kaolinite, depending on the quality of the surface water (Rodríguez et al., 2010; Tantawy, 2015). The typical chemical composition of AS was primarily Al_2O_3 . Other components such as SiO_2 , Fe_2O_3 and CaO result from contamination. AS has been widely found to contain significant amorphous content and exhibits a high loss on ignition (LOI). Tantawy (2015) summarised the thermal behaviour of AS as a sequence of chemical reactions, which are elimination of moisture, decomposition of organic matter, dehydration of colloidal $\text{Al}(\text{OH})_3$ and crystallization of amorphous silica and aluminium. Europe and the United States generate 100,000 tonnes of AS and over 2 million tonnes of solid residues per year (Okuda et al., 2014).

In some countries, such as Egypt and India, AS is often disposed of into nearby rivers or landfilled (Ahmad et al., 2016; Tony & Tayeb, 2016). These disposal methods involve waste of resources and potential water and soil pollution. A more efficient strategy lies in recycling AS waste within building materials. AS is very abundant and broadly accessible across many geographic regions that align with intensive building construction activities. Integrating AS waste in materials has great potential to lower the environmental impact of construction.

The utilization of AS in construction materials has been the subject of extensive research. Huang et al. (2005) incorporate AS into ceramic bricks at levels of up to 15% without compromising the quality of the final product. Sales et al. (2010) mixed AS with sawdust to produce a lightweight aggregate, and found it to reduce the thermal conductivity of

conventional concrete by 23%. Huang & Wang (2013) used AS as the main material to produce lightweight aggregates.

Furthermore, AS can serve as an active aluminium source in cement systems. Rodríguez et al. (2010) used atomization technology to treat AS and found that the organic matter within AS significantly hindered the cement reaction, leading to prolonged setting times. Geraldo et al. (2017) reported that the incorporation of raw AS into a metakaolin geopolymer also prolonged setting time and reduced mechanical performance. Wang et al. (2018) developed a low-strength material with raw AS. They found the raw AS significantly increased the water demand and prolonged the setting time but the addition of Ca-based admixtures notably shortened the stiffening time. Ching et al. (2021) explored the potential of using AS to replace PC in concrete. They found that even though AS reduced mechanical performance, it also reduced water absorption and chloride penetration.

The high organic matter content in raw AS is a major factor hindering its use in construction. Organic matter affected the setting of cement by adsorbing calcium ions released during hydration (Clare & Sherwood, 1954). Rodríguez et al. (2010) found despite a high proportion of $\text{Al}_2\text{O}_3 + \text{SiO}_2$, unburnt AS exhibited no activity in the Frattini test or when it was tested for alkali activation. AS can be calcined to remove organic matter. Tantawy (2015) further revealed that calcination can trigger dehydroxylation and the formation of boehmite and amorphous alumina polymorphs, thereby enhancing the reactivity of AS. Waijarean et al. (2014) report 800 °C as the optimal calcination temperature for AS. Calcination dehydroxylates and destroys 1:1 layer-lattice aluminosilicate structure occurred thereby increasing the reactivity of AS.

El-Didamony et al. (2014) added calcined AS to PC may increase the production of cementing phases but doses exceeding 5% can reduce the mechanical strength of cement specimens. Ahmad et al. (2018) note that increasing the dosage of 800°C-calcined AS significantly increased the porosity of cement leading to strength reduction. Suksiripattanapong et al. (2015) report the application of calcined AS in geopolymer fabrication. According to the authors, the strength of AS-FA geopolymers cured at 75 °C ranged from 12 to 20 MPa. Nimwinya et al. (2016) studied the potential of geopolymer fabrication with calcined AS and rice husk ash (RHA). The AS-RHA geopolymers exhibit prolonged setting times, and a specimen with a compressive strength of 19 MPa was produced and cured at 60 °C. Therefore, despite the high content of reactive aluminium, calcined AS does not yield desirable performance in neither PC nor geopolymer systems. These challenges have constrained the broader application of AS in construction materials.

2.3.4 Spent Fluid Cracking Catalyst (FCC)

The fluid catalytic cracking process is used in the petrochemical sector to convert petroleum crude oils into gasoline and other products (Wojciechowski & Corma 1986). The process uses zeolite-based catalysts which deactivate over the course of the cracking process losing their catalytic capacity, hence becoming a waste (Marafi & Stanislaus 2008; Macaskie et al. 2010; Rodríguez et al. 2013). The modern refinery FCC units operate 24 hours a day and circulate about 55,900 metric tons of catalysts per day (Gonzalez et al., 2016). The annual global use of catalysts in cracking processes has been estimated at 800,000 tons, with refineries being the principal consumer (Akcil et al. 2015; Wojciechowski & Corma, 1986). The use of refinery catalysts will increase by approximately 5% in the next decade (Cheng et al. 2015; Chiranjeevi et al. 2016).

FCC deactivates in two ways: reversibly as a consequence of side reactions that eventually give coke, and irreversibly: either as a result of sulphur, vanadium and nickel contamination in the crude oil feedstock or due to the dealumination of the zeolite catalyst (Cerqueira et al. 2008; Chiranjeevi et al. 2016). In either case, FCC is typically discharged every three to four weeks. This spent FCC catalyst is often classified as hazardous waste and traditionally disposed of in landfills (Ferella et al. 2016; Chen et al. 2004).

The main constituent of FCC catalyst is a crystalline, synthetic, Y-type zeolite, a faujasite with a Si/Al ratio = 1.5–3 which increases during the cracking process (Rouquerol, 1999). A typical modern cat cracking catalyst has four major components: • Zeolite • Matrix • Filler • Binder (Sadeghbeigi, 2020). According to the author, the matrix consists of alumina which can be active having catalytic activity. The filler is a clay, usually kaolin $[Al_2(OH)_2, Si_2O_5]$, added to give structural integrity and dilute its activity. The binder is the glue that holds the zeolite matrix and filler together. It may or may not have catalytic activity.

Zeolites consist of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra, joined to form open structures of large surface areas with crossing channels and cages which usually enclose water molecules and alkaline or alkali-earth cations (Rouquerol, 1999). Zeolite lattices have a network of very small pores, hence zeolites are sometimes referred to as molecular sieves (Sadeghbeigi, 2020). The cracking process causes significant changes in the chemical and structural composition of the zeolite (Sadeghbeigi, 2020): the zeolite is subjected to thermal and hydrothermal deactivation in the regenerator, and exposed to feedstock contaminants such as vanadium and sodium in the reactor.

It is well known that zeolites have significant pozzolanic activity, reacting with lime to form cementing hydrates. Therefore, they have been used as pozzolans for thousands of years, since at least Roman times or earlier. Liguori et al. (2019) summarise the reactions that occur in a zeolite-lime system as follows: dissolution of solids (lime and zeolite); ion exchange between the cations in the zeolite and the Ca^{2+} released by the lime; zeolite breakdown and conversion into a transient amorphous material; and precipitation of calcium aluminate hydrates (C-A-H) and calcium silicate hydrates (C-S-H). Today, natural zeolites are used to produce PC, where 6-35% of the clinker is replaced with a pozzolan to create CEM II A/B P/Q products (EN 197-1).

The pozzolanic activity of the synthetic zeolite comprising the spent catalyst (FCC) has been proven by previous authors (Pacewska et al., 1998; Payá et al., 1999). Su et al. (2000) and Payá et al. (2001) stated that the spent catalyst can replace up to 15–20% of cement without compromising the material quality. Payá et al. (2003) further pointed out that FCC has comparable pozzolanic activity to metakaolin (MK). Chen et al., (2004) reported that using 5-15% spent catalyst to replace PC increased the compressive strength by 10%-36%. Using spent FCC catalysts as mineral admixtures in concrete is quite feasible. Tseng et al. (2005) reported that heat treatment at 450-850°C and/or grinding can increase the reactivity of FCC. The strengths of mortars containing 10% calcined and calcined/ground FCC were 8-18% and 23-26% higher than those containing untreated within 3-28 days. Pacewska et al., (2011) reported the application of FCC in the calcium aluminate cements (CAC). The addition of FCC into CAC as a reactive admixture formed a new type of C-A-S-H, which might be a new potential approach to preventing the conversion of CAC. Al-Jabri et al. (2013) reported the 20% sand could be replaced by the spent catalyst without a negative influence on the mechanical performance.

The application of FCC in geopolymer fabrication also has been extensively studied. Tashima et al., (2013) investigated the influence of $\text{SiO}_2/\text{Na}_2\text{O}$ and $\text{H}_2\text{O}/\text{FCC}$ on the mechanical performance of the FCC-based geopolymer. The optimal activator solution for FCC was composed of 18.6% Na_2O and 21.0% SiO_2 . When the $\text{H}_2\text{O}/\text{FCC}$ was 0.4, the ultimate compressive strength of FCC geopolymer can reach 80 MPa.

Geopolymers made solely from FCC demonstrated prolonged setting times and sometimes required thermal curing. To address this issue, FCC was often mixed with other wastes to produce geopolymers. Liu et al. (2021) on the coupling effect of steel slag with FCC in geopolymer fabrication. They found that increasing the steel slag dosage improved the mechanical performance of the FCC-steel slag system due to the involvement of more Ca^{2+} ions. The primary hydration product in the resulting geopolymer was C(N)-A-S-H and unreacted steel slag was embedded in the cementing gel as skeleton material. Yu et al. (2021) produced geopolymers with FCC and silica fume at ambient temperature. They found that geopolymers with good early compressive strength properties (23.77 MPa) could be prepared by using FCC waste catalyst as the main raw material, 50% silica powder as the silica-correcting material, and water glass with a modulus of 1.2 as the alkaline activator. The incorporation of silica powder significantly influenced the mechanical and microstructural properties of the geopolymers.

2.3.5 Crop Biomass Ash (CBA)

Biomass is an inexhaustible and abundant renewable resource, continually replenished through photosynthesis. The use of biomass as a replacement for fossil fuels has great significance in the context of global warming because of its carbon neutrality. Amidst the global call for carbon neutrality by 2030, biomass power plants have regained prominence, with biomass electricity generation increasing from 162 to 685 terawatt-hours (World Bioenergy Association, 2022). Biomass power capacity in 2019 stood at approximately 17.8 GW in China and 16.2 GW in the US (REN21, 2020). Large biomass plants also have been installed in India (10.2 GW), Germany (8.4 GW) and the UK (7.7 GW) (REN21, 2020). By 2050, 33 to 50 percent of the world's primary energy consumption can be biomass-generated (Vassilev et al., 2013). However, behind the thriving industry lies a significant issue: the discharge of growing quantities of biomass ash.

Crop biomass ash (CBA) resulting from the combustion of local agricultural residues such as corn cob, wheat straw, rice husk and corn straw is rich in silica and aluminium (Vassilev et al., 2013). Given the relatively stable types and yields of locally grown crops, the composition and quantity of CBA obtained is regionally constant. However, the emerging ashes are a great challenge for local communities to dispose of. In the absence of appropriate disposal methods, these ashes are usually relegated to landfills.

More than 5 billion tonnes of agricultural residues are produced annually worldwide (Krishna & Mkondiwa, 2023). Among these, residues from wheat, corn and rice, known as the three major food crops, constitute more than three-quarters of the total production. Annually, it is estimated that wheat, maize, and rice generate approximately 1 billion tonnes, 1 billion tonnes, and 0.8 billion tonnes of dry matter in crop residues, respectively (Bentsen et al., 2014). Particularly in Asia, excessive residues are burned in open fields causing severe air pollution (Zheng & Luo, 2022).

One of the main pressures faced by the construction sector is the continuous use of Portland cement (PC) products which have high carbon emissions due to the burning of fuels and the decarbonization of raw materials involved in its production. Under current standards, biomass ash is excluded from PC concrete additions. However, research by Abdulkareem et al. (Abdulkareem et al., 2019) and Ates et al. (Ates et al., 2023) demonstrate the feasibility of developing a sustainable geopolymer from agricultural biomass ash.

The use of agricultural residual ash in geopolymer development has been extensively studied. Rice husk ash (RHA) could significantly improve the mechanical performance of geopolymer. Liang et al. (2019) reported that replacing 30% of metakaolin with RHA increased the compressive strength of a sodium silicate-activated geopolymer from 30.2 MPa to 47.47 MPa, a 57.18% increase. Liu et al. (2020) found a 24% increase in compressive strength after 28 days of curing when 15% RHA was added, noting that RHA also improved the thermal stability of the geopolymer by lowering the sintering temperature. The high reactivity of RHA could provide an extra silica source to promote the formation of gel phases thereby benefiting the mechanical performance of geopolymer (He et al., 2013). Furthermore, other types of ashes such as corncob ash (Oyebisi et al., 2020, 2022; Saloni et al., 2021), sugarcane bagasse ash (Castaldelli et al., 2016; Yadav et al., 2020) and wood ash (Abdulkareem et al., 2019) have been used partially to replace FA/metakaolin to develop geopolymer. However, it is important to acknowledge that producing these ashes is an energy-intensive process that requires controlled conditions—specific temperature, duration, and sufficient oxygen supply. Contrarily, biomass ash from power plants is often produced under higher temperature combustion conditions for power generation, which while contributing to its carbon-neutral status, also leads to high crystallinity and challenges in utilization.

Songpiriyakij et al., (2010) investigated the reactivity of biomass ash (BA) collected from power stations, finding that while the reactivity of BA was lower than that of fly ash, it still can serve as a potential source of Si for producing geopolymer. Geopolymer with a compressive strength of 56.0 MPa was made with 40% BA. Ates et al. (2023) ground and calcined biomass wood fly ash (BWFA) at 800 °C and mixed it with FA to produce geopolymer. Their test results showed that BWFA increased the porosity but also enhanced the mechanical performance of the geopolymer. BWFA contributes Ca to the geopolymer system, generating more calcite and CSH phases. Silvestro et al. (2023) collected three types of wood ashes from power stations, which had different chemical compositions but all had a high LOI. When 10% and 20% of metakaolin were replaced with wood ash, the compressive strength of the resulting geopolymers reached 83 MPa and 79 MPa, respectively. Due to the low reactivity of wood ash, the setting of geopolymers was delayed.

Overall, biomass ash varies greatly in chemical composition depending on the source of the biomass and is mineralogically highly crystalline. These differences and high crystallinity create difficulties in utilizing BA effectively. Therefore, more research is necessary to characterize BA from different sources and explore effective methods to enhance its reactivity.

2.3.6 Olive-pit Biomass Ash (OBA)

Olive is an important resource in Mediterranean countries. According to Galán-Martín et al. (2022), 10.57 Mha were devoted to olive trees in 2019 globally, almost half of which are located in four Mediterranean EU countries. Mediterranean olive production accounts for 41% of the world's production: 13.70 mt which are processed into 2.51 mt of olive oil and 0.85 mt of olives. During the production of olive oil, the olive is crushed and pressed or centrifuged to isolate the

fruit from the pit. In Spain, most olive mills (~99%) use two-phase decanters, which produce about 800-850 kg of pomace per ton of olives processed, compared to Italy, Greece and Portugal where three-phase decanters are the most common operation, producing about 45-52% of pomace by weight (García Martín et al., 2020). After oil extraction, the residual pomace is either used as feedstock to provide heat during oil manufacture, or as biomass in power plants (López et al., 2018). Considering an average residue yield rate (solid waste/olive oil = 2.5) and a 6-7% residue content (biomass ash/solid waste), it is estimated that EU countries will generate around 345,100 tons of OBA annually, contributing to global output of 526,750 tons (de Moraes Pinheiro et al., 2018). The accumulated ashes are a burden on both the business operation and the environment.

The feasibility of using OBA to develop sustainable low-carbon building materials was demonstrated by previous authors. Cabrera et al. (2014) found that, even with different combustion conditions, the composition of olive bottom ashes from different sources was similar, and that the use of bottom ash in civil facilities was feasible. Font et al. (2017) used a suspension of olive bottom ash and water to activate GGBS, and the resulting material reached a strength of 30 MPa after 7 days of curing at 60°C. Font et al. (2020) designed a thermally-cured, ternary alkali-activated mortar with GGBS, olive biomass ash, rice husk ash and pre-mixed activator which reached a compressive strength of over 50 MPa. Carrillo-Beltran et al. (2021) used olive biomass fly ash and chamotte, calcined at 950°C, to produce a geopolymer brick with a compressive strength of 50 MPa. Alonso et al. (2019) examined the radiology and leaching behaviour of olive biomass ash and demonstrated that an olive bottom ash-based binder complies with relevant requirements and the main leachate was K.

2.4 ALKALINE ACTIVATORS IN AAM/GEOPOLYMER PRODUCTION

Geopolymer systems rely on a wide range of alkaline activators: their second essential component. Generally, the activators are alkaline hydroxides, alkaline silicates, or blends of the two. High alkalinity and high soluble Si content trigger alkali activation and facilitate strength gain and densification. In high calcium systems such as slag-based AAMs, weak acid salts such as Na_2CO_3 (Collins & Sanjayan, 1998) or strong acid salts such as Na_2SO_4 (Wang et al., 1994) or $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Ma et al., 1995) can be used as activators or auxiliary activators.

NaOH is often used to activate aluminosilicate precursors such as metakaolin and FA for reasons including price, availability and low viscosity. The OH^- from the activators dissolves Si and Al ions in the precursors by breaking the Si-O-Si and Si-O-Al bonds in the silicates and releasing them into the solution (Glukhovskiy, 1967). The activator performance in aluminosilicate precursors is optimum when the concentration of NaOH is around 8M- 10M (Puertas et al., 2000; Wang et al., 2005).

Silicate activators, especially sodium silicate, are used to increase the availability of soluble Si at the beginning of the geopolymerisation reaction. The availability of soluble silicate is very important in these systems as it affects setting and mechanical strength, and changes the gel composition and microstructure of the material formed (Pacheco-Torgal et al., 2014). The general formula for soluble silicate is $\text{Na}_2\text{O} \cdot x\text{SiO}_2$, where x = molar ratio. Sodium silicate solution with a low molar ratio consists primarily of monomers (SiO_4^{4-}) and dimers ($\text{Si}_2\text{O}_5^{2-}$), while a solution with high molar ratio will have a high proportion of polymeric species (Bass & Turner, 1997). Furthermore, the pH of the silicate solution depends on the molar ratio.

Increasing the silicate content will decrease the pH of the solution thereby lowering the dissolution of the precursors.

Silicate activators increase the available Si to participate in geopolymerisation. The available $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the system influences the ratio of Si-O-Si / Si-O-Al bonds (He et al., 2016). Since the strength of the Si-O-Si bond is greater than that of the Si-O-Al bond (Xiao & Lasaga, 1994); increasing the availability of soluble Si enhances mechanical strength. Silva et al. (2007) found that increasing Si content results in a more extensive polymerisation that produces higher strength, while the available Al content controls the setting time. The ratio Si/Al significantly affects the properties of the resulting materials, and it is one of the most important parameters that govern the mechanical strength of AAMs (Duxson et al., 2005). The optimal ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ for superior strength of the resultant geopolymer is between 3.0 and 3.8 (Silva et al., 2007).

Furthermore, the alkalinity of the activator-precursor system strongly affects the geopolymer properties. The first step of geopolymerisation is the dissolution of the precursor. The rate of dissolution is highly dependent on the composition of the activator solution, in particular the pH value of the solution. Under alkaline conditions, the hydrolysis of silica-aluminate and ion-exchange processes occur concurrently, accelerating precursor dissolution. In high-Ca systems, such as alkali-activated slag, a high pH causes the deprotonation of hydrated Ca^{2+} which can then interact strongly with hydrolysed silicate and aluminate species. This interaction leads to condensation reactions and the formation of low-Ca/Si C-(A)-S-H (Newlands et al., 2017). The concentration of OH^- determines the rate at which Al and Si ions dissolve, a high concentration increases dissolution. KOH activator produces higher alkalinity - greater $[\text{OH}^-]$ - than NaOH, but NaOH has been reported to be more efficient at dissolving silicate and aluminate monomers in silico-aluminate precursors (Duxson et al., 2007). The concentration of OH^- is controlled by the silicate module ($M_s = \text{SiO}_2/\text{Na}_2\text{O}$). Davidovits (2018) claimed that, when sodium silicate is used, the resulting geopolymer is more consistent, homogenous and dense, and it has low porosity because the sodium silicate activator increases the availability of Si at the early stage of the reaction. However, the introduction of SiO_3^{2-} by the activator decreases the pH and increases viscosity, therefore it needs to be controlled, and the optimum M_s for sodium silicate activator has been established between 1.0 and 1.5 (Duxson et al., 2005).

Besides the $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{SiO}_2/\text{Na}_2\text{O}$ ratios, the curing regime and liquid/solid ratio also affect the properties of the resultant materials. The dissolution of precursors and the breaking of chemical bonds (mainly -Si-O-Si- and -Si-O-Al-) is a heat-absorbing process, therefore thermal curing can be favourable (Lancellotti et al., 2013; Palomo et al., 1999). Water plays a significant role in geopolymerisation. A high liquid/solid ratio favours the dissolution of raw materials and the hydrolysis of Si^{4+} and Al^{3+} compounds but hinders polycondensation (Zuhua et al., 2009).

The development of one-component geopolymer technology has expanded activators beyond alkali solutions, allowing the use of low-carbon and environmentally friendly solid activators and waste-based activators. Ma et al. (2019) used anhydrous sodium carbonate and sodium silicate to produce a one-part geopolymer. They found that using sodium carbonate (which has significantly less environmental impact) instead of sodium silicate prolonged the setting time and reduced early-age strength due to calcite formation. Choo et al. (2016) used red mud as an alkali activator to produce a low-carbon geopolymer with a compressive strength of around 1.7 MPa. Peys et al. (2016) found that ash derived from the combustion of maize stalk

and maize cob exhibited a high pH of 13-14 after mixing with water. Geopolymer made with metakaolin and maize ash yielded a compressive strength of 40 MPa using a pre-press cast and thermal curing method. Similarly, Ban et al. (2017) used high-calcium wood ash as an activator to produce a self-activating geopolymer with a compressive strength of 8 MPa. However, the authors did not provide the composition analysis of the resulting geopolymer. Vinai & Soutsos (2019) produced a silicate powder activator derived from waste glass powder and sodium hydroxide. They claimed that powder activators were 80% efficient in activating fly ash and fly ash/GGBS binders, and that the cost of concrete produced using their powder activator is either comparable or lower than that of equivalent PC. Their powder activator is also expected to have a significantly lower carbon footprint. Tchakouté et al. (2017) used RHA and waste glass to produce alternative activators. Specimens obtained using sodium silicate from waste glass exhibited a more cohesive geopolymer structure.

2.5 CARBON FOOTPRINT OF CONSTRUCTION MATERIALS

2.5.1 Background and Concept

The production of Portland cement consumes large amounts of energy and raw materials, and emits large amounts of CO₂. Although geopolymer technology reduces dependence on energy and raw materials by utilizing industrial by-products (or waste) containing aluminosilicate and silica phases, the production of alkaline activators also consumes substantial amounts of energy and raw materials. This overshadows the low-carbon sustainable character of geopolymers. Given that geopolymer is recognized as a potential sustainable material to replace Portland Cement, it is necessary to compare the sustainability of geopolymer with that of PC. Life Cycle Assessment (LCA) methods are widely used for this purpose.

Life Cycle Assessment (LCA) is a method for assessing the environmental load of processes and products (goods and services), over their life cycle, from cradle to grave (Heijungs et al., 1997). The LCA methodology, based on the ISO 14040 series of international standards, consists of four distinct analytical steps: definition of objectives and scope, creation of an inventory, assessment of impacts and final interpretation of results (ISO, 1997).

First, defining goals and scope involves outlining the purpose, audience and system boundaries. Second, the Life Cycle Inventory (LCI) involves the collection of all relevant energy and mass flow input and output data for each unit process, as well as air, water, and land emissions data. This phase includes calculating the materials and energy inputs and outputs of the building system. Thirdly, the Life Cycle Impact Assessment (LCIA) phase assesses the potential environmental impacts and estimates the resources used in the modelled system (Ortiz et al., 2009).

The categorization of Life Cycle Inventory (LCI) results involves assigning emissions, wastes, and resources used to selected impact categories, such as CO₂, CH₄, and CO. The converted LCI results are aggregated into indicator results, which are the final outcomes of the mandatory part of the Life Cycle Impact Assessment (LCIA). Optional steps include normalization, grouping, weighting, and additional LCIA data quality analysis.

There are two main approaches in LCIA: the problem-oriented approach (midpoint) and the damage-oriented approach (endpoint). The midpoint approach addresses environmental impacts related to climate change, acidification, eutrophication, potential photochemical ozone

generation, and human toxicity. These impacts can be assessed using methodologies such as CML baseline (2001), EDIP 97 & EDIP 2003, and IMPACT 2002+. The endpoint approach, on the other hand, categorizes environmental flows into various themes, modelling the damage to humans, the natural environment, and resources caused by each theme.

One of the challenges facing the construction industry is understanding the greenhouse gas footprint of materials through credible and transparent information. The Environmental Product Declaration (EPD) is a standardized (ISO 14025) and LCA-based tool for communicating the environmental performance of products. EPDs on building materials such as concrete, wood, and aluminium provide information related to raw material sourcing, energy use, material and chemical content, emissions to air, land and water, and waste generation.

2.5.2 Carbon Footprint of Geopolymer Materials

Teh et al. (2017) quantified the carbon footprint of cement and concrete production in Australia, including Ordinary Portland Cement (OPC), Standard Ordinary Portland Cement Concrete (SOPC), Mixed Cementitious Concrete (MCC), and Geopolymer Concrete (GCC). They concluded that geopolymer production is the most likely method to reduce environmental impacts compared to mixed cementitious concrete and OPC concrete. Geopolymer concrete based on fly ash (FA) and ground granulated blast furnace slag (GGBFS) can significantly reduce greenhouse gas emissions (GHGE) by 32% and 43% compared to standard OPC concrete with the same compressive strength.

Salas et al., (2018) reported a Life Cycle Assessment (LCA) of geopolymer concrete (GC) conducted after expanding the Life Cycle Inventory (LCI) from laboratory scale to industrial scale. The study considered the local power generation mix and the impact of different sources of alkaline activator (locally produced and imported). The results showed that the process with the highest impact in the LCA is the production of sodium hydroxide. When sodium hydroxide is produced under optimal conditions and using a hydroelectric power mix, the global warming potential (GWP) of geopolymer concrete is 64% lower than that of PC-based concrete.

Meshram & Kumar (2022) conducted a cradle-to-gate LCA of two geopolymer cements produced from blended fly ash and slag, as well as blended fly ash and cement under Indian scenarios. Compared to Ordinary Portland Cement (OPC), the authors conclude that geopolymer cements produced from fly ash and slag can reduce the global warming potential by 70%, the abiotic depletion potential of fossils by 49%, the abiotic depletion potential of elements by 34%, and the terrestrial ecotoxicity potential by 77%; and that the greatest environmental impact is due to the use of alkali solutions.

Shi et al. (2021) systematically quantified and compared the environmental impacts of fly ash geopolymer concrete (GPC) and PC concretes of different strength classes with LCA. They considered the sensitivities to strength and CO₂ emissions in terms of three key parameters: alkali exciter solution to fly ash ratio (S/F), sodium hydroxide concentration (C NaOH), and sodium silicate to sodium hydroxide ratio (SS/SH). They found that CO₂ emissions of geopolymer concrete depend mainly on the alkali solution, transport and thermal curing processes, while those of PC concrete depend mainly on the cement dosage. The CO₂ emissions of PC concrete increase continuously with increasing compressive strength, while CO₂ emissions of high-strength grades of geopolymer concrete do not increase significantly.

Munir et al. (2023) reported that the use of alkaline activators is a major contributor to the increased environmental burden of geopolymer concrete. Bajpai et al. (2020) reported that the GWP of geopolymer concrete was around 135 kg CO₂ eq. while the PC-based concrete was 597.54 kg CO₂ eq. The activator of the geopolymer contributed 59.97% of the environmental impact.

Despite the numerous LCA studies on geopolymers, there is significant variability in the choice of various carbon emission parameters, leading to different results that are difficult to directly compare. Shi et al. (2021) claimed the emission factors of sodium silicate and sodium hydroxide were 1.247 and 1.155 kg CO₂ eq. respectively, while Meshram & Kumar (2022) applied an emission factor of 0.696 kg CO₂ eq. for sodium silicate and Turner & Collins (2013) applied an emission factor of 1.915 kg CO₂ eq. for sodium hydroxide. Significant concerns are the lack of transparency in many studies regarding carbon emission factors for individual components and the process for calculating them, and these hinder more transparent comparisons of carbon emissions.

Another concern about geopolymer LCA is the carbon allocation for FA and GGBS. It is widely recognized that GGBFS and FA are waste products and have negligible environmental impacts compared to the overall environmental impacts of PC or geopolymer concrete. However, under the conditions set out in the EU Directive on the treatment of waste as a by-product, FA and GGBS should be categorized as by-products and not as waste (Chen et al., 2010). The hidden carbon emissions and other environmental impacts from steel production and coal-fired power generation behind GGBS and FA should be considered when they are seen as products with real economic value. When the choice was made to allocate the mass ratio of steel to GGBS generated during steel production, the environmental impacts of GGBS are higher than CEM I. When choosing to allocate carbon emissions based on the economic value of steel and GGBS, part of the load from steel production falls on the environmental indicators of abiotic depletion, human toxicity, photochemical oxidation, and freshwater and seawater ecotoxicity of GGBS, making the values higher than those of CEM I. However, the global warming impacts were still relatively low compared to the CEM I (Chen et al., 2010).

2.6 REFERENCE IN THIS CHAPTER

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Chapter 3: Materials and Methods

3.1 MATERIALS

3.1.1 Waste

Spent fluid catalytic cracking catalyst (FCC)

FCC was sourced from BP Energía España (Castellón Refinery, Spain). Spent catalysts are periodically discharged every few months to maintain reactor activity. According to the producers, the differences between batches of catalysts, in terms of the percentage of metal adsorbed and active surface, are minimal. FCC was used as received. No further grinding was applied.

Alum sludge (AS)

AS was collected from a drinking water treatment plant in Northern Ireland. When AS is discharged from the water treatment plant where it undergoes a series of compression and dewatering procedures. It was received in the form of a black lumpy solid with a water content of approximately 82.5% which was dried to a constant weight at 105°C and then ground in a ball mill for 2 hours. The resulting powder is named as raw alum sludge (AS) (Figure 3-1).

Some of the AS was pyroprocessed. As aforementioned, it was expected that calcination would remove organic matter and increase reactivity. Tantawy (2015) found that calcination enhances the pozzolanic activity of the AS, and that both temperature and dwelling time influence reactivity. Hence, a systematic study of the effect of pyroprocessing on this particular AS is required to enable the application. Therefore, the raw AS was calcined in an electrical furnace at temperatures of 450, 600, 800 and 1000°C for 1, 2, and 3 hours. Calcination produces a gradual colour change, from coffee/black to light yellow (Figure 3-1). The colour transition reflects the removal of carbon (organic matter) and the formation of colourless Al oxide.

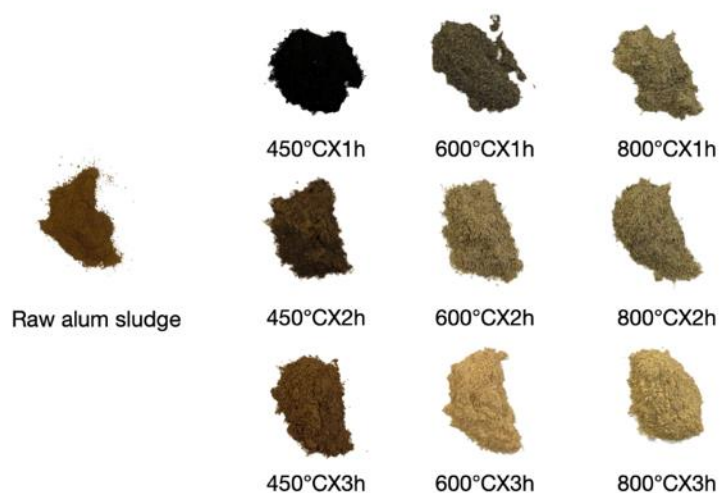


Figure 3-1 Colour change in the AS induced by calcination.

Olive-pit bottom ash (OBA)

The OBA was collected from an olive oil manufacturer in Spain. The oil factory uses olive cake as feedstock to provide heat on the premises. The company burns the cake in a boiler where combustion is roughly controlled. The raw OBA was received dry, consisting of fine ash and some large molten masses. To obtain a uniform powder, it was ground in a ball mill for two hours.

Crop biomass ash (CBA)

The biomass ash used in this study was supplied by Beijing Zhineng Xiangying Energy Conservation and Environmental Protection Technology Company. This biomass ash, designated as crop biomass ash (CBA), is a bottom ash derived from the combustion of local agricultural residues, including rice husks and maize stalks, for power generation. The stable source of biomass and the consistent incineration process ensure the uniformity of the composition and properties of the resultant ash. The exact combustion temperature of the ash is not known, and the combustion temperature of biomass boilers varies for different boiler types. However, for wood-chip boilers, it is typically 540 - 600°C for the initial burn which releases gases, and up to 1200°C for the re-burn of the gases in the calcination chamber. Therefore, internal temperatures usually range between 500°C and 1200°C (Gimelli & Luongo, 2014). The CBA, as received from the power plant, comprises large, sintered masses and fine powder. To achieve homogeneous powders, the CBA was ground in a ball mill for two hours.

Ground granulated blast furnace slag (GGBS)

An Irish GGBS of particle density = 1.80 mg/m³ was blended as a silica and calcium source. As reported by previous authors (Alelwee & Pavia, 2019, 2021b, 2021a; Walker & Pavía, 2011), the GGBS is totally amorphous (Figure 3-2) and shows outstanding activity and significant qualities for the production of alkali-activated cement, being ultra-fine (SSA=1950 m²/kg) and basic ($\text{CaO} + \text{MgO} / \text{SiO}_2 = 1.56$). Furthermore, it complies with the standard EN 15167-1 requirement for PC substitution in mortars, concretes and grouts and has ratios of $\text{CaO}/\text{SiO}_2 = 1.41$ and $\text{Al}_2\text{O}_3/\text{SiO}_2 = 0.34$ which are deemed suitable for alkali-activation.

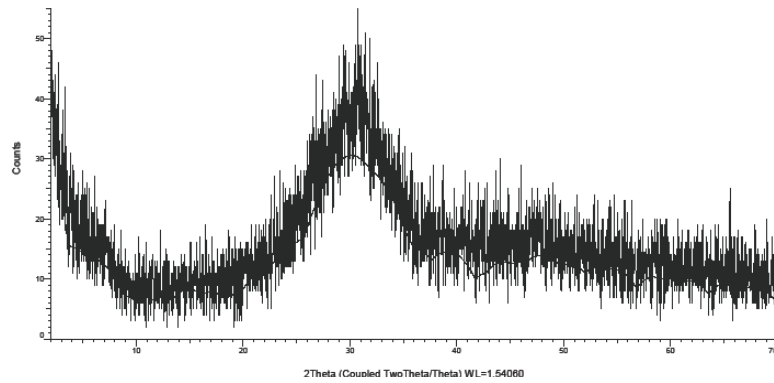


Figure 3-2 XRD trace of the GGBS with a marked halo indicating a high amorphousness and no crystalline phases (Alelweet & Pavia, 2021b).

The chemical composition of GGBS used in this study is presented in Table 3-1.

Table 3-1 Chemical composition of the GGBS (wt%).

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	MnO	TiO ₂	SO ₃	Cl	S ²⁻	Na ₂ O _{eqv.}
36.5	10.4	0.7	42.4	8.1	0.4	0.5	0.1	0.01	0.7	0.5

Fly ash (FA)

The fly ash (FA) was collected from a coal-burning power station at Money Point, Clare, Ireland. The chemical composition of FA is presented in Table 3-2. This FA was produced from the combustion of low sulphur coal at approximately 1100°C. The FA is pozzolanic, classified as class F (ASTM C618) and complies with the chemical requirements in EN450–1: Use of FA in concretes, mortars and grouts (Alelweet & Pavia, 2020).

Table 3-2 Chemical composition of FA expressed as % wt oxide.

Chemical composition	FA
SiO ₂	53.40
Al ₂ O ₃	21.18
Fe ₂ O ₃	9.99
CaO	4.14
MgO	1.86
Na ₂ O	0.70
K ₂ O	3.24
TiO ₂	1.35
MnO	0.07
P ₂ O ₅	0.84
LOI	4.92

The particle size distribution of FA is presented in Figure 3-3. The D₅₀ diameters by volume distribution are 14.97 µm for the FA. This fineness suggests a great specific surface area which is one of the main variables that govern short-term reactivity in pozzolanic reactions (Massazza, 2002, 2007).

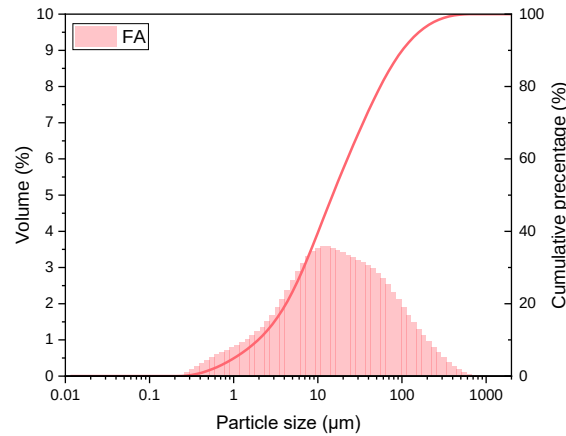


Figure 3-3 Particle size distribution of FA wastes.

The mineral composition of FA is presented in Figure 3-4. FA is semi-crystalline and displays a broad hump centred at $23^\circ 2\theta$ which indicates the presence of amorphous content. The FA contains significant amorphous material. The composition of the FA's glass, determined by devitrification, consists of mullite ($2\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and hematite (Fe_2O_3) (Alelweet & Pavia, 2020). Quartz (SiO_2 , PDF 04-016-2085) is the predominant crystalline phase. Due to its physical and chemical stability, quartz is generally inert in pozzolanic reactions, especially when the particle size exceeds $5\text{ }\mu\text{m}$ (Benezet & Benhassaine, 1999).

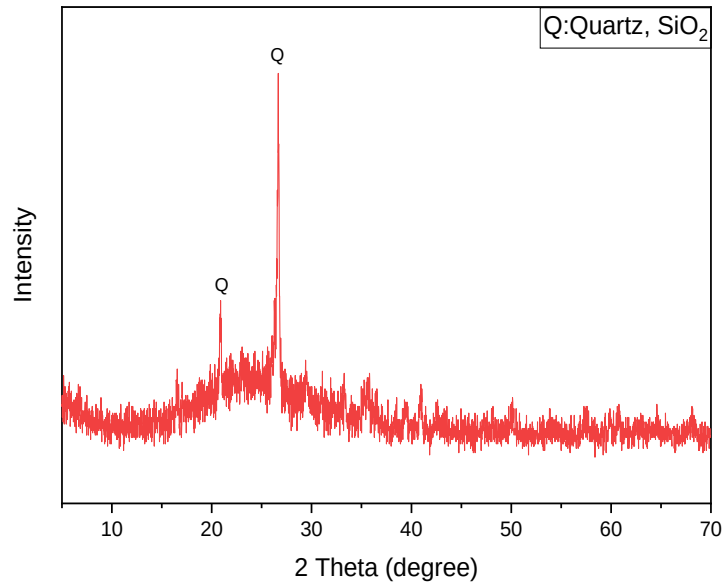


Figure 3-4 Mineral composition of FA.

3.1.2 Alkali Activator

Sodium silicate (NS)

Sodium silicate solution (27.8 wt.% SiO_2 , 8.5 wt.% Na_2O , 63.7 wt.% H_2O , general purpose grade) supplied by Fisher was used in the two-part geopolymer fabrication. In the one-part

geopolymer system, commercial sodium silicate anhydrous (NS) with various moduli ($M_s = \text{SiO}_2/\text{Na}_2\text{O}$ by molar ratio) ranging from 1.0 to 3.0 supplied by Henan Borun New Material Co., China was used.

Sodium hydroxide (NH)

Sodium hydroxide pearl (general purpose grade) supplied by Fisher was used in this study to prepare sodium silicate solution with different $\text{SiO}_2/\text{Na}_2\text{O}$ ratios and in the alkali-fusion process.

Sodium carbonate (NC)

Sodium carbonate anhydrous (Laboratory reagent grade, $\geq 99.5\%$ purity) supplied by Fisher was used as an activator in the one-part geopolymer system.

3.1.3 Other Materials

Hydrated lime (CH)

A hydrated commercial lime of European designation CL90s was used to fabricate waste-lime specimens for reactivity study. Furthermore, CH also was added in some geopolymers as a source of alkali to optimize the mix design.

Sand

The sand of siliceous composition (Figure 3-5) and grading similar to the standard CEN sand (EN 196-1, 1995) was used to fabricate the lime and geopolymer mortars required for testing.

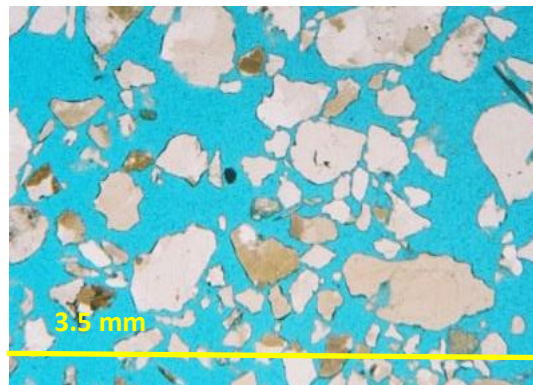


Figure 3-5 Petrographic micrograph of the sand including abundant angular quartz, microsilica and occasional feldspar. 2X. Polarised light.

Water

Municipal tap water was used to prepare lime and geopolymer samples. The activator solution for a two-part geopolymer was prepared in distilled water. Similarly, the Chapelle test was conducted using distilled water to prevent the dissolved carbon dioxide in tap water from interfering with the experimental results.

3.2 METHODS

3.2.1 Characterisation of the Wastes and the New Cements

Particle size distribution

The particle size distribution of the wastes was assessed using laser diffraction with a Mastersizer 3000 instrument by Malvern using water as the dispersing agent. The test procedure followed the methodology by Sperazza et al. (2004).

Chemical composition

The major chemical components of the wastes were analysed by X-ray fluorescence (XRF) and reported as weight percentages of oxides. The minor chemical components were analysed using inductively coupled plasma optical emission spectrometry (ICP-OES) and reported as concentrations of elements.

Mineral composition

The mineral composition of the waste, waste-lime pastes and geopolymers was determined with an X-ray diffraction apparatus using the powder method. The equipment used is a Bruker D5000 machine fitted with a 2.2 kW Cu long fine-focus X-ray tube. The angles were scanned over a 2θ range spanning from 5° to 70° .

Morphology

Scanning electron microscopy (SEM) in conjunction with energy dispersive X-ray spectroscopy (EDX) was employed to investigate the morphology of waste particles and the microstructure and chemical/mineral composition of the new cements produced in polymerization and pozzolanic reactions. The analyses are performed with a Zeiss ULTRA plus apparatus equipped with a 20mm² Oxford Inca EDX detector under SE mode. To prevent the charging of the specimens during the analyses, a layer of gold/palladium was applied to the specimens' surfaces.

Fourier-transform infrared spectroscopy

Fourier-transform infrared spectroscopy (FTIR) is used to investigate the nature of the new cements produced in polymerization and pozzolanic reactions. The analyses are conducted in a PerkinElmer Spectrum 100 FTIR apparatus equipped with an ATR accessory and a one-bounce diamond/KRS5 top plate. The spectra were obtained in the range of 4000 to 400 cm⁻¹ at a resolution of 4 cm⁻¹ averaging 32 scans for each measurement.

3.2.2 Waste Processing Methods

Pyroprocessing

When required by the composition and reactivity of the raw waste, some wastes are calcined in an electrical furnace at temperatures of 300-800 °C for 2 h and cooled naturally.

Oxidation

Oxidation treatments are used to improve the reactivity of certain wastes using a 15% hydrogen peroxide (H₂O₂) solution. The waste and H₂O₂ mixtures were aged at room temperature for 24h, and then dried in an oven at 105 °C.

Acid etching

Certain wastes are etched with a 0.1M HCl solution to enhance their reactivity. The waste / 0.1M HCl mix was aged at room temperature for 24h, then filtered and washed with distilled water. The residues were dried in an oven at 105 °C.

Alkali fusion

Alkali fusion was applied to certain raw wastes to increase their reactivity. 25% NaOH and 600 °C were used as the reactants.

3.2.3 Waste Reactivity Evaluation

Chemical method: Chapelle test

The pozzolanic reactivity of waste was measured according to the Chapelle test (Quarcioni et al., 2015). This is a standard test that measures the amount of portlandite (Ca(OH)₂) that the waste is capable of binding in an aqueous solution, as a measurement of the pozzolanic activity.

1 g of waste was mixed with 2 g of CaO and 250 ml of distilled, CO₂ free water. The suspension was shaken for 16 h at 90 °C in a water bath, and the free Ca²⁺ was dissolved with a saccharose solution and determined by means of titration with an HCl solution. Following this procedure, the consumption of CaO per gram of material was calculated according to Eq.3-1.

$$mg\ CaO\ per\ gram\ of\ material = \frac{112(v_3m_3-v_2)F_c}{m_4m_3m_2} \quad (Eq.3-1)$$

Where: m_2 = grams of pozzolanic material

m_3 = grams of CaO mixed with the pozzolanic material

m_4 = grams of CaO in the blank test

v_2 = milliliters of 0.1M HCl consumed by the sample solution

v_3 = millilitres of 0.1M HCl consumed by the blank test

F_c = correction factor for the 0.1M HCl standard solution

Mechanical method: Mechanical activity index

The mechanical activity index (MI) was used to indirectly measure reactivity as the ratio of the compressive strength of a waste-lime mortar to a standard lime mortar according to EN 450-1. The waste-lime mortar was made at a waste: lime: sand ratio of 1:1:3, while the standard lime mortar was made at a lime: sand ratio of 2:3 with the same water/binder ratio. The compressive strength was tested at 28 days with a Zwick loading machine in accordance with EN 459-2:2021.

3.2.4 Engineering Properties

Mixing, Casting and Curing

All the solids were mixed for 2 minutes. Subsequently, all the water was added and mixed for a further 5-10 minutes using a mechanical mixer. The fresh slurry was then cast into prismatic moulds sized 40x40x160 mm and covered with a layer of polyethylene to prevent the loss of moisture. The specimens were demoulded after 24 hours. They were cured at 20 ± 3 °C for 28 days.

Setting time

The setting times of geopolymer pastes were tested in accordance with EN 196-3:2016 using the Vicat apparatus.

Flowability

The flowability was measured using an initial flow table in accordance with EN 459-2:2021.

3.2.5 Mechanical Properties

The compressive and flexural strength of the geopolymers were measured with a Zwick loading machine according to EN 196-3:2016 after curing for 28 days. The mechanical properties were determined using averages from multiple replicate specimens: three for flexural strength and six for compressive strength.

3.2.6 Durability

Wet-dry cycle

A test method recommended by RILEM PEM-25 for wet-dry cycles was applied. The geopolymer was immersed in water at 20 °C for 16 hours, then placed in an oven at 105 °C to dry for 6 hours, followed by cooling for 2 hours. This cycle was repeated 15 times unless the cubes disintegrated before completing the cycles. The cubes were weighed after the final drying if they remained sufficiently intact. The compressive strength of the specimens was measured before and after the wet-dry cycles.

Sulphate attack

A test method recommended by RILEM PEM-25 for the sulphate cycle was applied. The geopolymer specimens were immersed in a 14% solution of sodium sulphate decahydrate for 2 hours at 20 °C, then placed in an oven at 105 °C to dry for 10-15 hours. This cycle was repeated 15 times unless the cubes disintegrated before completing the cycles. The cubes were weighed after the final drying. The compressive strength of the specimens was measured before and after the sulphate attack cycles.

High-temperature resistance

The specimens were incrementally heated to temperatures of 450°C, 600°C and 800°C, at a rate of approximately 10°C/min starting from room temperature. Upon reaching the target temperature, it was sustained for 60 minutes. Subsequently, the furnace was turned off, allowing the specimens to cool to room temperature within the furnace.

The residual compressive strength was measured after calcination. XRD, FTIR and SEM were applied to analyse the microstructure change after high-temperature calcination.

3.2.7 Environmental Impact

A cradle-to-gate life cycle assessment (LCA) was conducted to illustrate the environmental impact of geopolymer production. The functional units and system boundaries can be found in Section 9.1.

Chapter 4: Characterisation of Raw Wastes

Identification and understanding of the properties of the raw materials is the first step in developing geopolymers. In this chapter, the chemical, physical, and mineralogical properties of four selected solid wastes are characterized and compared to commonly used SCMs such as fly ash (FA) and ground granulated blast furnace slag (GGBS) to provide a more intuitive understanding.

4.1 THE PRINCIPLES OF WASTE SELECTION

Various waste materials were collected and characterized to assess their suitability as precursors for the development of geopolymers. Key factors such as safety, chemical composition, and stability were considered during the selection process.

Safety was the primary criterion, as certain wastes, despite having favorable chemical compositions, contained harmful substances. For instance, waste residues from silane production, although enriched with 58–75% amorphous SiO_2 , were deemed unsuitable due to the presence of potentially hazardous organic compounds.

In addition to safety, the chemical composition of the waste was critical. Wastes rich in silicon (Si) and aluminium (Al), particularly those with an amorphous mineral structure, were preferred for geopolymer development. Highly alkaline wastes, especially those rich in potassium (K) and calcium (Ca), were also evaluated for their potential to enhance the geopolymerization process.

The stability of the waste's composition and properties was another essential consideration. Variability in waste composition from batch to batch could lead to inconsistent geopolymer properties, rendering the waste unsuitable. For example, aluminium processing sludge (APS), collected from aluminium profile processing plants, showed significant variation in composition depending on the specific processes involved. While some batches were Al-rich and amorphous, others contained large amounts of Si and were semi-crystalline.

Ultimately, four waste types were selected based on their stable composition, high availability, and local production. These materials were further analyzed for their potential in geopolymer development and represent diverse waste streams with consistent characteristics.

4.2 SPENT FLUID CRACKING CATALYST (FCC)

The chemical composition and grading of the FCC are included in Table 4-1. The FCC is largely composed of SiO_2 and Al_2O_3 . When compared with other pozzolans and supplementary cementitious materials (Figure 4-1), the FCC displays high Al, moderate Si content and traces of Ca. The FCC composition is similar to metakaolin, both consisting of over 90% SiO_2 and Al_2O_3 . The chemical composition of the FCC exceeds the current chemical requirements for the use of pozzolans and cementitious materials in building standards (Table 4-2), implying

that the FCC has the potential to produce a highly active pozzolan. Also, the Mg and P_2O_5 contents are very low, hence meeting standard requirements (Table 4-2). The chemical composition of the spent FCC catalyst in this study agrees with others in the literature: 50 % of SiO_2 and 45 % of Al_2O_3 ; with the remaining 5 % distributed among other minor components (Gonzalez et al. 2016).

Table 4-1 Chemical composition and grading of the FCC.

Chemical composition (XRF)	wt%	Heavy metal content (ICP-OES)	ppm	Notes
SiO_2	41.7	V	634	
Al_2O_3	49.0	Ni	336	
Fe_2O_3	1.28	Co	30	
CaO	0.19	Cu	20	~trace
MgO	0.07	As	20	~trace
Na_2O	0.29	Zn	26	
K_2O	0.16	Cd	<0.5	trace
Cr_2O_3	0.04	Hg	1	trace
TiO_2	1.00	Tl	<10	trace
MnO	0.01	Pb	18	~trace
P_2O_5	0.26	Particle size distribution/specific surface area (laser diffraction)		
SrO	<0.01	D [3,2] particle size		66.9 μm
BaO	0.02	D [4,3] particle size		78.1 μm
Others	2.50	D ₅₀ particle size		72.3 μm
LOI at 1000 °C	3.70	Specific surface area		85.44 m ² /kg

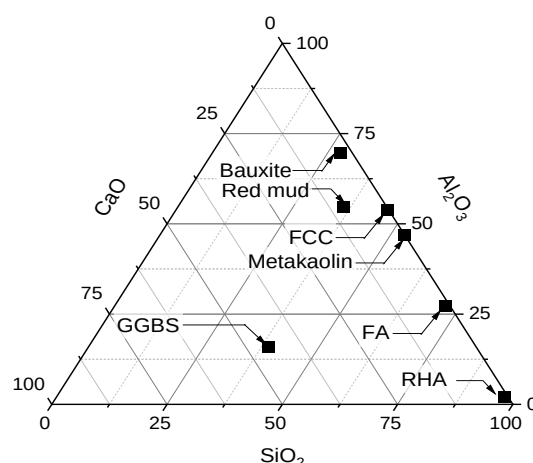


Figure 4-1 Chemical composition of the FCC waste, compared with some pozzolans and supplementary cementitious materials in Walker & Pavía (2011); Alelweet & Pavia (2022).

A study of the heavy metal content was carried out. Heavy metals are naturally occurring elements with many industrial applications. As a result, they are widely found in our environment, and this has raised concerns over their toxicity. Environmental contamination by heavy metals can occur through metal corrosion, atmospheric deposition, soil erosion and heavy metal leaching, contamination from water resources, industrial activity in metal processing, coal-burning power plants, petroleum combustion, nuclear power stations, high-

tension lines, plastics, textiles, microelectronics, wood preservation and paper processing plants (Tchounwou et al. 2012). Some of the metallic elements in FCC waste such as cobalt, copper, chromium, iron, magnesium, manganese and zinc, are essential nutrients required for physiological functions, but arsenic, cadmium, lead and mercury are considered toxic (Tchounwou et al. 2012). In the FCC studied, there are only traces (<10 ppm) of cadmium, mercury, thallium and lead, and arsenic is close to the tracing concentration (Table 4-1). Only nickel and vanadium are present in small amounts. These heavy metals entered the FCC from the petroleum feedstock during the catalyst process. The toxicity of vanadium is considered low, and only in certain compounds vanadium can become toxic. Evidence suggests that vanadium and vanadium compounds are not carcinogenic, and vanadium is not classified as carcinogenic by the Environmental Protection Agency (RAIS, 2020). Nickel is found naturally, and it is essential to plants. It is widely used in several industries such as alloys, stainless steel and batteries (electric vehicles). Nickel is not cumulative, but it is processed by the kidneys and removed from the body. Average daily exposure does not pose a threat to human health, but oral consumption or chronic inhalation may be toxic (Buttice 2015).

Table 4-2 FCC compliance with standard requirements for the use of FA, GGBS and natural pozzolans in concretes and other materials. All results in % by mass.

	$\Sigma \text{SiO}_2, \text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3$	SO_3	MgO	Cl^-	LOI	Total P_2O_5
EN 450 - FA requirements	≥ 70	≤ 3	≤ 4	≤ 0.10	< 5	< 5.5
ASTMC618-pozz.requirements	50-70	4-5	-	-	< 10	-
EN 15167-GGBS requirements	-	< 2.5	≤ 18	≤ 0.10	≤ 3	-
FCC	92	-	0.07	-	3.7	0.2
FA (Alelweet & Pavia 2020)	89	1.4	1.0	0.04	4.9	0.5
GGBS (Pavia & Alelweet 2021)	49-44	2.2	8	0.03	< 1	0.4

As indicated by the loss on ignition (LOI) test (Table 4-3), the FCC has low organic matter content probably due to the temperature at which the catalyst cracking process takes place. The catalyst cracking process occurs between 493 and 760°C (Marafi & Stanislaus 2008; Macaskie et al. 2010; Rodríguez et al. 2013).

Table 4-3 LOI of the FCC.

Temperature	% weight loss	Equivalence
0 to 105 °C	1.35	Water
105 to 550 °C	0.00	Organic material and water loss from clay minerals
550 to 950 °C	0.77	Release of $\text{H}_2\text{O}/\text{CO}_2$
Residue remaining after 950 °C	97.88	Oxide/silicate residue

The particle size distribution of the FCC is shown in Figure 4-2. The results show that it is coarser and more monogranular (lower spread of particle sizes) than other pozzolans and supplementary cementitious materials such as FA and GGBS. The close $D_{[3,2]}$ and $D_{[4,3]}$ values indicate that the FCC particles are regular and rounded.

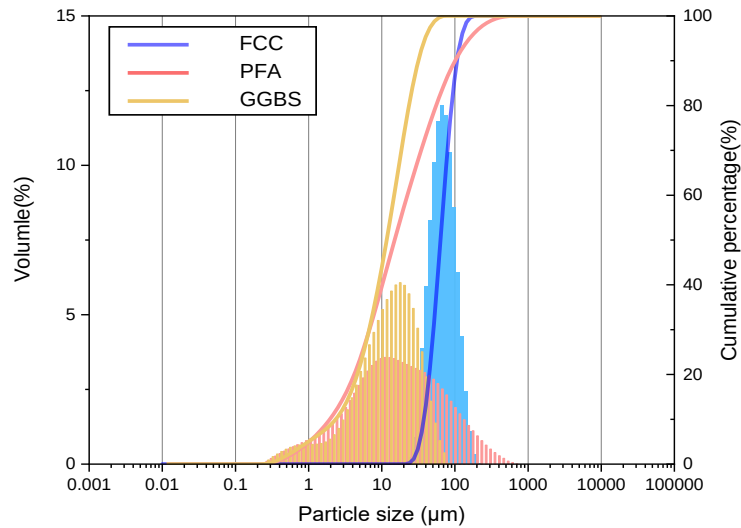


Figure 4-2. Particle size distribution of the FCC compared with FA and GGBS.

The SEM evidenced that the FCC particles tend to spherical shapes and that their size and shape are consistent (Figure 4-3), agreeing with the laser diffraction results. Further magnification reveals rough, porous surfaces of significant specific surface area- SSA. The SSA of the FCC particles is lower than other pozzolans and SCMs (Table 4-4). However, it is largely underestimated because the laser assumes that the particles are solid and spherical rather than very porous. Therefore, a correction factor of 2 is applied based on Gómez-Tena et al. (2014) who determined this factor, for rounded particles, based on experimental laser diffraction and BET (Brunauer, Emmett and Teller) measurements.

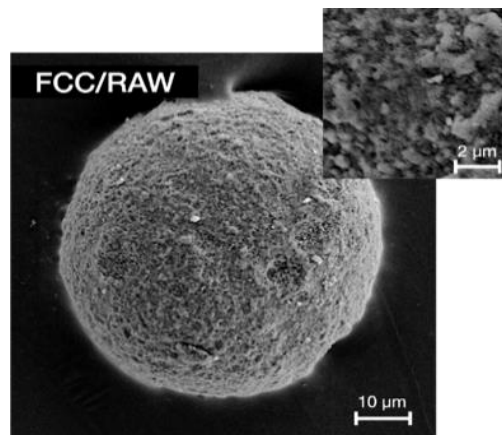


Figure 4-3 Shape and surface of the raw FCC particles.

Table 4-4 SSA of the FCC particles compared with other pozzolans and SCMs in * Alelweet & Pavia 2022; **Pavía et al. 2014

Material	Specific surface area (SSA) m ² /g
FCC	0.08 (laser value) 0.17 (with conversion factor)
Bauxite*	17.92
Red Mud*	9.35
GGBS*	1.95
FA*	6.50
CEM II*	1.88
RHA**	13.70

The main crystalline phase in the FCC is the zeolite faujasite (Figure 4-4 and Figure 4-5). As aforementioned, faujasite is a microporous aluminosilicate composed of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra. It has a high porosity and the ability to exchange intercluster ions, being considered at least as reactive as vitreous pozzolans (Pacewska et al. 2002). Two high-temperature aluminosilicate polymorphs, sillimanite and kyanite, were also identified (Figure 4-5). These are residues from the catalytic cracking process as they are used as active fillers during the process (Kolesnikov & Frolova 1982; Rodríguez et al. 2013). Traces of anatase (TiO_2) were also found. Anatase is added as an active phase to trap vanadium in order to prevent its passivating effect (Hernández-Beltrán et al. 2000).

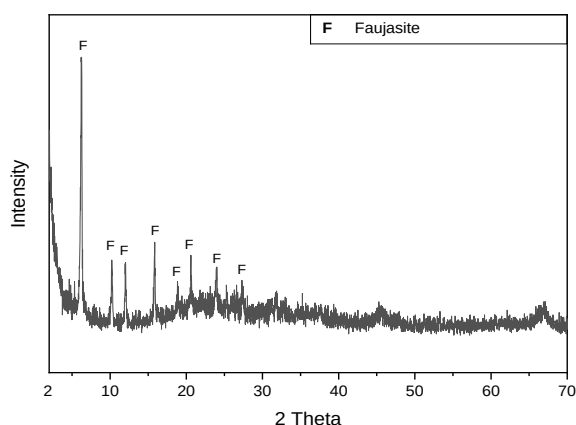


Figure 4-4 Mineral assemblage (main phases) in the raw FCC.

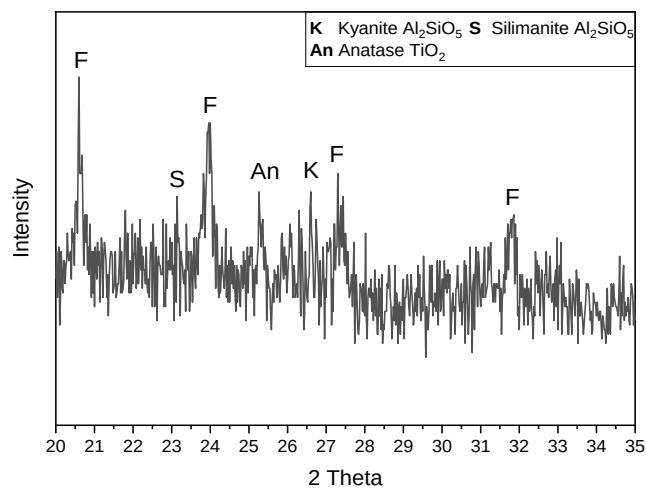


Figure 4-5 Subsidiary mineral phases in the raw FCC.

4.3 ALUM SLUDGE (AS)

As expected, the main component of the AS is aluminium (Table 4-5). The composition of the AS investigated is similar to the Irish AS, both with lower silica and iron than others worldwide (Table 4-5). It has a much lower Ca content than cements such as PC and CAC (Table 4-5). It can also be seen from Table 4-5, that European sludges have much higher Al_2O_3 than SiO_2 content, whereas, in South America and Asia, the silica is much greater.

Table 4-5 Chemical composition of the AS in this research compared with PC, CAC and other AS in the literature. XRF results are represented as wt% by oxide.

	AS investigated	AS Ireland (Lingl Laboratory Report L18-08, 2018)	AS York UK (Shamaki et al., 2021)	AS Zhengzhou China (Tie et al., 2010)	AS Colombia (Bohórquez González et al., 2020)	PC (Bohórquez González et al., 2020)	CAC (Hewlett & Liska, 2019)
SiO ₂	3.19	2.36	10.28	44.4	60.91	21	3-8
Al ₂ O ₃	28.30	35.50	44.24	33.7	19.72	5	36-42
CaO	0.17	0.99	2.50	7.73	1.48	64	36-42
Fe ₂ O ₃	1.03	1.04	2.51	5.50	11.59	3	12-20
K ₂ O	0.05	0.13	0.43	1.84	2.42	0.7	0.15
MgO	0.09	0.12	0.34	1.64	1.47	2	1
TiO ₂	0.03	0.04	0.16	0.58	0.96	<1	<2
SO ₃	<0.10	0.07	1.24	-	0.23	2.5	-
MnO	0.04	0.96	0.15	-	-	-	-
Na ₂ O	0.06	0.05	0.15	0.39	-	0.2	0.10
P ₂ O ₅	0.08	0.27	0.44	0.31	-	-	-
LOI %	66.10	58.50	36.4	-	-	-	-

With respect to the particle size distribution, the AS is slightly coarser than other pozzolans and supplementary cementitious materials such as FA and GGBS (Figure 4-6 and Table 4-6). The vast difference among D[3,2], D[4,3] and Dx(50) suggests that the AS particles are irregular conforming with the SEM analyses (Figure 4-7). The specific surface area (SSA) of the AS particles is high but lower than FA and GGBS.

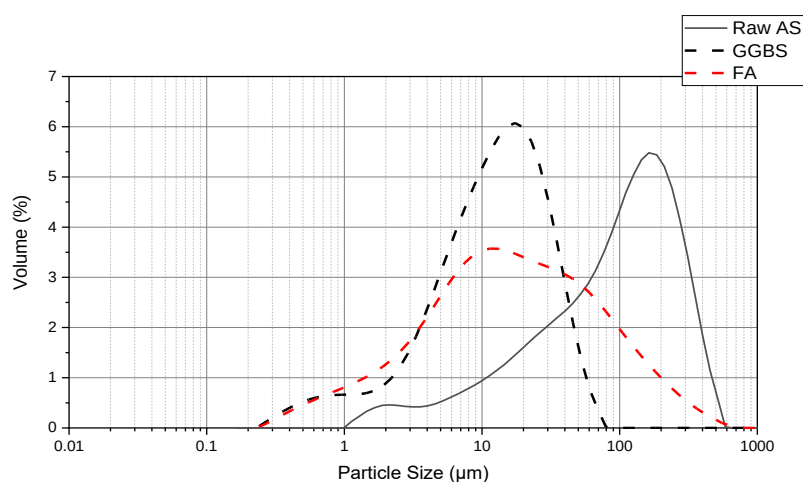


Figure 4-6 Particle size distribution of the raw AS as % by volume by laser diffraction.

Table 4-6 Specific surface area and particle size distribution* of the raw AS compared with FA and GGBS.

Notation	SSA	D [3,2]	D [4,3]	Dx (10)	Dx (50)	Dx (90)
AS Raw	0.22 m ² /g	26.1 µm	138 µm	12.6 µm	111 µm	307 µm
GGBS	1.34 m ² /g	4.49 µm	14.79µm	2.35 µm	11.67 µm	31.63 µm
FA	1.27 m ² /g	4.72 µm	38.48µm	1.95 µm	14.97 µm	100.64 µm

*:Results are represented as percentiles, where Dx (50) is the maximum particle diameter below which 50% of the sample volume exists.

According to the SEM analysis, the AS particles are irregular and angular (Figure 4-7), with high specific surface areas.

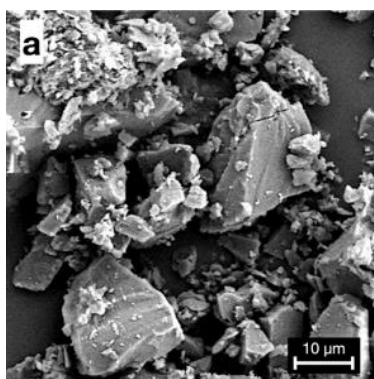


Figure 4-7 SEM micrographs of raw AS.

The XRD analyses (Figure 4-8) indicate that the raw AS is amorphous. The diffractograms show the typical characteristic of amorphous diffraction patterns: except for the sharp peaks of quartz crystals, there is only a gentle variation in the intensity of the scattered X-rays over the entire scan, the intensity decreases as the angle increases, gradually approaching the background value of the instrument at high angles. According to the Scherrer formula (Patterson, 1939), this phenomenon is due to the extreme fineness of the crystals which causes the diffraction peaks to broaden considerably, overlap and blur each other.

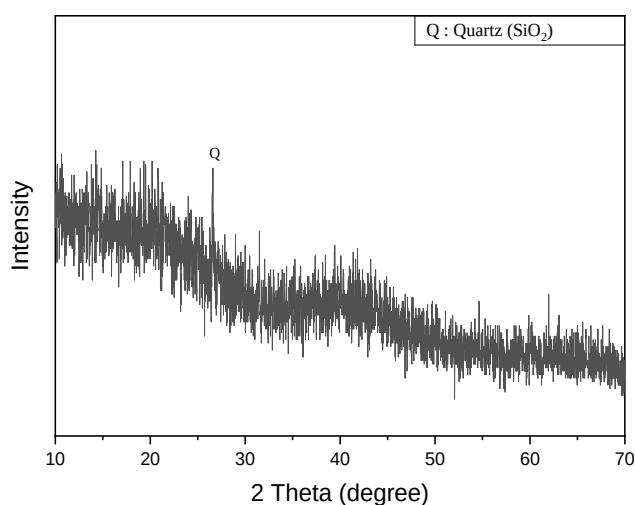


Figure 4-8 X-Ray Diffractogram of raw and calcined AS.

The loss on ignition (LOI) test evidenced that the major weight loss of the raw AS occurs between 105 and 550 °C, at 54.6% (Table 4-7) due to the volatilisation of organic matter. However, a minor weight loss is owed to the dehydroxylation of the Al hydroxides. According to Tantawy (2015), the dehydroxylation of Al(OH)₃ to boehmite AlOOH begins at 258°C and peaks at 489 °C. The weight loss between 550 and 950°C (34.5%) is probably due to further dehydroxylation which begins above 587°C and peaks at 625°C, during which boehmite is converted to Al₂O₃ (Tantawy, 2015). The large LOI of AS can adversely impact its reactivity.

Table 4-7 LOI of the raw AS.

Temperature	% weight loss	equivalence
0 to 105°C	8.0	Water
105 to 550°C	54.6	organic material and (minor) water loss from clay minerals
550 to 950°C	2.9	release of H ₂ O due to dehydroxylation
Residue remaining after 950°C	34.5	oxide/silicate residue

4.4 CROP BIOMASS ASH (CBA)

The chemical composition of CBA analysed by XRF appears in Table 4-8. CBA is composed of SiO₂ (68.40%), Al₂O₃ (12.85%) and Fe₂O₃ (5.01%). The presence of alkali metal oxides within the CBA is relatively low, accounting for less than 5% of the composition. The alkali content may be underestimated due to agglomeration. According to Niu et al. (2016), K, Na, and C display a propensity to nucleate and aggregate, forming submicron particles that subsequently condense in the ash.

The CBA ash exhibits a deficiency in phytonutrients including calcium, magnesium, sodium, potassium and phosphorus which limits the recycling potential of CBA in agricultural contexts. Few European countries have established regulations or recommendations pertaining to the utilization of ash as fertilizer. For instance, Finnish legislation mandates that ash used as fertilizer must possess a total phosphorus and potassium concentration exceeding 2%, while the calcium content should amount to at least 6% (Huotari, 2012; López et al., 2018). Consequently, CBA does not appear to hold promising prospects for reuse within agricultural applications.

Table 4-8 Chemical composition of CBA by XRF as wt% by oxide.

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Cr ₂ O ₃	TiO ₂	P ₂ O ₅	SrO	BaO	LOI
68.40	12.85	5.01	1.75	1.24	1.86	3.57	0.01	0.75	0.38	0.02	0.07	3.63

Furthermore, an assessment of element concentrations was conducted through inductively coupled plasma optical emission spectrometry (ICP-OES) as detailed in Table 4-9. Elements with pronounced biotoxicity including mercury (Ag), cadmium (Cd), lead (Pb), chromium (Cr) and arsenic (As) exhibit exceedingly low concentrations. As per information provided by the supplier, the CBA originates from the combustion of corn stover and rice husk. Research findings by Duan et al. (2021) indicate that the root system of maize has the capacity to mitigate the mobilization of heavy metals towards the stem. Moreover, even when grown in polluted soil, the concentration of heavy metals does not pose a potential non-carcinogenic risk to human health. Similarly, the work of Liu et al. (2007) attested to the low accumulation concentration of heavy metals within the husk and stem of crops. Hence, it

can be inferred that ash originating from these crops holds a safe profile in terms of heavy metal content.

Table 4-9 Chemical composition of CBA by ICO-OES.

Element	Unit	Concentration	Element	Unit	Concentration
Ag	ppm	<0.2	Li	ppm	10
As	ppm	9	Mo	ppm	<1
B	ppm	10	Ni	ppm	18
Ba	ppm	170	Pb	ppm	16
Be	ppm	0.9	S	%	0.01
Bi	ppm	2	Sb	ppm	<2
Cd	ppm	<0.5	Sc	ppm	7
Co	ppm	10	Sr	ppm	65
Cr	ppm	32	Th	ppm	<20
Cu	ppm	13	Tl	ppm	<10
Fe	%	2.38	U	ppm	<10
Ga	ppm	10	V	ppm	47
Hg	ppm	1	W	ppm	<10
La	ppm	20	Zn	ppm	56

The particle size distribution analysed by laser diffraction of CBA and GGBS is included in Figure 4-9. The average particle sizes D_{50} of CBA and GGBS were $62.3 \mu\text{m}$ and $11.7 \mu\text{m}$. The specific surface areas of CBA and GGBS were evaluated as 317.5 and $1340 \text{ m}^2/\text{kg}$.

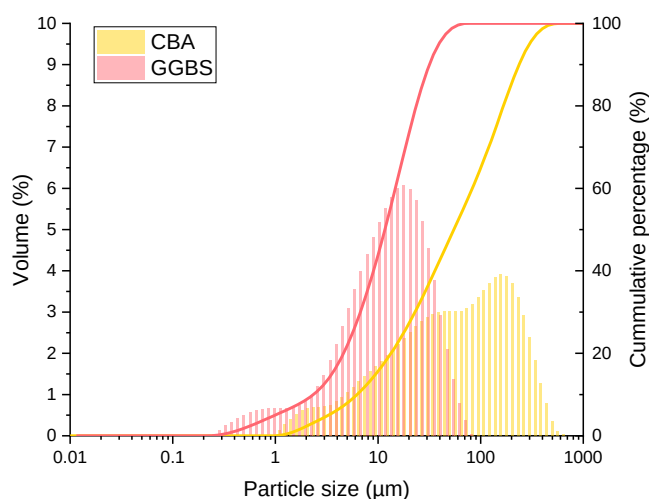


Figure 4-9 Particle size distributions of CBA and GGBS.

As it can be seen from the SEM analyses (Figure 4-10), the CBA particles are porous and irregular. A notable vascular structure was observed in some of CBA particles, and other particles with a smooth surface are likely to be unburned biomass. The structure of a CBA particle which was thermally treated under 600°C to eliminate the unburned carbon shows a fragile and porous framework with increased specific surface area (Figure 4-11).

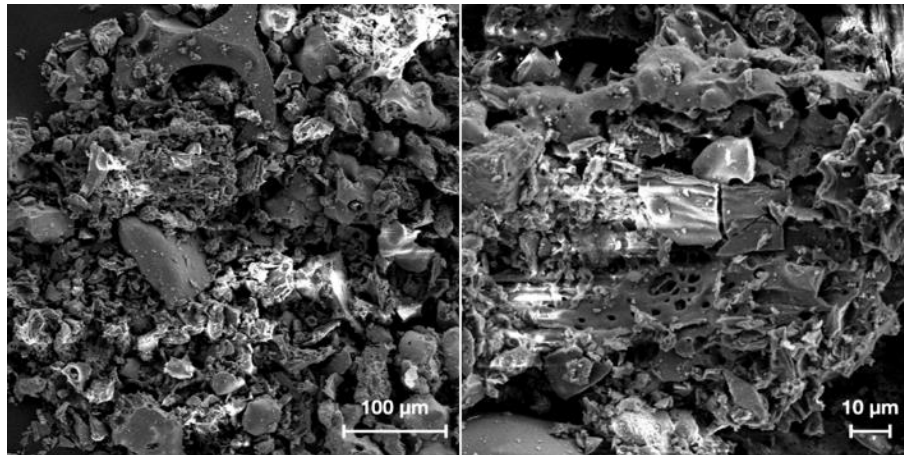


Figure 4-10 SEM micrograph of CBA powders.

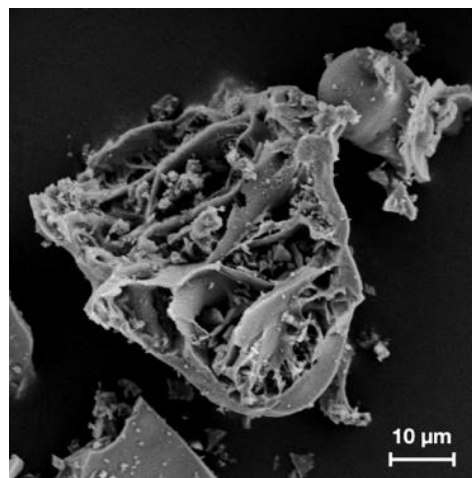


Figure 4-11 SEM micrograph of CBA thermal treated under 600 °C.

The mineral composition of the CBA was examined with X-Ray Diffraction. The results appear in Figure 4-12. Quartz and albite are the main crystalline phases detected in the CBA powder. Quartz and albite are widely found in various biomass ash and were considered to be due to fuel and soil contaminants (Boström et al., 2012; Wang et al., 2012). A hump centred at $25^\circ 2\theta$ indicates the presence of an amorphous phase.

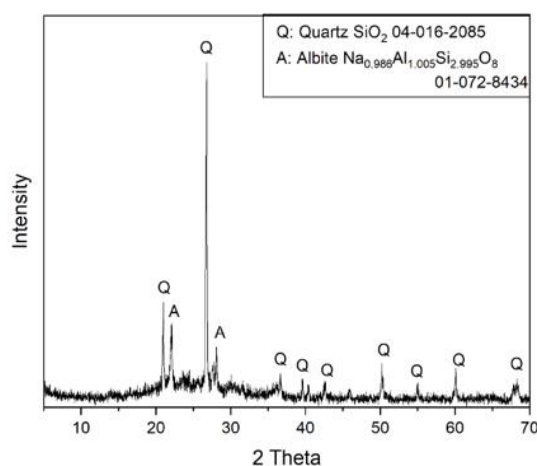


Figure 4-12 Mineral composition of CBA.

The loss on ignition (LOI) results appear Table 4-10. The CBA has LOI of 3.87% at 1000 °C. The main weight loss which occurred between 105 °C and 450 °C, represents the mass loss due to oxidation of unburnt biomass. As indicated by the XRD pattern shown in Figure 4-12, the main crystalline phases in CBA, quartz and albite, are stable at high temperature up to 1200 °C, they hardly contribute to weight loss at high temperatures (Feng et al., 2012).

Table 4-10 Loss on ignition of CBA powder.

Temperature	Weight loss
0-105 °C	0.80%
105-450 °C	3.31%
450-600 °C	0.25%
600-800 °C	0.31%
800-1000 °C	0.00%
Total (105-1000 °C)	3.87%

4.5 OLIVE-PITS BIOMASS ASH (OBA)

The chemical composition of the OBA appears in Table 4-11. As it can be seen from this table, it compares well with others in the literature, with the main constituents being CaO and K₂O. In comparison to other OBAs, the SiO₂ and Al₂O₃ contents are relatively low. The $\Sigma SiO_2 + Al_2O_3 + Fe_2O_3$ is far below the 70% standard pozzolanic activity requirement in ASTM C618-22. Therefore, it is assumed that the OBA has negligible pozzolanic activity.

Table 4-11 Chemical composition of the OBA compared with others in the literature. * LOI at 950 °C.

Reference	This research	de Moraes Pinheiro et al., 2018	Alonso et al., 2019	Eliche-Quesada & Leite-Costa, 2016	Rosales et al., 2022	El Boukili et al., 2022
Source	Spain	Spain	Spain	Spain	Spain	Morocco
SiO ₂	5.26	5.33	23.61	10.88	33.91	44.00
Al ₂ O ₃	0.73	0.70	5.41	1.68	6.62	7.14
CaO	19.95	27.77	20.61	13.07	31.71	19.29
Fe ₂ O ₃	2.48	3.45	6.12	1.38	3.02	3.26
Na ₂ O	0.43	0.78	1.29	0.13	0.34	-
MgO	3.87	5.13	6.02	1.92	5.05	3.46
K ₂ O	23.00	32.12	17.31	38.01	15.37	2.58
P ₂ O ₅	4.91	2.68	4.40	3.67	3.05	0.03
SO ₃	-	1.67	0.80	1.40	-	0.80
LOI	27.9*	18.90	13.40	25.53	-	18.90

The particle size distribution of the raw OBA appears in Figure 4-13. The OBA is slightly coarser than the GGBS. The average particle size $D_{[50]}$ of OBA is 45.9 μm while the GGBS reached 11.67 μm . Both the ash and the slag particles feature vast specific surface areas. The specific surface area of the ash is 422.8 m^2/kg measured with laser diffraction. However, the laser value requires a correction factor (X4) because the laser presumes that the ash particles are solid and spherical (Gómez-Tena et al. 2014). This results in a SSA of 1691 m^2/kg for the ash. The SSA of the GGBS is 1340-1950 m^2/kg (measured with BET).

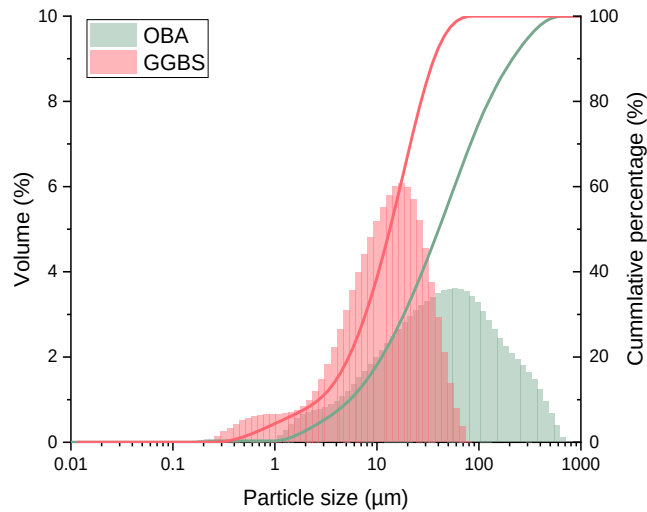


Figure 4-13 Particle size distribution of the OBA and the slag.

The SEM analyses (Figure 4-14) show that the OBA consists of irregular particles of varying sizes and high specific surface area with occasional coarse agglomerates. There are also some smooth surface particles of higher density and lower porosity. Detailed analyses (Figure 4-14b) revealed a porous nature, similar to other biomass bottom ashes (Assad Munawar et al., 2021; Ondrasek et al., 2021).

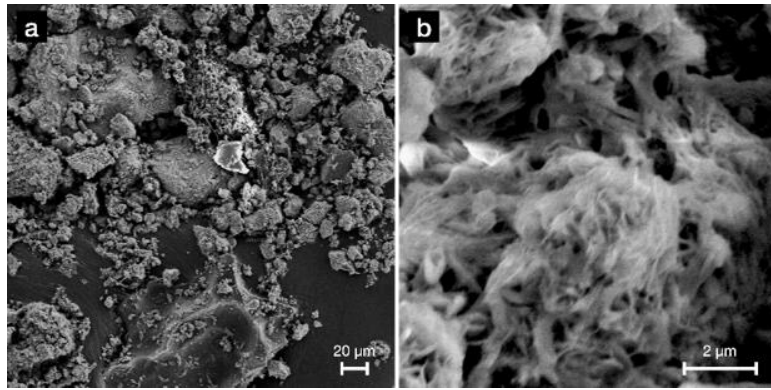


Figure 4-14 Representative SEM micrographs of OBA: a) general; b) detail.

The OBA contains biochar (C), unburned biomass ($C_xH_yO_z)_n$ and carbonate (M_2CO_3). To evaluate the total carbon in the OBA, a modified loss on ignition (LOI) test is proposed as shown in Figure 4-15(a). The standard LOI test procedure is given in Figure 4-15(b) as a reference.

The modified method involves calcining the OBA at 600°C, for 6 hrs in a reducing atmosphere, to remove moisture and convert the biomass into pure C (or coke). The reducing atmosphere prevents the C to evolve as CO_2 . Therefore, the weight loss Δm_1 is due to the release of O, H and some C in the biomass' organic components. The resultant OBA was then calcined in an oxidising atmosphere for 6 hours to eliminate all the coke contained therein. Therefore, the weight loss Δm_2 is the total carbon content in the biochar and unburnt biomass. The OBA was finally calcined at 800°C, in the same conditions, and the weight loss (Δm_3) attributed to carbonate decomposition.

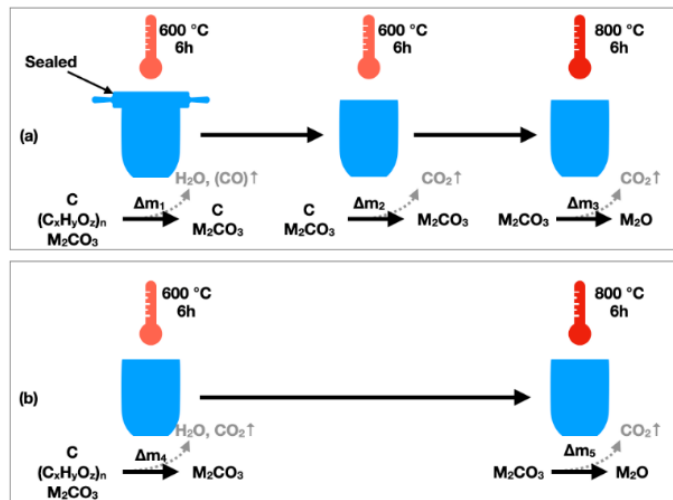


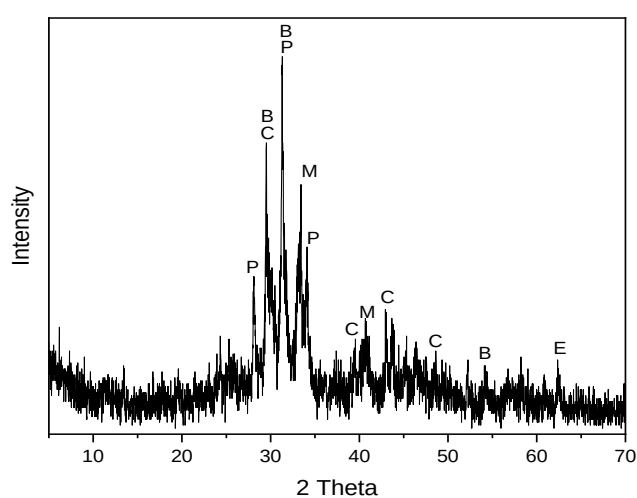
Figure 4-15 (a) Modified loss on ignition (LOI) test procedure. (b) Standard LOI test procedure.

Table 4-12 presents the LOI of the OBA. Between 105°C and 600°C, it lost 21.87% of its initial mass. According to Fernandez et al. (2016), the pyrolysis of olive pits occurs between 473K (199.85 °C) and 823K (539.85 °C). Therefore, the weight loss between 105 and 600°C is attributed to the combustion of unburned particles and organic matter.

Table 4-12 Loss on ignition of the OBA

Temperature	Weight loss	Equivalent
105 °C – 600 °C	21.87%	Δm_1 (reducing atmosphere): 12.30% Δm_2 (oxidising atmosphere): 9.57%
600 °C – 800 °C	7.68%	Decomposition of carbonates
800 °C – 1000 °C	12.92%	Decomposition of carbonates and silicates
Residue	57.53%	Oxides

The mineral composition of the OBA appears in Figure 4-16. It comprises mainly carbonates (calcite, butshliite) and potassium calcium magnesium phosphate. Calcium and magnesium silicates (merwinite and enstatite) are also present.



P: Potassium Calcium Magnesium Phosphate $\text{KCa}_9\text{Mg}(\text{PO}_4)_7$ [PDF 04-017-5717]

C: Calcite CaCO_3 [PDF 00-047-1743] **E:** Enstatite MgSiO_3 [PDF 04-009-8359]

B: Butshliite $\text{K}_2\text{Ca}(\text{CO}_3)_2$ [PDF 00-025-0626] **M:** Merwinite $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$ [PDF 04-011-6738]

Figure 4-16 Mineral composition of the OBA

4.6 SUMMARY

In this section, four types of wastes have been characterised.

FCC primarily consists of 41.7% SiO_2 and 49.0% Al_2O_3 , making it a promising precursor for developing geopolymer. It is mineralogically semi-crystalline, with the zeolite faujasite as its main crystalline component. Zeolites are generally considered the most reactive pozzolans. FCC particles are nearly spherical with a porous structure and a large surface area, which favours their reactivity.

AS has a very high organic matter content, as indicated by an extremely high LOI (66.1%). This organic matter is expected to interfere with geopolymerization, necessitating further treatment. AS also has a high Al content, likely in the form of amorphous $\text{Al}(\text{OH})_3$, which dehydroxylates during heating, impacting chemical properties and activity. Therefore, pyroprocessing may be a promising method for treating AS.

CBA is primarily composed of SiO_2 (68.4%) and Al_2O_3 (12.85%). It is highly crystalline, with quartz and albite as the main crystalline components. This high crystallinity may adversely affect reactivity. Further treatment is required to increase its reactivity.

OBA consists of K_2O (23.0%) and CaO (19.95%), with a LOI of 27.9%. Due to its low Si and Al content, it may not be a suitable precursor for geopolymer development. However, its high alkali content implies potential for use as a low-carbon activator. Modified LOI tests indicate that OBA contains a significant amount of unburned carbon, suggesting that using this material for geopolymer preparation could sequester carbon, leading to the production of low-carbon geopolymer. OBA has a complex mineralogical composition and a semi-crystalline structure, with the main components being crystalline carbonates of Ca and K.

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Chapter 5: Treatment and Reactivity of Wastes

The reactivity of waste is crucial for its application as SCMs and precursors. Increasing the reactivity of wastes facilitates geopolymerization and pozzolanic reaction; therefore, various treatments aimed at enhancing the reactivity of wastes are investigated in this chapter. Reactivity is examined using chemical and mechanical methods based on the reaction of the waste with hydrated lime which provide valuable data on initial reactivity and allow to rate the waste in relation to standardised SCMs and other pozzolanic materials. This is a critical measure of the potential of wastes as precursors and allows for an initial screening of the materials.

5.1 SPENT FLUID CRACKING CATALYST (FCC)

As aforementioned, FCC is semi-crystalline, hence it was treated to improve its reactivity. This section intends to optimise FCC activity by increasing particle reactions using adequate activation procedures which are proposed and carried out based on the characteristics of the FCC. The reactivity of FCC after calcination, oxidation, acid etching and alkaline fusion is measured with chemical and physical methods. The tests are conducted in a lime system because it is a simpler chemical system, where reactions are well known and can be better followed, and research variables are controlled. However, the results apply to both lime and PC systems because pozzolanic and supplementary cementitious materials (SCMs) react with lime, either added in the paste or released on PC clinker hydration.

The mixing design and treatments used appear in Table 5-1. The notation is based on the FCC's treatment. Numbers denote the temperature of calcination while H_2O_2 and HCl denote the oxidizing and acid etching treatments respectively. Two different alkali-fusion methods were employed using sodium carbonate (NC) and sodium hydroxide (NH).

Table 5-1 Mix design for the strength test. The setting time, XRD and SEM specimens are the same mixes without sand. ** Water / binder: The binder includes FCC and CL90s.

Notation	Treatment	Composition				
		FCC	CL90s	Sand	Water	w/b**
FCC/raw	None	1	1	3	1.5	0.75
FCC/300	Calcination at 300 °C for 2h	1	1	3	1.5	0.75
FCC/400	Calcination at 400 °C for 2h	1	1	3	1.5	0.75
FCC/500	Calcination at 500 °C for 2h	1	1	3	1.5	0.75
FCC/600	Calcination at 600 °C for 2h	1	1	3	1.5	0.75
FCC/700	Calcination at 700 °C for 2h	1	1	3	1.5	0.75
FCC/800	Calcination at 800 °C for 2h	1	1	3	1.5	0.75
FCC/H ₂ O ₂	Oxidation with 15% H ₂ O ₂ for 24h	1	1	3	1.5	0.75
FCC/HCl	Etching with 0.1N HCl for 24h	1	1	3	1.5	0.75
FCC/NC	Fusion with 20%Na ₂ CO ₃ at 600 °C for 2h	1	1	3	1.8	0.90
FCC/NH/450	Fusion with 15%NaOH at 450 °C for 2h	1	1	3	1.5	0.75
FCC/NH/600	Fusion with 15%NaOH at 600 °C for 2h	1	1	3	1.5	0.75
Lime/0.75	-	0	2	3	1.5	0.75
Lime/0.90	-	0	2	3	1.8	0.90

5.1.1 Characterization of Treated FCC

Zeolites undergo structural changes when calcined including (i) removal of water and/or organic molecules; (ii) transformation into a metastable phase; (iii) structural collapse and (iv) amorphization (Cerqueira et al. 2008). However, the XRD evidenced that no significant changes take place in the mineralogy of the FCC up to 800°C (Figure 4-4). This agrees with (Li and Rees 1986) who demonstrated that, despite its open structure, faujasite is extremely stable at high temperatures up to 900-1000°C.

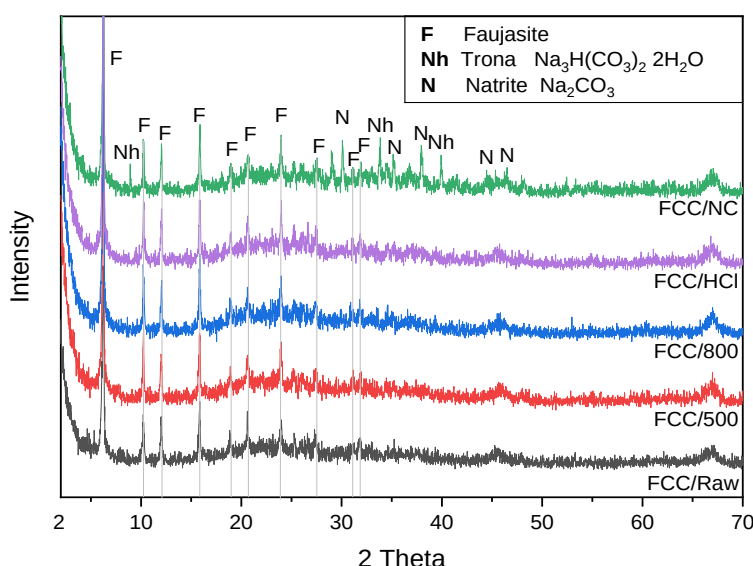


Figure 5-1 Mineral assemblage (main phases) in the raw, calcined and etched FCC.

As it can be seen from Figure 5-2, fusion with Na_2CO_3 at 600°C (FCC/NC/600) produces sodium carbonates natrite (Na_2CO_3) and trona (NaHCO_3) which coexist with faujasite indicating that the fusion between the zeolite and the carbonate did not take place during the treatment. This is due to the melting point of sodium carbonate (c. 820°C , Newkirk and Aliferis, 1958) being greater than the calcination temperature (600°C). This agrees with Feng et al. (2012) and Choi et al. (2019) stating that the calcination temperature needs to be far beyond the melting point of Na_2CO_3 for the carbonate to break and the resulting Na^+ and CO_3^{2-} to react with the pozzolan.

In contrast, fusion with NaOH , at both 450 and 600°C , altered the mineral composition of the FCC (Figure 5-2). At 450°C , the FCC has become totally amorphous, and the characteristic peaks of the zeolite have disappeared. At 600°C , part of the amorphous phase has transformed into crystalline sodium aluminium silicate ($\text{Na}_{1.15}\text{Al}_{1.15}\text{Si}_{0.85}\text{O}_4$, N-A-S). The FCC has reacted with NaOH , probably due to the hydroxide's melting point (c. 320°C) being lower than the calcination temperature: the Na^{2+} and OH^- released from the NaOH during fusion have collapsed and disordered the faujasite crystals, part of which later reorganise to form crystalline sodium aluminium silicate.

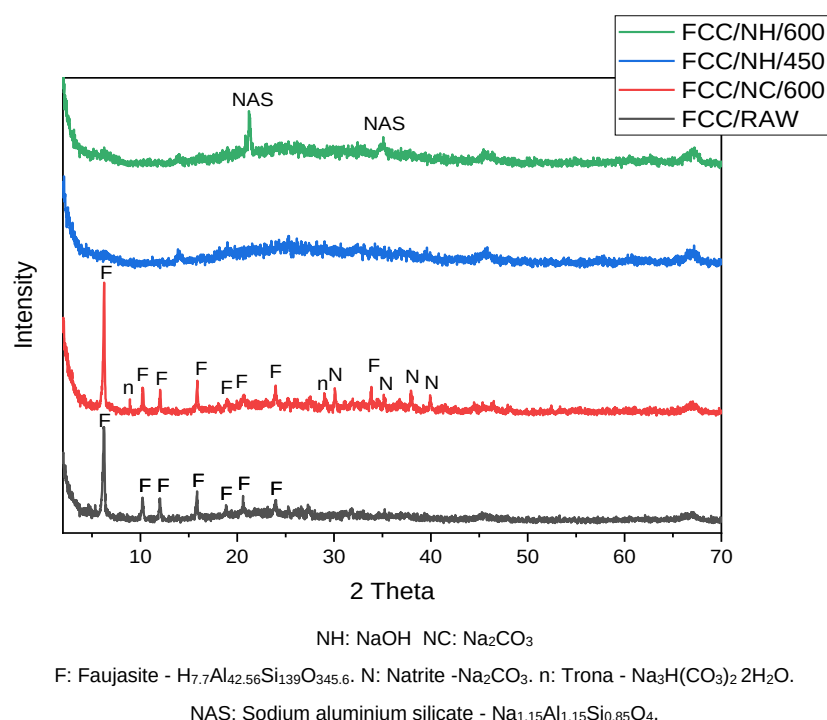


Figure 5-2 Mineral assemblage of the alkali-fused FCC.

Physical changes were evidenced with the SEM. Oxidation considerably increased surface roughness (Figure 5-3a) probably due to the removal of surface coke. Oxidation can remove organic compounds from FCC particles, mostly coke generated during the cracking process (Vaičiukynienė et al. 2015). Acid etching smothered the rough FCC particles (Figure 5-3b). This generally agrees with Shi and Day (2001), who report that acid treatment can dissolve pozzolans and form a gel on their surface. However, the SEM showed no new-formed gels on the etched surfaces, agreeing with the XRD results showing no changes in the mineralogy of the acid-etched FCC. Calcination at 800°C smothered the surface (Figure 5-4), and the macropores in the raw FCC are no longer evident at 800°C .

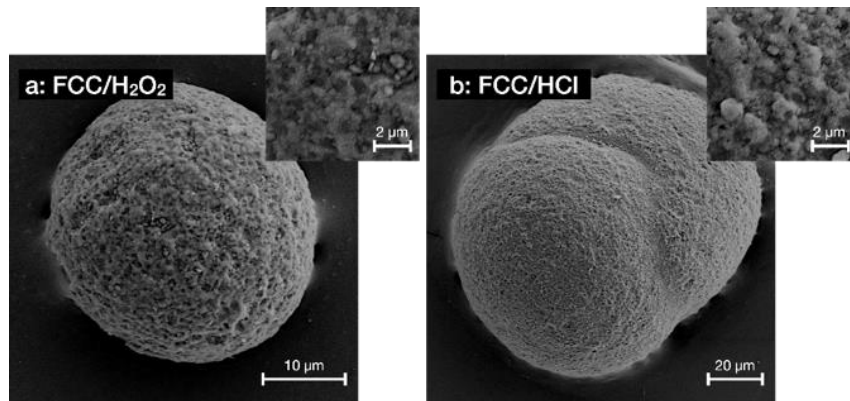


Figure 5-3 SEM micrographs of (a) oxidised, (b) HCl-etched FCC particles.

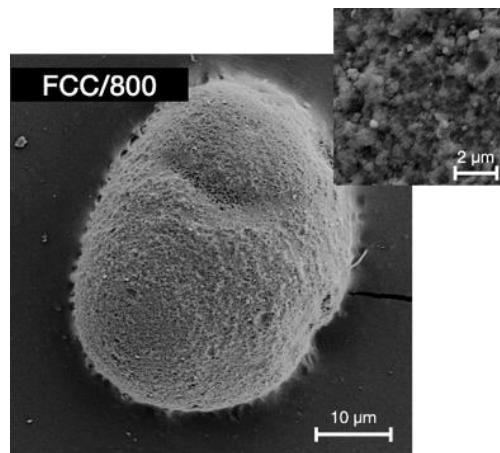


Figure 5-4 SEM micrograph of FCC particles calcined at 800 °C.

5.1.2 Reactivity by the Chapelle Test

All the FCCs consume significant Ca^{2+} (Figure 5-5) indicating high early dissolution rate and high pozzolanic activity. The acid-etched FCC displays the highest consumption, hence the strongest pozzolanic activity, while the oxidised FCC has the lowest. The alkali-fused FCC was not tested as the unreacted CO_3^{2-} and/or OH^- produced during alkaline fusion would interfere with the results.

Calcination does not significantly impact the early reactivity of the FCC (Figure 5-5), but the highest calcination temperatures (700-800°C) slightly lower Ca^{2+} consumption, probably due to the partial collapse of the FCC particles (smoother particle surfaces and disappearance of macropores, determined with SEM - Figure 5-4) lowering the SSA. Tseng et al. (2005) state that FCC particles collapse when calcined, and that pore channels break, pores close and the SSA declines lowering reactivity.

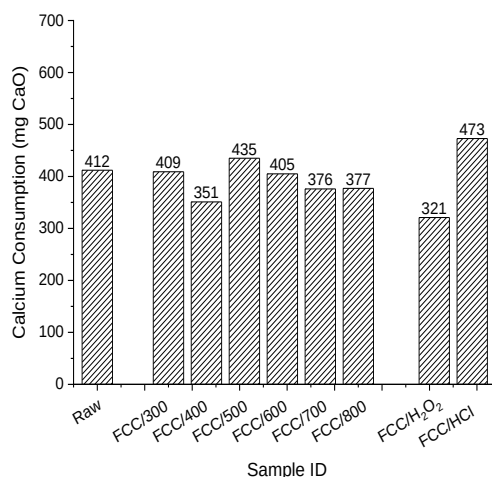


Figure 5-5 Ca²⁺ consumption of the raw and treated FCC.

Oxidation lowers early pozzolanic activity. This disagrees with Abubakar et al. (2020) and Vaičiukynienė et al. (2015) who regard oxidation as an efficient method for removing coke (deposited on FCC during catalytic cracking) and increase reactivity. The FCC in this study contains little organic matter (only 1% wt loss between 105 and 950°C) hence oxidation did not show a significant beneficial effect on activity.

The results show that HCl-etching enhances early activity. Shi and Day (2001) state that HCl etching can form a silica gel on the pozzolan surface that increases reactivity.

When compared with other pozzolanic materials tested with an identical method (Table 5-2), the FCC shows early activity comparable to fly ash (FA), red mud (RM) and bauxite. Despite the coarse spheres comprising the FCC, the FCC particles bind as much Ca²⁺ in pozzolanic reactions as highly reactive Al-based materials of layered structures such as RM and bauxite.

Table 5-2. Comparison of pozzolanic activity based on the Chapelle test. *Alelweet et al. 2021; **Alelweet & Pavia 2022.

Notation	Treatment	Ca ²⁺ Consumption mg CaO / g of pozzolan
FCC/Raw	none	412
FCC/500	Calcination at 500 °C	435
FCC/HCl	HCl etching	473
RM/Raw*	none	190
RM/400*	Calcination at 400 °C	346
FA*	none	431
Bauxite**	none	525
Bauxite**	Calcination at 300 and 550°C	635/1034

5.1.3 Reactivity by the Mechanical Activity Index (MI)

In all cases, the MI is much greater than 1, indicating high pozzolanic activity (Figure 5-6). The MI results show that FCC has high reactivity, superior to pozzolans such as FA, red mud and

RHA but lower than metakaolin (Table 5-3). The MI of the alkali-fused FCC is comparable to GGBS.

The HCl-etched FCC has a slightly lower MI, possibly due to the loss of some active Al and Si through dissolution into the acid solution. Calcination does not significantly alter the MI which slightly fluctuates as the temperature increases agreeing with the Chapelle test and mineralogy results. Oxidation does not alter the MI as, due to the lack of carbon in FCC, the oxidation treatment had little impact on the FCC's activity.

Alkali fusion greatly enhanced the MI which achieved high values of 22-24, in particular NaOH-fusion at 600°C (FCC/NH/600). This treatment broke down the zeolite structure and generated a reactive amorphous phase and sodium aluminium silicate (N-A-S, Figure 5-2) which are responsible for the high MI (24). NaOH-fusion at 450°C (FCC/NH/450) which also broke and amorphized the faujasite (Figure 5-2) provided a similar, slightly lower MI (22). This suggests that the hydration of the N-A-S (only present at the highest fusion temperature) slightly contributes to strength up to 28 days. The high MI (23) of the carbonate-fused FCC (FCC/NC/600) is due to the presence of carbonates forming a calcite binder that increases density and strength.

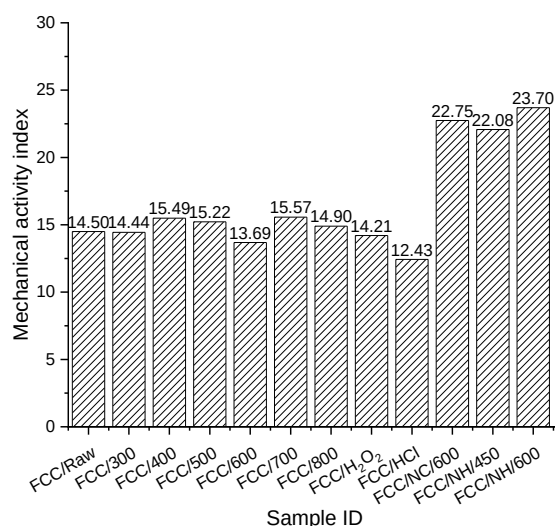


Figure 5-6 Mechanical activity index of the FCC mortars

Table 5-3. MI of the FCC compared with other pozzolanic and cementitious materials. * Walker & Pavía 2011; ** Alelweet et al. 2021

	FCC/ Raw	FCC/NH/600	GGBS*	FA*	Metakaolin*	RHA*	Red Mud**
MI	14.5	23.7	29.5	3.4	38	12	6-8

5.1.4 Composition of the cements in the FCC-lime Pastes

In the raw and calcined FCC specimens, the XRD evidenced that the cements include monocarboaluminate (Calcium Aluminium Oxide Carbonate Hydrate, $\text{Ca}_4\text{Al}_2\text{O}_6\text{CO}_3 \cdot 11\text{H}_2\text{O}$) and minor calcite (Figure 5-7) while the SEM/EDX shows semi-amorphous gels and plate C-A-H crystals in dense matrices (Figure 5-8 and Figure 5-9). The calcite cement is scarce because the Ca^{2+} from the lime has combined with aluminium to form carboaluminates. The

silica in the zeolite has formed hydrates (C-S-H /C-A-S-H) which are clear from the SEM/EDX results but do not appear in the XRD analyses probably due to their low crystallinity and scarcity. Monocarboaluminates belong to the group of AFm phases and are relatively common in Al-rich systems containing carbonate. According to Lothenbach et al. (2008) and Moon et al. (2012) monocarboaluminates have a high bulk modulus that can improve the strength of the cement matrix by lowering porosity.

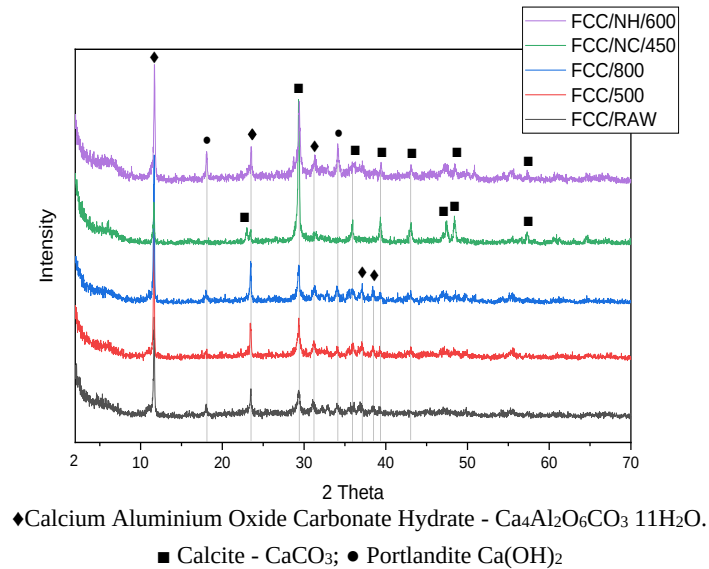


Figure 5-7 Mineral composition of the cementing phases in the FCC-lime pastes at 28d.

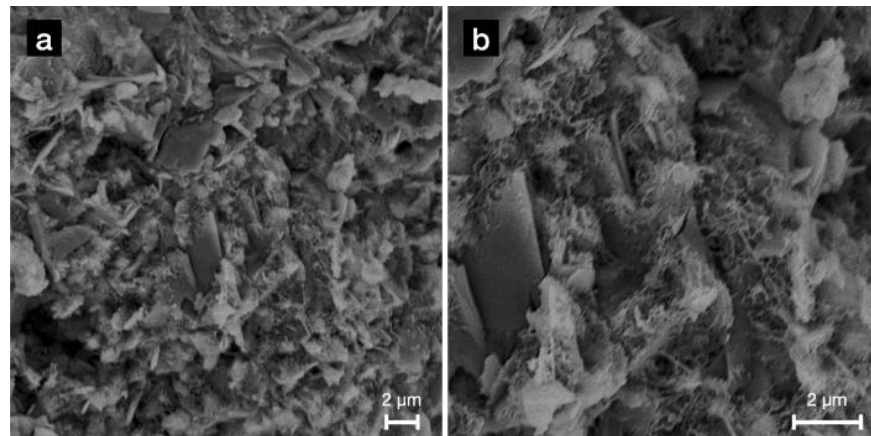


Figure 5-8 Cementing phases in the pastes made with calcined FCC (FCC/400): (a) general (b) detail of hydrates with plate and gel structures.

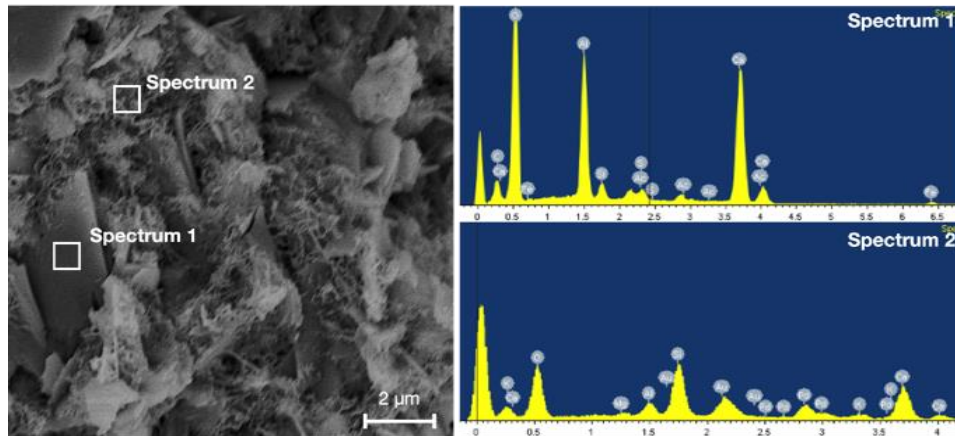


Figure 5-9 Elemental composition of the cements in Figure 5-8: hexagonal calcium carboaluminate hydrates (spectrum 1) and C-S-H cements (spectrum 2).

In the carbonate-fused FCC, the XRD analyses indicate that calcite is the dominant cementing phase mixed with some carboaluminates. The excess CO_3^{2-} has combined with the free Ca^{2+} to form calcite. The SEM/EDX analyses show a cement of N-A-S-H gel mixed with abundant euhedral calcite (Figure 5-10). The SEM also evidenced unreacted FCC (Figure 5-10a) agreeing with the results above showing that the carbonate didn't react with the FCC during the fusion due to the fusion temperature being below the carbonate's melting point.

This great difference in the nature of the cements of the raw/calcined and the carbonate-fused FCC explains their difference in strength. The dominant calcite cement in the carbonate-fused FCC filled space quickly, improving the 28-day strength while, in the raw and the calcined FCC pastes, the C-S-H (or C-A-S-H) cements formed slowly due to the relatively slow dissolving rate of the zeolite contributing to the strength growth in the long term.

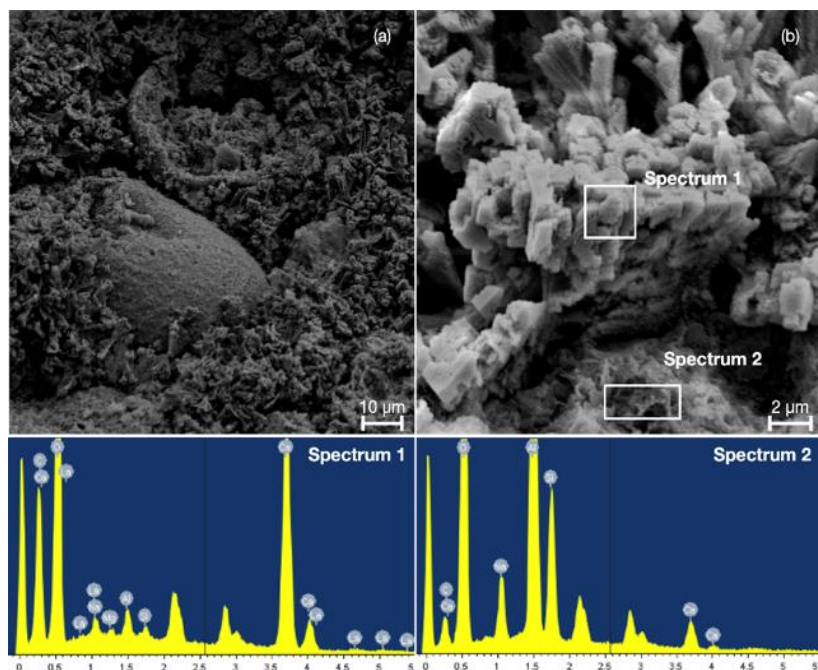


Figure 5-10 Microstructure and composition of the pastes made with carbonate-fused FCC: (a) general (b) detail of calcite (spectrum 1) and N-A-S-H cement (spectrum 2).

The oxidised FCC paste (FCC/H₂O₂) includes fewer cementing hydrate gels and little densification (Figure 5-11). In comparison with the calcined FCC (Figure 5-9), the matrix of FCC/H₂O₂ is less dense and more porous, agreeing with the lower strength results.

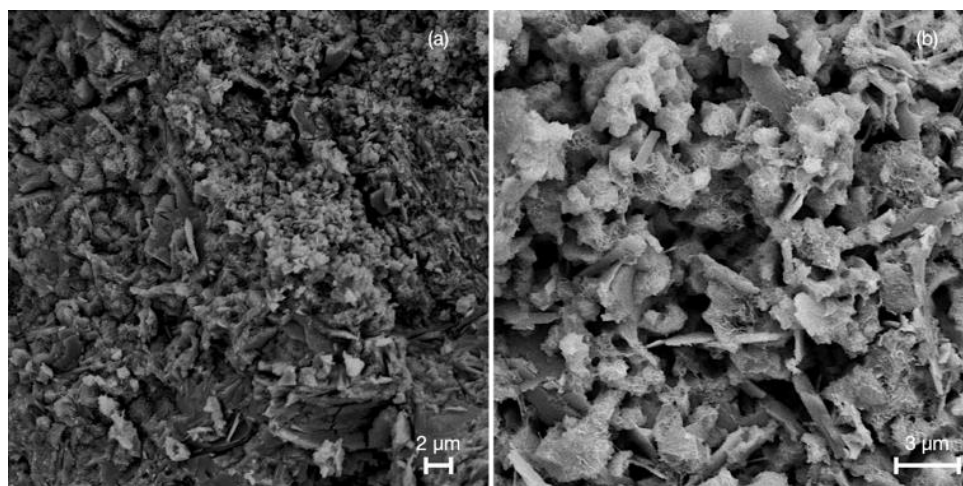


Figure 5-11 Structure and cements in the pastes made with oxidised FCC (FCC/H₂O₂) (a) general (b) detail.

In the NaOH-fused FCC paste, the XRD analyses evidenced cements of carboaluminate hydrates, calcite and portlandite (Figure 5-2). The SEM analyses show hydrates covered with a small amount of calcite crystals. According to the EDX results, the hydrates are C-A-S-H gels with high Ca/Si and Si/Al ratios (Figure 5-12). They have a significantly higher Si/Al ratio than the cementing hydrates in the carbonate-fused FCC (Figure 5-10) which is responsible for their higher strength (Figure 5-6). This agrees with the results above, indicating that NaOH-fusion breaks down the zeolite further than any other treatments, and dissolves Si which formed cementing hydrates of greater strength.

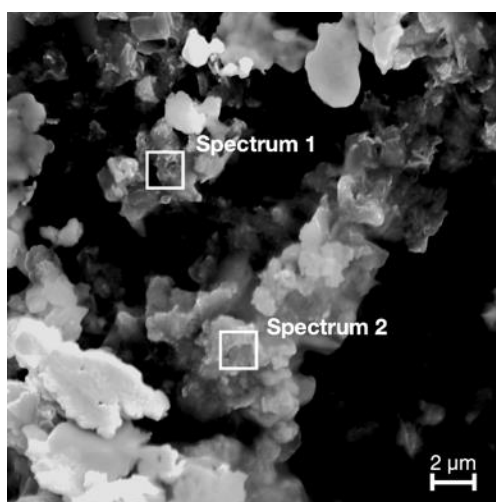


Figure 5-12 Detail of the dense hydrates in the NaOH fused FCC specimens.

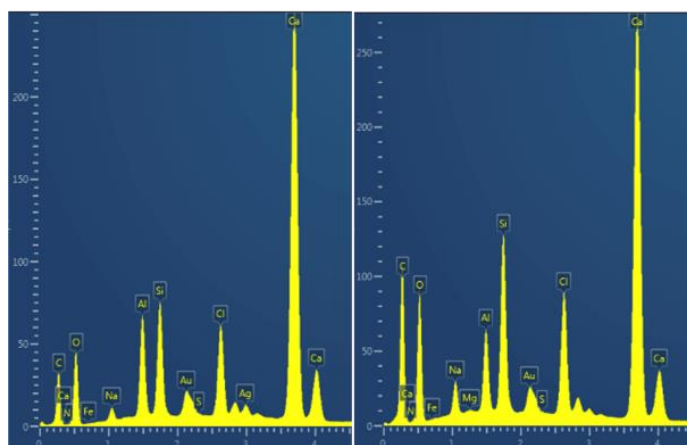


Figure 5-13 Elemental composition of the hydrates by EDX.

5.2 ALUM SLUDGE (AS)

As aforementioned, AS contains significant organic matter which may hinder geopolymerisation. Calcination can remove the organic matter and alter the reactivity of AS. Therefore, in this section, AS is calcined at 450, 600, 800 and 1000 °C and the reactivity of the resultant AS is evaluated with chemical and mechanical methods. The mixing design appears in Table 5-4. The notation is based on the AS treatment, where the first number indicates the calcination temperature and the second number is the proportion of GGBS. Since AS is rich in Al and deficient in Si, GGBS is used as a Si source.

Table 5-4. Mix design for strength and setting times testing.

Notation	Detail	Composition (parts by wt)					
		AS	GGBS	Lime	Sand	Water	w/b*
AS Raw	Raw	1	0	1	3	1.5	0.75
AS 600	Calcined at 600 °C for 2h	1	0	1	3	3.4	1.70
AS 600/50	Calcined at 600 °C for 2h	0.50	0.50	1	3	2.4	1.20
AS 800	Calcined at 800 °C for 2h	1	0	1	3	1.5	0.75
AS 800/25	Calcined at 800 °C for 2h	0.75	0.25	1	3	1.5	0.75
AS 800/50	Calcined at 800 °C for 2h	0.50	0.50	1	3	1.5	0.75
GGBS	-	0	1	1	3	1.5	0.75
Lime	-	0	0	2	3	1.5	0.75

* Water/binder ratio (w/b) = Water / (AS+GGBS+Lime)

5.2.1 Characterization of Treated AS

The impact of calcination on the particle size distribution is shown in Figure 5-14 and Table 5-5. The SSA of AS is relatively low, with raw AS having a SSA of 0.22 m²/g. However, as the calcination temperature increased, a notable rise in SSA was observed. At 600°C, the SSA increased to 0.51 m²/g, reaching a peak of 0.57 m²/g at 1000°C. The increase in SSA indicates that higher calcination temperatures enhance the surface properties of AS, likely due to the removal of organic matter and the breakdown of larger particles into finer ones.

The particle size distribution also changed significantly with varying calcination temperatures. The D [3,2] value, which represents the surface area-weighted mean diameter, showed a

decrease from 26.1 μm in raw AS to 10.1 μm at 1000°C. Similarly, the volume-weighted mean diameter, D [4,3], decreased from 138 μm in raw AS to 116 μm at 1000°C. The Dx(10) value decreased from 12.6 μm in raw AS to 6.95 μm at 1000°C, indicating a reduction in the size of the smaller particles in the distribution. The Dx(50) value, or median particle diameter, dropped from 111 μm in raw AS to 76.4 μm at 1000°C. The Dx(90) value, representing the larger end of the particle size distribution, decreased from 307 μm in raw AS to 285 μm at 1000°C. These reductions suggest that higher calcination temperatures effectively reduce the average particle size of AS.

GGBS and FA were used as a reference. The raw and calcined AS are coarser than FA and GGBS (Figure 5-14). GGBS has an SSA of 1.34 m^2/g and significantly finer particles, with D [3,2] and D [4,3] values of 4.49 μm and 14.79 μm respectively. Similarly, FA has an SSA of 1.27 m^2/g , with D [3,2] and D [4,3] values of 4.72 μm and 38.48 μm respectively.

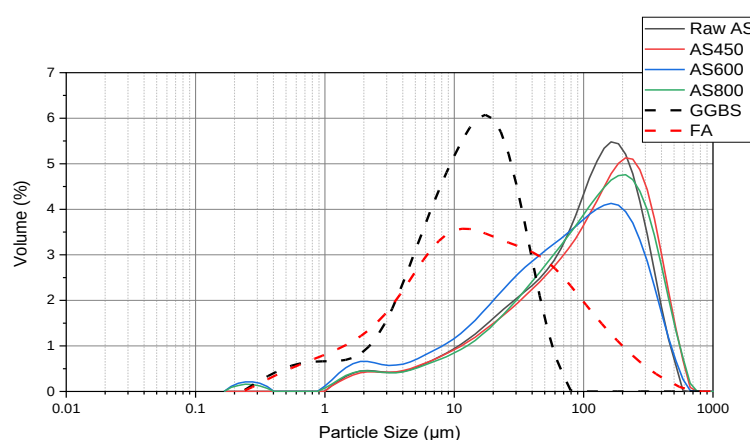


Figure 5-14 Particle size distribution of the raw and pyroprocessed AS compared with FA and GGBS as % by volume by laser diffraction.

Table 5-5 Specific surface area and particle size distribution of the raw and pyroprocessed AS compared with FA and GGBS.

Notation	SSA	D [3,2]	D [4,3]	Dx (10)	Dx (50)	Dx (90)
AS Raw	0.22 m^2/g	26.1 μm	138 μm	12.6 μm	111 μm	307 μm
AS 450	0.21 m^2/g	27.4 μm	160 μm	13.0 μm	123 μm	366 μm
AS 600	0.51 m^2/g	11.2 μm	121 μm	7.38 μm	79.1 μm	298 μm
AS 800	0.37 m^2/g	15.3 μm	154 μm	12.0 μm	113 μm	358 μm
AS 1000	0.57 m^2/g	10.1 μm	116 μm	6.95 μm	76.4 μm	285 μm
GGBS	1.34 m^2/g	4.49 μm	14.79 μm	2.35 μm	11.67 μm	31.63 μm
FA	1.27 m^2/g	4.72 μm	38.48 μm	1.95 μm	14.97 μm	100.64 μm

*Results are represented as percentiles, where Dx (50) is the maximum particle diameter below which 50% of the sample volume exists.

The micrographs of raw and calcined AS particles visually confirmed the influence of calcination on the particle size change as shown in Figure 5-15 and Figure 5-16. The raw AS (Figure 5-15a) showed large, irregularly shaped particles with considerable agglomeration, characterized by a relatively smooth surface. After calcination at 600°C (Figure 5-15 b), the particles appeared more fragmented and smaller compared to the raw AS, displaying

increased surface roughness and porosity, which suggests that the heat treatment begins to break down larger agglomerates into finer particles. The detailed view in Figure 5-16 highlighted this fragmentation, showing a porous structure with numerous small particles adhering to larger fragments. At 800°C (Figure 5-15 c), the particles became even finer and more uniformly distributed, with a significant reduction in size. The denser texture and sharper edges of the particles suggested that while calcination caused the breakdown of particles, higher temperatures may have prompted re-densification of AS. At 1000°C (Figure 5-15 d), the particles reach their smallest and most well-defined form, featuring a highly fragmented structure with sharp, well-defined edges and a highly dense surface. This suggested that calcination at 1000°C effectively maximizes the breakdown of larger particles into very fine fragments, greatly increasing the specific surface area. However, particles calcined at temperatures above 800°C also appear denser, which could be attributed to crystallization induced by high temperatures. This increased density might result from the reorganization of the material's internal structure during the calcination process.

Higher temperatures result in a finer particle size distribution and increased surface area, as reflected in the corresponding particle size distribution data. The transformation from larger, smoother particles in the raw AS to smaller, more irregularly shaped and porous particles and then sharp-edged dense particles at higher calcination temperatures demonstrates the impact of thermal treatment on AS.

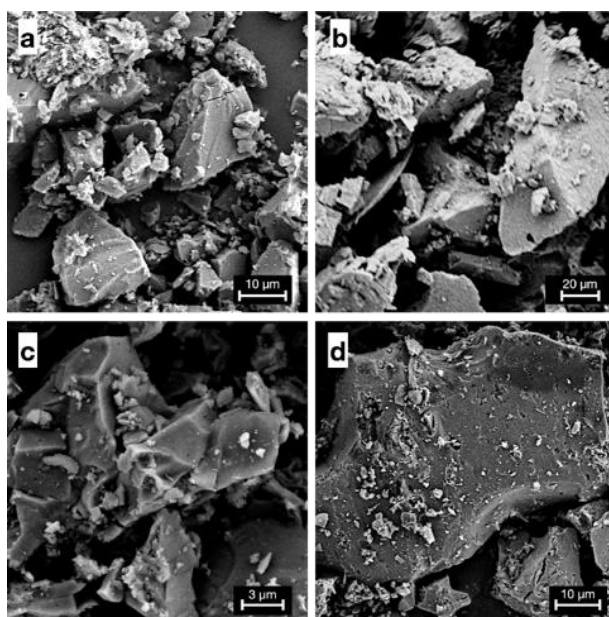


Figure 5-15 SEM micrographs of (a) raw AS and AS calcined at (b) 600 °C, (c) 800 °C, and (d) 1000 °C.

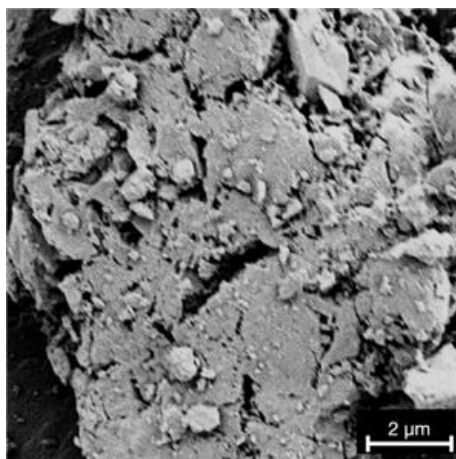


Figure 5-16 SEM micrograph of detailed AS/600 surface.

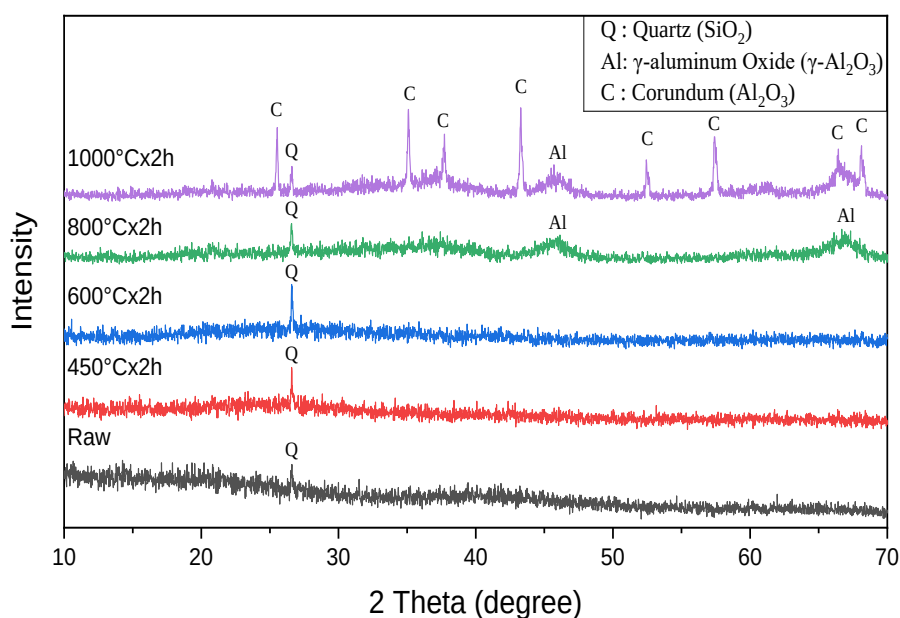


Figure 5-17 X-Ray Diffractogram of raw and calcined AS.

The XRD analyses (Figure 5-17) indicate that the raw AS is amorphous and that it remains primarily amorphous up to 800°C. At 800°C, two new diffuse humps appear at 46 and 67° 2 θ which show a good match with $\gamma\text{-Al}_2\text{O}_3$, this semi-amorphous phase is the predecessor of crystalline corundum (Al_2O_3) whose sharp peaks are evident at 1000°C (Figure 5-17). This agrees with Tantawy (2015), who states that amorphous $\text{Al}(\text{OH})_3$ will undergo a series of dehydroxylation reactions to eventually transform into crystalline Al_2O_3 . Typically, the conversion occurs above 1100°C (Rozhkovskaya et al., 2021). However, the presence of sulphate and organic compounds has lowered the temperature agreeing with previous authors (Lee et al., 2013; Matori et al., 2012; Mishra, 2002).

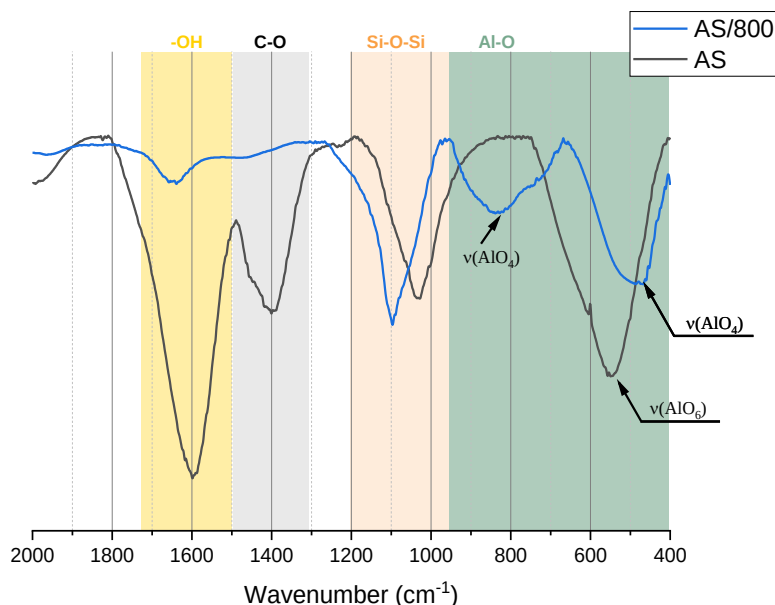


Figure 5-18 FTIR spectra of AS and AS/800.

The FTIR of AS and AS/800 in Figure 5-18 further revealed their microstructure. The absorption band located between 1500 cm^{-1} and 1750 cm^{-1} corresponds to surface hydroxyl groups from $\text{Al}(\text{OH})_3$ and H_2O (Lee & Condrate Sr, 1995). The abundant -OH groups in the AS are attributed to its hydrophilic nature. This hydrophilicity poses challenges for dewatering AS (Wu et al., 1997, 2003; Li et al., 2016) and it is responsible for a high water demand when used in construction materials (see below). Calcination dehydroxylates the AS significantly reducing its hydroxyl groups (AS/800 in Figure 5-18) (Lei & Pavia, 2023c). This reduction lowers the water demand of AS. The absorption band centred around $\sim 1400\text{ cm}^{-1}$, associated with C-O groups from organic matter and carbonates, disappears after calcination as the C evolves. The bands between $\sim 900\text{ cm}^{-1}$ and 1200 cm^{-1} , attributed to Si-O-Si groups, shift to higher wavenumbers due to calcination. This suggests potential crystallization of SiO_2 (Tantawy, 2015). Furthermore, bands from 500 cm^{-1} to 900 cm^{-1} are associated with the stretching vibrations of Al-O bonds in AlO_6 octahedra and AlO_4 tetrahedra units (Adamczyk & Długoń, 2012; Vasconcelos et al., 2012). After calcination, a conversion tendency from 6-fold to 4-fold coordination of Al was noted, indicating dehydroxylation and structural turbulence within Al_2O_3 units due to high-temperature treatment.

5.2.2 Reactivity by the Chapelle test

The pozzolanic activity measured by the Chapelle test is included in Figure 5-19. The results show that all the ASs consume significant Ca^{2+} . As Ca^{2+} consumption is mostly due to cation exchange and pozzolanic reactions, they all exhibit pozzolanic activity. However, in the raw AS, the abundant organic matter (when dissolved in the alkaline conditions imposed by the lime) also combines Ca^{2+} . The consumption of Ca^{2+} by the organic matter (rather than the pozzolanic reaction) agrees with the low strength of the raw AS specimens shown below.

Despite the XRD diffractogram not showing any mineralogical changes up to 800°C (Figure 5-17), it is clear from the Chapelle test results that reactivity is greatest at 600°C , and increases with the dwelling time so that the 600°C AS burned for 3 hours renders the greatest activity (Figure 5-19). Burning at 600°C for 3h increased the Ca^{2+} consumption of the raw AS by 109.8%

(from 551 to 1156 mg). This increased reactivity is due to the activation of some Al hydroxides and the riddance of organic matter. Ca^{2+} consumption drops at 800°C and further drops at 1000°C. This agrees with the XRD results showing that part of the amorphous Al hydroxides become semi-amorphous $\gamma\text{-Al}_2\text{O}_3$ at 800°C to later transform into crystalline, inert corundum (Al_2O_3) at 1000°C.

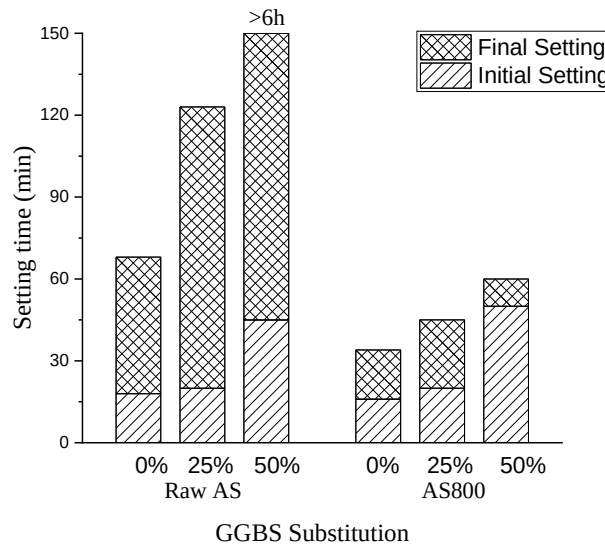


Figure 5-19 Portlandite consumption of raw and pyroprocessed AS. x1 x2 x3: dwelling time (hrs).

Expanding calcination time has an inconsistent effect on the pozzolanic activity of AS because it increases activity at 450-600 °C but lowers it at 800°C. This effect is however logical, because, at 800°C, increasing calcination time transforms more amorphous Al hydroxide into crystalline, inert Al_2O_3 (Figure 5-17), hence lowering activity. While, on the contrary, prolonged calcination at 450-600°C, produces more reactive Al phases and furthers the removal of organic matter, hence enhancing reactivity. Furthermore, despite increasing the Ca^{2+} consumption of the 450°C and the 600°C AS (by 10.59 and 13.00% respectively), extending calcination time for a further hour increased the energy consumed by 50%. Therefore, the calcination time was set at 2 hours to continue the study.

5.2.3 Reactivity by the Mechanical Activity Index (MI)

The pozzolanic activity of the AS, measured with the mechanical activity index (MI), appears in Figure 5-20. The AS calcined at 450°C and 600°C cannot be mixed with reasonable w/b ratios due to exothermic reaction and flash set as discussed below. Therefore, their MI is not measured. All the MIs are over 1.00 indicating pozzolanic activity. After calcination at 800 °C for 2h, the MI increased from 1.90 to 5.40, indicating the enhancement of the pozzolanic activity. The high MI values are caused by the presence of reactive phases and the absence of organic matter which no longer inhibits pozzolanic reaction so that hydrates can form and contribute to strength. The raw AS shows a low index despite the high Ca^{2+} consumption evidenced by the Chapelle test which agrees with the organic matter competing for Ca^{2+} and interfering with the pozzolanic reaction. In comparison with other pozzolans and supplementary cementitious materials, such as fly ash (FA), rice husk ash (RHA) and ground granulated blast-furnace slag (GGBS), AS has low MI due to the low silica content.

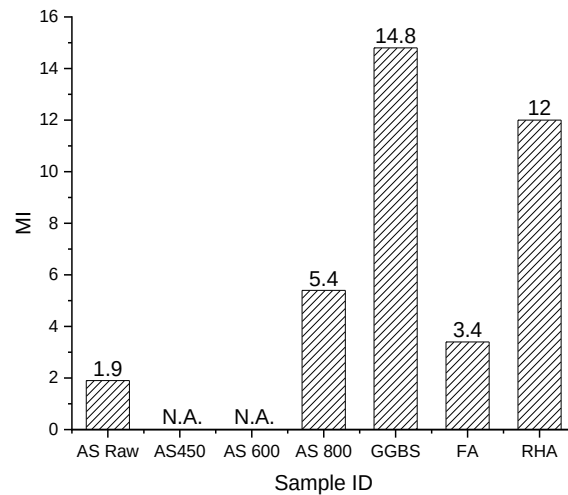


Figure 5-20 MI of the raw and pyroprocessed AS (800°C) compared with other pozzolans and supplementary cementitious materials.

5.2.4 Properties of AS materials blended with GGBS

As aforementioned, the mechanical index of the AS is low due to its low silica content. Therefore, it was blended with GGBS, as a silica source, to improve mechanical properties.

The water demand of AS and AS-GGBS pastes appears in Figure 5-21 and Figure 5-22. The pastes made with AS calcined at 450°C and 600°C show considerably higher water demand due to flash setting. When mixed with lime and water, they react exothermically transforming into breadcrumb-like solids. The presence of highly reactive Al phases is likely the reason for the flash setting: it is well known that Al phases (in PC clinkers) dissolve fast, largely controlling the water demand, setting and rheology of PC materials. The flash set of the 600°C AS indicates that sudden hydration of aluminium phases is taking place, similarly to the abrupt hydration of aluminate i.e. tricalcium aluminate (C_3A , $3CaO \cdot Al_2O_3$) in PC clinkers. The flash set indicates high reactivity agreeing with the Chapelle and XRD tests evidencing high Ca^{2+} consumption and amorphous diffraction patterns respectively. Even using 50% GGBS to replace AS600, the w/b ratio could not be reduced to a reasonable value.

In contrast, the water demand of the 800°C AS is lower agreeing with its larger crystalline content and lower pozzolanic activity. The AS materials show a greater water demand than equivalent GGBS mixes.

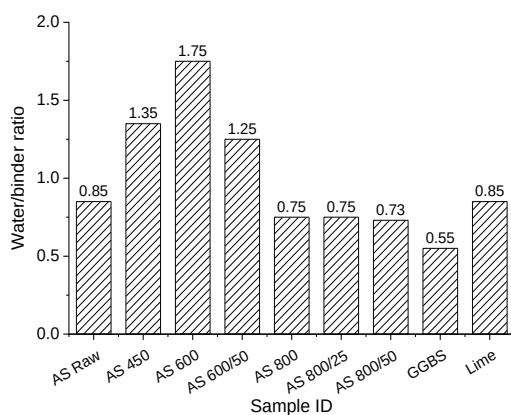


Figure 5-21 Water demand of raw, pyroprocessed (450/600/800°C) and blended (25/50% GGBS) AS mixed to a 165 mm flow diameter.

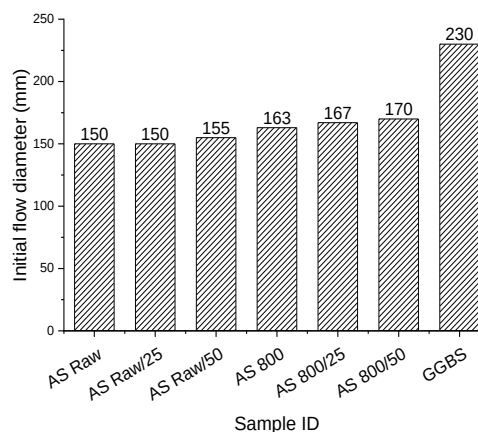


Figure 5-22 Variation of the initial flow diameter at w/b=0.75.

The setting times of the 450°C and 600°C calcined AS specimens could not be measured due to their flash set. The initial setting times of the raw and the 800°C AS are comparable (Figure 5-23). However, the 800°C AS materials reach their final set much faster, agreeing with the reactivity results and lack of carbon. Partially replacing AS with GGBS delays setting (Figure 5-23), and the delay is proportional to the amount of GGBS in the paste. This is due to the major chemical composition of GGBS (SiO_2 and CaO) increasing the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, hence depressing the initial dissolution of Al and aluminate hydrate formation that causes a speedy set.

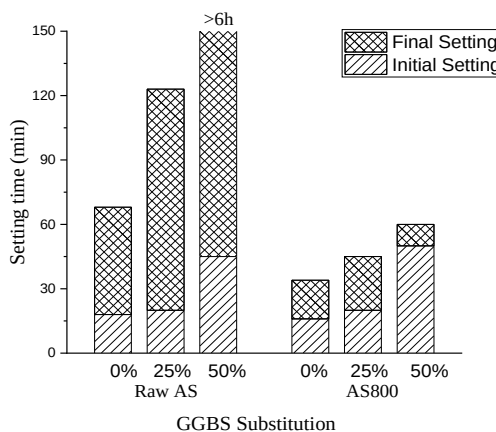


Figure 5-23 Setting times of raw, pyroprocessed and GGBS-blended AS.

The compressive and flexural strengths of the AS specimens are included in Figure 5-24 and Figure 5-25. The raw AS has low strength, similar to the lime paste, due to the hindrance of the organic matter. Even after 140 days, only a small strength development is observed. The 600°C AS also reached low strength which is due to its high water demand (w/b). Therefore, the 600°C AS is not suitable to be combined with PC or lime as a SCM because it increases water demand and the risk of flash setting. Despite a slight reduction in long-term strength (Figure 5-24), the 800°C AS displays the best potential with respect to flowability and mechanical strength. The reduction in the long-term strength of the 800°C AS is probably due to the conversion of metastable calcium aluminate hydrates into more stable hydrates of lower

strength. This has been reported in PC materials, metakaolin-based geopolymers and calcium aluminate cements (CAC) (Antonovič et al., 2013).

The 800°C-AS specimens with 50% GGBS replacement show significantly higher compressive and flexural strength, and the increase is proportional to the amount of GGBS in the specimen. The strength increase can be attributed to the increase of the Si/Al ratio which enables the formation of calcium silica hydrates in lieu of the calcium aluminate hydrates of lower strength that would otherwise occur. In addition, GGBS substitution avoids the late strength reduction due to metastable hydrate conversion. The GGBS reduces the conversion of calcium aluminate hydrates into hydrates of lower strength seen in the AS. Several authors have reduced hydrate conversion and the subsequent strength decrease in CACs with blast furnace slag, microsilica or metakaolin replacements (Hidalgo et al., 2009).

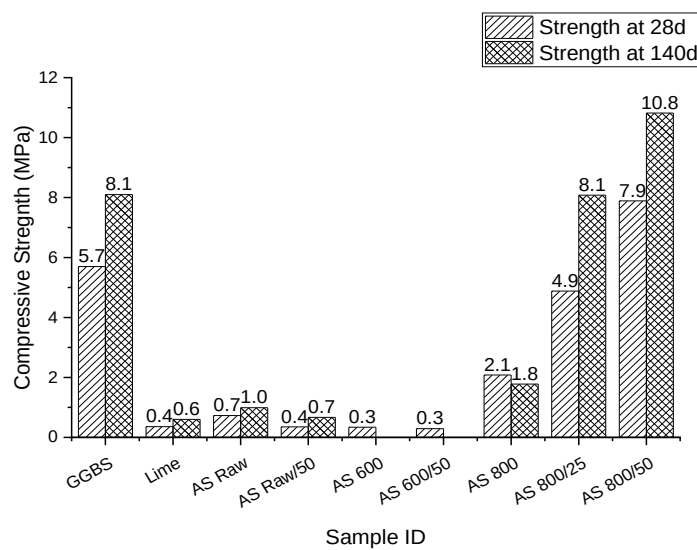


Figure 5-24 Compressive strength of raw, pyroprocessed and GGBS-blended AS at 28 and 140 days.

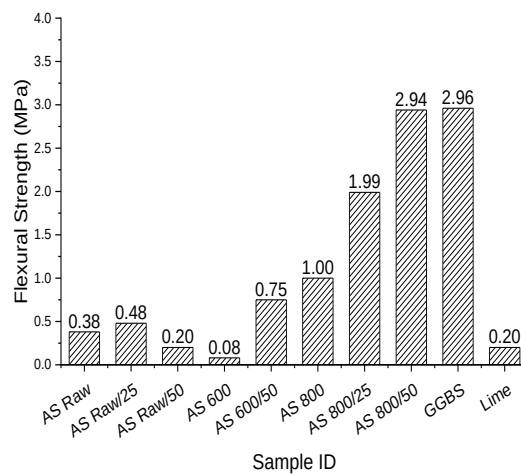


Figure 5-25 Flexural strength at 28 days.

5.2.5 Microstructure and Cements in the AS materials blended with GGBS

The mineral composition of the AS and the AS-GGBS pastes appears in Figure 5-26. As it can be seen, the main cementing material of the raw AS/lime pastes is calcite (CaCO_3) resulting from the carbonation of the hydrated lime $\text{Ca}(\text{OH})_2$ which agrees with the lower pozzolanic activity shown in the reactivity tests. The SEM displayed the open structure and high porosity typical of carbonated lime pastes (Figure 5-27), and the EDX confirmed abundant euhedral and cubic calcite microcrystals (rhombohedral system). The EDS consistently showed significant Al (Figure 5-28). Al phases were not detected by XRD, but are occasionally recorded with SEM, as incipient Al hydrates of low crystallinity (Figure 5-27b).

In contrast, in the 800°C-AS/lime pastes, the XRD trace (Figure 5-26) shows the presence of calcite and calcium carboaluminate hydrate ($\text{Ca}_4\text{Al}_2\text{O}_6\text{CO}_3 \cdot 11\text{H}_2\text{O}$, $\text{C}_4\text{AC} \cdot \text{H}_{11}$, calcium monocarboaluminate). The carboaluminate hydrates have formed by the reaction of CO_3^{2-} ions from the carbonated lime with the reactive aluminates in the 800°C-calcined AS. Carboaluminate hydrates are carbonate-AFm phases relatively common in Al-rich systems containing carbonate. Previous authors have reported the formation of carboaluminate hydrates, in secondary hydration reactions, in PC-limestone cement (Bonavetti et al., 2001; Ipavec et al., 2011), blended cements (Antoni, 2013), and ternary cements with calcined clay or fly ash and limestone (Tironi et al., 2017). The formation of carboaluminate hydrates enhances the mechanical and durability properties of blended cements even at low clinker content (Krishnan et al., 2019).

The calcium monocarboaluminate ($\text{C}_4\text{AC} \cdot \text{H}_{11}$) detected by XRD in the AS 800°C cement is the most commonly observed carbonate AFm phase in PC systems (Bonavetti et al., 2001). Furthermore, this phase is stable. According to Matschei et al. (2007), carbonate AFm phases are thermodynamically more stable than hydroxy or sulphate phases. The SEM/EDS analyses confirm the presence of calcite and calcium carboaluminate hydrates (Figure 5-28). The hydrates appear as hexagonal plates (Figure 5-29) similar to the hexagonal calcium aluminate hydrates ($\text{CaAl}_2\text{O}_4 \cdot \text{H}_2\text{O}$ - CAH_{10} and $\text{Ca}_2\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ - C_2AH_8) typically found in hydrated calcium aluminate cements (CAC).

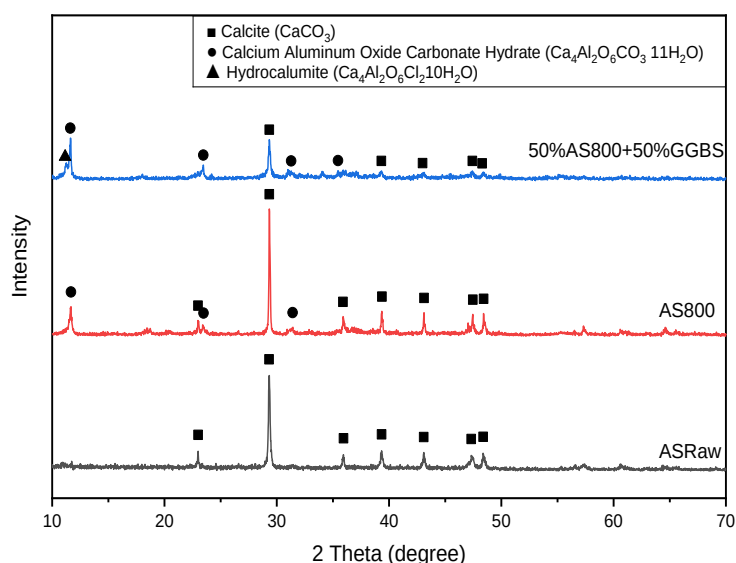


Figure 5-26 Mineral composition of the cement in the AS/lime materials made with raw and pyroprocessed AS, with and without GGBS replacement (by X-Ray diffraction at 28 days).

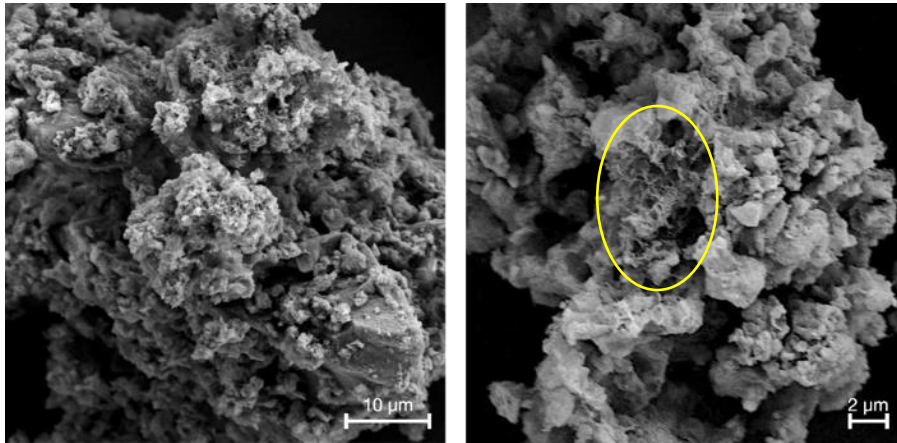


Figure 5-27 a/b Microstructure of the carbonated cement in the raw-AS/lime specimens mainly consisting of microcrystalline calcite resulting from extensive carbonation (a) with occasional incipient Al hydrates of low crystallinity (b).

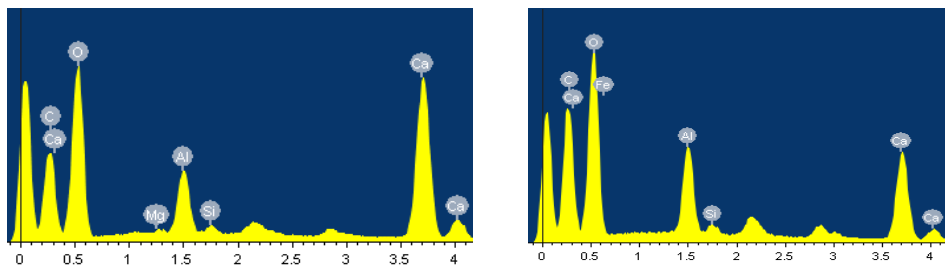


Figure 5-28 a/b Chemical composition of the carbonated pastes in the raw-AS/lime specimens including significant Al present as incipient, low-crystallinity hydrates (Figure 5-27).

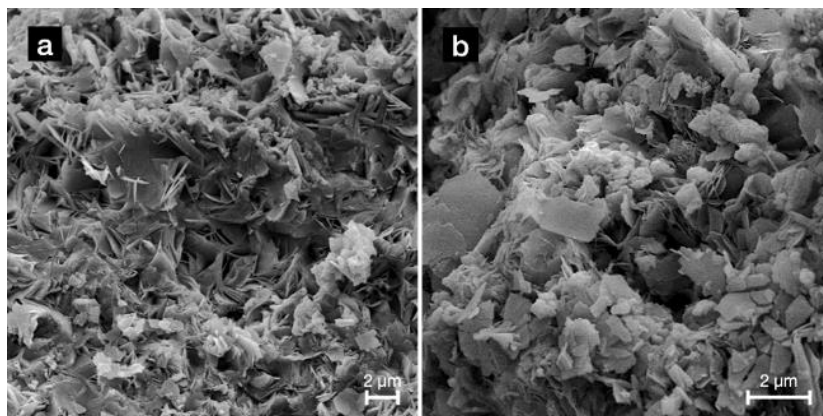


Figure 5-29 Typical microstructure of the cements in the 800°C-AS/lime paste consisting of calcium carboaluminate hydrates plates mixed with microcrystalline calcite.

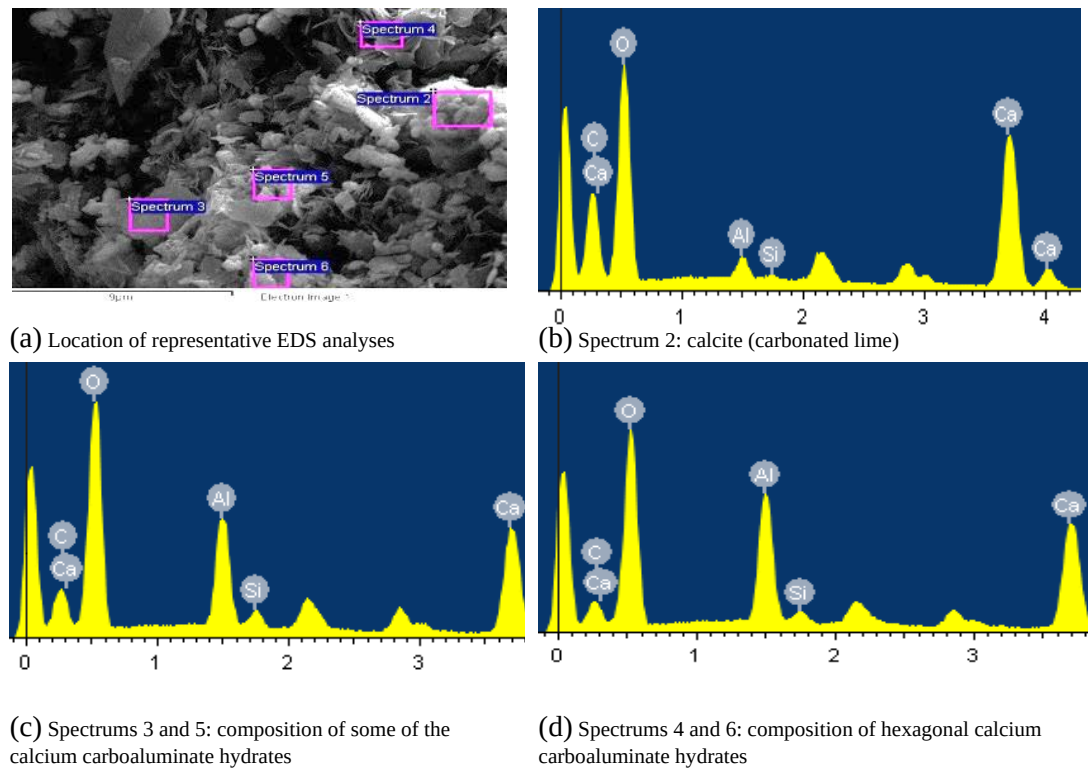


Figure 5-30 EDS analyses result of 800°C-AS/lime pastes.

When 50% of the 800°C-AS is replaced with GGBS, the XRD results show that the calcite cements reduce substantially, the carboaluminate hydrates increase, and an additional phase appears: hydrocalumite, $\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ (Figure 5-26). Hydrocalumite is a cement hydrate (AFm-phase) with high adsorbent capacity. It is defined as an anion-exchange mineral belonging to the layered double hydroxide group and is widely used in environmental remediation because of its high adsorption capacity (Manikonda et al., 2019). However, hydrocalumite was not found in the SEM/EDS analyses. Instead, the SEM/EDS showed hydrates of greater Si content and higher crystallinity than those in the 800°C-AS/lime cements (Figure 5-32). Therefore, the GGBS has changed the nature of the hydrates. The appearance and composition of the hydrates in the SEM/EDS analyses (Figure 5-31 and Figure 5-32 d) conforms with stratlingite (gehlenite hydrate, C2ASH8), an AFm-type phase with a layered structure that crystallises in the trigonal system and can form perfect hexagonal plates (Okoronkwo & Glasser, 2016). This agrees with former authors that changed the nature of the hydrates in aluminat cements using Si-rich replacements such as GGBS (Hidalgo et al., 2009).

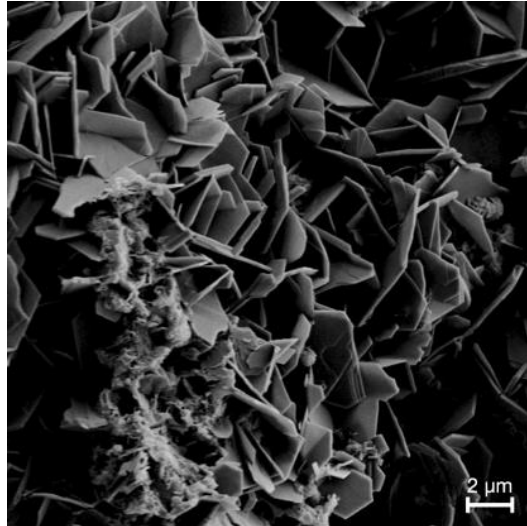
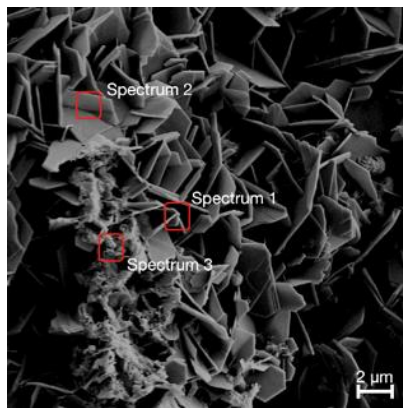
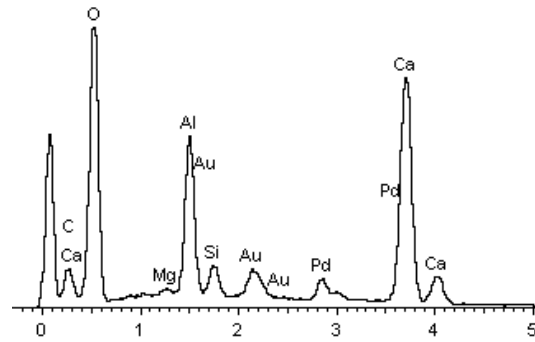


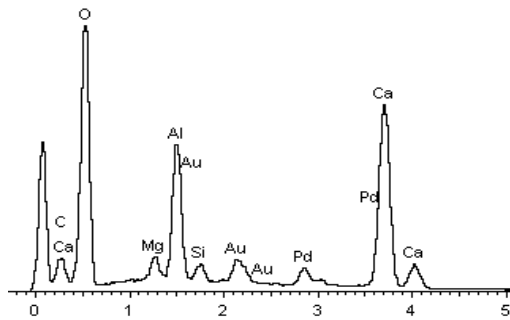
Figure 5-31 Hexagonal calcium aluminate hydrates in the 800°C-AS pastes with 50% GGBS replacement.



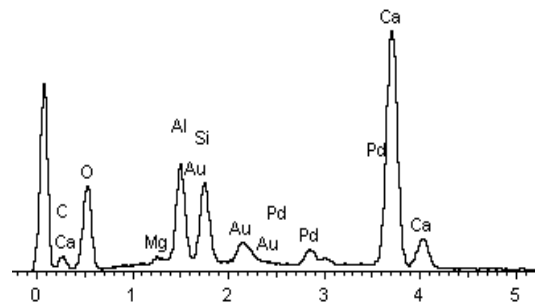
(a) Location of representative EDS analyses.



(b) Spectrum 1: consistent with calcium carboaluminate hydrates.



(c) Spectrums 2: composition of some of the calcium carboaluminate hydrates.



(d) Spectrums 3: a larger Si and lower C content indicating a shift to a higher Si hydrate that can be strätlingite C_2ASH_8 .

Figure 5-32 EDS analyses result of 800°C-AS/lime pastes with 50% GGBS replacement.

5.3 CROP BIOMASS ASH (CBA)

CBA is characterized by its high crystallinity, which may result in low reactivity. To enhance the reactivity, an alkali-fusion process was applied to break down the crystalline phase in CBA.

As described in the Methods section, the alkali-fusion process involves mixing CBA with a specific amount of sodium hydroxide and heating the mixture to 600 °C. Various alkali percentages, ranging from 15% to 75%, were tested to determine the optimal value for CBA. The mix design used in this section is presented in Table 5-6. The nomenclature in this section is based on the processing parameters of the alkali fusion, with the first number indicating the alkali content (wt%) and the second number indicating the duration of calcination (h).

Table 5-6 Alkali fusion treatment, mixing design and water demand.

Notation	Alkali fusion treatment			Mixing ratio				
	Waste type	Alkali dosage	Duration (h)	Waste (g)	CL90s (g)	Sand (g)	Water (g)	w/b
CBA-raw		0%	-				390	0.65
CBA-15-2		15%	2h				390	0.65
CBA-25-2		25%	2h				390	0.65
CBA-50-2	CBA	50%	2h	300	300	900	390	0.65
CBA-75-2		75%	2h				480	0.80
CBA-50-3		50%	3h				390	0.65
CBA-75-3		75%	3h				480	0.80

5.3.1 Characterization of Alkali-fused CBA

The mineral composition of the raw and the alkali-fused CBA is illustrated in Figure 5-33 and the mineral changes are summarised in Table 5-7. The analyses revealed patterns like those observed in the APS. Fusing CBA with less than 50% alkali does not result in any significant alteration in mineral composition. Fusion with 15%-25% NaOH decreases the intensity of the characteristic peaks of quartz and albite; and forms new phases of sodium aluminosilicate and sodium silicate ($\text{Na}_{1.15}\text{Al}_{1.15}\text{Si}_{0.85}\text{O}_4$, PDF 04-010-3962 and $\text{Na}_{0.98}\text{Al}_{0.98}\text{Si}_{1.02}\text{O}_4$, PDF 04-016-6555).

A notable shift in mineral composition was evident when the CBA was fused with 50% NaOH: Sodium silicate (Na_2CO_3 04-007-9571) replaced quartz as the primary crystalline phase and albite disappeared. When CBA is fused with 75% NaOH, quartz further decreases, and sodium silicate becomes more prominent. Although a small amount of sodium carbonate (Na_2CO_3 , PDF 04-007-9571) was detected, indicative of an excess of sodium in the reaction system, the amount of sodium residue in the CBA fused with 75% NaOH was notably lower than that in APS fused with the same alkalinity.

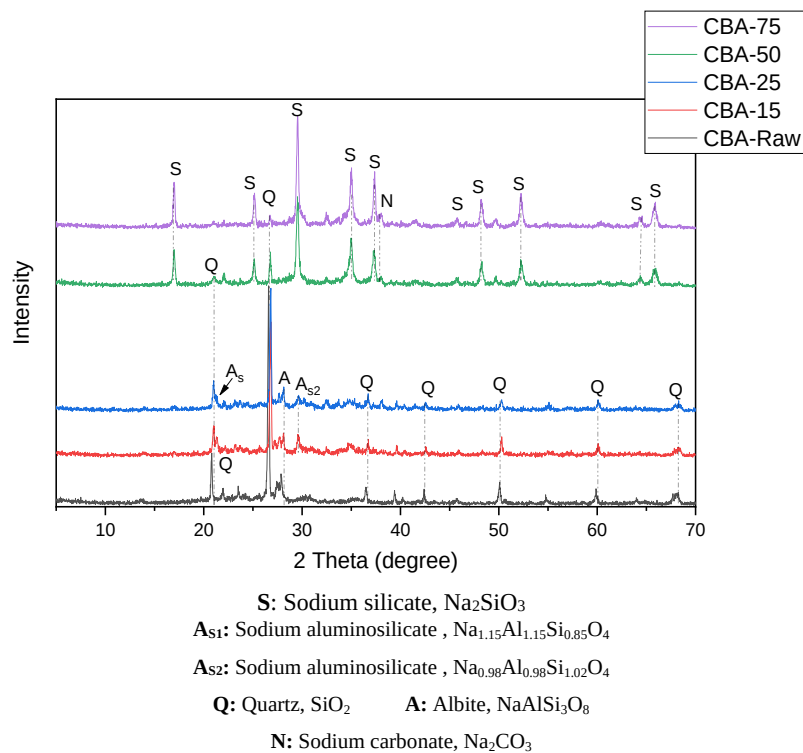


Figure 5-33 Mineral composition of the raw and alkali-fused CBA.

Table 5-7 Changes in the mineral assemblage of CBA waste due to alkali-fusion.

	Main phases	New-formed phases
CBA-Raw	Quartz, Albite	
CBA-15	Quartz (↓), Albite (↓)	Sodium aluminosilicate
CBA-25	Quartz (↓), Albite (↓)	Sodium aluminosilicate
CBA-50	Quartz (↓)	Sodium silicate
CBA-75	Quartz (↓)	Sodium silicate (↑), Sodium carbonate

The relative crystallinity of CBA after alkali fusion appears in Figure 5-34. A sharp decrease in crystallinity is evident with increasing alkali dosage. Fusion with 15% NaOH nearly halved the crystallinity of CBA. The most significant reduction in relative crystallinity occurs with a 50% NaOH treatment, where the crystallinity of CBA dropped from approximately 56% to 16%.

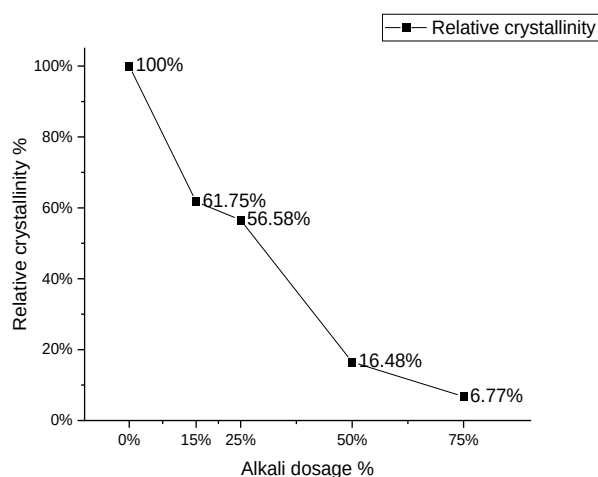


Figure 5-34 Variation in relative crystallinity of CBA after alkali-fusion.

The FTIR spectra for the raw and alkali-fused CBA are included in Figure 5-35. In the raw CBA, the main absorption band spanned from 825 cm^{-1} to 1280 cm^{-1} , centred at 1024 cm^{-1} . This band is attributed to the asymmetric stretching of Si-O-Si(Al) bonds, indicating a predominance of SiQ^3 units alongside a broad distribution of various SiQ^n units. Upon fusion with 15-25% NaOH, the main absorption band shifted to approximately 960 cm^{-1} . This shift reflects the disruption of SiO_4 tetrahedrons due to the replacement of SiQ^3 units with SiQ^2 . As the concentration of NaOH increases to 50-75%, the original main band split into two separate bands at 962 cm^{-1} and 877 cm^{-1} , representing the dominant SiQ^2 and presumably SiQ^0 units inferred from the XRD results. Concurrently, the range of the Si-O-Si(Al) asymmetric stretching bands narrows significantly to $740\text{--}1130\text{ cm}^{-1}$, indicative of the substantial breakdown of the highly cross-linked SiQ^4 and SiQ^3 units.

Furthermore, the band assigned to the asymmetric stretching of C-O bonds in carbonates was first observed after alkali fusion. This band maintained a single symmetry shape, suggesting that the carbonates exist as free ions. X-ray diffraction analyses did not detect any carbonates, even with alkali dosages reaching 75%, a finding consistent with the FTIR analysis. This indicates a lack of carbonate crystallization under the conditions studied, suggesting that any carbonate formation remained at the ionic or molecular level without significant structural integration into the ash matrix.

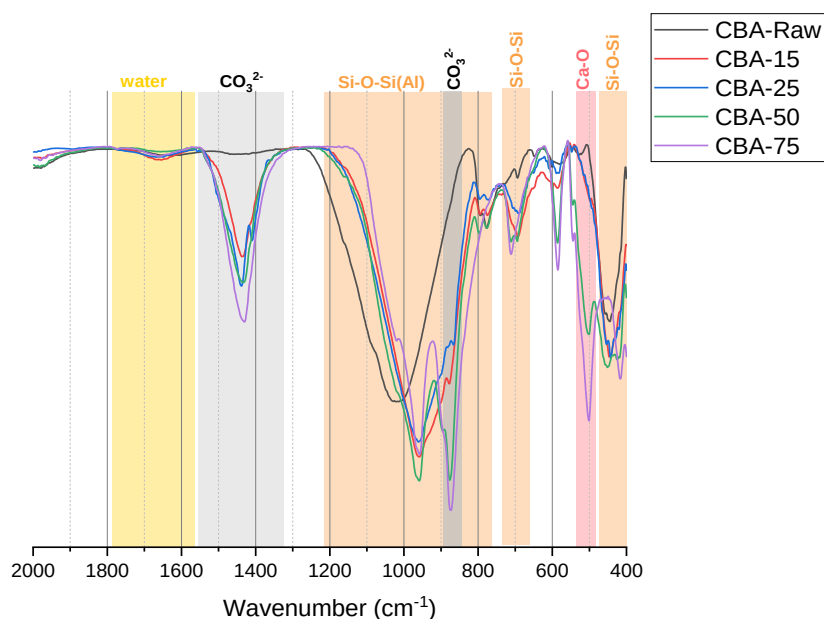


Figure 5-35 FTIR spectra for the raw and alkali fused CBA.

5.3.2 Reactivity by the Chapelle Test

Due to the presence of sodium hydroxide, the reactivity of the alkali fused CBA cannot be examined with the Chapelle test as the excessive hydroxide and carbonate would interfere with the results.

The reactivity of raw CBA by the Chapelle test is presented in Table 5-8 and compared to other pozzolans and SCMs. According to the results (Table 5-8), the CBA consumes calcium indicating some pozzolanic activity. However, in comparison with other pozzolans and SCMs, the reactivity of CBA is low. Pozzolans and SCMs including: fly ash (FA); spent fluid cracking catalyst (FCC); red mud calcined at 750 °C (RM/750); bauxite calcined at 800 °C (Bauxite/800); alum sludge calcined at 800 °C (AS/800) and GGBS, exhibit calcium consumption substantially higher than the CBA.

Table 5-8 Reactivity of CBA (measured with chemical and mechanical methods) compared with pozzolanic materials.

Material	Calcium consumption (mg CaO/g pozzolan)	Resource
CBA	127	-
FA	431	(Lei & Pavia, 2023c)
FCC	412	(Lei & Pavia, 2023a)
RM/750	346	(Alelweet et al., 2021)
Bauxite/800	620	(Alelweet & Pavia, 2022)
AS/800	782	(Lei & Pavia, 2023c)

5.3.3 Reactivity by the Mechanical Activity Index (MI)

The pozzolanic activity of the raw and alkali-fused wastes, measured with the mechanical activity index (MI), appears in Figure 5-36. The MI values are high, indicating notable pozzolanicity. The MI values are high when compared with other pozzolanic/ cementing materials. The highest values are comparable to those reached by alkali-fused spent fluid cracking catalyst FCC (Lei & Pavia, 2023b). Prolonging the fusion time to 3 hours does not generally enhance the MI significantly. The raw CBA exhibits the lowest activity (smallest MI). However, alkali fusion significantly enhanced the MI of CBA even at low NaOH dosage: fusing CBA with 15% NaOH improved its MI from 2.04 to 12.13, an increase of 494.61%. Therefore, despite the XRD not showing any significant change in mineralogy between the raw and the 15%NaOH-fused CBA, 15%NaOH fusion effectively enhances the CBA reactivity. Increasing the alkali dosage to 25% lowers the MI of CBA slightly, and increasing the dosage to 50% provides the maximum MI. However, over this threshold, the MI tends to lower probably due to the crystallization of considerable carbonate as detected by XRD and FTIR.

Table 5-9 Comparison with the MI of other pozzolanic and cementitious materials. (NH- NaOH)

	FCC/ Raw (Lei & Pavia, 2023b)	FCC/NH/600 (Lei & Pavia, 2023b)	GGBS	Metakaolin (Walker & Pavia, 2011)	RHA (Walker & Pavia, 2011)	RM (Alalweet et al., 2021)	AS 800 (Lei & Pavia, 2023c)
MI	14.5	23.7	29.5	38	12	6-8	5.4

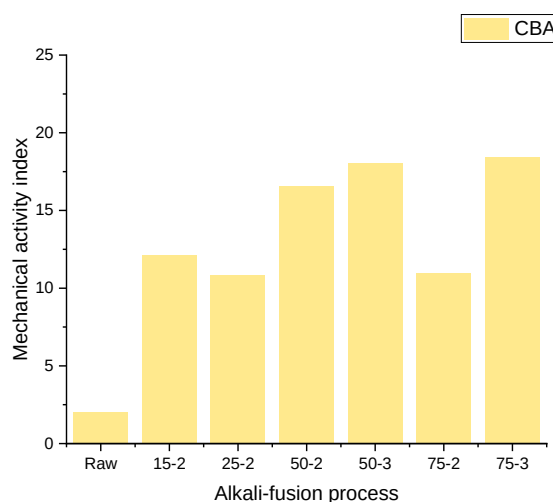


Figure 5-36 Mechanical activity index of raw and fused CBA, APS and FA wastes (2–3-hour fusion).

Figure 5-37 includes the mineralogy of the CBA-lime pastes. The raw CBA paste comprises quartz, calcite and portlandite, and a small amount of C-A-C-H is the only hydration product of the pozzolanic reaction. In the pastes made with alkali-fused CBA, a noticeable decrease in quartz and a rise in C-A-C-H are noted. When increasing alkalinity to 50% (CBA-50-2) nontronite hydrates appear, and pirssonite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2(\text{H}_2\text{O})_2$ - PDF 04-025-3514) crystallizes due to excessive sodium. Nontronite is an iron-rich smectite which occurs due to the activation of the iron in the wastes by the alkali fusion process. In an alkaline medium, it can later be converted to zeolite and C-S-H or C-A-S-H (Gaucher & Blanc, 2006).

Therefore, C-A-C-H, nontronite, portlandite and calcite are the main cementing phases formed upon pozzolanic reaction. When the wastes are fused, the pozzolanic reaction produces more abundant and diverse hydrates: the amount of C-A-C-H enlarges and nontronite appears. Finally, increasing alkalinity during fusion multiplies the hydrates and forms residual alkali carbonates gaylussite and pirssonite.

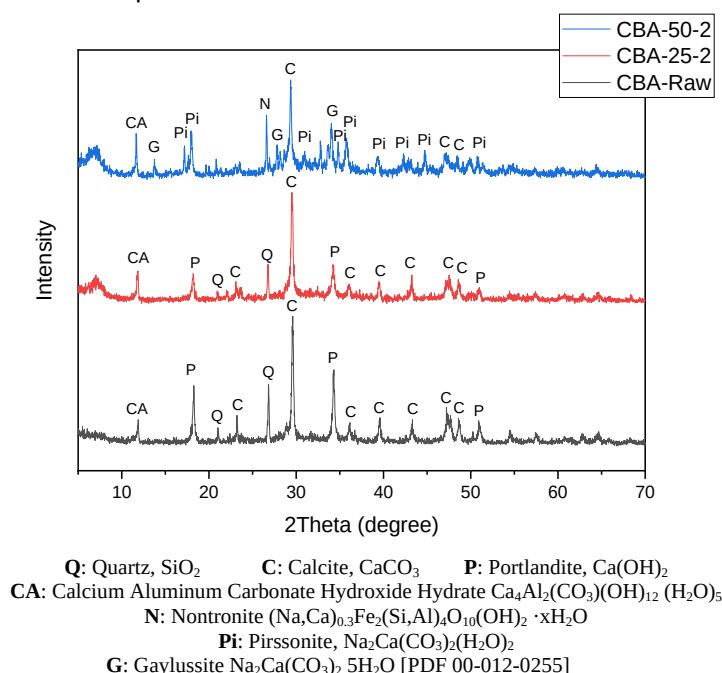


Figure 5-37 Mineral composition of raw and alkali fused CBA-lime pastes at 28d.

The micrographs of the CBA/50-lime pastes (Figure 5-38) display dense and homogeneous matrices. Profuse hydrate gels were observed, evidencing a strong pozzolanic reaction. The cements exhibit a high content of Na, Si, and Ca, indicating effective activation of CBA by alkali fusion. The abundance of hydrates further confirms the successful enhancement of CBA's reactivity through this process.

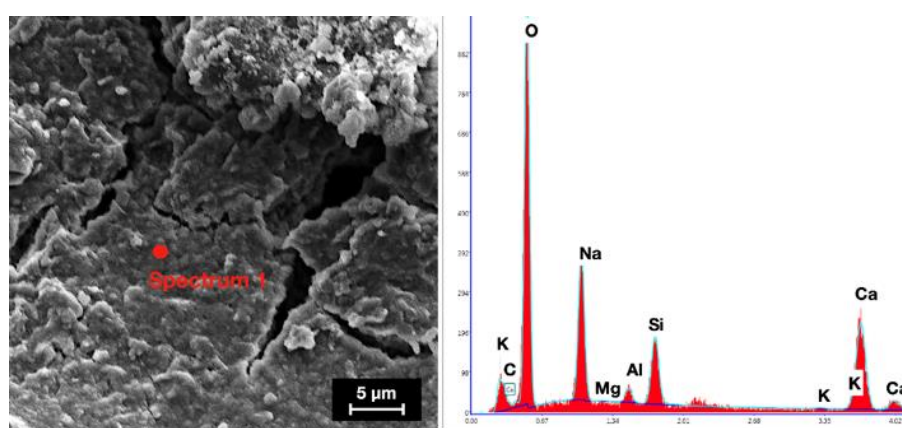


Figure 5-38 Micrograph of CBA/50-lime paste.

5.4 SUMMARY

In this section, the reactivity of three types of waste was examined with chemical and mechanical methods. Different treatments were designed for each waste to further enhance reactivity. Based on the experimental results in this section, the findings are summarized as follows:

Although FCC is semi-crystalline, its zeolite structure makes it highly reactive. FCC is structurally stable up to 800 °C; calcination at this temperature does not destroy its crystalline structure or enhance its reactivity. Similar results were observed for oxidation and acid etching treatments. In contrast, alkali-fusion with sodium hydroxide destroys the zeolite's crystalline structure. Using 15% sodium hydroxide is sufficient to vitrify the crystalline structure of FCC. The MI of FCC after alkali-fusion with 15% sodium hydroxide increased from 14.5 to 23.7. However, the use of sodium hydroxide and the high temperature of the treatment result in significant carbon emissions.

Calcination removes organic matter in AS and dehydroxylates the Al units, producing unstable transition phases. Calcination below 600 °C significantly improves the reactivity of AS, but the high reactivity of Al causes flash set, making it unsuitable for use in building materials. Calcination at 800 °C promotes the development of a semi-amorphous γ - Al_2O_3 phase which slightly reduces the reactivity of AS but allows it to be used normally without interfering with the normal setting of the paste. As AS is rich in Al but deficient in Si, its MI is very low. Incorporating GGBS into calcined AS as a source of Si shows good synergistic effects. Mortars prepared with 50% calcined AS and 50% GGBS exhibit mechanical properties higher than those of 100% GGBS mortars.

Due to its highly crystalline mineral structure, CBA exhibits very low reactivity. Alkali-fusion proved to be an effective method to enhance reactivity. After alkali-fusion, the original highly cross-linked Si chains were gradually broken to produce low-aggregation Si units. XRD results showed that alkali-fusion increased the reactivity of CBA by the gradual conversion of quartz into soluble, reactive sodium aluminosilicate and sodium silicates. When fusing with 50% sodium hydroxide, reactive sodium silicate replaced quartz as the main mineral component. However, the use of high doses of sodium hydroxide generates larger carbon emissions, and while further digesting the crystalline SiO_2 it also introduces excessive Na ions which can negatively affect activity.

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Chapter 6: Traditional Geopolymer System: Two-part Geopolymer

Two-part geopolymers are made with precursors activated by sodium silicate solution. This technique has been investigated for decades. This established route for the synthesis of geopolymers was initially adopted to synthesize two-part geopolymers using spent fluid cracking catalyst (FCC) and crop biomass ash (CBA) as precursors. The effect of the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio and Na^+ concentration of the activator, and the mixing ratio with other precursors on the properties of the resulting geopolymer are studied. In subsequent sections, the term “geopolymer” is used to describe the synthesised sustainable binder.

6.1 SPENT FLUID CRACKING CATALYST (FCC)

As aforementioned, raw FCC has high reactivity; therefore, it has the potential to serve as precursor to develop geopolymers.

In this section, GGBS and FA (silica-rich wastes) were used to balance the low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the raw FCC. To optimise the geopolymer system, this section investigates the effect of the activator's Na^+ concentration and $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio, and the relative proportions FCC/GGBS/FA on the mechanical properties of the geopolymer. The composition and microstructure of the cementing gel resulting from the polymerisation process are studied with X-ray diffraction (XRD), Fourier transform infrared spectrometry (FTIR) and scanning electron microscopy (SEM).

The mixing design used in this section is presented in Table 6-1. The notation is based on the components of the geopolymer (F for FCC, G for GGBS and FA for fly ash) preceded by a number that indicates the percentage of precursor. The last two numbers indicate the parameters of the activator: the first number indicates the concentration of Na^+ (mol/L) and the second number indicates the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio (molar ratio).

Table 6-1 Geopolymer mix design.

Group	Notation	Precursor (g)			Activator			Sand	w/b
		FCC	GGBS	FA	Concentration of Na ⁺ (mol/L)	SiO ₂ /Na ₂ O (molar ratio)			
A1	40F60G/10/1.2	160	240	0	10	1.2			0.6
	40F60G/8/1.2	160	240	0	8	1.2	1200		0.6
	40F60G/6/1.2	160	240	0	6	1.2			0.6
B1	40F60G/8/1.4	160	240	0	8	1.4			0.6
	40F60G/8/1.2	160	240	0	8	1.2	1200		0.6
	40F60G/8/1.0	160	240	0	8	1.0			0.6
C1	40F60G/6/1.0	160	240	0	6	1.0	1200		0.6
	40F60G/6/1.2	160	240	0	6	1.2			0.6
D1	80F20G/8/1.2	320	80	0	8	1.2			0.6
	60F40G/8/1.2	240	160	0	8	1.2	1200		0.6
	40F60G/8/1.2	160	240	0	8	1.2			0.6
A2	60F40FA/10/1.2	240	0	160	10	1.2			0.6
	60F40FA/8/1.2	240	0	160	8	1.2	1200		0.6
	60F40FA/6/1.2	240	0	160	6	1.2			0.6
B2	60F40FA/8/1.4	240	0	160	8	1.4			0.6
	60F40FA/8/1.2	240	0	160	8	1.2	1200		0.6
	60F40FA/8/1.0	240	0	160	8	1.0			0.6
D2	80F20FA/8/1.2	320	0	80	8	1.2			0.6
	60F40FA/8/1.2	240	0	160	8	1.2	1200		0.6
	40F60FA/8/1.2	160	0	240	8	1.2			0.6

6.1.1 Component Optimisation in the Spent FCC Geopolymer System

The optimization of the FCC geopolymer system involves the optimisation of the Na⁺ concentration and SiO₂/Na₂O ratio in the activator, and the ratio of FCC to GGBS/FA in the precursor.

The impact of Na⁺ concentration in the activator on the mechanical performance of the geopolymers appears in Figure 6-1. In the FCC-GGBS system (Group A1, Figure 6-1a), the Na⁺ concentration of 8 mol/L yields the highest compressive strength of 51.47 MPa. The highest flexural strength of 8.67 MPa is achieved at 6 mol/L, though this concentration lowers compressive strength by 11.15% when compared to the 8 mol/L Na⁺ concentration. Increasing Na⁺ to 10 mol/L raises flexural strength by 20.74% but decreased compressive strength by 3.94%. In the FCC-FA system (Group A2, Figure 6-1b), 8 mol/L Na⁺ concentration produced the highest compressive and flexural strengths. Increasing Na⁺ to 10 mol/L lowered compressive and flexural strength by 3.08% and 11.33% respectively, while reducing Na⁺ to 6 mol/L significantly lowered mechanical performance, with strengths dropping to 7.63 MPa and 1.73 MPa, for compressive and flexural respectively.

Increasing Na⁺ concentration from 6 mol/L to 8 mol/L enlarges compressive strength in both the GGBS (high-Ca) and the FA (low-Ca) system, and the strength increase in the FA system is substantial (Figure 6-1b). The results agree with Rashad & Zeedan (2011). According to the authors, in a low-Ca system, compressive strength significantly depends on the activator concentration, with higher concentration improving strength. The results also agree with

previous authors claiming that low-Ca materials such as FA are particularly affected by the system's alkalinity, requiring increased alkalinity to start reactions (Palomo & Grutzeck, 1999; Provis & Van Deventer, 2009; Puertas et al., 2000).

Conversely, when increasing Na^+ concentration to 10 mol/L the performance of both geopolymer systems tends to slightly deteriorate (Figure 6-1). Rashad et al. (2016) observed a similar pattern in a high-Ca system. The authors claim that increasing Na^+ concentration enhanced the reaction between silicate and Ca, forming calcium silicate hydrate (C-S-H) thereby increasing strength. However, over a certain threshold, increasing Na^+ concentration did not further enhance mechanical strength.

Burciaga-Díaz et al. (2010) report that, in a metakaolin-GGBS system, when Na_2O content exceeded 10%, detrimental carbonation occurred with associated cracking in the matrix due to the excessive Na^+ which decreased mechanical performance. According to Singh et al. (2016) overly high alkalinity at high Na^+ concentration may cause polycondensation of silicates prior to the polymerisation reaction resulting in low strength.

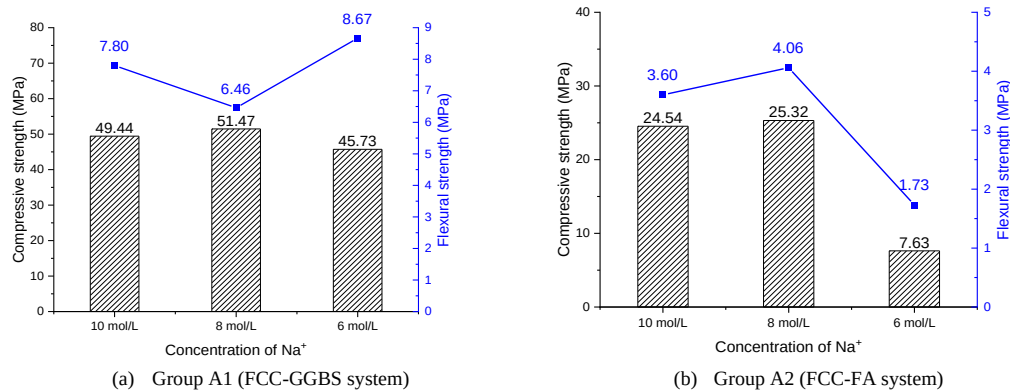


Figure 6-1 Effect of varying Na^+ concentrations in the activator on mechanical strength

Based on the results above, the Na^+ concentrations of 6 mol/L and 8 mol/L in the FCC-GGBS system and 8 mol/L in the FCC-FA system are selected for further optimization.

The effect of different $\text{SiO}_2/\text{Na}_2\text{O}$ ratios on the FCC geopolymers appears in Figure 6-2. Adjusting the $\text{SiO}_2/\text{Na}_2\text{O}$ activator ratio significantly affects both the alkalinity and the availability of silicate in geopolymer systems: lowering the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio increases alkalinity while reducing the silicate content, and vice versa. An overly increase in $\text{SiO}_2/\text{Na}_2\text{O}$ ratio can lead to the agglomeration of silicate species which form condensed silicate, rising the proportion of Q^2 and Q^3 units in the silicate solution. Agglomeration can impair activation and negatively affect the rheology of the geopolymer paste (Duxson et al., 2005). Lowering $\text{SiO}_2/\text{Na}_2\text{O}$ ratio results in the presence of Q^0 and Q^1 units due to depolymerization under high alkali conditions (Zhang et al., 2020).

In the FCC-GGBS (high-calcium) system (Group B1 and C1, Figure 6-2a), the mechanical properties generally improved with an increase in the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio. When Na^+ is fixed at 8 mol/L, increasing $\text{SiO}_2/\text{Na}_2\text{O}$ ratio enhances compressive strength and provides the highest strength of 57.01 MPa at $\text{SiO}_2/\text{Na}_2\text{O} = 1.4$. Reducing the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio from 1.4 to 1.2 produced a 10.76% reduction in compressive strength and 14.32% reduction in flexural

strength; and further decreasing the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio to 1.0 only led to minor variations: 3.10% flexural strength increase and slight decrease in compressive strength.

The dissolution and reactivity of GGBS are less dependent on alkalinity due to its inherent hydraulic properties. According to Wang et al. (Wang et al., 1994), for an activated basic slag, mechanical performance improves with increasing Ms up to an optimal value of 1.25. They also found that slags activated with highly alkaline, NaOH solutions exhibit poorer mechanical performance than those activated with silicate, highlighting the critical role of available silicate in strength development over mere alkalinity. However, in lower alkalinity scenarios where Na^+ concentration is 6 mol/L, compressive strength did not consistently increase with higher $\text{SiO}_2/\text{Na}_2\text{O}$ ratios: increasing the ratio from 1.0 to 1.2 lowered compressive strength by 4.65% but significantly increased flexural strength by 31.36%. This indicates that increasing the quantity of silicate in the activator does not compensate for a low, silicate content triggered by the deficient dissolution of a precursor in low alkaline conditions. The significant improvement in flexural strength caused when raising $\text{SiO}_2/\text{Na}_2\text{O}$ ratio may be related to the high silica avoiding the negative effect of Na_2O content on the cracking of the matrix.

In the FCC-FA system (Group B2, Figure 6-2b), the best mechanical performance was found at $\text{SiO}_2/\text{Na}_2\text{O} = 1.2$. Increasing or decreasing the $\text{SiO}_2/\text{Na}_2\text{O}$ worsened mechanical performance. Specifically, elevating the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio to 1.4 results in substantial strength loss (32.46% compressive strength and 28.82% flexural). In this high $\text{SiO}_2/\text{Na}_2\text{O}$ scenario (Ms=1.4), the reduced alkalinity limited the dissolution of FA, hence lowering strength (Figure 6-2b). This agrees with the results above. As aforementioned, FA systems are more dependent on the activator's alkalinity than GGBS systems, and their compressive strength significantly depends on the activator concentration, with higher alkalinity improving mechanical strength. Furthermore, a low $\text{SiO}_2/\text{Na}_2\text{O}$ ratio = 1.0 also diminished mechanical performance due to insufficient silicate being available to form cementing gels that provide strength to geopolymers. This agrees with previous authors (Shekhawat et al., 2019). Furthermore, Somna et al. (2011) and Sukmak et al. (2013) report that high alkalinity can cause premature precipitation of aluminosilicate gels before geopolymerisation, leading to weaker structures. The FCC-FA system results also agree with Cho et al. (2017) who confirmed the sensitivity of FA to alkali concentration, Ms value and curing conditions and emphasized the critical role of a precise composition to optimize geopolymer properties.

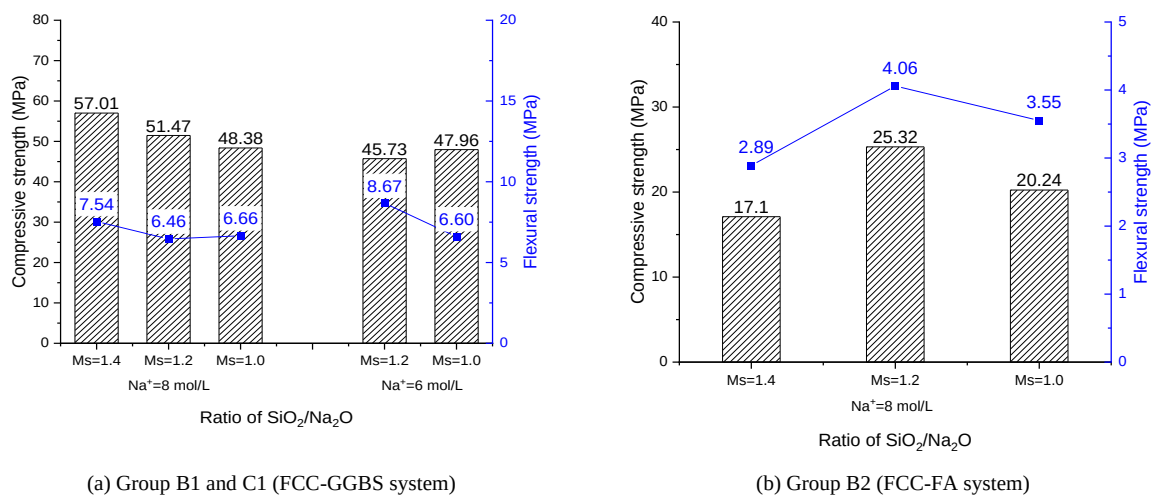


Figure 6-2 Effect of different $\text{SiO}_2/\text{Na}_2\text{O}$ ratios in activator on mechanical strength

In summary, the FCC-GGBS system demonstrates superior robustness and works well with a wider range of Na^+ concentrations and $\text{SiO}_2/\text{Na}_2\text{O}$ ratios of activator without significant impact on mechanical properties. Therefore, within a certain parameter range, changes in activator composition do not markedly impact the FCC-GGBS geopolymer. Higher Na^+ concentration and greater $\text{SiO}_2/\text{Na}_2\text{O}$ ratios generally mean higher costs and more carbon emissions, as activators contribute a major part of the cost and carbon footprint of geopolymers. Given the robust nature of the FCC-GGBS system, opting for lower Na^+ concentrations and $\text{SiO}_2/\text{Na}_2\text{O}$ ratios is advisable to balance performance with cost-efficiency and sustainability.

In contrast, the FCC-FA system is more sensitive to the activator composition. Any deviation from the optimal activator composition markedly deteriorates the mechanical properties of the FCC-FA geopolymer. Therefore, a strict activator composition is essential to guarantee the desirable mechanical performance and reliability of the geopolymer system. Based on the results above, Na^+ concentration = 8 mol/L and $\text{SiO}_2/\text{Na}_2\text{O}$ = 1.2 were selected to further optimise the FCC geopolymer system.

The effect of varying FCC-GGBS/FA ratios on mechanical strength appears in Figure 6-3. In the FCC-GGBS geopolymers, the compressive strength continuously increased with rising GGBS substitution, up to the highest value of 51.47MPa, attained by the geopolymer made with 40% spent FCC catalyst and 60% GGBS (Figure 6-3a) which also provided the highest flexural strength (6.46MPa).

In contrast, the FCC-FA system exhibits an anomalous pattern: the highest flexural strength was achieved when the FCC:FA ratio was 80:20 but increasing FA substitution results in a significant reduction in flexural strength. At 40% FA content, the flexural strength decreases to 4.06 MPa, a reduction of 21.32%, and the specimens failed to develop any strength when further increasing FA to 60%. However, the geopolymer made with 60% spent FCC and 40% FA reached a significant compressive strength of 25.32 MPa.

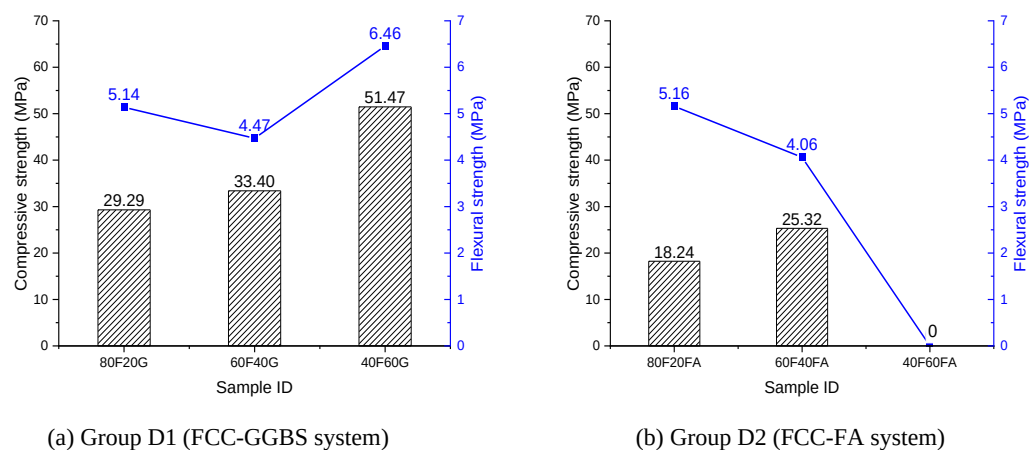


Figure 6-3 Effect of varying FCC-GGBS/FA ratios on mechanical strength

Therefore, substitution of spent FCC catalyst with GGBS enhances strength development but increasing FA content over 40% has an adverse effect on the strength of the resultant geopolymers. GGBS, with a latent hydraulic content and being totally amorphous, is more reactive than the semi-crystalline FA; and these mineral differences cause different dissolving

patterns (Alelweet & Pavia, 2020; Lei & Pavia, 2023). GGBS rapidly reacts with alkalis releasing Si, Al and Ca species to participate in polymerization reactions, while FA displays a delayed dissolution, requiring around 24h to begin slowly dissolving (Lei & Pavía, 2022). The quick dissolution of GGBS effectively alters the initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the system. The initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of FCC was calculated as 1.45; however, when incorporating 60% GGBS, this value increases to 2.28. Therefore, GGBS provides Si for the polymerization, especially in early stages, to form Si-rich gels that contribute to strength development. In contrast, the delayed dissolution of FA halts strength development and lowers the ultimate strength of FCC-FA geopolymer. Furthermore, the high Ca content of GGBS contributes to the formation of C-S-H and C-A-S-H gels that produce strength (Burciaga-Díaz et al., 2010; Duxson, Mallicoat, et al., 2007; Fernández-Jiménez et al., 2003; Palomo & Grutzeck, 1999; Provis & Van Deventer, 2009).

6.1.2 Microstructure of FCC Geopolymer

The composition and microstructure of the FCC geopolymers were examined with XRD, FTIR and SEM/EDX. The mineral composition of FCC-GGBS geopolymer is presented in Figure 6-4. In all the XRD traces, the characteristic peaks of the faujasite originally comprising the spent FCC catalyst have disappeared. This indicates that the original zeolite phases in the FCC catalyst have dissolved into Si and Al species to participate in polymerization reactions. A hump centred at approximately $2\theta = 29.5^\circ$ appears in all the FCC-GGBS geopolymers, indicating lack of long-range order and a totally amorphous nature. Furthermore, according to the results, variations in the activator composition did not significantly impact the mineralogy of the geopolymer.

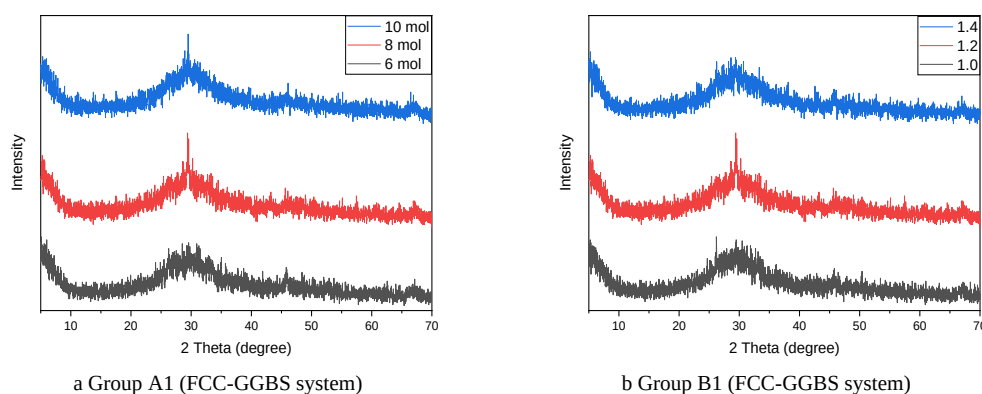


Figure 6-4 Mineral composition of FCC-GGBS geopolymers made with activators of varying Na^+ concentration and $\text{SiO}_2/\text{Na}_2\text{O}$.

The 60%FCC+40%FA geopolymer (60F40FA), activated with a sodium silicate solution of Na^+ concentration= 8 mol/L and modulus of 1.2, was selected as the optimal formula to be compared with the FCC-GGBS geopolymer. The mineral composition of 60F40FA appears in Figure 6-5. An intensive peak of quartz was found which may originate from the unreacted part of FA. A hump centred at $2\theta = 26.5^\circ$ is also present, located at a greater angle than in the FCC-GGBS geopolymer.

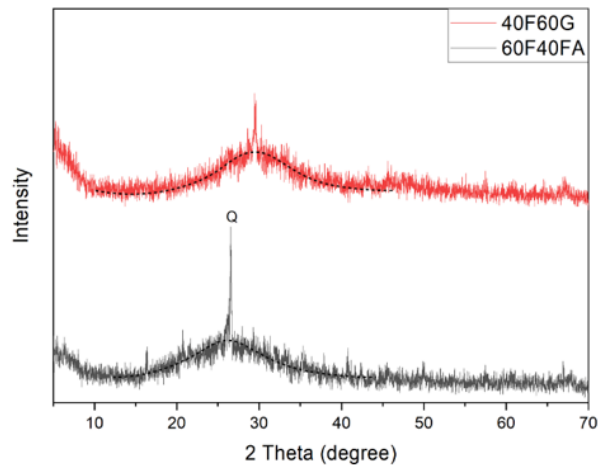


Figure 6-5 Mineral composition of FCC-FA geopolymer compared with an equivalent FCC-GGBS geopolymer. F- spent FCC catalyst; G-GGBS.

The FTIR spectra of the FCC geopolymers are included in Figure 6-6. A Portland cement specimen (CEM II/A, w/b=0.6) was analysed as a reference. The spectra of PC and FCC geopolymers show analogous absorption bands. The band centred at 1650 cm^{-1} is associated with the O-H bending modes of molecular water (Lecomte et al., 2006a). The band located at $\sim 1450\text{ cm}^{-1}$ is assigned to the anti-symmetric stretching of CO_3^{2-} in carbonate (Gunasekaran et al., 2006). The PC specimens showed the most pronounced absorption in the carbonate bands, followed by the FCC-FA geopolymer. Even though the FCC-GGBS geopolymer contained a considerable amount of Ca originating from GGBS, it shows negligible absorption in the carbonate band. The presence of carbonate in PC is probably due to the carbonation of $\text{Ca}(\text{OH})_2$, a hydration product of Portland cement. The carbonate in the FCC-FA geopolymer may arise from the carbonation of the alkali activator. Typically, low-Ca geopolymer is less sensitive to atmospheric carbon than high-Ca geopolymer (Sufian Badar et al., 2014). However, the FTIR spectra results disagree, showing a considerable carbonate absorption band for the low-Ca, FA geopolymer. This suggests that an improperly activated low-Ca geopolymer is vulnerable to carbonation while a properly activated high-Ca geopolymer is resistant to carbonation since Ca^{2+} participates in polymerization before it is exposed to atmospheric CO_2 .

The main band of PC and geopolymers, located at $\sim 1000\text{--}940\text{ cm}^{-1}$, is attributed to the anti-symmetric Si-O-Si(Al) stretching vibrations (Lecomte et al., 2006a). The broadness of this band indicates an amorphous nature. In FCC-FA geopolymer, the main band appears at a higher wavenumber, with more intense absorption. The Si-O stretching modes for SiQ^n units are characterized by infrared absorption bands at approximately 1200, 1100, 950, 900, and 850 cm^{-1} for $n = 4, 3, 2, 1$ and 0, respectively (Clayden et al., 1999). The infrared absorption bands of Si-O shift to a higher wavenumber due to the presence of more extensive cross-links, and shift to a lower wavenumber due to silicon substitution by aluminium (Lecomte et al., 2006a). This suggests that the cementing gel in FCC-FA geopolymer has a higher degree of polymerisation than the PC and FCC-GGBS geopolymer, and it is likely to consist of molecular polymerisation units such as Q^2 and Q^3 .

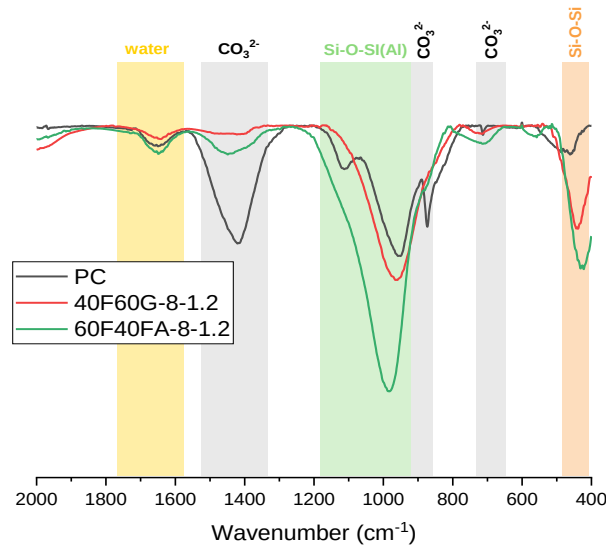


Figure 6-6 FTIR spectra of FCC geopolymers compared with CEM II.

The SEM/EDX analyses revealed significant distinctions between the FCC-GGBS and FCC-FA geopolymers as shown in Figure 6-7. The FCC-GGBS geopolymer exhibited a compact and dense matrix with no residual, unreacted FCC particles. The EDX analyses consistently showed high Si, Al, Na and Ca contents in the amorphous cement, indicating the presence of C(N)-A-S-H gel. The ratio of Si/ Al/ (Ca+Na) was calculated at 2.49: 1: 1.93. The high Si content in the cementing gels proves that the FCC and GGBS were substantially activated. The microcracks are attributed to the shrinkage of the geopolymer.

The FCC-FA geopolymer displays a totally different microstructure including a considerable number of unreacted FCC and FA particles which indicate poor activation of the FCC-FA system. The ratio of Si/Al/Na in the gel content was calculated as 2.51: 1: 1.06. The apparent coarse-grained matrix agrees with the poorer mechanical performance shown by the FCC-FA geopolymer.

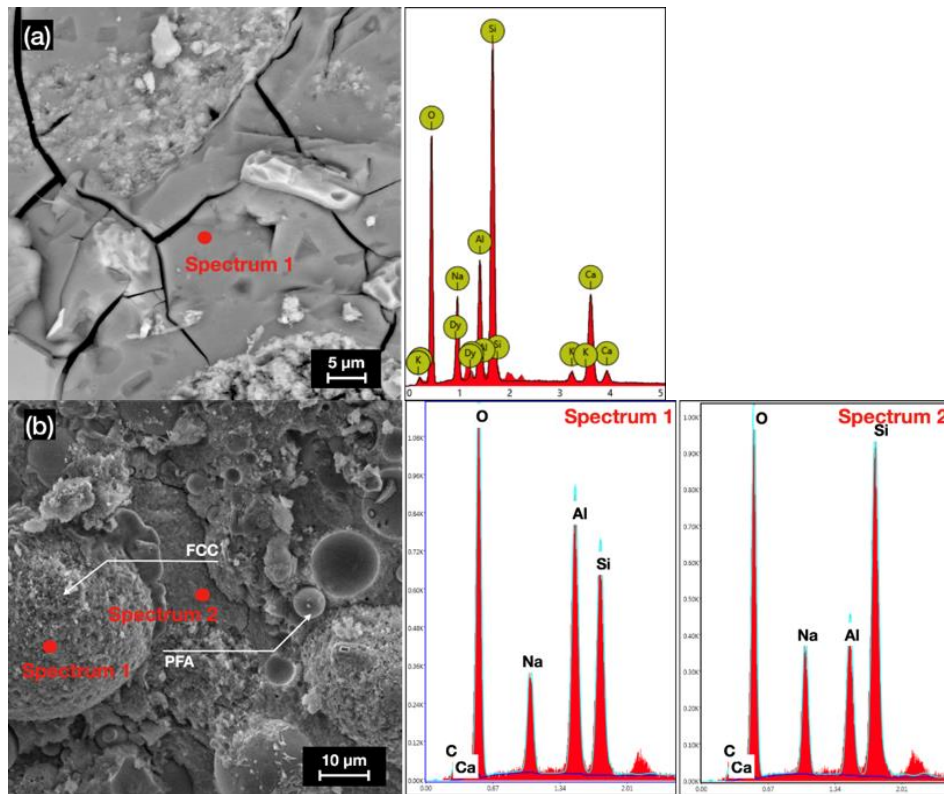


Figure 6-7 FCC geopolymer composition and microstructure. (a) FCC-GGBS geopolymer 40F60G 8/1.2 and (b) FCC-FA geopolymer 60F40FA 8/1.2

6.2 CROP BIOMASS ASH (CBA)

As aforementioned, CBA has low reactivity due to the high crystallinity of its mineral components. Alkali fusion is an effective method for enhancing the reactivity of CBA as demonstrated in the previous chapter. Therefore, in this section, raw and alkali-fused CBA were used as precursors to develop geopolymers.

The mix design used in this section is presented in Table 6-2. The nomenclature of the samples is the same as before (with C standing for CBA, fC for alkali-fused CBA, and G for GGBS) and the number in front indicating the percentage of precursor. The last two numbers indicate the concentration of Na^+ and the percentage of $\text{SiO}_2/\text{Na}_2\text{O}$ in the activator solution. As aforementioned, to obtain alkali-fused CBA, raw CBA was calcined with NaOH at 600°C.

Table 6-2 Mix design of CBA-based geopolymer. (w/b = 0.6. C = CBA; fC = alkali fused CBA; G = GGBS)

Group	Notation	Precursor (g)			Activator		Sand (g)
		Raw	CBA Alkali-fused	GGBS	Na ⁺ Concentration mol/L.	SiO ₂ /Na ₂ O ratio	
A	100C	400			10	1.2	1200
A	100fC		400		10	1.2	
B	70C30G	280		120	10	1.2	
B	70fC30G		280	120	10	1.2	
B	50C50G	200		200	10	1.2	
B	50fC50G		200	200	10	1.2	
B	30C70G	120		280	10	1.2	
B	30fC70G		120	280	10	1.2	
C	100fC/8/1.0		400		8	1.0	
C	100fC/8/1.2		400		8	1.2	
C	100fC/8/1.4		400		8	1.4	
C	100fC/10/1.0		400		10	1.0	
C	100fC/10/1.2		400		10	1.2	
C	100fC/10/1.4		400		10	1.4	
C	100fC/12/1.0		400		12	1.0	
D	30fC70G/8/1.0		120	280	8	1.0	
D	30fC70G/8/1.2		120	280	8	1.2	
D	30fC70G/8/1.4		120	280	8	1.4	
D	30fC70G/10/1.0		120	280	10	1.0	
D	30fC70G/10/1.2		120	280	10	1.2	
D	30fC70G/10/1.4		120	280	10	1.4	
D	30fC70G/12/1.0		120	280	12	1.0	

6.2.1 Performance of CBA-based Geopolymer

The flowability of CBA-based geopolymers is presented in Figure 6-8. The geopolymer made with 100% CBA, both raw and alkali fused, has low workability, showing the lowest initial flow diameters of 100 mm. This observation aligns with similar findings in rice husk ash (RHA)-based geopolymers, as reported by Patel & Shah (2018a, 2018b) and Nishanth & Patil (2022). RHA shares a similar morphology with CBA due to their analogous origin. The low workability agrees with the high particle porosity observed through the SEM. The CBA absorbs significant water quickly due to the porous nature of its particles, diminishing flowability. The incorporation of GGBS improves the flowability of the CBA geopolymer mortars. It is well known that GGBS has high workability and tends to enhance the flow of composites (Walker & Pavía, 2011). On the contrary, alkali-fusion lowers the flowability of the geopolymer. When adding water to the fused CBA, sodium residues from the NaOH used in the fusion, carbonate with atmospheric carbon to form sodium carbonate crystals which resist flow, hence lowering workability.

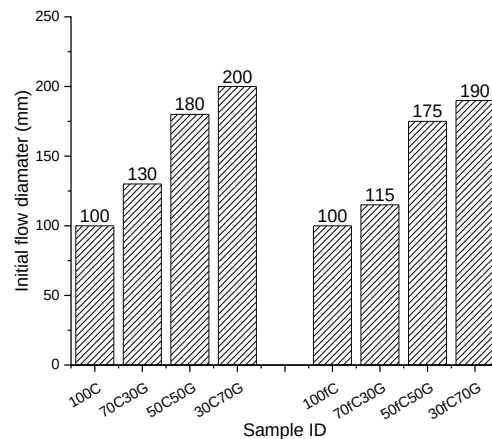


Figure 6-8 Flowability of CBA and CBA-GGBS geopolymers.

The strength of the CBA geopolymers at 28d appears in Figure 6-9 and the standard deviation is given in Table 6-3. The geopolymers made with raw CBA increase strength with increasing CBA substitution with GGBS. After 28 days, the geopolymer made with 100% raw CBA (100C) yields the lowest compressive and flexural strength of 7.46 MPa and 2.99 MPa respectively. The incorporation of GGBS improved mechanical performance: replacing 30%CBA with GGBS increased compressive and flexural strengths to 13.32 MPa and 4.14 MPa respectively, corresponding to improvements of 78.55% and 38.46%. Further replacing CBA with GGBS increased mechanical strength: at 50% GGBS replacement, the compressive and flexural strengths rose to 18.91 MPa and 6.52 MPa respectively. Increasing GGBS content (to 70%) yields a further enhancement, with values reaching 29.83 MPa and 7.35 MPa for compressive and flexural strength respectively.

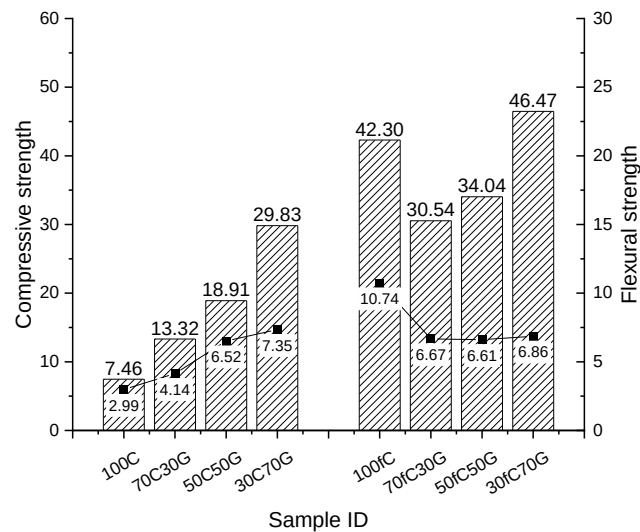


Figure 6-9 Effect of alkali-fusing the CBA on the mechanical performance of CBA and CBA-GGBS geopolymers (MPa) (Groups A and B in Table 6-2: $[Na^+] = 10 \text{ mol/L}$ and $M_s = 1.2$).

Table 6-3 Standard deviation of mechanical properties in Figure 6-9.

Notation	Compressive strength	Flexural strength
100C	1.29	0.37
70C30G	1.30	0.23
50C50G	2.02	0.54
30C70G	1.38	0.65
100fC	1.66	1.37
70fC30G	0.82	0.56
50fC50G	3.06	0.41
30fC70G	1.63	0.62

The geopolymers made with alkali fused CBA show enhanced performance. The geopolymer made with 100% alkali fused CBA (100fC) achieved compressive and flexural strengths of 42.30 and 10.74 MPa respectively, improving by 467.02% and 259.20% respectively when compared to the geopolymer made with raw CBA. Replacing alkali-fused CBA with GGBS slightly lowers mechanical strength: at 30% GGBS content, compressive strength decreased

from to 30.54 MPa and increasing GGBS to 50% did not significantly alter mechanical performance. However, at 70% GGBS content, a notable improvement in compressive strength was found at 46.47 MPa.

The geopolymers made with alkali-fused CBA display higher strengths than their raw CBA counterparts, therefore, alkali-fusing the ash releases active silica from the ash that forms cementing hydrates that contribute to the strength of the CBA geopolymer. The active silica and calcium released by the GGBS also participate in the polymerization reaction increasing strength. However, the strength increase triggered by GGBS substitution is more consistent and pronounced in the raw CBA group, indicating that the synergistic effect between GGBS and CBA becomes weaker when the CBA is fused.

The crucial role of precursor dissolution, providing silicon and aluminium species essential for the subsequent gelation and polymerization processes, is well established in geopolymer technology (Duxson, Fernández-Jiménez, et al., 2007). The limited dissolution of the crystalline phases (quartz and albite) comprising the CBA, results in the inferior mechanical performance of raw CBA geopolymers. Silicate crystals such as quartz and albite are highly stable chemically and thermally, and require strong acidic/alkaline conditions to partially dissolve. Therefore, within the alkalinity range of the activator in this research, the silicates in the CBA contribute little or nothing to polymerisation. Improving the reactivity of the CBA precursor with alkali fusion enhances geopolymer performance much more efficiently than adding active silica (slag). Alkali fusion breaks down the CBA's silicate structures releasing active radicals that participate in polymerisation reactions improving the geopolymer performance.

The geopolymers made with alkali-fused CBA (100fC and 30fC 70G groups) were selected to further investigate the optimum activator composition due to their excellent mechanical performance. The effect of the activator composition, i.e. Na^+ concentration and $\text{SiO}_2/\text{Na}_2\text{O}$, on the geopolymer performance is presented in Figure 6-10. The geopolymers made with activators of ratio $\text{SiO}_2/\text{Na}_2\text{O}=1.0$ produced a flash set regardless of the $[\text{Na}^+]$. Flash set produced premature hardening and lack of workability so that strength could not be measured. Flash set of geopolymer is rarely reported and, when reported, it is linked to high pH and high-calcium (Class C) fly ash-based geopolymers (Antoni et al., 2017; Satria et al., 2017; Tailby & MacKenzie, 2010). In contrast, in this research, flash sets occurred at both high-calcium (Group D- 70%GGBS) and low-calcium content (Group C- 100 fC), when the activator $\text{SiO}_2/\text{Na}_2\text{O}$ was 1.0. The relatively low ratio of $\text{SiO}_2/\text{Na}_2\text{O} = 1.0$ implies high alkalinity. A clear pattern exists where the most alkaline activator ($\text{SiO}_2/\text{Na}_2\text{O} = 1.0$) triggered the flash set of the geopolymer. The high alkalinity caused rapid precursor dissolution which produced a flash set.

The geopolymers made with alkali-fused CBA (100fC group) performed best when the $\text{SiO}_2/\text{Na}_2\text{O}$ was 1.2. Increasing silica content beyond this ratio worsened mechanical performance, suggesting that an excessive $\text{SiO}_2/\text{Na}_2\text{O}$ ratio provides insufficient alkalinity for effective precursor dissolution while providing excess soluble silica. This imbalance likely promotes polymerization of silica species within the activator, hindering the dissolution of the precursor. The results also indicate that maintaining the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio while increasing the Na^+ concentration of the activator slightly improves strength development.

The geopolymers made with alkali-fused CBA and GGBS (30fC70G group) constantly display outstanding mechanical performance (38-47 MPa compressive strength at 28 d.). The best mechanical performance was observed in the geopolymer activated with a 10 mol/L solution

having a $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 1.2. However, the combined effect of the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio and Na concentration on strength is inconsistent. At low Na^+ concentration (8 mol/L), raising the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio from 1.2 to 1.4 significantly increased the geopolymer strength from 38.07 to 45.79 MPa. However, at higher Na^+ concentration (10 mol/L) it lowers it (from 46.47 to 43.64 MPa). The combination of low Na^+ concentration with low $\text{SiO}_2/\text{Na}_2\text{O}$ ratio likely contributes less available SiO_2 which lowers strength, while the higher alkalinity (10 mol/L) combined with the high $\text{SiO}_2/\text{Na}_2\text{O}$ ratio can saturate Si in the system preventing its polymerisation and cement formation which decrease strength.

The presence of GGBS significantly enhanced strength and stabilized the system against fluctuations in activator composition. Unlike the dramatic strength reductions seen in the low-calcium system (100fC group) when lowering alkalinity and increasing the silica content beyond $\text{SiO}_2/\text{Na}_2\text{O} = 1.2$, the strength of the 30fC70G geopolymers remains stable over the whole range of ratios investigated (1.0-1.4), and increasing $[\text{Na}^+]$ does not significantly impact strength.

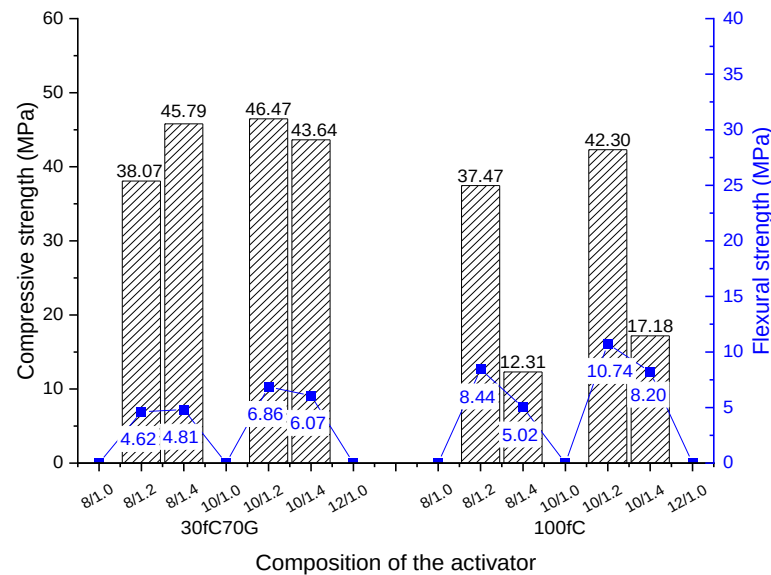


Figure 6-10 Effect of activator's alkalinity and silica modulus on the mechanical performance of CBA and CBA-GGBS geopolymers (Groups C and D).

Table 6-4 Standard deviation of mechanical properties in Figure 6-10.

Precursor	Activator	Compressive strength	Flexural strength
30fC70G	8/1.2	2.12	0.42
	8/1.4	3.20	0.12
	10/1.2	1.63	0.62
	10/1.4	2.08	0.28
100fC	8/1.2	3.67	0.47
	8/1.4	1.37	0.67
	10/1.2	1.66	1.37
	10/1.4	2.57	0.11

6.2.2 Microstructure of the CBA-based Geopolymer

The mineral compositions of CBA and CBA-GGBS geopolymers appear in Figure 6-11. The raw CBA geopolymer (100C) includes quartz and albite. These are unreacted remnants of the crystalline phases originally comprising the CBA and hence imply low reactivity. The intensity and sharpness of the peaks suggest significant crystalline content which may contribute to strength to some extent but does not form cementing gels that induce high mechanical performance which agrees with the strength results above (7.46MPa at 28d.). The geopolymer made with alkali-fused CBA (100fC) (Figure 6-11a) has lower crystallinity and a more amorphous structure that correlates with the formation of cementing gels characteristic of geopolymers and agrees with the greater mechanical performance seen above (39.35 MPa at 28 d.).

As can be seen from Figure 6-11b, replacing CBA with GGBS largely changed the mineral composition and structure of the geopolymer, from crystalline into amorphous, regardless of the CBA being fused or not. The amorphous nature is consistent with the general structures of geopolymers and alkali-activated materials (Lecomte et al., 2006b). The amorphous content represents ample cementing gel which enhances mechanical performance. The results evidence that the mineralogy and structure of the geopolymer (i.e. crystallinity vs amorphousness) do not necessarily mirror the mechanical properties: despite the abundant amorphous cement produced by the GGBS in the 30C 70G and 30fC 70G geopolymers (70% GGBS substitution), their strengths (13.32 MPa and 35.07 MPa respectively) are lower than the strength of the crystalline geopolymer (100fC) which reached 39.35 MPa.

Both GGBS and alkali fusion vitrify the structure of the geopolymers. However, GGBS vitrifies the structure to a much greater extent than alkali fusion. The results also indicate that alkali fusion at low temperature (600°C) breaks tectosilicate structures as strong and stable as quartz, as it can be seen from the reduction of the intensity of the quartz peak in the traces corresponding to the alkali-fused geopolymers (Figure 6-11a, b).

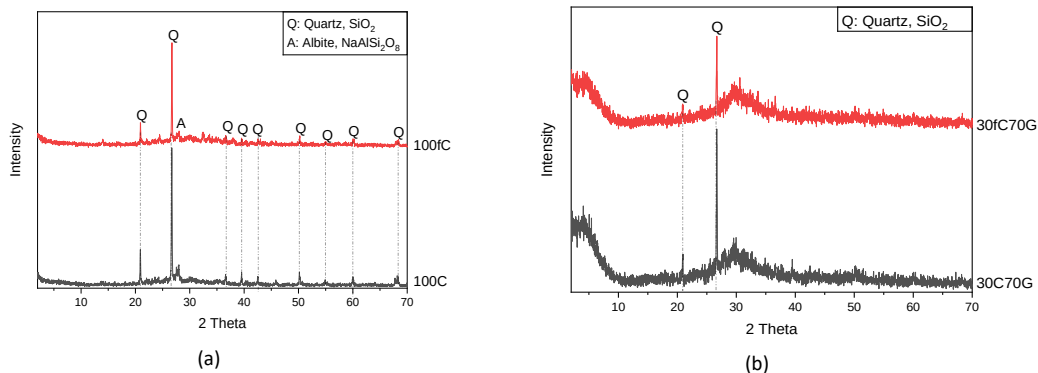


Figure 6-11 Mineral composition of (a) 100% CBA and (b) CBA-GGBS geopolymer.

The microstructure of the geopolymers appears in Figure 6-12 and Figure 6-13. Despite the drastic change in mineralogy and microstructure, from crystalline into amorphous, when GGBS was added (Figure 6-11), SEM analyses show vitreous geopolymer cements in all the geopolymers. The EDX analyses (Figure 6-12 and Figure 6-13.) revealed high Si and Na content in the vitreous geopolymer suggesting that they are a product of polymerisation consistent with previous authors. The main polymerisation reaction product of low-calcium (aluminosilicate-rich) precursors is an alkaline aluminosilicate hydrate gel (N-(A)-S-H) (Duxson, Fernández-Jiménez et al., 2007; Pacheco-Torgal et al., 2008; Provis & Van Deventer, 2013).

In the geopolymers made with 100% CBA, alkali fusion improved the quality of the matrix by substantially reducing cracking (Figure 6-12). An intricate network of cracks, occasionally interconnecting and breaking plates apart, is apparent in the raw CBA geopolymers (100C) while a denser matrix without obvious cracking appears in the alkali-fused CBA geopolymers (100fC). The vitreous cement of the alkali-fused CBA geopolymer (100fC) consistently shows a higher concentration of Si and Na which agrees with the presence of abundant Si-rich gel that is consistent with the enhanced mechanical performance seen in the strength results above. Particulate clusters appeared sporadically in the raw CBA geopolymer. These are unreacted remnants of CBA particles, as suggested by the high Si and a low Na content evidenced with EDX; and are consistent with the lower reactivity and lower mechanical performance of raw CBA geopolymers evidenced above. The alkali-fusion process significantly improved the reactivity of CBA in geopolymerisation reactions. However, some porous and sponge-like regions appear in the 100fC matrix, presumably unreacted, alkali-fused CBA particles (Figure 6-12).

Micrographs of the CBA-GGBS geopolymers are included in Figure 6-13. Adding GGBS made the vitreous geopolymer matrices more homogenous and denser, with fewer unreacted particles; however showing similar cracking. The cracks are due to autogenous unrestrained shrinkage and are typical of alkali-activated materials such as geopolymers. The cracks evidenced are shrinkage cracks inherent to the polymerisation process, caused by the loss of water inducing volume change during polymerisation (Pacheco-Torgal et al., 2014). Shrinkage cracks are common in alkali-activated slag and FA/GGBS geopolymers (Lima et al., 2022), and prone to occur in low Ca/Si matrices (Zhu et al., 2018).

In CBA-GGBS geopolymers, the incorporation of $[Ca^{2+}]$ in cementing gels can transform N-A-S-H into C-A-S-H gel which increases density and enhances mechanical performance (Wang et al., 2019) but can exacerbate shrinkage (Zhang et al., 2022). Ye & Radlińska (2016) also

report the collapse and redistribution of C-A-S-H gel leading to significant shrinkage. Furthermore, shrinkage relates to the content of Na_2O in high Ca systems and alkali fusion introduced significant Na^+ which triggered more intense autogenous shrinkage agreeing with (Neto et al., 2008).

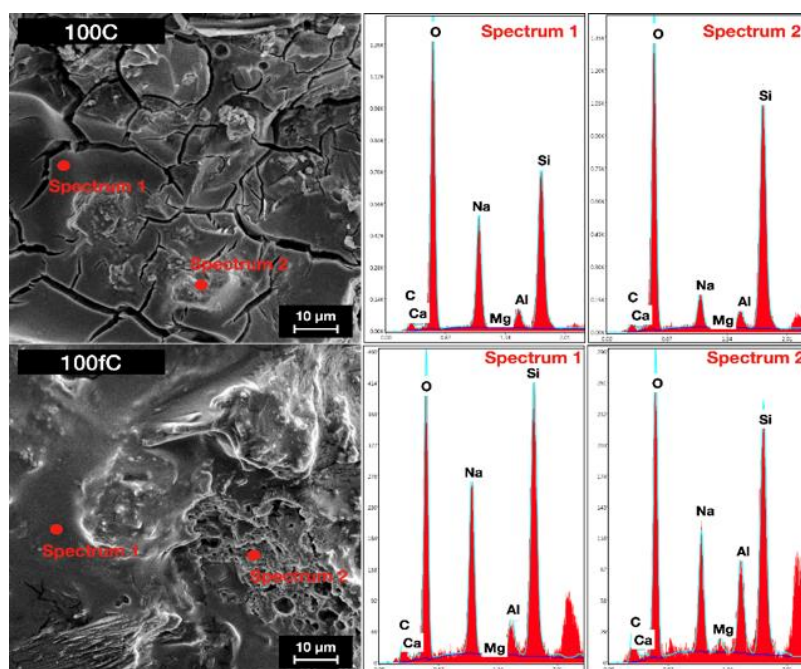


Figure 6-12 Micrographs of 100% CBA geopolymers. Top: raw CBA. Bottom: alkali-fused CBA.

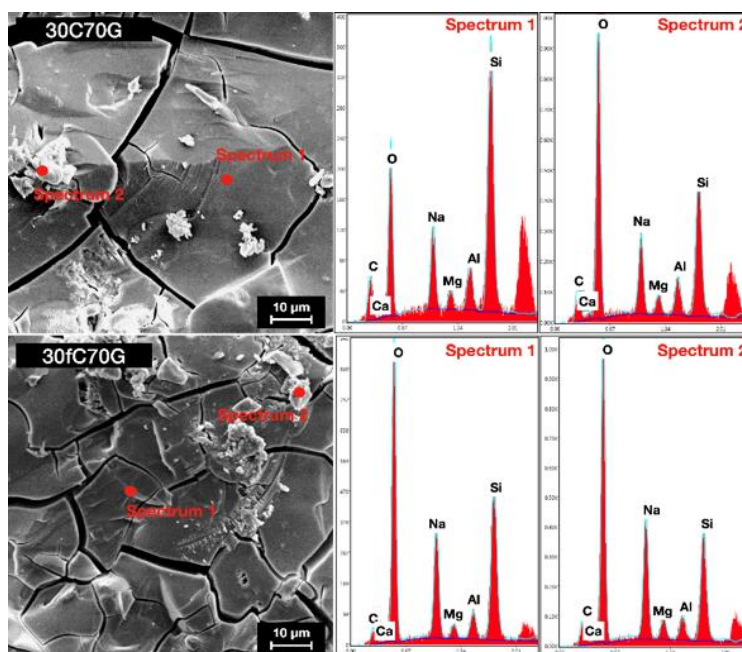


Figure 6-13 Micrographs of CBA-GGBS geopolymers. Top: raw CBA. Bottom: alkali-fused CBA.

The FTIR spectra of the geopolymers and the alkali-fused CBA powder (af-C) appear in Figure 6-14. The spectra are dominated by absorption bands located at $800\text{--}1200\text{ cm}^{-1}$ which are due to the stretching vibrations of Si-O-Si(Al) . The wide $800\text{--}1200\text{ cm}^{-1}$ bands in the CBA powder (af-C) and the CBA geopolymer (100fC) suggest a wide distribution of Si units with varying

bonds. In contrast, in the CBA-GGBS geopolymer (30fC70G), the main band is relatively narrow and shifted towards lower wave numbers indicating the substitution of Al into the Si-O-Si structure. The absorption band of Si-O-Si(Al) in the CBA-GGBS geopolymer is notably enhanced. This agrees with the significant contribution of GGBS to the geopolymerisation process evidenced in the results above.

The characteristic bands for carbonate occur in the spectral regions $1400\text{--}1600\text{ cm}^{-1}$ (ν_3 ; asymmetric stretch vibration) and $873\text{--}880\text{ cm}^{-1}$ (ν_2 ; out-of-plane bend vibration) (Fleet, 2009). Therefore, the bands located at $1350\text{--}1550\text{ cm}^{-1}$ are assigned to the anti-symmetric stretching of carbonate. Two distinct patterns were found: a broad band with a nearly symmetrical centre at 1392 cm^{-1} (30fC70G geopolymer) and two sharp bands with asymmetrical centres at 1440 and 1409 cm^{-1} (af-C powder and 100fC geopolymer). The $\nu_3(\text{CO})$ stretch mode in 30fC70G is characteristic of free carbonate ions (Fleet, 2009). The presence of free carbonate ions is attributed to the absorption of atmospheric carbon dioxide by the abundant Ca^{2+} in GGBS. The carbonate bands centred at 1440 and 1409 cm^{-1} (in the af-C powder and 100fC geopolymer) are narrower waves of higher wave numbers. These characteristics indicate that the carbonate is tightly connected to the matrix and may even be bound to it (Fleet, 2009). Therefore, the FTIR results indicate that the GGBS is more reactive than the alkali-fused CBA and that the Ca and Al in the system promoted polymerisation and participated in the reaction.

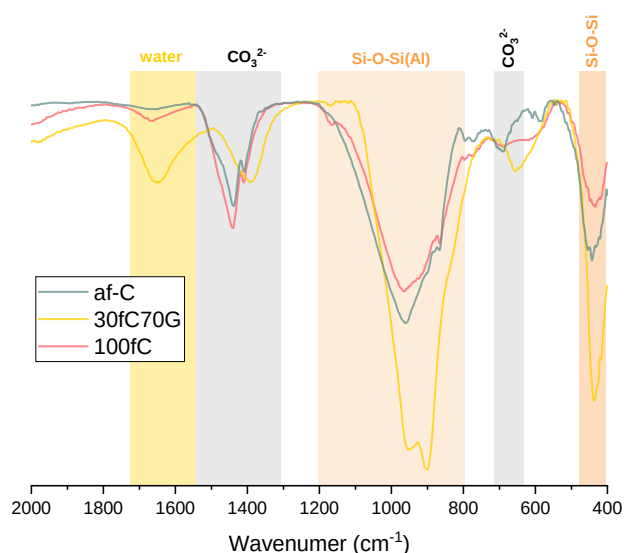


Figure 6-14 FTIR spectra of CBA and CBA-GGBS geopolymers and alkali-fused, CBA powder (af-C)

6.3 SUMMARY

In this section, FCC and CBA were used as precursors to develop two-part geopolymers. Based on the experimental results above, the conclusion is as follows:

FCC two-part geopolymer:

The FCC-GGBS system has superior robustness. A sodium silicate activator with Na^+ concentration ranging from 6 to 10 mol/L and $\text{SiO}_2/\text{Na}_2\text{O} = 1.0$ to 1.4 is suitable for the system and produces geopolymers of excellent mechanical performance consistently reaching values between approximately 45 and 57 MPa at 28 days.

The FCC-GGBS geopolymer has a dense matrix consisting of amorphous cement constantly showing high Si, Al, Na and Ca content and concurring with the presence of C(N)-A-S-H gel that contributes to its excellent mechanical performance. The FCC and GGBS activate well in the geopolymer: the faujasite originally comprising the spent FCC catalyst dissolved into the alkaline activator and participated in the geopolymerisation, developing amorphous cementing gels consisting of Si-O-Si(Al) links with varying degrees of polymerization.

The FCC-FA system is more sensitive to the composition of the activator. Any deviation from the optimal formulation caused a strength reduction of the FCC-FA geopolymer. The FCC-FA geopolymer failed to develop strength when the FA content raised to 60%. The rough and large grain of the geopolymer gel including unreacted FCC particles agreed with its lower mechanical performance. FA is not suitable for use with spent FCC in geopolymerisation.

CBA two-part geopolymer:

The geopolymers made with alkali-fused CBA and GGBS constantly display outstanding mechanical performance (38-47 MPa compressive strength at 28 d.). The availability of SiO₂ plays a significant role in strength development. The GGBS stabilized the geopolymer system against fluctuations in activator composition. The active Si, Al and Ca released by GGBS participate in the polymerization reaction, increasing strength of the geopolymer.

The geopolymers made with raw CBA alone reached the lowest strengths of 7.46 MPa and 2.99 MPa (compressive and flexural respectively). However, partially replacing raw CBA with GGBS raised strength to over 29 MPa and 7 MPa respectively.

Alkali-fusing the CBA greatly enhanced reactivity and improved polymerisation, and the geopolymer made with 100% alkali-fused CBA achieved compressive and flexural strengths of 42.30 and 10.74 MPa. Alkali fusing the raw CBA is an effective method for improving the mechanical performance of CBA geopolymers. Even at low temperature (600°C), alkali fusion breaks silicate structures as strong and stable as the quartz and feldspar originally comprising the CBA.

GGBS is more reactive than the alkali-fused CBA: GGBS amorphized the mineral composition/structure of the geopolymer to a much greater extent than the alkali-fused CBA. However, there is no direct proportionality between the increase of geopolymer vitreousness and improved mechanical performance because the 100% alkali-fused CBA geopolymer, with a crystalline structure, was nearly as strong as the vitreous CBA-GGBS geopolymer (38-47 MPa).

The most alkaline activator compositions (SiO₂/Na₂O = 1.0) caused rapid precursor dissolution which produced flash set of the geopolymer.

The geopolymers show a vitreous structure of cementing gels, with high Si⁴⁺ and Na⁺ contents, consistent with alkaline silico-aluminate hydrate gel (N-(A)-S-H) which is a typical product of polymerisation. FTIR spectrums show ample Si-O-Si(Al) bonds in the geopolymer made with alkali-fused CBA. The presence of GGBS significantly increased the absorption intensity of these bonds, indicating the presence of more abundant C(N)-A-S-H which improved mechanical properties.

6.4 REFERENCE IN THIS CHAPTER

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Chapter 7: One-part Geopolymer System

One-part geopolymers are more practical than their traditional (two-part) counterparts because they can be easily batched and mixed which facilitates commercialisation and application on site. The aim of this research is that industry uses the low-carbon materials developed. Therefore, one-part geopolymers are investigated to facilitate the application of research results. AS, CBA and OBA are used as precursors because of their great potential in geopolymer technology as demonstrated in the former chapters. They are also chosen because of their wide availability and consistent composition as explained in the background chapter.

7.1 ALUM SLUDGE (AS) ONE-PART GEOPOLYMER

In the previous chapter, AS was found to contain a high amount of organic matter and aluminium. Calcination at 800 °C effectively removed the organic matter and regulated the reactivity of AS to prevent abnormal setting.

The high reactivity of calcined AS positions it as a promising precursor for preparing a one-part geopolymer. This section aims to recycle and valorise AS by developing a one-part geopolymer. In this study, calcined AS was employed as the reactive source, with sodium carbonate and sodium silicate used as activators. The effect of activator composition (including $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio and modulus of the sodium silicate) on the microstructure and mechanical performance were investigated.

The mix design used in this section is presented in Table 7-1. The mixes are designed and split into groups A to E so that each group explores a design variable. In group A, the influence of different moduli of sodium silicate on the performance of AS-based geopolymer was investigated. Group B examines the influence of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios on the geopolymer performance by adjusting the sodium carbonate dosage. The design of groups C and D is based on the results of groups A and B. The groups investigate the effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ by adjusting the dosage of sodium silicate at varying AS content (of 20% and 30%).

Table 7-1 Mix design of one-part AS geopolymers (g).

	Binder (g)					Sand (g)	Water (g)	w/b*	SiO ₂ /Al ₂ O ₃ **	Na ₂ O/Al ₂ O ₃ **
	AS/800	GGBS	NS	Ms	NC					
A1	87.3 (30%)	203.8 (70%)	158.8 (54.6%)	1.0	0.0 (0.0%)	1500.0	320.0	0.8	2.5	1.36
A2	82.2 (30%)	191.7 (70%)	111.5 (40.7%)	2.0	64.6 (23.6%)	1500.0	225.0	0.5	2.5	1.36
A3	80.6 (30%)	188.0 (70%)	96.9 (36.1%)	3.0	84.5 (31.5%)	1500.0	225.0	0.5	2.5	1.36
B1	75.0 (20%)	300.0 (80%)	75.0 (20%)	2.0	0.0 (0.0%)	1500.0	225.0	0.5	2.5	0.43
B2	70.6 (20%)	282.4 (80%)	70.6 (20%)	2.0	26.4 (7.5%)	1500.0	225.0	0.5	2.5	0.70
B3	66.3 (20%)	265.3 (80%)	66.3 (20%)	2.0	52.0 (15.7%)	1500.0	225.0	0.5	2.5	1.00
B4	62.5 (20%)	250.2 (80%)	62.5 (20%)	2.0	74.7 (23.9%)	1500.0	225.0	0.5	2.5	1.30
B5	59.2 (20%)	236.7 (80%)	59.2 (20%)	2.0	94.9 (32.1%)	1500.0	225.0	0.5	2.5	1.60
B6	70.7 (20%)	282.7 (80%)	0.0 (0.0%)	2.0	96.6 (27.33%)	1500.0	225.0	0.5	1.65	1.00
C1	68.9 (20%)	275.7 (80%)	27.6 (8%)	2.0	77.8 (22.6%)	1500.0	225.0	0.5	2.0	1.0
C2	66.3 (20%)	265.3 (80%)	66.3 (20%)	2.0	52.0 (15.7%)	1500.0	225.0	0.5	2.5	1.0
C3	64.0 (20%)	255.9 (80%)	102.3 (32%)	2.0	27.8 (8.7%)	1500.0	225.0	0.5	3.0	1.0
D1	92.7 (30%)	216.3 (70%)	80.3 (26%)	2.0	60.6 (19.6%)	1500.0	225.0	0.5	2.0	1.0
D2	88.9 (30%)	207.4 (70%)	121.5 (41%)	2.0	32.3 (10.9%)	1500.0	225.0	0.5	2.5	1.0
D3	85.4 (30%)	199.2 (70%)	159.3 (56%)	2.0	6.2 (2.1%)	1500.0	225.0	0.5	3.0	1.0

7.1.1 Effect of the Activator Composition on the Performance of AS Geopolymer

Effect of varying moduli (Ms)

As can be seen from the results in Figure 7-1, increasing the moduli raises workability but beyond the threshold of Ms=2, the geopolymers are unable to develop any strength. The lack of strength is because, at Ms=3 there is not sufficient alkalinity to dissolve AS and GGBS and polymerization fails to initiate. The modulus determines alkalinity, and industry grades having a ratio higher than 2.94 are considered neutral. On the contrary, high alkalinity, due to low Ms, triggers rapid dissolution of the Al phase, forming crystal phases such as calcium aluminate hydrates (C-A-H) which hinder flow (Lei & Pavia, 2023).

Under the same SiO₂/Al₂O₃ and Na₂O/Al₂O₃ ratios, the specimens made with Ms=2.0 yield optimal mechanical performance in both compressive and flexural strength as shown in Figure 7-1(b). The geopolymer activated with sodium silicate of Ms=1.0 has the lowest flowability, even when the w/b ratio was increased to 0.80 (Table 7-1). An exothermic reaction with heat evolution took place during mixing. This is typical of too sudden and overly high reactivities that can lead to flash set which impedes flow which agrees with the low flow measured.

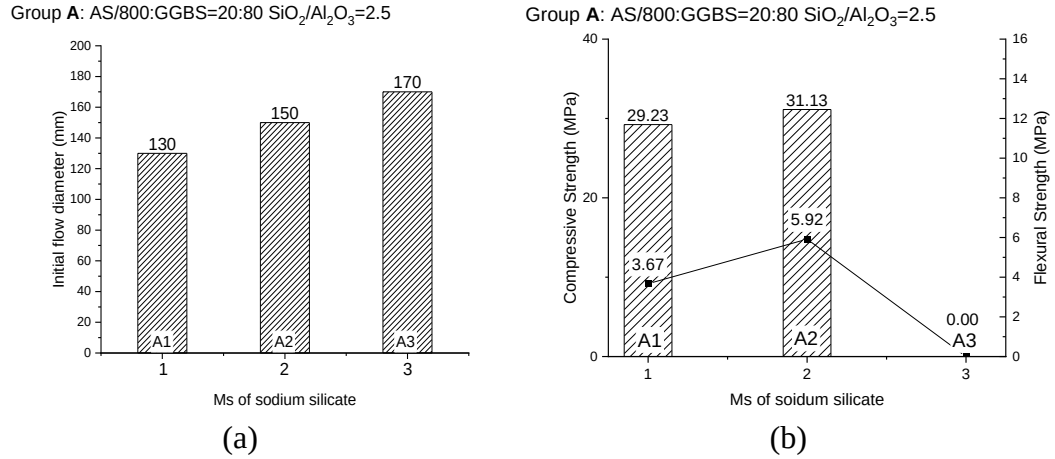


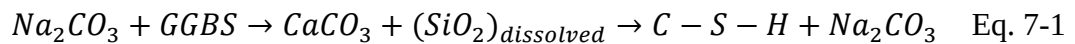
Figure 7-1 Properties of AS geopolymers activated with sodium silicate with varying Ms: (a) flowability, (b) mechanical strength.

Effect of sodium carbonate activator

In group B, the main variable is the amount of Na_2CO_3 activator -NC- which determines the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$. Specimens B1 are activated with sodium silicate (NS) only (hence they have the lowest $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 0.43$) while specimens B6 are solely activated with sodium carbonate therefore having the greatest $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 1.65 (Table 7-1). At constant $\text{SiO}_2/\text{Al}_2\text{O}_3$ (specimens B1-B5) the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio is governed by the dosage of sodium carbonate.

The strength and workability of the resultant geopolymers appear in Figure 7-2. The highest flowability is obtained when the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ is between 0.7 and 1.0. Increasing $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ significantly reduced workability. This likely caused by an overly high NC content: although sodium carbonate is highly soluble in water, large quantities are difficult to fully dissolve during mixing.

The highest compressive strength of 66.5 MPa is achieved at $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.00$. Strength decreases when $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ deviates from 1.0. The specimens activated solely with either sodium silicate (B1) or sodium carbonate (B6) yield poor mechanical performance indicating the important synergistic role of NC and NS in one-part repolymerization. NC plays a vital role in slag activation. Adesina (2021) notes the reaction mechanism of carbonate-activated slag as shown in Eq. 7-1. The CO_3^{2-} from NC combined the Ca^{2+} from GGBS promote dissolution and form carbonates such as calcite or gaylussite. Shi & Day (1995) report that the hydration of alkali-activated slag is determined by the action of the anion or anion group of the activator and the Ca^{2+} dissolved from the slag rather than by the initial pH of the activator.



Similarly, soluble silicate is equally important in geopolymerisation, especially in the presence of large amounts of highly reactive aluminium (AS). Soluble silicate provides ample raw material for polymerisation to form C-A-S-H gels at the early stages of the reaction which enhance mechanical performance. However, an overly high silicate concentration can inhibit the rapid reaction between the active AS and the NC activator in the initial stage and form a calcium monocarboaluminate phase which causes flash set (Lei & Pavía, 2022).

When $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ dropped below 1.0, the low alkalinity was not enough to trigger polymerization leading to low strength (B1 and B2).

The Al ions from the AS enter C-S-H by replacing Si on the tetrahedral sites. The charge imbalance caused by the replacement of Si^{4+} by Al^{3+} is balanced by the valence compensation of bound alkali metal ions, Na^+ in this system. The results suggest that $\text{Na}/\text{Al} = 1.0$ is optimal and greater ratios lower strength and workability. Excessive Na^+ in the geopolymer matrix may precipitate as salt and cause problems such as loss of strength and efflorescence.

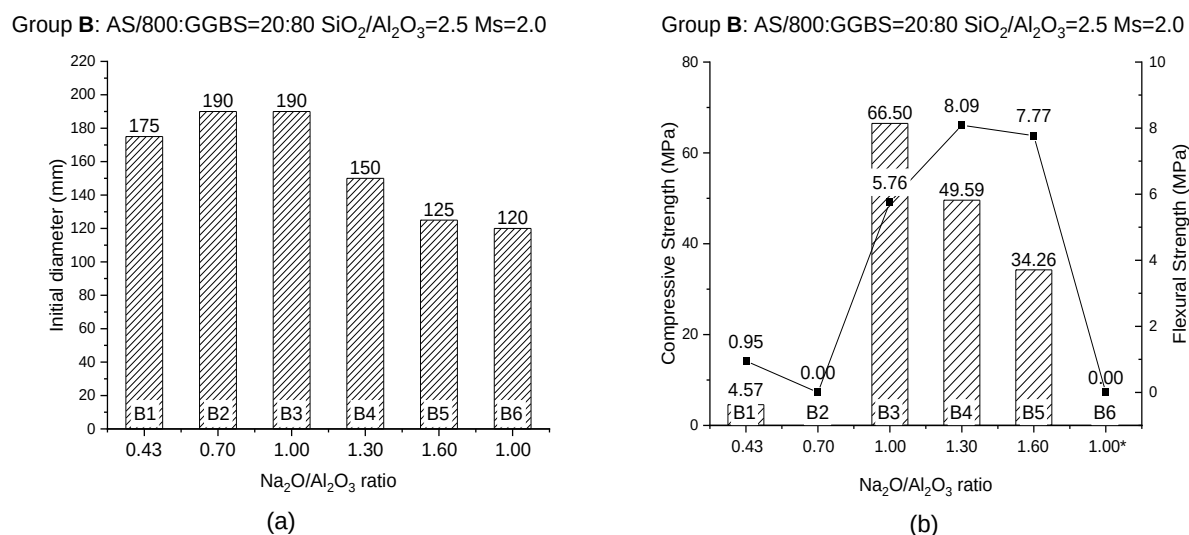


Figure 7-2 Properties of one-part AS geopolymers with varying $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$: (a) flowability, (b) mechanical strength.

The structure and chemical composition of the amorphous matrix of Group B geopolymers are summarized in Figure 7-3 and Figure 7-4. Specimens B1 (with no NC) are not fully activated showing a heterogeneous, highly porous matrix where microcrystalline salts occasionally appear (Figure 7-3). Increasing the NC activator densifies the geopolymer matrix: the B4 specimens ($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.30$) display a more compact and less porous matrix (Figure 7-4). The magnified SEM photographs highlight the differences between the two matrices even more. The geopolymer becomes denser, more homogenous and more vitreous, with fewer crystals. Hence, increasing NC improves the quality the quality of the geopolymer.

The EDX analyses show high Na and Al content in the C-S-H cement (Figure 7-3 and 7.4). Hence, the abundant Al in the AS has replaced Si in the C-S-H, and Na from the activator has compensated the imbalance caused by the replacement. The EDX occasionally evidenced Na^+ salts at the highest $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of 1.3 (Figure 7.4).

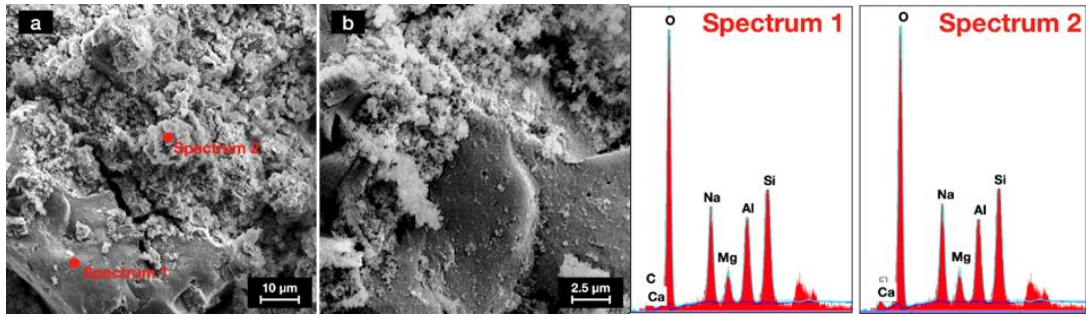


Figure 7-3 SEM micrographs and EDX analysis of B1 ($\text{SiO}_2/\text{Al}_2\text{O}_3=2.5$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3=0.43$).

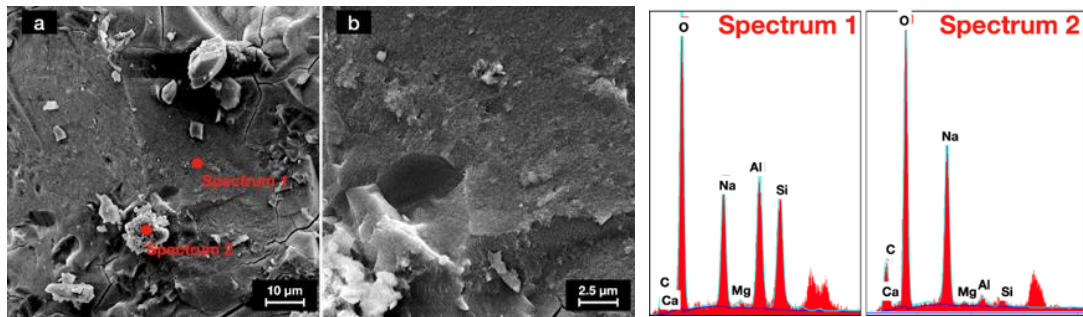


Figure 7-4 SEM micrographs and EDX analysis of B4 ($\text{SiO}_2/\text{Al}_2\text{O}_3=2.5$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3=1.3$).

The mineralogical composition of the geopolymers, analyzed with XRD and included in Figure 7-5, indicates that increasing NC promotes the formation of carbonates calcite and gaylussite (the latter at greater NC content); and that the carbonate content increases with the amount of NC in the geopolymer. The mineralogical composition agrees with the reaction mechanism of carbonate-activated slag proposed in Equation 7-1 where calcite and gaylussite are the products of the reaction between the CO_3^{2-} from NC and the Ca^{2+} from GGBS.

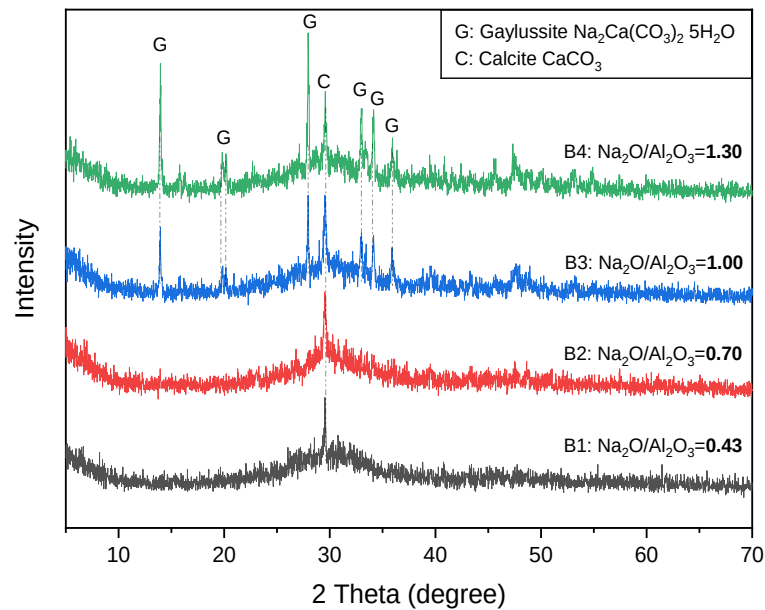


Figure 7-5 Mineral compositions of B1-B4 with different $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios.

The microstructure and cementing phases of the geopolymers in group B was further studied with FTIR. The results appear in Figure 7-6. The main band located between 800 cm^{-1} and 1200 cm^{-1} was assigned to the anti-symmetric stretching vibration of Si-O-Si(Al) bands. The centre of the band at 952 cm^{-1} indicates the dominance of SiQ^2 units and the broad band suggests a disordered structure with a wide distribution of SiQ^3 to SiQ^0 units. The band located between 1300 cm^{-1} and 1550 cm^{-1} is assigned to the anti-symmetric stretching mode of C-O in carbonate. The amount of carbonate increased with rising $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio agreeing with the results above.

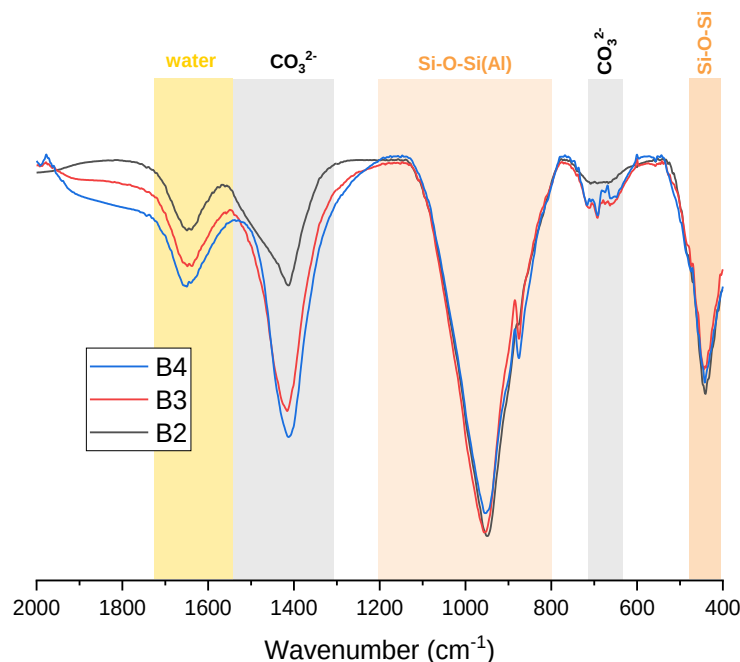


Figure 7-6 FTIR spectra of one-part AS geopolymers (B2-B4) with different $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios.

Effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios on the AS geopolymer

The study of the geopolymers in groups A and B enables to determine that the modulus of 2 ($M_s = 2.0$) and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of 1.0 are optimal activator composition parameters for the AS geopolymer. In groups C and D these remain constant and varying $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios are investigated. The flowability, indicated by the initial flow diameter, of Group C and D is presented in Figure 7-7. Except for specimen C1, workability is not influenced by the change of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. Specimen C1, with the lowest silicate (8%) and highest carbonate (22.6%) contents, has the lowest flow probably due to the quick reaction between the active AS and carbonate forming carbonate crystals that impede flow.

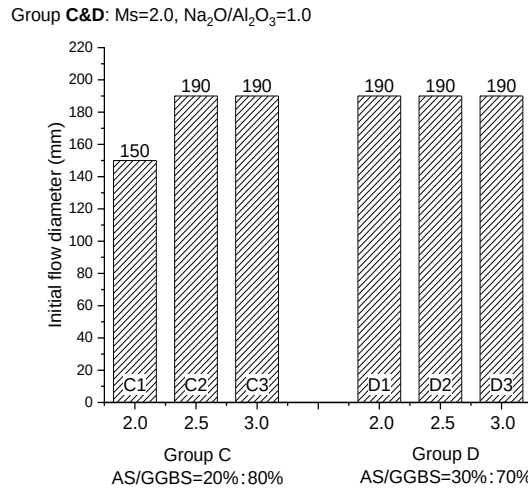


Figure 7-7 Flowability of AS-based geopolymers with varying SiO₂/Al₂O₃.

The mechanical strength of one-part AS geopolymer with different SiO₂/Al₂O₃ ratios appears in Figure 7-8. Group D (AS/GGBS=30/70) has more AS and less slag than Group C (AS/GGBS=20/80). All the geopolymers attained high compressive strengths at 28d ranging from 40 to over 66 MPa, except for specimen C1 which reached 9 MPa. Similarly, flexural strengths are also significant ranging from 5 to over 6 MPa except for specimen C1 that reached 2.55 MPa. Irrespective of the %AS in the geopolymer, the ratio SiO₂/Al₂O₃ = 2.5 achieved the highest compressive strength and amongst the highest flexural strengths and increasing or reducing the ratio reduced compressive strength. In group C, dropping SiO₂/Al₂O₃ to 2.0, substantially decreased compressive strength from 66.50 MPa to 9.05 MPa, but raising SiO₂/Al₂O₃ to 3.0 only caused a slight reduction of 0.9%. However, in group D, deviating the SiO₂/Al₂O₃ ratio from 2.5 only led to small strength reductions of 8-13%.

Flexural strength roughly mirrors the compressive strength trend. In Group C, flexural strength increases with the SiO₂/Al₂O₃ ratio: by c.70% when the ratio increases from 2 to 2.5 but only by 9.91% when the ratio increased from 2.5 to 3.0. However, in Group D, varying the SiO₂/Al₂O₃ ratio did not strongly impact strength which consistently reached c.5-6 MPa.

In general, lower AS content enhanced mechanical strength (group C) but higher AS content (group D) improves the robustness of the geopolymer against variations in the SiO₂/Al₂O₃ ratio. At higher AS dosage, more NS activator is required to maintain the SiO₂/Al₂O₃ ratio which balances mechanical strength so that changes became more gradual and less dramatic. With less AS, the boundaries of the effectiveness of the geopolymer system appeared to be narrower, as evidenced from the significant reduction in mechanical performance observed in C1.

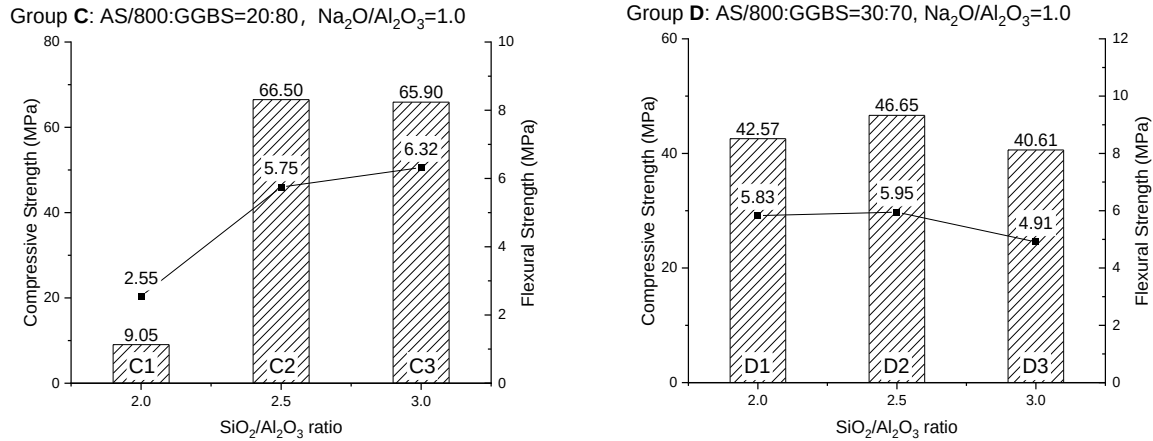


Figure 7-8 Mechanical strength of Group C and D at 28d.

7.1.2 Microstructure of the optimized One-part AS Geopolymer (Ms = 2.0 and Na₂O/Al₂O₃ = 1.0)

In groups C/D, the NC and NS activator contents vary to reach SiO₂/Al₂O₃ values between 2 and 3. The mineral composition of group C specimens appears in Figure 7-9. The primary crystalline phase is gaylussite (Na₂Ca(CO₃)₂ · 5H₂O, PDF #00-020-1085). Calcite (CaCO₃, PDF #04-008-0198) occurs in the specimen with SiO₂/Al₂O₃ at 2.5. Both carbonates result from the reaction between the Ca²⁺ ions dissolved from GGBS and the sodium carbonate activator.

In comparison to the other two groups, new characteristic peaks of calcite and less intensive peaks of gaylussite were found in the specimens with SiO₂/Al₂O₃ at 2.5 probably because more Na⁺ ions integrated into amorphous substances such as N-A-S-H gel, rather than precipitating as sodium salts.

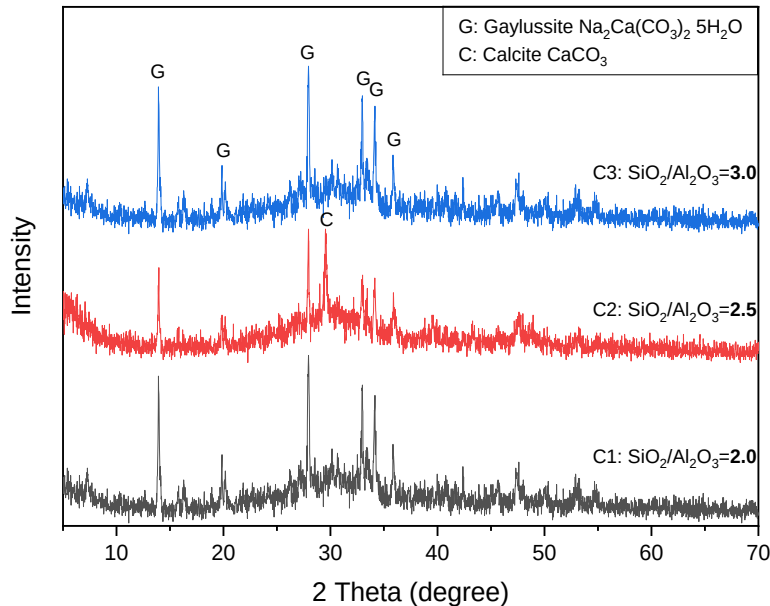


Figure 7-9 Mineral compositions of C1-C3 with different SiO₂/Al₂O₃ ratios at 28d.

The FTIR spectra of Group C are presented in Figure 7-10. Alteration of SiO₂/Al₂O₃ did not significantly change the microstructure of the AS based geopolymer as indicated by their similar FTIR spectra. The band between 800 cm⁻¹ and 1200 cm⁻¹ is the main absorption band

in all specimens, which was assigned to the stretching vibration of Si-O-Si(Al). The band located from 1300 cm^{-1} to 1550 cm^{-1} was associated with the asymmetric stretching vibrations of the C-O bond of the carbonate. A clear pattern is that the amount of carbonates decreases with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$, however, the XRD results in Figure 7-9 show identical patterns for the lowest and the highest ratios. The presence of excess carbonates can adversely affect strength development and durability.

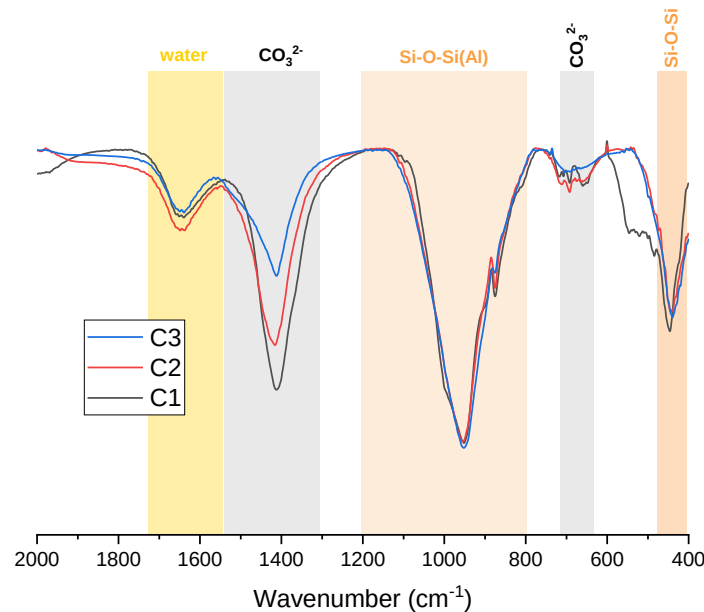


Figure 7-10 FTIR spectra of C1-C3 with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios at 28d.

The surface morphology and chemical composition of the amorphous matrices in groups C and D appear in Figure 7-11 to Figure 7-15. All specimens consist of dense amorphous matrices with scattered salts. No unreacted AS/800 and GGBS particles were found due to their high reactivity and fast dissolution rate (Lei & Pavía, 2022). Cracks through the matrix were detected, and it seems that cracking is more pronounced in the high $\text{SiO}_2/\text{Al}_2\text{O}_3$ matrix. This is probably autogenous shrinkage cracking like in all geopolymers (Li et al., 2020).

The high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio indicates the presence of C-A-S-H and N-A-S-H gels. To differentiate their properties with analyses is difficult. In an alkali media, Ca-O bonds (464kJ/mol) break first due to their lower dissociation energy followed by Al-O (512kJ/mol) and finally Si-O (798kJ/mol) (Stevenson, 1955). In the geopolymer system, Ca^{2+} was first released into the solution and formed calcium salts calcite and gaylussite (Figure 7-9) and Al species ($\text{Al}(\text{OH})_4^-$) followed.

In a $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ system (N-A-S-H), the Al species polymerise but excessive Al content can form Na-Al-Si precipitates which worsen mechanical performance (Silva et al., 2007). However, in the $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ system (C-A-S-H), the Al species do not directly form cementing gel but mainly replace tetrahedral Si in the C-S-H gel; and Na^+ neutralises the charge imbalance caused by Al^{3+} substituting Si^{4+} (Faucon et al., 1996).

In cement chemistry, a suitable amount of Al ions form longer linear chains of C-(A)-S-H gel (Pardal et al., 2012); and up to 15% Si can be replaced with Al (Diamond et al. 1964). However, as reported by Puertas et al. (2011), C-(A)-S-H gels in PC and alkali-activated slag systems

have different composition and microstructure. C-(A)-S-H formed from alkali-activated slag has higher Al content, higher Q^3 units and longer chain length.

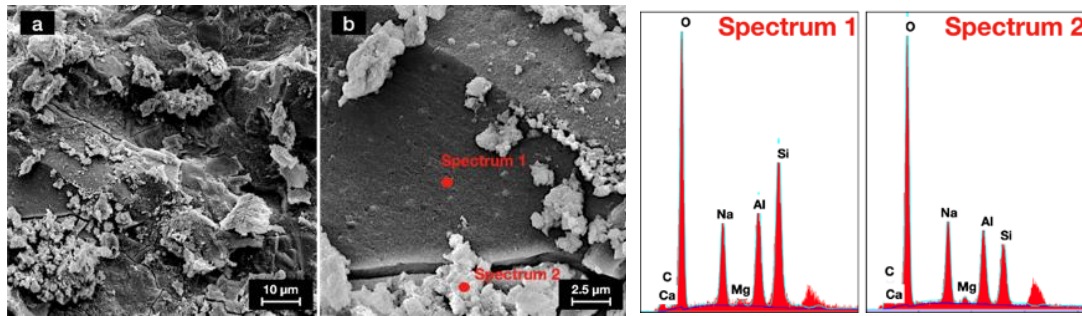


Figure 7-11 SEM micrographs and EDX analysis of C1 ($\text{SiO}_2/\text{Al}_2\text{O}_3=2.0$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3=1.0$).

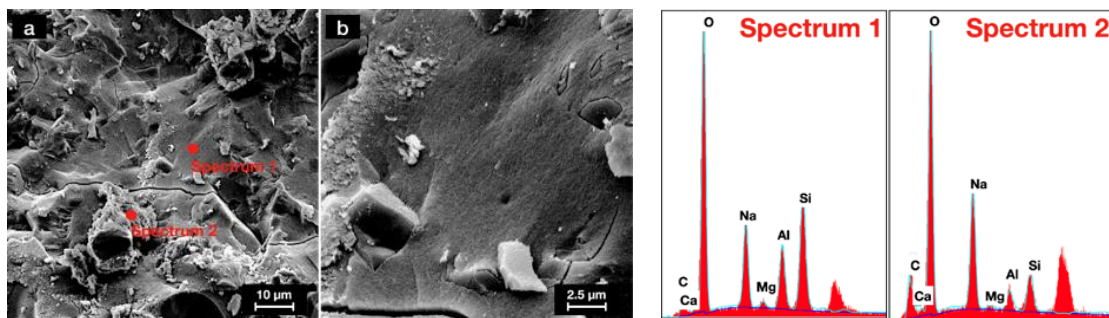


Figure 7-12 SEM micrographs and EDX analysis of C2 ($\text{SiO}_2/\text{Al}_2\text{O}_3=2.5$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3=1.0$).

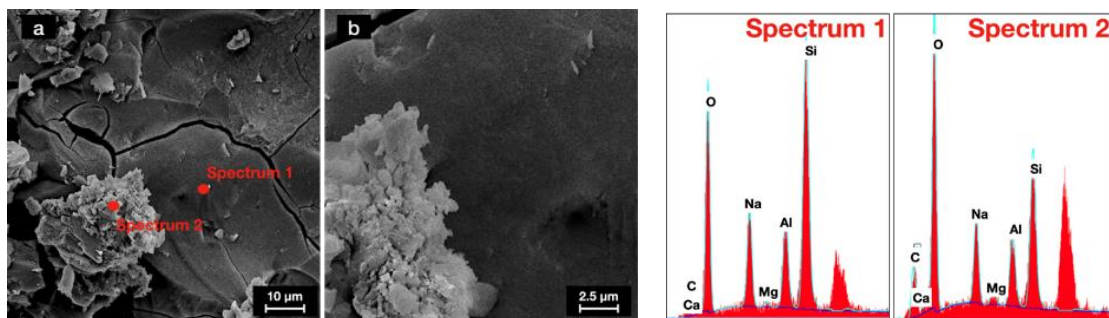


Figure 7-13 SEM micrographs and EDX analysis of C3 ($\text{SiO}_2/\text{Al}_2\text{O}_3=3.0$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3=1.0$).

The morphology and chemical composition of group D geopolymer (Figure 7-14) shows an amorphous dense matrix. The $\text{Ca}/(\text{Si}+\text{Al})$, $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios measured with EDX analysis are 0.42, 6.4 and 2.0 respectively. The ratios are higher than in group C (specimen C2). In C2, the AS:NC was 1:1 by weight, while in D2, the ratio was increased to 3:4 to maintain the $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the design. More reactive Al and soluble silicate in the initial reaction system facilitated polymerization. However, this may have also produced more cracks, as illustrated in Figure 7-14. The mineral composition of D2 is similar to group C, with gaylussite and calcite as the main crystalline phases (Figure 7-15).

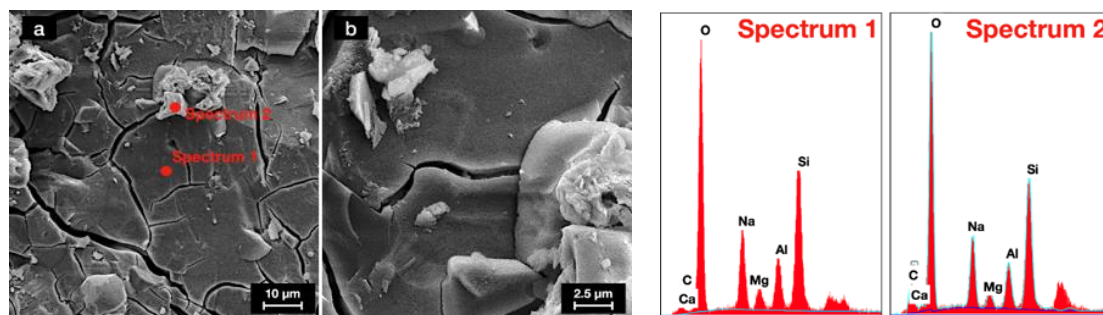


Figure 7-14 SEM micrographs and EDX analysis of D2 ($\text{SiO}_2/\text{Al}_2\text{O}_3=2.5$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3=1.0$).

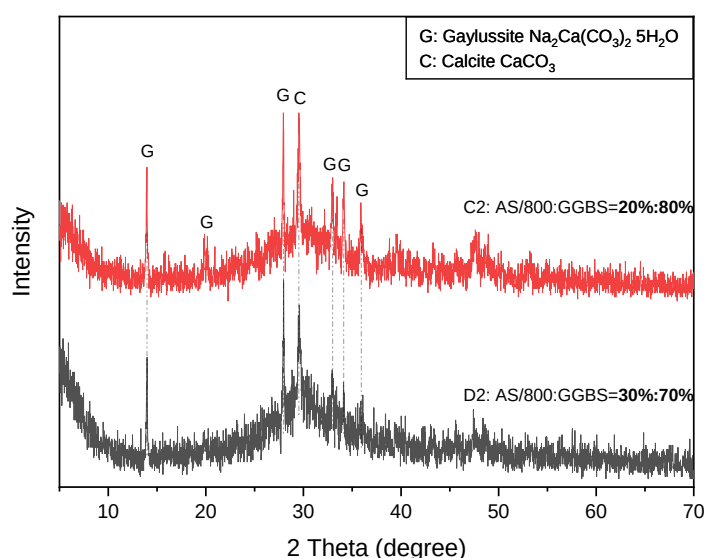


Figure 7-15 Mineral compositions of C2 and D2 with different AS/800 usage.

7.2 CROP BIOMASS ASH (CBA) ONE-PART GEOPOLYMER

In the previous chapter, raw and alkali-fused CBA were successfully used as precursors for producing two-part geopolymers. In this section, the potential of CBA as a precursor for developing one-part geopolymers is evaluated. GGBS is chosen as the silica source due to its high reactivity, standard status, commercial availability and accessibility. Various ratios of ash to slag and activators are explored to optimize performance. The microstructure and mineralogy of the resulting geopolymer cements are thoroughly investigated.

The mixing design used in this section is presented in Table 7-2 and Table 7-3 for raw and alkali-fused CBA respectively. The nomenclature is based on composition. "C" denotes raw CBA, "fC" is CBA fused with 25% NaOH, "ffC" is the CBA fused with 50% NaOH, "G" - GGBS, "C"- carbonate and "S" - sodium silicate. The numbers indicate the amount of each component. For example, 30fC70G4C10S consists of 30% fC and 70% GGBS, activated by 4% sodium carbonate and 10% sodium silicate.

Table 7-2 Mix design of raw CBA, one-part geopolymer mortars (g).

Notation	Precursor		Activator		Sand	Water	w/b
	GBBS	CBA	NC	NS			
30C70G10C	280	120	40	0	1200	200	0.50
50C50G10C	200	200	40	0	1200	260	0.65
70C30G10C	120	280	40	0	1200	260	0.65
70C30G5C	280	120	20	0	1200	200	0.50
70C30G5C10S	280	120	20	40	1200	200	0.50
70C30G5C15S	280	120	20	60	1200	200	0.50
70C30G5C20S	280	120	20	80	1200	200	0.50

Table 7-3 Mix design of alkali-fused, CBA geopolymer mortar.

Notation	fC	ffC	GBBS	NC	NS	Water	Sand	w/b
50fC50G4C	200		200	16		240		
50fC50G6C	200		200	24		240		
50fC50G8C	200		200	32		240		
50fC50G10C	200		200	40		240		
70fC30G4C	280		120	16		240		
50fC50G4C	200		200	16		240		
30fC70G4C	120		280	16		240	1200	0.6
30fC70G4C10S	120		280	16	40	240		
30fC70G4C15S	120		280	16	60	240		
30fC70G4C20S	120		280	16	80	240		
100ffC4C		400		16		240		
70ffC30G4C		280	120	16		240		
50ffC50G4C		200	200	16		240		

7.2.1 Properties of Raw-CBA One-part Geopolymers

Table 7-4 presents the setting times of one-part, CBA geopolymers with varying slag content and activator type. The results evidence that the sodium silicate (NS) activator speeds up the set. The paste made with 30% CBA, 70% GGBS and 10% sodium carbonate (NC) (30C70G10C) shows a prolonged setting time, with an initial setting time of 5h 7min and a final setting time of 8h. Adding sodium silicate (NS) accelerates setting: the pastes with 10% NS and 5% NC (30C70G5C10S) set faster taking only 1h 57min and 2h 43min to reach the initial and final set respectively. Increasing the dosage of NS to 20% (30C70G5C20S), further accelerates the setting: the paste achieved the initial set after 53 min and the final set after 1h 15min. The NS increased the pH in the system promoting the dissolution of the precursors, hence increasing the availability of active Si^{4+} , Ca^{2+} and Al^{3+} for hydrate production to cause set.

Table 7-4 Setting times of one-part CBA-GGBS geopolymers.

	Initial setting time	Final setting time
30C70G10C	5h7min	8h
30C70G5C10S	1h57min	2h43min
30C70G5C20S	53min	1h15min

The mechanical performance of one-part, raw CBA geopolymer is presented in Table 7-5. According to the results, the threshold of CBA content is 30% by weight. The geopolymers with 30% CBA achieved flexural and compressive strengths of 3.69 and 30.70 MPa respectively. However, replacing slag with CBA beyond this threshold results in strength loss: the mortars with 70% CBA failed to develop any strength after 28 days of curing. This agrees with the reactivity test results indicating that CBA has low pozzolanic activity. Therefore, in the raw CBA, one-part geopolymers, excessive CBA dosage results in insufficient cement which undermines strength. The results also indicate that reducing the NC activator from 10% to 5% lowers flexural and compressive strengths by 3.79% and 26.32% respectively (Table 7-5).

Partial replacement of carbonate with silicate activator significantly improved compressive strength. Specifically, adding 10% NS (30C70G5C10S) increased compressive strength from 22.62 MPa to 24.89 MPa (10.03% increase). Further increasing the NS dosage to 15% dramatically raised the compressive strength by 72.47%, reaching 42.93 MPa. However, increasing the NS dosage to 20% only results in a slight improvement, rising to 46.09 MPa. In contrast, the development of flexural strength exhibited a different pattern. The highest flexural strength (4.67 MPa) was achieved at NS dosage of 15%. Any further NS increase reduced flexural strength. The introduction of the silicate activator lowers the concentration of CO_3^{2-} in solution increasing the alkalinity of the system which speeds up the dissolution of the ash and the slag, hence delivering active Si^{4+} , Ca^{2+} and Al^{3+} species to form hydrates that accelerate the setting process. The acceleration of precursor dissolution and hydrate formation by the NS agrees with former authors who investigated the alkali activation of metallurgic slags with NC and NS (Bernal et al., 2016; Jiao et al., 2018; Yuan et al., 2017a).

Table 7-5 Mechanical performance of raw-CBA, one-part geopolymers. (MPa, F- failed.)

Notation	Flexural Strength 28d	SD	Compressive Strength 28d	SD
30C70G10C	3.69	0.57	30.70	0.91
50C50G10C	0.44	0.05	1.22	0.14
70C30G10C	F	F	F	F
30C70G5C	3.55	0.22	22.62	1.24
30C70G5C10S	4.19	0.69	24.89	1.34
30C70G5C15S	4.67	0.36	42.93	2.75
30C70G5C20S	3.52	0.61	46.09	4.44

7.2.2 Mineral Composition and Microstructure of the Reaction Products in One-part, raw-CBA geopolymers

The microstructure and cement composition of several geopolymers are investigated to determine the effect of varying ash content and activator type on the geopolymer properties. The mineral composition of the reaction products formed in pastes of varying ash and activator content appear in Figure 7-16. The main crystalline phases are calcite (CaCO_3), gaylussite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$), quartz (SiO_2) and cristobalite (SiO_2). A hump centered at around $2\theta =$

29° indicates the presence of an amorphous cementing phase probably corresponding to a poorly crystalline C-S-H, the main reaction product in alkali-activated slag pastes (Fernández-Jiménez et al., 1999; Fernández-Jiménez & Puertas, 1997). The hump is better defined in the polymers with greater slag content. The geopolymer cement becomes slightly more crystalline when adding NS activator (slim increase in gaylussite and calcite), however, the amount of amorphous or poorly crystalline cementing hydrates remains approximately the same, agreeing with the similar strengths results for the 30C70G10C and the 30C70G5C10S geopolymers (Table 7-5).

Carbonates calcite and gaylussite are common hydration products in alkali-activated slags resulting from the reaction between Ca^{2+} , released mainly from the slag dissolution, and CO_3^{2-} released by the carbonate activator (Bernal et al., 2016; Fernández-Jiménez et al., 2003; Jiao et al., 2018; Yuan et al., 2017a). Gaylussite has been considered a transition phase that eventually forms more stable products such as calcite and hydrotalcite (Akturk et al., 2019). Cristobalite is a high-temperature, low-pressure silica polymorph stable above 1470 °C (Heaney, 1994). In this CBA, cristobalite originates from the uncontrolled combustion of biomass crops. The quartz likely originates from soil contamination in the biomass.

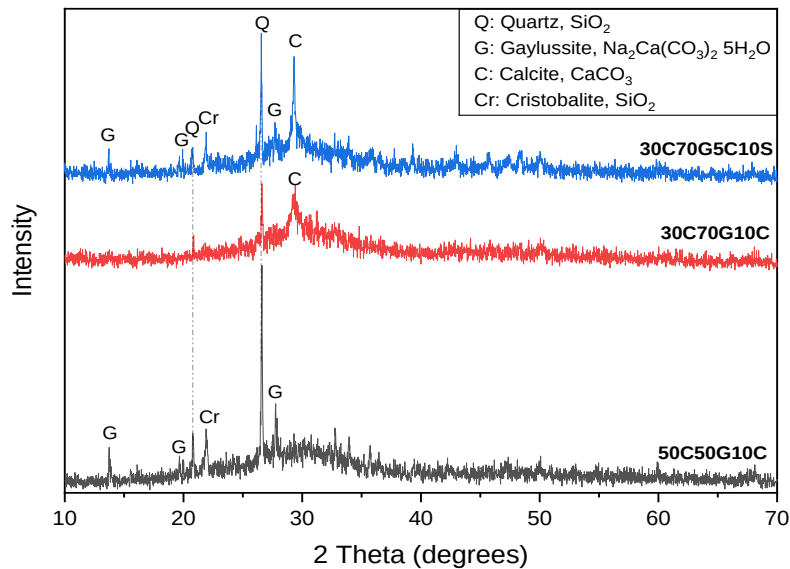


Figure 7-16 Mineral composition of one-part, raw-CBA geopolymer cements at 28d.

The microstructure and cement composition of one-part, raw-CBA geopolymers are investigated with XRD, SEM/EDX and FTIR below. The 70%GGBS / 30%CBA pastes activated with 10%NC (30C70G10C) analysed with SEM/EDX appear in Figure 7-17. The micrographs revealed a dense and amorphous cementing phase. Higher magnifications occasionally evidenced the remains of unreacted ash particles (Figure 7-17b and Spectrum 3 in Figure 7-18) and scattered salts (Figure 7-17b and Spectrum 1 in Figure 7-18). The EDX analyses showed high concentrations of Ca, Si, Al, Mg and Na in the amorphous cement, suggesting the presence of N-A-S-H and C-A-S-H gels (Figure 7-17b and Spectrum 2 in Figure 7-18). The ratios in the cement are $\text{Si}/\text{Al} = 2.44$ and the $\text{Ca}/(\text{Si}+\text{Al}) = 0.75$.

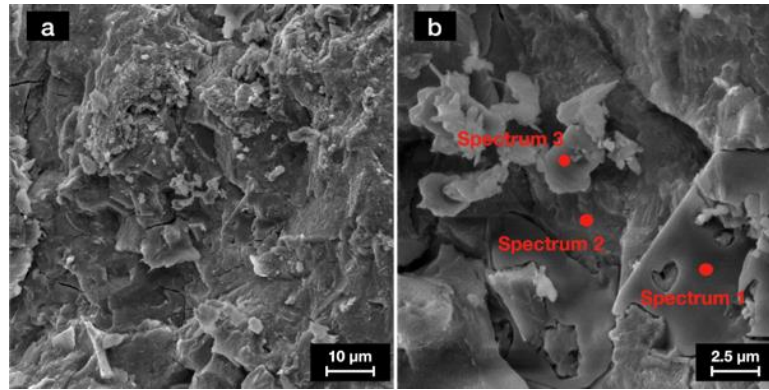


Figure 7-17 Microstructure of the cement in the 30C70G10C (GGBS/CBA/NC) geopolymer at 180 days.

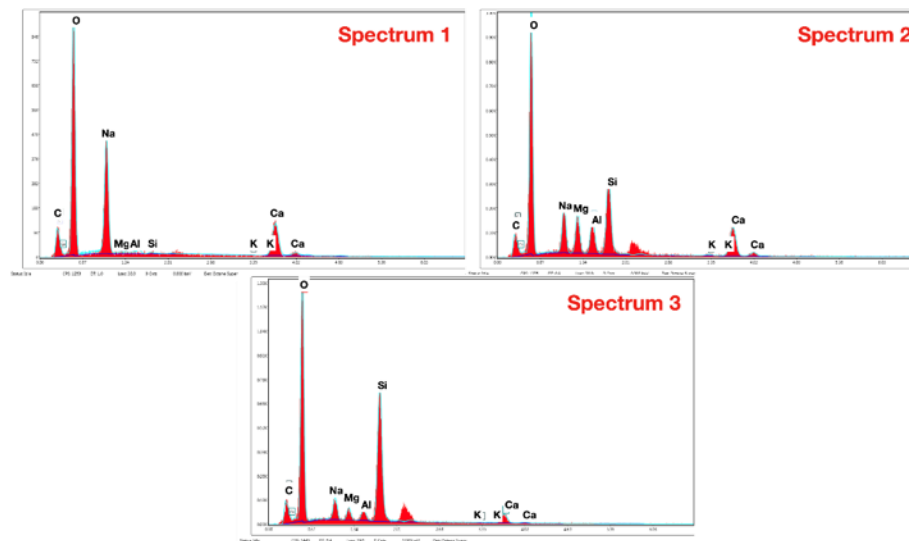


Figure 7-18 Chemical composition of the reaction products in the 30C70G10C geopolymer-marked in Figure 7-17.

Increasing NS activator results in a slightly denser matrix (30C70G5C10S-Figure 7-19). The cementing phase revealed high concentrations of Si, Ca, Al and Na; and higher Si / Al and Ca / (Si+Al) ratios (4.43 and 0.82 respectively) than those in the geopolymer activated with NC only (Figure 7-17). The NS activator increased the Si content in the cement raising the Si/Al from 2.44 (carbonate-activated geopolymer) to 4.43. However, the Ca/(Si+Al) only increased slightly. The results indicate that the soluble silicate in the activator provides Si^{4+} for the polymerization process to produce a denser cement with greater Si content. Simultaneously, the reduced NC content results in less Ca^{2+} being fixed by the carbonate anions to form carbonate cements, and more Ca^{2+} being combined in the hydrates which raises the Ca/(Si+Al) ratio of the C-A-S-H.

The addition of a small amount of NS activator (10%) (30C70G5C10S) increases the cement density but provides similar strength than the NC activator. Geopolymers with further NS contents were not analysed with SEM/EDX but the tendency to increase cement density with rising silicate activator content can be clearly established, which agrees with the faster set and the higher strength for the 15% and 20%NS geopolymers (Table 7-4 and Table 7-5). This trend agrees with former authors studying the activation of slags (Brough & Atkinson, 2002; Chang, 2003). Activating slag with sodium silicate (NS) results in a main reaction product of C-S-H

where highly condensed Si ions form 3D structures (Si ions in Q^3 sites) which provide strength to the material (Fernández-Jiménez et al., 2003). When the slag's activator is sodium carbonate (NC), the C-S-H also includes highly condensed Si, but it provides lower strength than the silicate activator (Fernández-Jiménez et al., 2003). Some cracks were found in the 30C70G5C10S matrix. As aforementioned, autogenous shrinkage cracks are inherent to the polymerisation process and caused by the loss of water inducing volume change during polymerisation. C-A-S-H gel collapsed and redistributed during drying can also promote shrinkage (Ye & Radlińska, 2016). Furthermore, shrinkage is considered to relate to the content of Na_2O in the high Ca system. The activator introduced high Na^+ which may trigger more intense autogenous shrinkage (Neto et al., 2008). The cracking of the matrix may be responsible for the reduction in flexural strength when high amount of activator was used as indicated by the mechanical test results (Table 7-5).

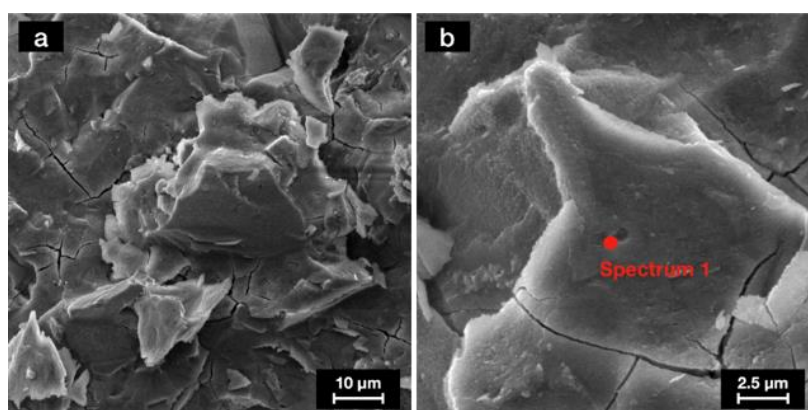


Figure 7-19 Microstructure of the cement in the 30C70G5C10S (CBA/GGBS/NC/NS) geopolymer at 180 days.

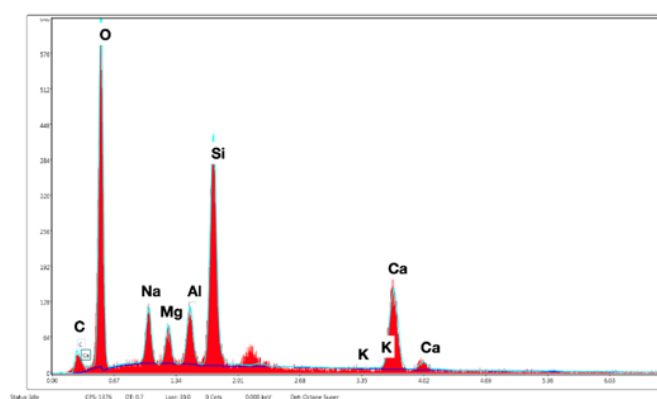


Figure 7-20 Chemical composition of the cements in the 30C70G5C10S geopolymer marked in Figure 7-19.

Increasing the amount of ash relative to the slag completely changed the microstructure of the geopolymers, producing highly porous and loosely stacked matrices with insufficient cement (50C50G10C, Figure 7-21) and unreacted precursors; unlike the dense amorphous cements found in the geopolymers with greater slag content (Figure 7-17 and Figure 7-19). This loose structure is responsible for the poor mechanical performance of the 50C50G10C geopolymer mortars (Table 7-5).

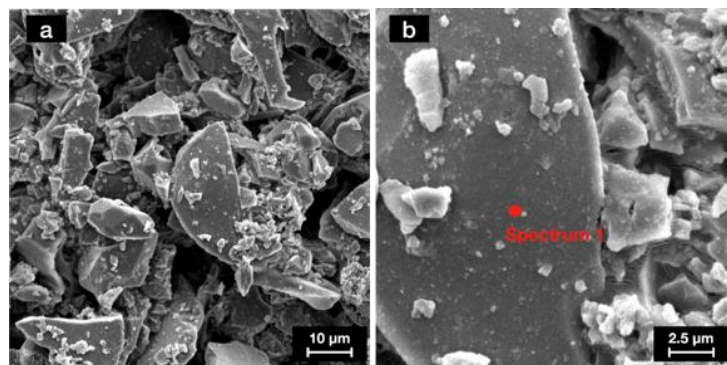


Figure 7-21 Microstructure of the cement in the 50C50G10C (CBA/GGBS/ NC) geopolymer at 180 days.

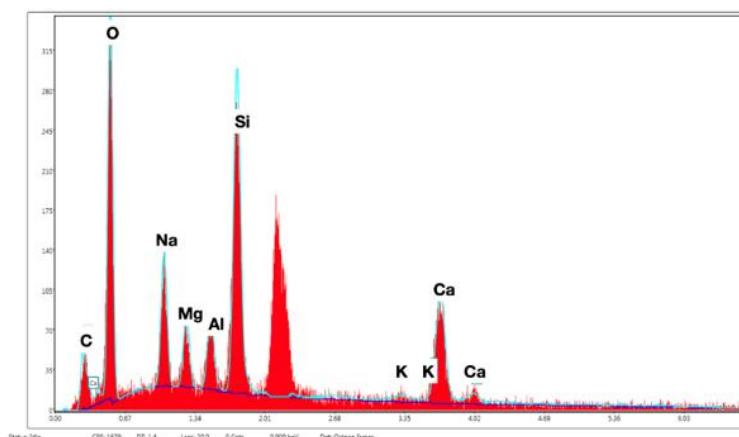


Figure 7-22 Chemical composition of unreacted slag in geopolymer cement 50C50G10C marked in Figure 7-21.

The CBA powder and 30C70G5C10S geopolymers (28 d) were studied with FTIR, and the results are presented in Figure 7-23. In the ash, the main bands (centred at $\sim 1015\text{ cm}^{-1}$, 778 cm^{-1} and 445 cm^{-1}) are attributed to Si-O-Si bonds and SiO_4 tetrahedron links indicating the presence of quartz and some amorphous silica (McKeown et al., 2002). A tiny band centred at 694 cm^{-1} suggests the presence of carbonate probably present in the unburnt biomass (Gunasekaran et al., 2006).

After geopolymerisation, a new broad band centred at $\sim 1437\text{ cm}^{-1}$ appears which is associated with the asymmetric stretching vibration of the C-O bond in the carbonates (Gunasekaran et al., 2006). This is consistent with the calcite and gaylussite reaction products determined with XRD in the geopolymer cement. In addition, the characteristic band of quartz centred at 778 cm^{-1} disappears, and the intensity of the Si-O-Si(Al) band increases, evidencing the occurrence of geopolymerisation. The original Si-O-Si bands present in the CBA powder (centred at 1015 cm^{-1}) shift to a lower wavenumber ($\sim 958\text{ cm}^{-1}$) in the geopolymer, indicating substitution of Si with Al in the Si-O-Si structure which corresponds to the formation of C-A-S-H cements by the polymerisation and is consistent with the SEM/EDX analyses of the geopolymer cements. C-A-S-H cements were expected given the Al content in the ash ($\sim 13\%$ wt) and the slag (10%wt) determined with XRF.

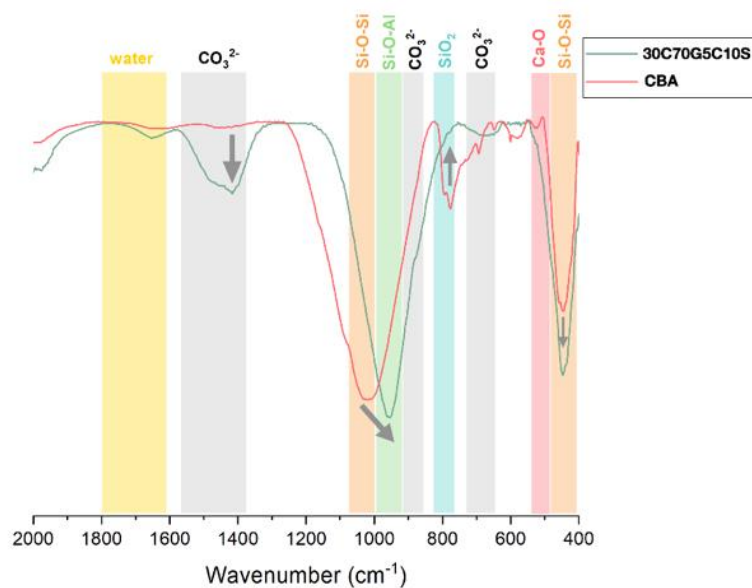


Figure 7-23 FTIR spectra for the CBA powder and 30C70G5C10S pastes at 28d.

7.2.3 Properties of Alkali-fused CBA One-part Geopolymers

Effect of Sodium carbonate activator on the performance of the alkali-fused CBA geopolymer

Figure 7-24 illustrates the impact of varying sodium carbonate dosage on the mechanical properties of geopolymers. Increasing the sodium carbonate content from 4% to 10% does not significantly impact compressive strength with attains values of c. 33-38 MPa. The lowest strength of 33 MPa is attained when using at 8% (8NC). Flexural strength development also shows a fluctuating pattern somehow contrary to the compressive strength with the highest value of 5 MPa reached at 8NC (when compressive strength was lowest).

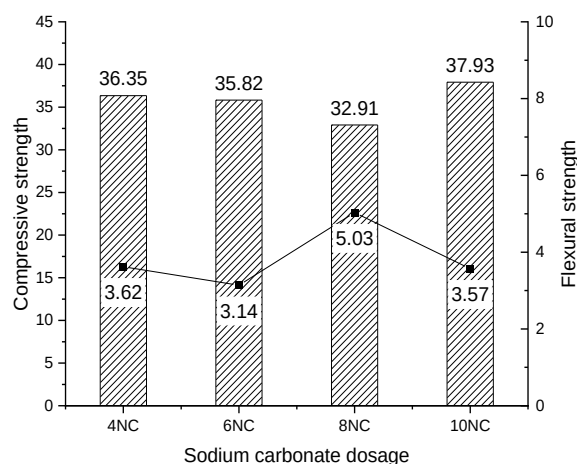


Figure 7-24 Mechanical performance of alkali-fused CBA geopolymer activated with varying sodium carbonate

The mineral composition of the geopolymers activated with 4% and 10% sodium carbonate is presented in Figure 7-25. Quartz and gaylussite were identified as the main crystalline phases in both geopolymers. Quartz originates from the remains of the inert phase originally comprising the alkali-fused CBA and has low reactivity in pozzolanic or geopolymerization reactions. Gaylussite is a transitional phase formed by the reaction between GGBS and sodium carbonate (Bernal et al., 2015). This phase is widely detected in activated slags (Akturk et al., 2019; Yuan et al., 2017b). A hump centred at $29^\circ 2\theta$ indicates the presence of amorphous gels. Increasing the sodium carbonate from 4% to 10% did not significantly alter the mineral composition.

As aforementioned, Adesina (2021) concluded the reaction mechanism of carbonate-activated slag is shown in Eq. 7-2. The initial pH of the activator solution plays an important role in dissolving the slag and promoting the early formation of some hydration products. However, further hydration of alkali-slag cements is dominated by the reaction of the anion or anion group in the activator and the Ca^{2+} dissolved from slag rather than the initial pH of the activator solution (Shi & Day, 1995). The pH increases slightly when increasing sodium carbonate concentration in the solution (National Center for Biotechnology Information, 2024). This agrees with the results showing that increasing the sodium carbonate does not significantly improve the mechanical performance of the activated slag (Figure 7-24). Similarly, Yuan et al. (2017) also report that increasing the amount of sodium carbonate only slightly accelerated the reaction.

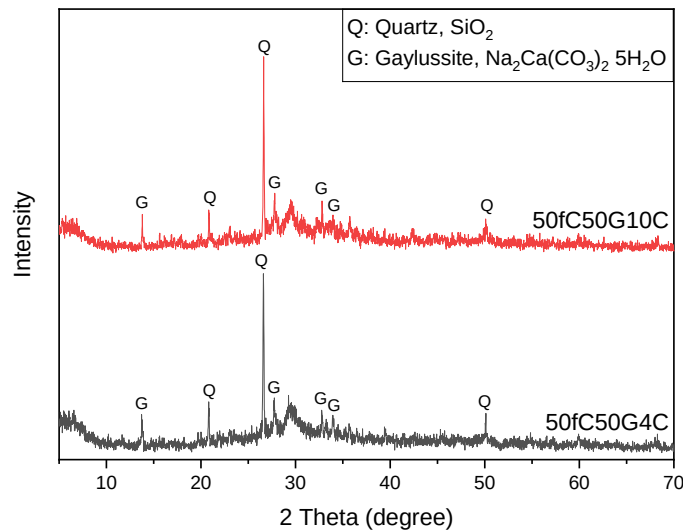
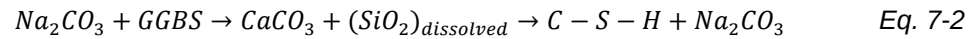


Figure 7-25 Mineral composition of geopolymer activated by 4% and 10% sodium carbonate.

The micrographs of geopolymers with 4% and 10% sodium carbonate (50fC50G4C and 50fC50G10C) are presented in Figure 7-26. Both geopolymers exhibit dense, compact and vitreous matrices, indicating effective geopolymerization. EDX analyses revealed that the cements are rich in Si, Al, Ca, Na and Mg. However, varying degrees of cracking were observed in both geopolymers. SEM observations indicate that increasing sodium usage notably exacerbated the tendency to crack. This is consistent with previous findings: the shrinkage of geopolymer relates to sodium usage, and cracking resulting from shrinkage negatively impacts strength development (Lei et al., 2024). A lower usage of activator lowers

both carbon emissions and the cost of the geopolymer. Therefore, the amount of carbonate was fixed at the lowest level of 4% in subsequent tests.

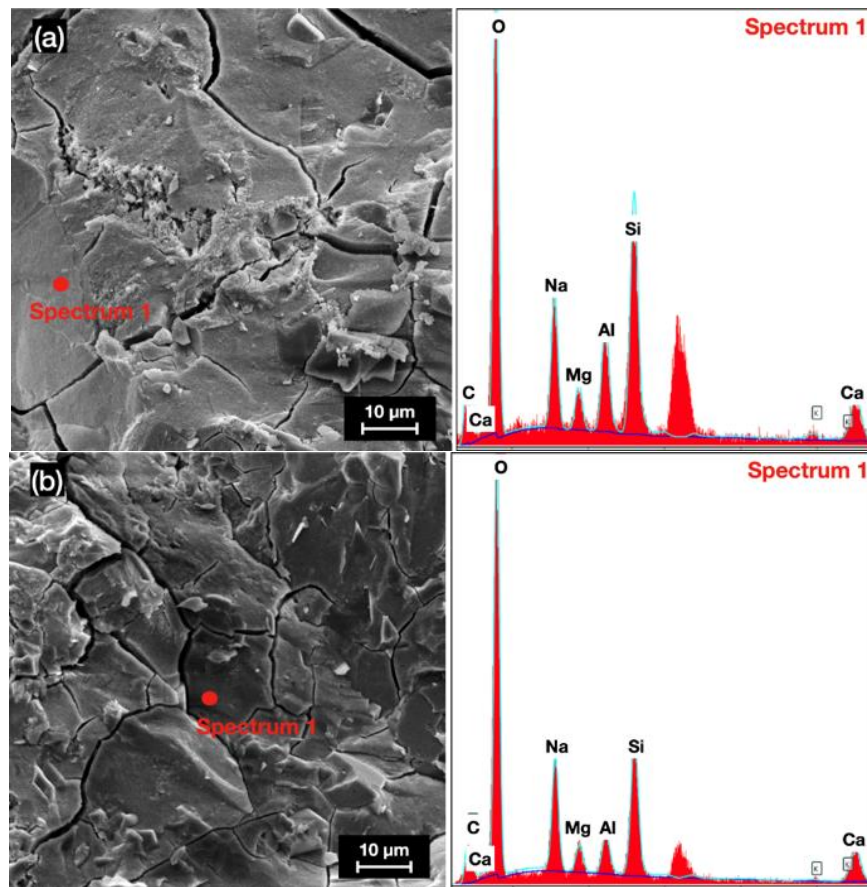


Figure 7-26 Micrograph of geopolymer activated by (a) 4% sodium carbonate and (b) 10% sodium carbonate.

Effect of GGBS: alkali-fused CBA ratio on the performance of the alkali-fused CBA geopolymer

Based on the previous test results, the mechanical performance of geopolymers made with different GGBS: alkali-fused CBA ratios and activated with 4% sodium carbonate is presented in Figure 7-27.

The composition of 30% GGBS and 70% alkali-fused CBA (70fC30G) shows the lowest strengths of 9.91 MPa and 2.44 MPa for compressive and flexural respectively. When the proportion of GGBS increased to 50% (50fC50G) both compressive and flexural strengths rose significantly to 36.35 MPa and 3.82 MPa respectively. This represents an increase of approximately 267% in compressive strength and 57% in flexural strength compared to the 70fC30G composition. Further increasing the GGBS content to 70% in the 30fC70G mix results in a compressive strength of 38.72 MPa, a modest gain of about 6.5% from the 50fC50G, while the flexural strength increased slightly to 3.97 MPa, an approximate 3.9% rise. Therefore, increasing the percentage of GGBS in the precursor composition significantly enhances the mechanical properties of the geopolymer up to a threshold of 50%, beyond which the strength gain is marginal.

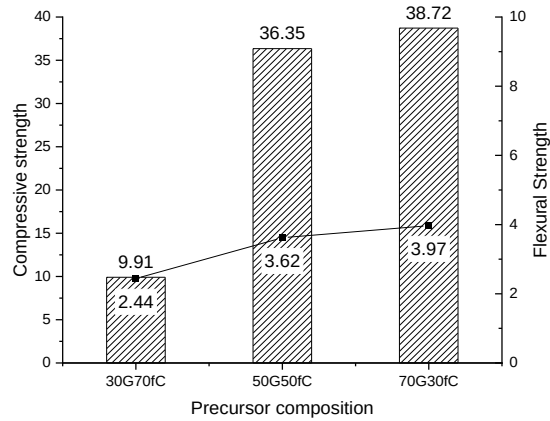


Figure 7-27 Mechanical performance of one-part geopolymer with different precursor compositions.

Figure 7-28 illustrates the mineral composition of geopolymers with varying slag: ash ratios. Increasing the amount of GGBS relative to ash, significantly vitrifies the geopolymer structure. This is likely due to the soluble silicate in the slag promoting the formation of cementing gel which develops strength. The intensity of the quartz peak decreased as the amount of ash in the mix lowers, and the amount of gaylussite also decreases.

Previous work compared the reactivity of alkali-fused CBA and GGBS with a mechanical method. The mechanical index (MI) evidence late activity as strength development. The MI compared the compressive strengths of standard lime mortar, lime/alkali-fused CBA mortar and lime/GGBS mortars. The MI of GGBS is 14.8 (Lei & Pavia, 2023). Alkali fusion increased the MI of CBA from 2.0 to 10.8 (Lei et al., 2024). The superior MI of GGBS agrees with the GGBS increasing the overall reactivity of the geopolymerisation system and enabling higher geopolymer strength as evidenced above.

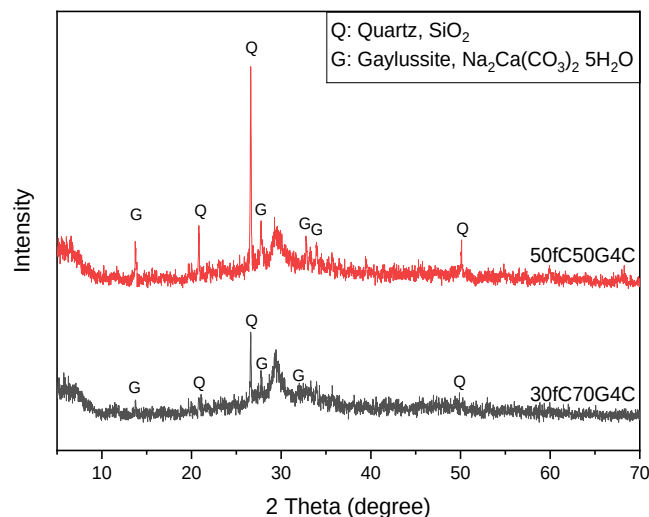


Figure 7-28 Mineral composition of alkali-fused CBA geopolymers with 50 and 70% slag.

The SEM/EDX analyses of the alkali-fused, CBA geopolymers with different GGBS substitutions show significant differences in their microstructural integrity - Figure 7-29. In Figure 7-28(a), the geopolymer matrix exhibits significant cracking and a less cohesive

structure which is attributed to the high content of sodium brought by the 70% alkali-fused CBA. Figure 7-29(b), with a balanced ratio of GGBS to alkali-fused CBA (50%:50%), shows reduced cracking and improved cohesion compared to Figure 7-29(a). The addition of GGBS promoted the formation of cementing gel and reduced the sodium content brought by the CBA thereby enhancing structural integrity. Figure 7-29(c) presents the most cohesive matrix with minimal cracking, demonstrating that the increased GGBS percentage significantly enhances microstructure.

Furthermore, increasing the amount of slag in the geopolymer raises the Mg^{+} in the system and produces geopolymer cements with significantly higher MgO content as shown in the 70% GGBS geopolymer (30fC70G4C) in (Figure 7-29c). Haha et al. (2011) report that MgO accelerates the reaction and forms a higher volume of hydrates. Therefore, it is proposed that the high MgO content plays a positive role in the development of strength and crack suppression in this system.

These microstructural observations correlate directly with the mechanical property results. Figure 7-29(a) suggests a weaker matrix due to extensive cracking, corresponding to the lower mechanical strength attained (Figure 7-27). Figure 7-28(b) and 7(c) show reduced cracking and cohesive and dense matrices, correlating with the high GGBS content and enhanced mechanical strength (Figure 7-27).

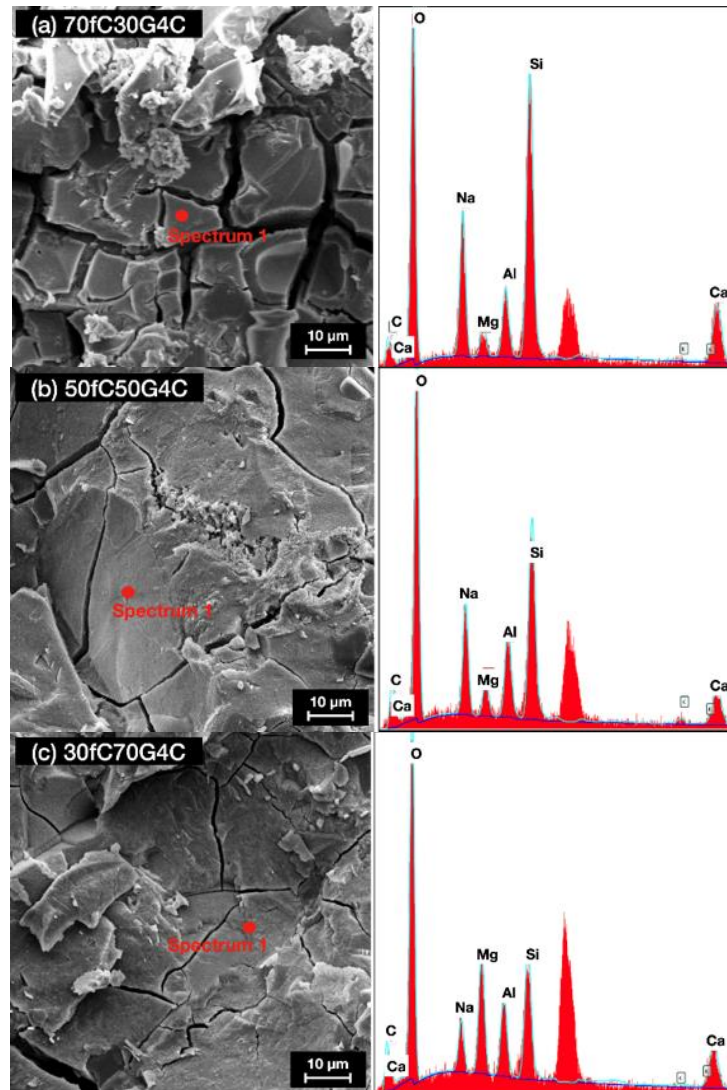


Figure 7-29 Micrographs of alkali-fused CBA geopolymers with different GGBS substitutions.

Effect of Sodium silicate activator on the performance of the alkali-fused CBA geopolymer

The geopolymer made with 70% GGBS and 30% fC activated by 4% NC was selected to investigate the influence of the silicate activator. The sodium silicate activator increases the soluble silicate in the system. The mechanical performance is shown in Figure 7-30. The results clearly show that adding the silica activator increases the strength of the geopolymers. The control sample, at 0% sodium silicate (0NS), attained 38.72 MPa and 3.97 MPa for compressive and flexural strength respectively but adding 10% sodium silicate (10NS) significantly raised compressive strength to 52.80 MPa (an increase of approximately 36.4%). The flexural strength, however, slightly decreases (by c. 9%) to 3.59 MPa. Rising the sodium silicate to 15% (15NS) slightly lowers compressive strength (by 1.9%) to 51.81 MPa but flexural strength slightly increases to 3.73 MPa, an improvement of 3.9%. The highest dosage of 20% sodium silicate (20NS) produces the greatest strengths of 58.33 MPa compressive strength and 5.20 MPa flexural strength.

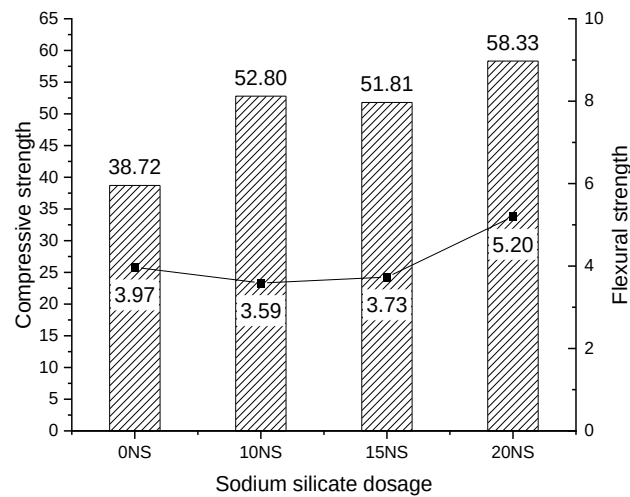


Figure 7-30 Mechanical performance of alkali-fused CBA geopolymers activated with 4% NC and varying NS.

The mineral composition of the geopolymer activated with Na carbonate alone is compared with the NC/NS activated geopolymer in Figure 7-31. Incorporating the sodium silicate activator does not significantly alter the mineral composition of the geopolymer. Quartz and a small amount of gaylussite are detected as the main crystalline phases in all geopolymers.

As seen from the results above, alkali-fusion transforms the quartz comprising the CBA into reactive silicate phases. Adding extra reactive silicate phase in the form of Na silicate activator was expected to produce more C-S-H. However, the results of the XRD analyses do not evidence this.

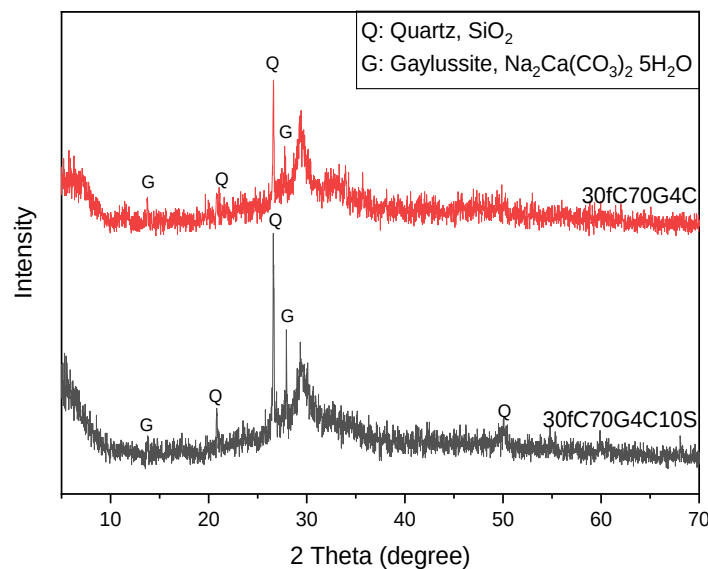


Figure 7-31 Mineral composition of the alkali-fused CBA geopolymer activated with NC alone compared with the NC/NS activated geopolymer.

The FTIR analyses results, presented in Figure 7-32 further contributes to reveal the microstructure of the geopolymer activated with NS. The spectrum of fC (CBA fused with 25% alkali) is used to compare.

The main band, located from 800 cm^{-1} to 1200 cm^{-1} , which is assigned to the asymmetric stretching vibrations of Si-O-Si bonds becomes narrower after geopolymerisation. With the same centre, the Si-O-Si(Al) band was found located between 760 cm^{-1} and 1120 cm^{-1} . According to previous authors (Clayden et al., 1999; Lecomte et al., 2006) the variation in the Si-O-Si stretching pattern corresponds to different SiQ^n units (where n denotes the number of bridging oxygens), with specific absorption bands near 1200, 1100, 950, 900, and 850 cm^{-1} for SiQ^4 , SiQ^3 , SiQ^2 , SiQ^1 , and SiQ^0 units respectively. This band shifts to lower wavenumbers as silicon is substituted by aluminium in the silicate's second coordination layer, a result of the lower bonding energy of Al-O compared to the Si-O bond. Therefore, the dissolution and polymerisation process rearranged the microstructure of CBA. After geopolymerisation, the SiQ^2 and SiQ^1 dominate, and the amount of SiQ^4 units decreased due to the incorporation of GGBS. A considerable Al substitution occurs to form C-A-S-H gel as evidenced by the spread of the spectrum towards the lower wavenumber.

The region between 1300 cm^{-1} and 1550 cm^{-1} in the infrared spectra is characteristic of the asymmetric stretching of C-O bonds in carbonates. The C-O bands indicate the presence of carbonate, agreeing with the gaylussite determined with XRD.

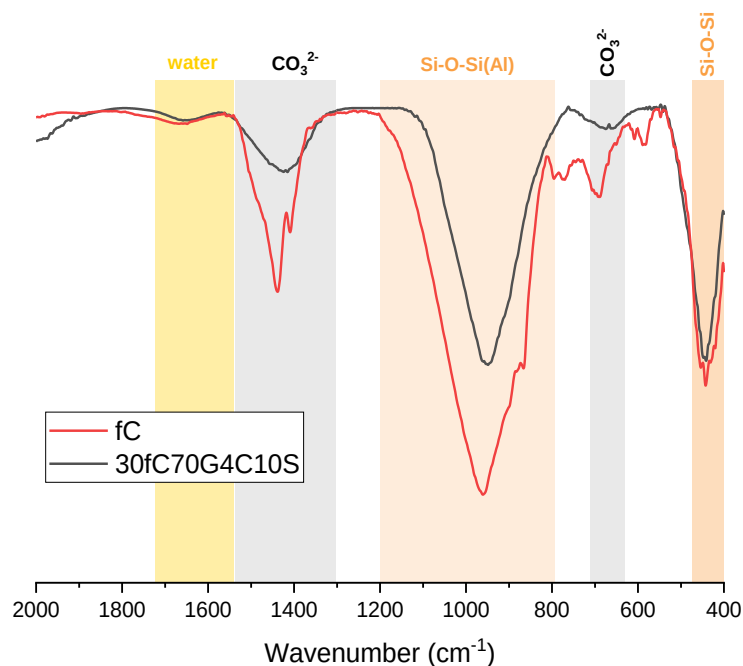


Figure 7-32 FTIR spectra of alkali-fused CBA geopolymer activated with 10% silicate (30fC70G4C10S) compared with alkali-fused CBA powder (fC).

The overall trend indicates that while increasing sodium silicate dosage can substantially enhance compressive strength, the increments become less pronounced with higher dosages. The diminishing mechanical performance improvement at higher levels of sodium silicate suggest a threshold of 10% for Na silicate activator content. In terms of flexural strength, there is a significant boost at the highest sodium silicate concentration (20%) and the strength variations at lower concentrations are not substantial.

Effect of Alkali dosage in the fusion process on the geopolymer performance

Varying the alkali dosage when fusing the CBA significantly influenced the properties of the resultant CBA geopolymer. The mechanical performance of geopolymer made by CBA fused with 25% and 50% alkali appears in Figure 7-33. The results show a consistent trend in the compressive strength results where the highest alkali content enhances strength irrespective of the slag content. Therefore, the increase in alkali percentage from 25% to 50% enhances compressive strength, and the CBA geopolymers with 50% GGBS attain the greatest strength of 42.98 MPa.

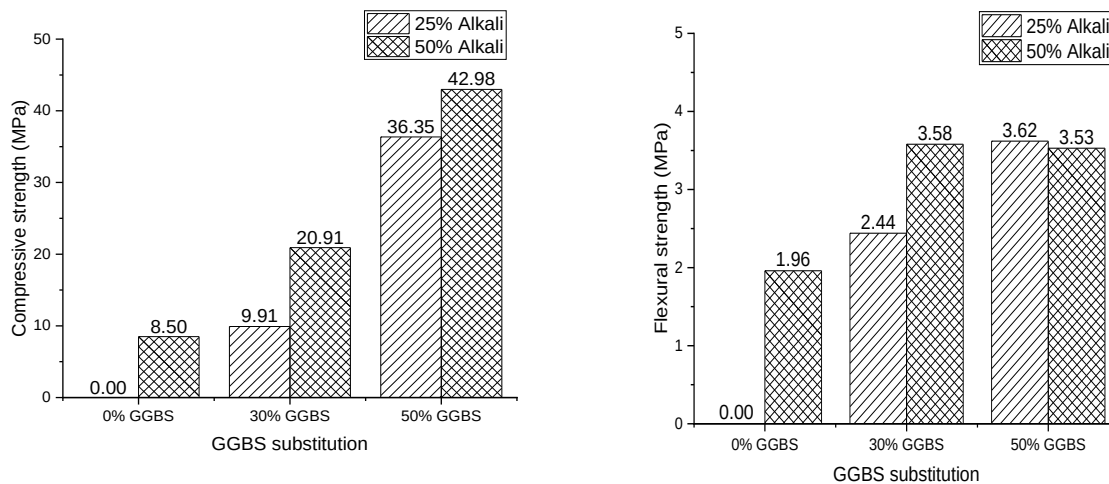


Figure 7-33 Mechanical performance of geopolymer made with CBA fused with different amounts of alkali.

The flexural strength results show a comparable trend. Raising the alkali percentage from 25% to 50% improves flexural strength, particularly at 30% GGBS substitution (Figure 7-33). However, the 50% GGBS geopolymer is not responsive to raising the alkali percentage during fusion reaching similar strengths.

Raising the alkali percentage during fusion enhances the strength of the ash geopolymer with low slag content (0-30% GGBS) but at greater slag contents, the effect becomes smaller. In the geopolymer with no GGBS (0% GGBS), the specimens made with 25% alkali-fused CBA did not yield any strengths over 28 days but using 50% alkali to fuse CBA significantly improved the reactivity of CBA thereby improving mechanical performance of the resulting geopolymer and also allowing to use higher proportion of CBA to fabricate the geopolymer.

The mineral composition of high alkali fused CBA (ffc) based geopolymer is presented in Figure 7-34. With 30% GGBS substitution, quartz, thermonatrite, and gaylussite were found as the main crystalline phases. The presence of thermonatrite indicated the excessive sodium introduced by the alkali-fusion process. When the GGBS substitution was 50%, thermonatrite was not detected and the intensity of quartz peaks decreased obviously in comparison to the geopolymer made with CBA fused with 25% alkali. The higher usage of alkali digested the quartz phase and converted it to a reactive phase contributed to the higher reactivity of the precursors and then to the higher mechanical performance. However, using a high amount of ffc ($\geq 50\%$) led to an excessive content of sodium. The formation of sodium salt may cause the deduction of mechanical performance and potential durability issues.

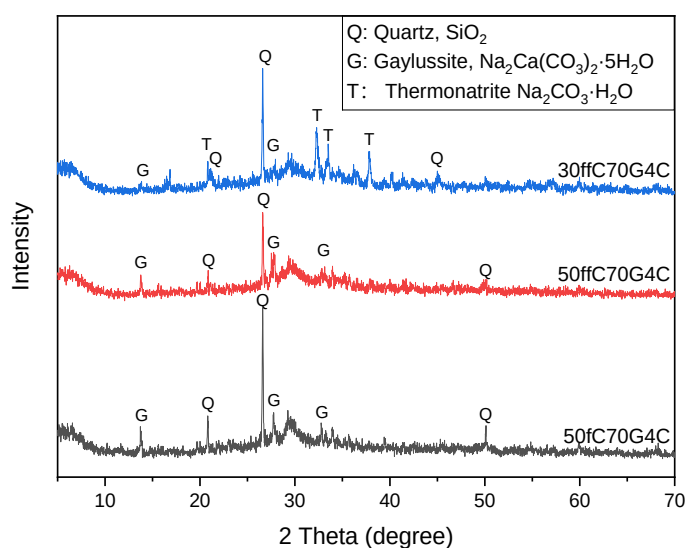


Figure 7-34 Mineral composition of alkali-fused CBA based geopolymer.

The FTIR spectrum provided more information on the microstructure of the 50ffC50G4C geopolymer in Figure 7-35. The main band located from 800 to 1200 cm^{-1} is assigned to the stretching vibrations of Si-O-Si(Al). The highest absorption wavenumber was recorded at 944 cm^{-1} indicating the dominate presence of SiQ^2 units. In addition, a band centred at 1408 cm^{-1} was assigned to the anti-symmetric stretching of carbonate suggesting the presence of carbonate due to the carbonation of the excessive sodium.

The SEM micrographs of ffC group geopolymers are presented in Figure 7-36. With 30% GGBS substitution, a cracked and fragmented matrix was found in Figure 7-36(a). A significantly high sodium content was detected by EDX in the matrix. Excess sodium exacerbates matrix cracking and forms additional carbonates that adversely affect strength development. However, when the substitution of GGBS increased to 50%, a denser and compacted matrix was found indicating better geopolymerisation occurrence. Although cracking is still observed, the trend of cracking is greatly moderated compared to 70ffC30G4C in Figure 7-36. Still, in comparison to the 50fC50G4C geopolymer in Figure 7-29(b), the cracking in 50ffC50G4C is more pronounced. Although the higher mechanical properties of 50ffC50G4C were obtained due to the higher reactivity of CBA, this tendency to crack may have a detrimental effect on its durability.

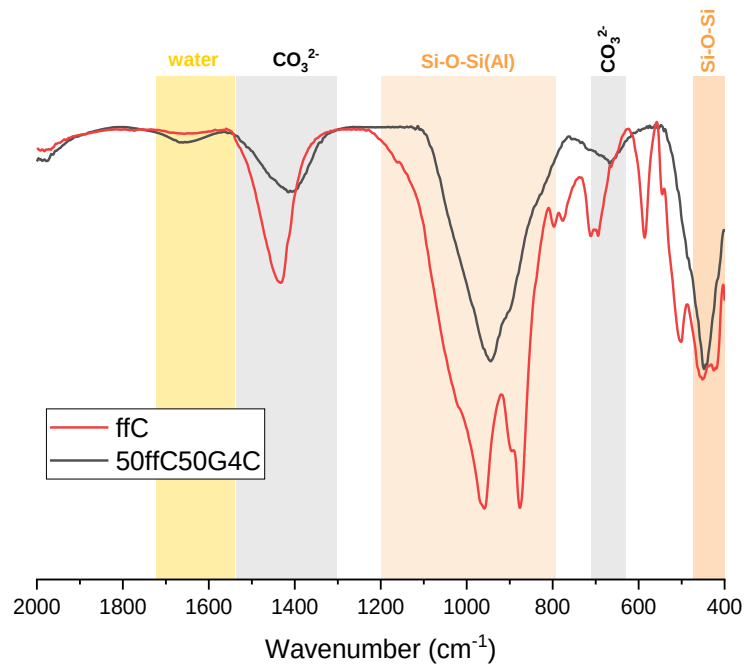


Figure 7-35 FTIR spectra of ffC and 50ffC50G4C.

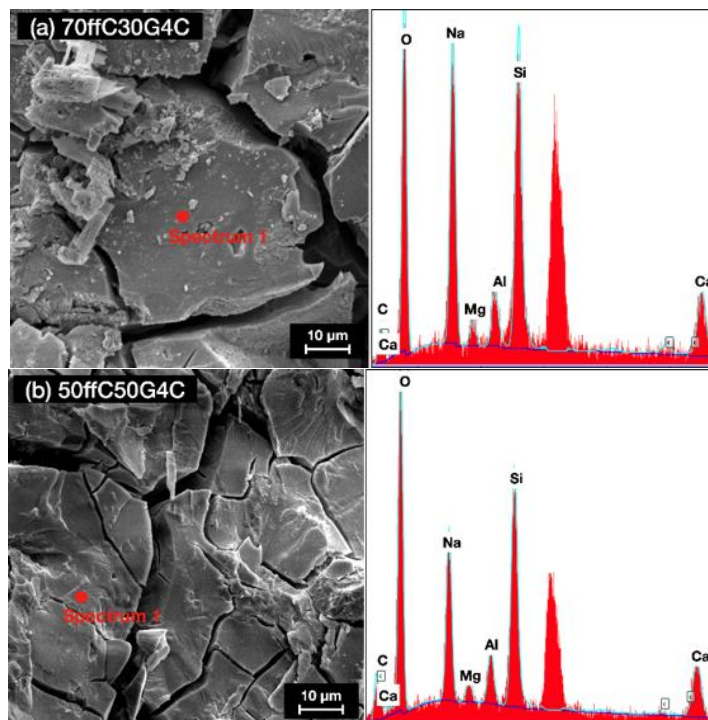


Figure 7-36 Micrograph of geopolymer made by CBA fused with 50% alkali.

7.3 OLIVE-PITS BIOMASS ASH (OBA) ONE-PART GEOPOLYMER

As concluded from the results in the previous chapter, OBA has high alkali content (19.95% CaO and 23.00% K₂O) and significant potential to serve as a novel activator to develop one-part geopolymer. This section produces cement with solid OBA and GGBS both alone and with small amounts of auxiliary activators. It doesn't use any calcination or thermal curing to

lower energy input and hence the carbon footprint of the resultant cement. It examines the influence of the OBA/slag ratio and the auxiliary activator composition on the binder performance and optimises the mixing method to improve the resultant OBA cement.

The mixing design used in this section is presented in Table 7-6 and Table 7-7. The convention for sample notation appears in Figure 7-37. The notation includes the percentages of OBA, GGBS and auxiliary activators, and the mixing method.

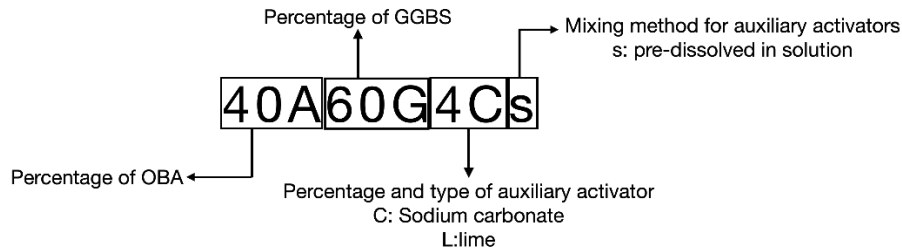


Figure 7-37 Convention of notation of OBA-based geopolymer.

Table 7-6 Mix design of OBA-based mortars: Batch I (g)

Notation	Binder		Auxiliary Activator		Water	Sand	w/b
	OBA	GGBS	Na ₂ CO ₃	Lime			
60A 40G	300	200	-	-	250	1000	0.5
50A 50G	250	250	-	-	250	1000	0.5
40A 60G	200	300	-	-	250	1000	0.5
40A 60G 4C	200	300	20	-	250	1000	0.5
40A 60G 6C	200	300	30	-	250	1000	0.5
40A 60G 8C	200	300	40	-	250	1000	0.5
40A 60G 10C	200	300	50	-	250	1000	0.5
35A 60G 5L	175	300	-	25	250	1000	0.5
30A 60G 10L	150	300	-	50	250	1000	0.5

Table 7-7 Mix design of OBA-based mortars: Batch II (g)

Notation	Binder		Auxiliary Activator Solution			Sand	w/b
	OBA	GGBS	Sodium carbonate	Lime	Water		
40A 60G 4Cs	200	300	20	-	250	1000	0.5
40A 60G 6Cs	200	300	30	-	250	1000	0.5
40A 60G 8Cs	200	300	40	-	250	1000	0.5
40A 60G 10Cs	200	300	50	-	250	1000	0.5
35A 60G 5Ls	200	300	-	20	250	1000	0.5

7.3.1 Properties of OBA-GGBS Cements with Varying OBA:GGBS Ratio

The initial flow diameter and mechanical strength of OBA-GGBS mortars with varying ash/slag ratios appear in Figure 7-38. Replacing GGBS with OBA has no significant effect on the mortar rheology, with only a slight reduction in flow at a 60% substitution rate. However, increasing OBA has a negative impact on the mechanical properties (Figure 7-38b): when the amount of

ash increased from 40% to 60%, the compressive strength reduced from 15.43 MPa to 9.13 MPa, a reduction of 40.83%, and the flexural strength diminished from 3.93 MPa to 2.51 MPa, a decline of 36.13%.

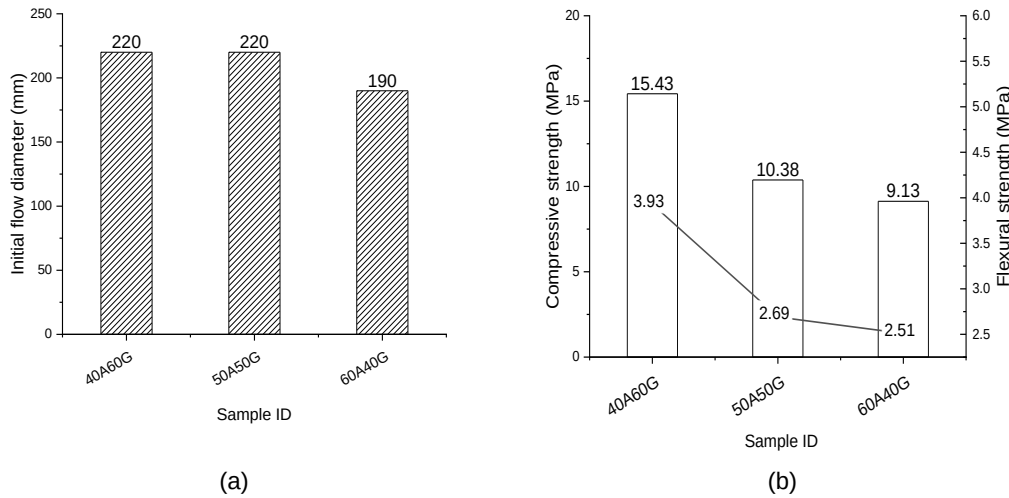
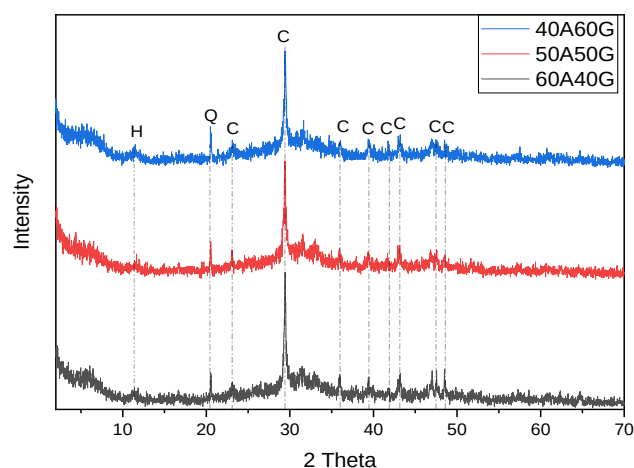


Figure 7-38 Initial flow diameter and mechanical strength of OBA-GGBS mortars at 28d.

The mineral composition of the OBA-GGBS cements with varying OBA/GGBS ratios appears in Figure 7-39. This shows that varying the ash-slag ratio does not significantly alter the mineral composition of the cement. The crystalline cement phases comprise calcite (CaCO_3), minor quartz (SiO_2) and hydrotalcite. Hydrotalcite is a common secondary reaction product of slag/ash activation (the main product being a C-(A)-S-H gel like the gel generated on PC hydration) (Wang and Scrivener, 1995; Palomo et al., 1999; Puertas and Fernández-Jiménez, 2003; Fernández-Jiménez et al., 2003). Hydrotalcite is a stable phase, one of the main reaction productions of alkali-activated slags when sufficient Mg is present (Kim et al., 2013). It often appears as sub microscopic crystals scattered in C-A-S-H gel resulting from the reaction of high calcium slag and NaOH / Na silicate and in PC + slag blends (Garcia Lodeiro et al., 2015).

A hump centred at $2\theta=31.1^\circ$ occurs in all pastes indicating the presence of amorphous C-S-H or C-(A)-S-H. Similar reflections are identified as C-S-H, the main reaction product of alkali-activated slags (Ben Haha et al., 2011). Similar broad diffuse humps, in the region $2\theta = 20-38^\circ$ are considered glassy phases resulting from the alkaline activation of slag (Khate and Chaudhary, 2007; Duxson et al., 2007). The position of the C-S-H hump can indicate the degree of polymerisation of the cement. According to Davidovits (2020), geopolymer cement obtained by polymerisation of an alumina-silica system typically shows a diffuse peak at $2\theta = 27-29^\circ$ which shifts depending on the degree of polymerisation: the greater the polymerisation the greater the shift towards lower angles. A well-developed, three-dimensional geopolymer showed the hump at $2\theta = 22-24^\circ$ while, in a less polymerised cement, it appears at $30-34^\circ$. The cements here show the peak at $\sim 31^\circ$ suggesting a medium to low polymerisation for the OBA-slag paste.



H: Hydrotalcite $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ [PDF 00-041-1428]
 C: Calcite CaCO_3 [PDF 00-066-0867] Q: Quartz SiO_2 [PDF 00-001-0378]

Figure 7-39 Mineral composition of OBA-GGBS pastes with varying ash/slag proportions at 28d.

The typical microstructure of the ash-slag cement with the highest strength, 40A60G (40%OBA), appears in Figure 7-40. It is a compact, continuous, amorphous cement with scattered salts, consistent with the XRD analyses. No unreacted slag particles or pores are found. The chemical analyses of the cement evidenced notable concentrations of K, Ca, Si and Al suggesting the presence of C(K)-A-S-H. The SEM analyses revealed cracks, a common feature in alkali-activated materials attributed to water loss and homogeneous shrinkage subsequent to the polymerization reaction (Provis and Van Deventer 2013; Bílek et al. 2023).

The pH of an OBA water solution is 12.67-13.07. A high alkalinity is consistent with other OBAs in the literature Alonso et al. (2019). This elevated alkalinity is mainly due to the high solubility of Potassium Calcium Magnesium Phosphate, a main component of the ash. The OBA affords a greater alkalinity than some commercial activators such as sodium silicate which have low solubilities and result in low polymerisation. The OBA-slag cement conforms to an alkaline system comparable to alkali-activated slags thanks to the activation power of the OBA. The alkalinity provided by the OBA releases Ca^{2+} , Si^{4+} and some Al^{3+} from the GGBS which contribute to the formation of calcite, hydrotalcite and C(K)-A-S-H cements (Figure 7-40). The Ca-O bond in slag is weaker than the Si-O / Al-O bonds. However, the GGBS in this research is highly amorphous and reactive (Alelweet & Pavia, 2021) hence the OBA has released active Ca^{2+} , Si^{4+} and Al^{3+} . Calcite cement is abundant agreeing with former authors. According to Dung et al. (2019), active Ca^{2+} tends to form calcite prior to the formation of hydrotalcite and C-S-H gels.

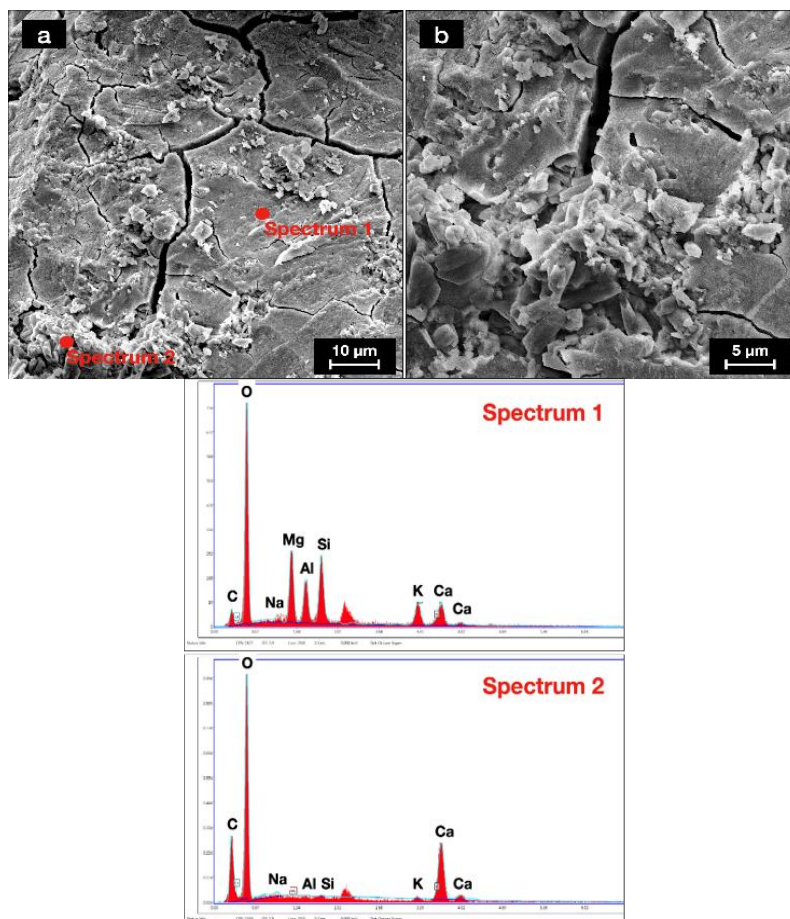


Figure 7-40 SEM micrographs of 40A60G paste and elemental EDX analyses at 180 days.

7.3.2 Properties of OBA-GGBS Cements Including Auxiliary Activators

To enhance the properties of the OBA-slag cements, auxiliary activators (sodium carbonate and hydrated lime) were added to the mix with the highest strength, 40A60G. The mechanical properties of the resultant materials appear in Figure 7-41. Doping with sodium carbonate (Na_2CO_3 - NC) enhances compressive strength development. With 4% NC, the compressive strength of the OBA-GGBS paste increased by 11.60% (from 15.43 to 17.22 MPa). The compressive strength raised with growing NC dosage. Increasing NC content to 10% raised compressive strength to 22.25 MPa, an increase of 44.20% compared to the reference group (0%NC). Flexural strength development did not follow the same pattern. 4% NC content yielded the highest flexural strength of 5.06 MPa, while 6%NC content achieved the lowest (3.54 MPa), a lower value than the reference group.

Using 5% lime as an auxiliary activator increased strength by 22.55%, from 15.43 MPa to 18.91 MPa. The release of extra Ca^{2+} by the lime enhances the reaction. However, when the amount of lime grows to 10%, compressive strength lowers from 18.91 MPa to 15.66 MPa, a lower value like the reference group. The bending strength follows the same trend as the compressive strength, decreasing with increasing lime content.

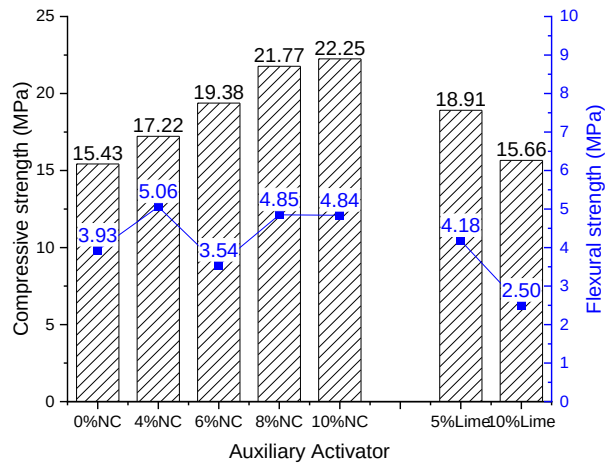


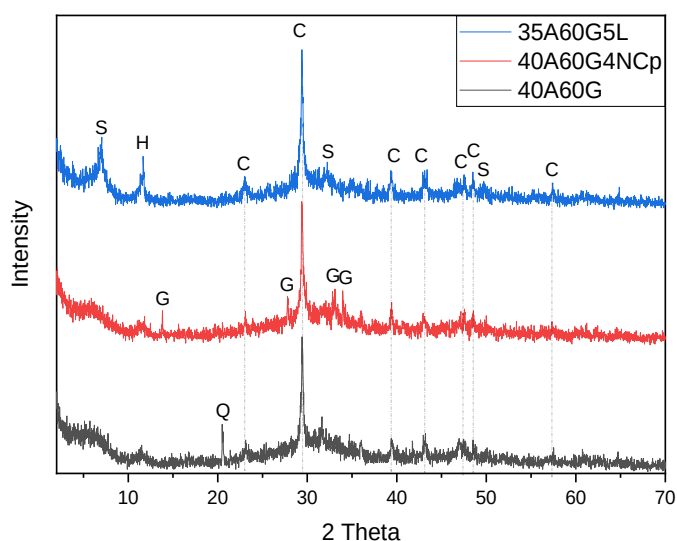
Figure 7-41 Mechanical strength of OBA-GGBS pastes with auxiliary activators.

The mineral composition of the OBA-GGBS cements including auxiliary activators appears in Figure 7-42. Calcite (CaCO_3) is still the main cementing mineral. However, the NC activator produced gaylussite and the lime activator increased hydrotalcite and produced crystalline C-S-H.

Gaylussite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$) is a common secondary reaction product in 30%PC/70%FA systems activated with NC (Garcia-Lodeiro et al., 2013); and a product of the reaction between GGBS and NC which transforms into a more stable carbonate phase in subsequent reactions (Yuan et al., 2017b; Dung et al., 2019). The formation of gaylussite implies a preferential reaction between the CO_3^{2-} from the activator and the active Ca^{2+} released by the early dissolution of the slag and ash. This agrees with former authors (Garcia-Lodeiro et al. 2013; Abdalqader et al., 2016) stating that the type of anion in the activator has a significant effect on the nature of the secondary products; and that NC favours the formation of gaylussite and AFm phases. Therefore, in the OBA-GGBS system, NC is an efficient activator that promotes dissolution and subsequent cement formation which enhances strength development (Figure 7-41).

Using a lime activator enlarges hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$) cement and produces crystalline C-S-H (Figure 7-42) which increases the strength of the control mix. As aforementioned, hydrotalcite is a stable, main reaction product of alkali-activated slags when sufficient Mg is present. GGBS contributes Mg^{2+} for the formation of hydrotalcite (~8%- Table 1). Similarly, the OBA (~4% Mg) likely contributes active Mg^{2+} for hydrotalcite formation.

The low solubility of lime can lead to unsoundness in lime based-alkali-activated slag mortars (Yang et al., 2012). However, the elevated alkalinity of the ash-slag system in this research (pH~13 or over) should increase lime solubility, hence unsoundness, at 5% lime content, is not a concern.



C: Calcite: CaCO_3 [PDF 00-066-0867] Q: Quartz SiO_2 [PDF 00-001-0378]
G: Gaylussite $\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ [PDF 00-012-0255]
H: Hydrotalcite $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ [PDF 00-041-1428]
S: Calcium Silicate Hydrate $\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ [PDF 00-034-002]

Figure 7-42 Effect of lime/NC activator on the mineral composition of OBA-GGBS cement - 28d.

The microstructures of the OBA-GGBS cements with lime and NC appear in Figure 7-43 and Figure 7-44 respectively. They are compact, continuous, amorphous structures like the OBA-GGBS cements with no activators. However, the amount of salt crystals increased probably due to the extra $\text{Ca}^{2+}/\text{Na}^{2+}$ added. The SEM shows that the NC cement is denser. It exhibits a smooth, flat cross-section, with occasional nano-sized cracks, unlike the other groups. These are typical features of stiff, brittle materials of high strength and hardness, agreeing with their higher strength results (Figure 7-41). The EDX analyses show significant Na in the cement implying the presence of N-A-S-H. Therefore, active Na^{2+} (dissolved from the activator) promotes the formation of N-A-S-H gels which enhance mechanical performance.

The EDX analyses also show that the NC activator significantly increased the Ca and Si concentrations in the cements from 7.34% and 8.09% respectively, in the ash/slag pastes without an auxiliary activator (40A60G), to 15.54% and 13.50% respectively (40A60G4C). This indicates that NC enhances GGBS dissolution and polymerisation. The upsurge of Si increases the density of the cement (Kovalchuk et al., 2008).

The EDX analyses demonstrate that both activators increase the amount of K in the cement. The EDX analyses suggest the presence of C(K)-A-S-H and a slightly higher Ca/Si ratio than in ash/slag paste alone (40A60G). The OBA is high in K therefore, the presence of C(K)-A-S-H indicates that both activators dissolve the ash effectively, in particular the NC.

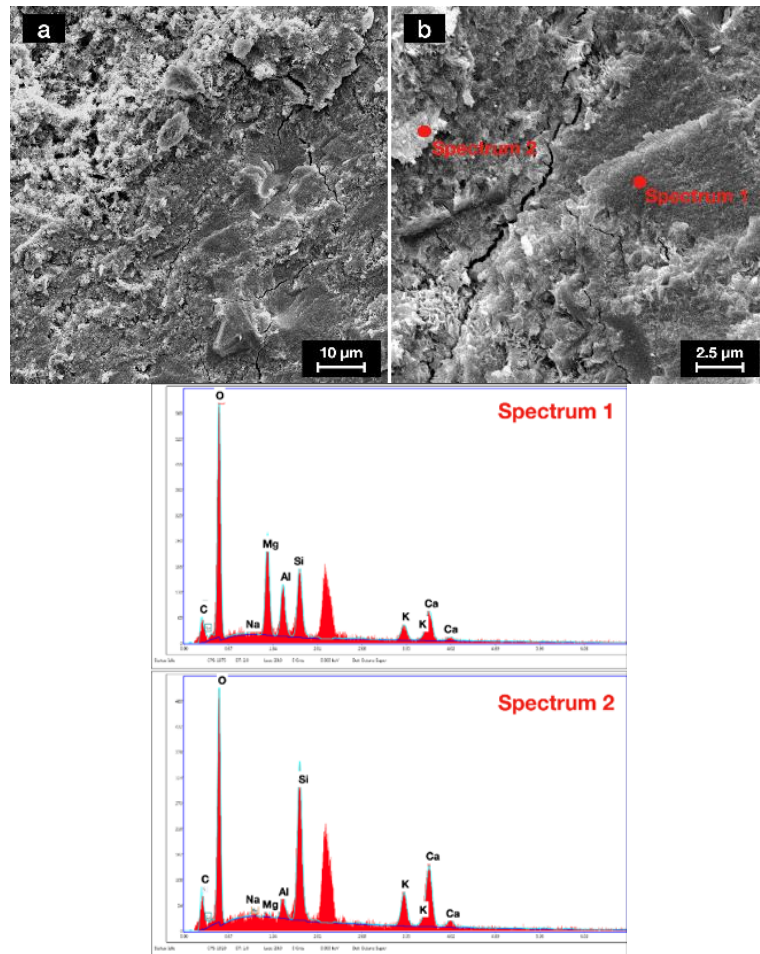


Figure 7-43 Microstructure and composition of OBA-GGBS cement with lime activator (35A60G5L)-180 d.

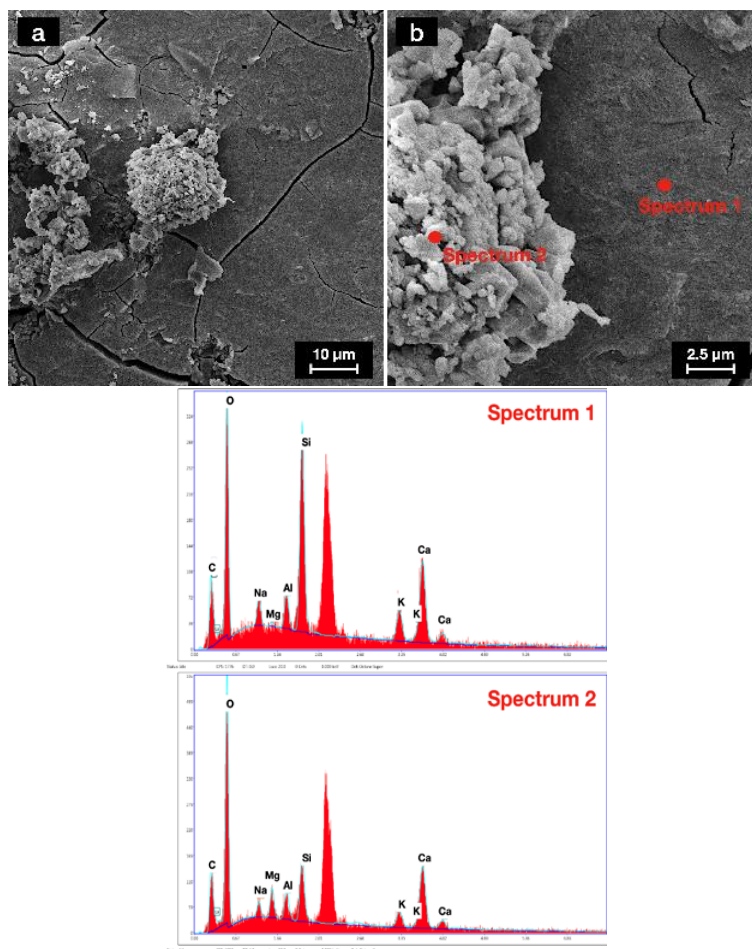


Figure 7-44 Microstructure and composition of OBA-GGBS cement with Na carbonate activator (40A60G4C) at 180 days.

7.3.3 Mixing Method Optimisation

This section investigates whether pre-dissolving the lime/NC activator improves the geopolymerization reaction and strength development. It compares specimens made without NC (40A60G) and 4% NC mixed as solid powder, with specimens made with 4% pre-dissolved NC.

As seen in Figure 7-45, compressive strength significantly improved by pre-dissolving NC. Adding 4% pre-dissolved carbonate increased compressive strength of the OBA-GGBS mix and the OBA-GGBS with 4% NC powder by 138.76% and 113.94% respectively. The cement with 10% pre-dissolved NC reached 43.94 MPa. This accounts for a strength increase of 184.77% for the OBA-GGBS mix and 97.48% for the OBA-GGBS with 4% NC powder. Rising NC content from 4 to 10% increased the compressive strength of the pre-dissolved mortar by 19.27%, and by 29.21 % when the NC was in powder form. Pre-dissolving the lime activator raised the compressive strength OBA-GGBS mortar with no activator by 41.60% and the strength of the mortar with lime as powder by 15.55%. The limited improvement, compared to pre-dissolving NC, is probably due to the lower solubility of lime.

The flexural strength of pre-dissolved mortars did not follow the same trend. Pre-dissolving generally has a negative effect on flexural strength development. Adding 4% pre-dissolved NC decreased the flexural strength of the OBA-GGBS mortar by 10.18% but increased the flexural

strength of the NC powder mortar by 28.75%. Adding 10% pre-dissolved NC improved the strength of the NC-powder specimens by 23.16%. Pre-dissolving lime exhibits a slight negative effect on flexural strength development, with a reduction of 6.87%.

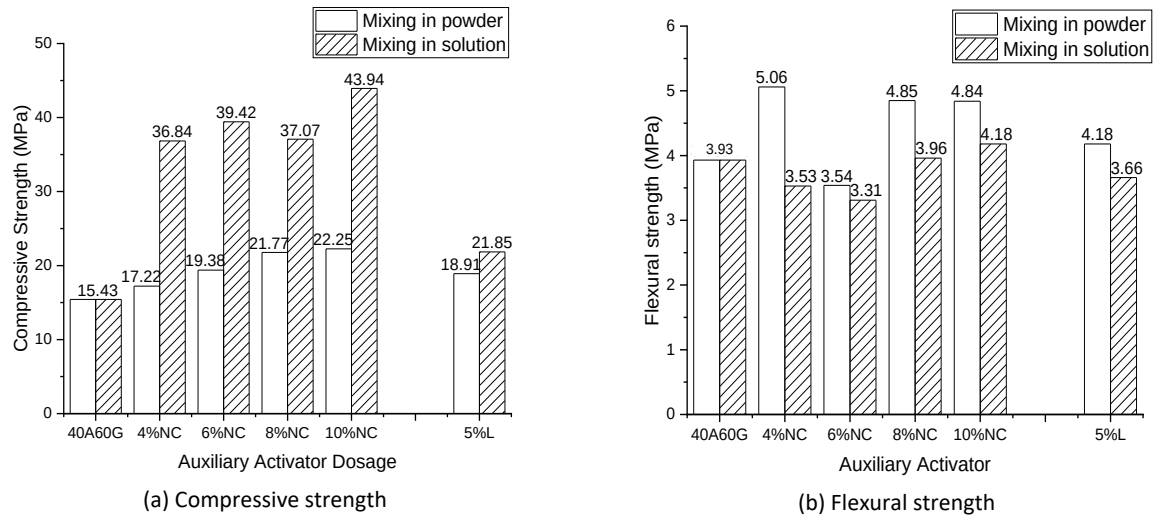
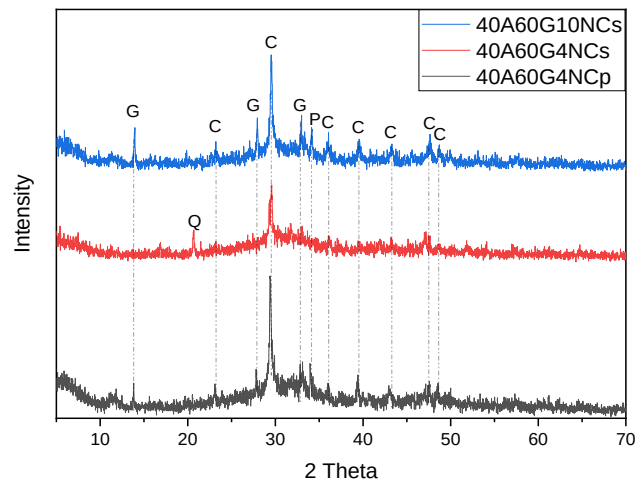


Figure 7-45 Mechanical performance of OBA-GGBS cements with pre-dissolved auxiliary activators at 28d.

The composition and microstructure of the cements produced with solid vs pre-dissolved NC, studied with XRD, SEM/EDX and FTIR, appear in Figure 7-46 - Figure 7-48. The cement mineralogy in Figure 7-46 shows that the pre-dissolution of NC improves its efficiency as an activator because it reduces the peaks of calcite. When less carbonate cement precipitates, more active Ca^{2+} is available to form cement such as amorphous C-S-H that remains undetected in the XRD trace. This agrees with the strength increase (Figure 7-45).

The microstructure and elemental composition of the cements formed using 4% and 10% pre-dissolved NC appear in Figure 7-47 and Figure 7-48 respectively. In either case, the cements are dense and amorphous and show occasional cracks. More abundant salt crystals are evident at 10% NC dosage. The EDX/SEM analyses indicate that increasing NC dosage does not substantially alter the nature of the cement but causes salt to precipitate (Figure 7-48, EDX spectrum 2). The amount of Ca^{2+} and Si^{4+} , measured on EDX spectra, in the 4% NC cement (14.90% and 13.54% respectively) and the 10% NC cement (15.68% and 15.07%) are similar. A greater NC content increases alkalinity facilitating the dissolution of OBA and GGBS. However, the 10% NC content, causes a surplus of unreacted activators that leads to salt precipitates.



C: Calcite: CaCO_3 PDF 00-066-0867 **Q:** Quartz SiO_2 PDF 00-001-0378

G: Gaylussite $\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ PDF 00-012-0255

P: Potassium Sodium Calcium Chloride Carbonate $\text{K}_6\text{NaCa}_2(\text{CO}_3)_5\text{Cl}(\text{H}_2\text{O})_6$ PDF 04-017-5717

Figure 7-46 Effect of pre-dissolving NC activator on the mineralogy of OBA-GGBS cements 28d.

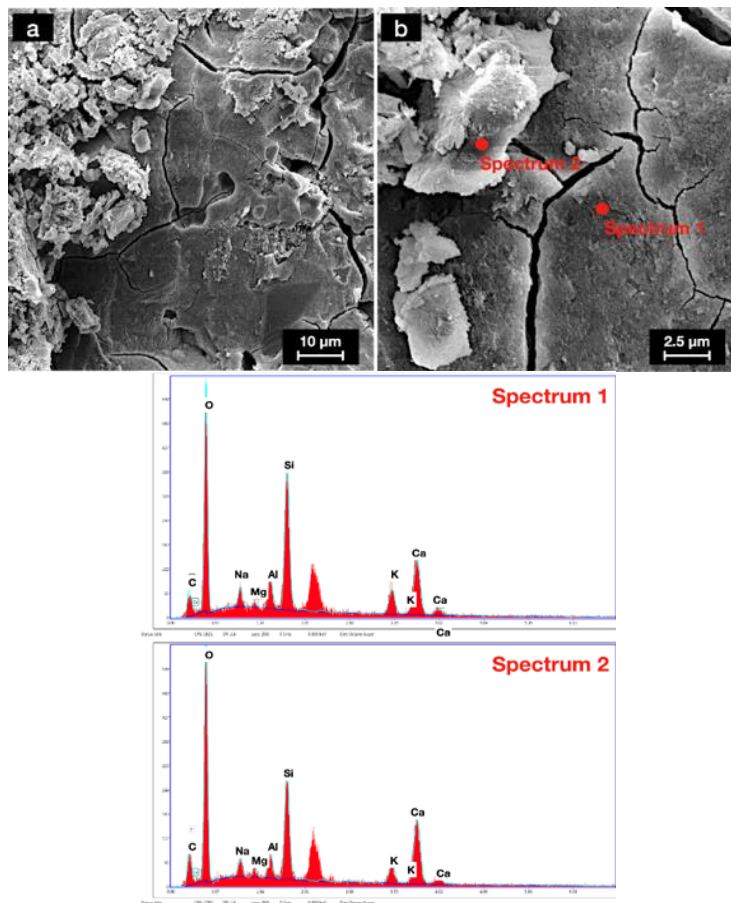


Figure 7-47 Microstructure and elemental composition of OBA-GGBS cement with 4% pre-dissolved NC activator (40A60G4Cs) at 180 days.

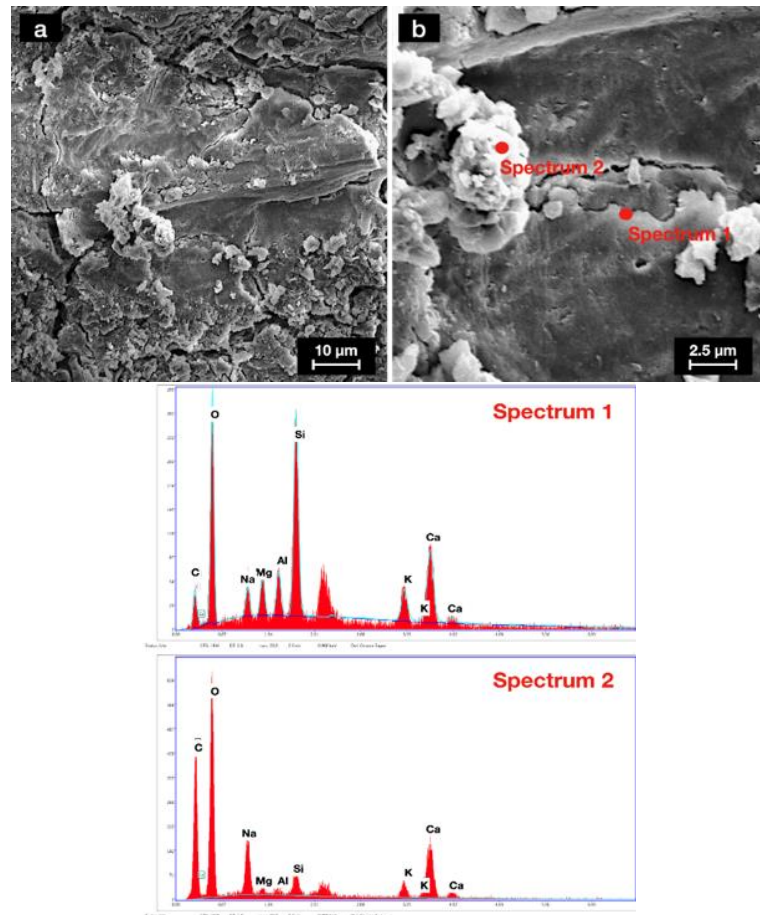


Figure 7-48 Microstructure and elemental composition of OBA-GGBS cement with 10% pre-dissolved NC activator (40A60G10Cs) at 180 days.

The FTIR spectra of the cements assist the XRD and SEM/EDX results (Figure 7-49). The bands centred at ~ 874 and ~ 1410 cm^{-1} correspond to the out-of-plane deformations and asymmetric stretching vibration of the C—O bond of carbonate, agreeing with the XRD results. The $1300\text{--}1500$ cm^{-1} band range on the IR spectrum is attributed to the presence of calcium and calcium sodium carbonates (Fernández-Jiménez and Puertas, 2001). The band at ~ 1650 cm^{-1} corresponds to the stretching vibration of the O-H bonds in chemically bound water in various hydration products. This band appears in all the specimens confirming the presence of cementing hydrates.

The occurrence of the bands centred at ~ 445 cm^{-1} and 944 cm^{-1} agree with previous authors and are assigned to the O-Si-O vibration from $[\text{SiO}_4]^{4-}$ in C-A-S-H. The band at 445 cm^{-1} is assigned to the O-Si-O vibration from $[\text{SiO}_4]^{4-}$ in C-A-S-H. The vibration band at $961\text{--}969$ cm^{-1} is created by the SiO_4 groups in C-A-S-H gels (Fernández-Jiménez et al., 2003; Puertas et al., 2004, 2011; Garcia Lodeiro et al. 2009).

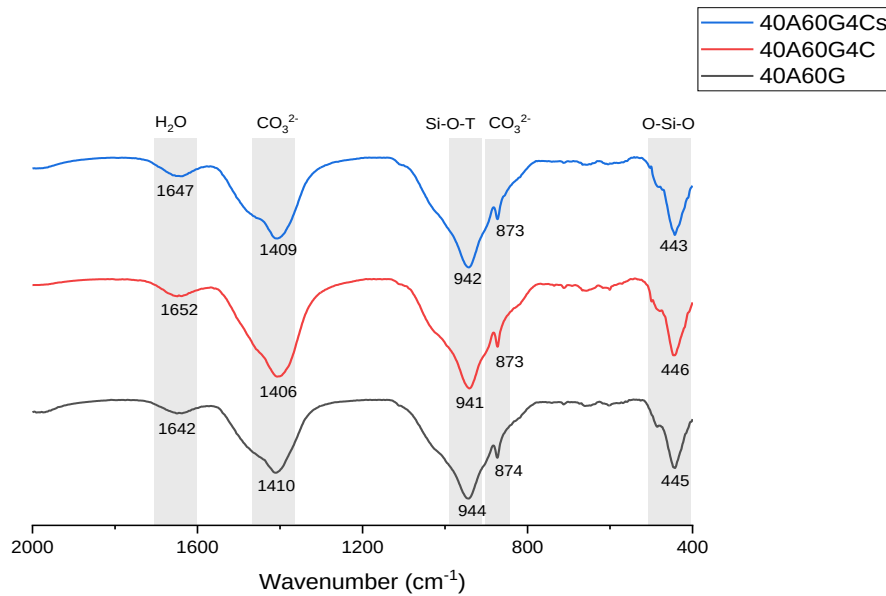


Figure 7-49 FTIR spectra of OBA-GGBS cements without and with (solid and pre-dissolved) NC activator.

7.4 SUMMARY

In this chapter, three types of wastes served as precursors to develop one-part geopolymer. Based on the experimental results, conclusions are as follows:

AS one-part geopolymer:

Sodium silicate with a modulus of 2.0 is the most suitable activator for the AS-GGBS geopolymer. A higher modulus of silicate led to low alkalinity, inhibiting geopolymerization, while a lower modulus caused excessive alkalinity, resulting in too rapid setting.

The optimal $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio for the geopolymer is 1.0. Deviations from this value decreased the strength of geopolymers. Sodium ions balance the charge deficit due to the substitution of Al^{3+} for Si^{4+} . Excess sodium led to the formation of excessive salt phases, adversely affecting structural integrity and homogeneity.

The presence of sodium carbonate activator was vital for the AS-GGBS geopolymer. Carbonate triggered the dissolution of GGBS, initiating geopolymerization in the one-part system. The sodium silicate activator had an irreplaceable and synergistic effect with sodium carbonate, providing soluble silicate necessary to form more cementing gels during geopolymerization, and inhibiting the rapid reaction of the activated alumina with carbonates leading to flash set and undermining workability.

A $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 2.5 was found optimal for the AS-GGBS geopolymer. Increasing the SiO_2 content beyond this ratio did not improve mechanical performance. Higher AS replacement (>20%) decreased mechanical strength but increased the robustness of the geopolymer system, requiring more activators to balance the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

A dense and compact matrix constitutes the optimally designed geopolymer. Gaylussite and calcite were identified as the main crystalline phases. Rich Si-O-Si(Al) bonds detected in FTIR spectra indicate the presence of C(N)-A-S-H gels. Modifying the design parameters did not alter the microstructure of the resulting geopolymer, as indicated by FTIR and XRD. However, SEM observations revealed a significant amount of salt phases, which may adversely affect mechanical performance.

CBA one-part geopolymer:

Up to 30% of raw CBA can be blended with GGBS to produce sound, one-part geopolymers activated with sodium carbonate and sodium silicate. Beyond this threshold, the geopolymer matrix experiences a strength reduction due to insufficient cement content. A one-part geopolymer consisting of 30% CBA and 70% GGBS activated with 10% sodium carbonate achieved a compressive strength of 30.70 MPa at 28 days. However, it exhibited a prolonged setting, taking up to 5 hours to initially set and 8 hours to finally set.

The inclusion of sodium silicate significantly improved the mechanical performance and accelerated the setting process of the one-part geopolymer. A formulation activated with 20% sodium silicate and 5% sodium carbonate reached a compressive strength of 46.09 MPa at 28 days, with setting times reduced to 57 minutes for the initial setting and 1 hour 15 minutes for the final setting.

The SEM/EDX analyses revealed a dense and amorphous matrix comprising the raw CBA-GGBS geopolymer. Increasing the sodium silicate activator facilitated the polymerization process providing denser cement with greater Si content.

Contrary to the raw CBA geopolymer, increasing the sodium carbonate activator does not enhance the strength of the geopolymer made with alkali-fused CBA. However, like the raw CBA geopolymer, increasing the substitution rate of slag and adding sodium silicate are effective strategies to improve mechanical properties. Specifically, adding 10% sodium silicate increases the compressive strength of the geopolymer by 36.4%, reaching 52.80 MPa, but further increasing the amount of sodium silicate does not significantly enhance the mechanical properties.

Since alkali fusion improves the reactivity of CBA, alkali-fused CBA can replace up to 50% of GGBS. This extends the applicability of CBA compared to raw CBA. However, as the CBA substitution rate increases, the matrix tends to crack. This can be attributed to two main factors: the lower reactivity of CBA compared to GGBS results in a reduced gelling component, and the extensive use of Na to alkali-fuse the CBA introduces excessive Na ions, leading to shrinkage and cracking of the matrix.

A properly activated alkali-fused CBA-based geopolymer matrix is dense and homogeneous, which correlates with its excellent mechanical properties. The matrix is predominantly amorphous, with only a few gaylussite crystals observed. Furthermore, FTIR spectra indicate that the geopolymer matrix is primarily composed of SiQ^2 and SiQ^1 structures.

When the amount of alkali used in the fusion process is increased from 25% to 50%, the CBA substitution rate can be further increased to 70%. However, due to the excessive Na^+ ions, significant matrix cracking occurs, which may adversely affect durability.

OBA one-part geopolymer:

The OBA-slag cement is comparable to an alkali-activated slag system thanks to the outstanding activation performed by the OBA which provides enough alkalinity to release Ca^{2+} , Si^{4+} and Al^{3+} from the GGBS to form calcite, hydrotalcite and C-(A)-S-H cement.

Adding sodium carbonate (NC) and lime as supplementary activators enhances the strength of OBA-GGBS cements. Both activators dissolve the ash and slag, but the NC is the most efficient. An optimal threshold of 5% lime content was evidenced beyond which escalating lime dosage lowers strength.

The dominant mineral component of the OBA-GGBS cement is calcite, accompanied by substantial amorphous content. Alterations in the structure and composition of the cement were observed upon doping with 4% sodium carbonate which enabled the generation of gaylussite and N-A-S-H cement. Moreover, including lime as an auxiliary activator increased hydrotalcite and calcite cement and produced crystalline C-S-H.

The incorporation of NC significantly raised compressive strength, and there is a notable positive correlation between the amount of NC and the strength improvement. The NC activator increased dissolution, and produced a denser and stronger cement with increased Si and K concentration that includes N-A-S-H and C(K)-A-S-H. The pre-dissolved NC activator is the most efficient, producing less calcite for the same amount of NC. By adding 4% pre-dissolved NC, compressive strength increased by 138.76% (compared to OBA-GGBS mortar without auxiliary activator) and 113.94% compared to the material with NC in powder form. Adding 10% pre-dissolved NC further enhanced strength, and produced more abundant calcite, gaylussite and potassium sodium calcium chloride carbonates.

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Chapter 8: Durability of Waste Based Geopolymer

Constructions are susceptible to aggressive influences that weather their material constituents over time. The effect of thermal and humidity variations, liquid water and salt crystallization are amongst the most significant. This research investigates the resistance of the geopolymers developed to these damaging agents by performing three durability tests including wet-dry cycles, sulphate attack tests and resistance to high-temperature tests.

8.1 WET-DRY CYCLE

Constructions are susceptible to various aggressive influences, with wet-dry cycling being one of the most significant. Rainfall, groundwater and tidal action cause concrete and other materials to repeatedly transition between dry and water-saturated states. The wet-dry cycling test is a critical experimental procedure to assess the durability of concrete when exposed to moisture fluctuations over extended periods. This test simulates the natural conditions of alternating wetting and drying, thereby revealing the physical and chemical changes in the concrete. These tests effectively predict the durability of materials during their service life, enhancing both the safety and longevity of these structures in particular bridges, tunnels and marine structures. Therefore, it is crucial to assess the resistance of geopolymer to thermal and hydric changes to ensure their durability and safety in construction applications.

The geopolymer blends used in this section are shown in Table 8-1. The optimized geopolymer formulations from the previous chapters were further studied in this chapter. The notation of each geopolymer follow the previous nomenclature: F = FCC, C = CBA, fC = alkali-fused CBA with 25% NaOH, ffC = alkali-fused CBA with 50% NaOH, A = OBA, G = GGBS, S = sodium silicate, C = sodium carbonate, Cs = pre-solubilized sodium carbonate. Numbers before the letters indicate percentages, and numbers with slashes indicate components of the activator solution. The AS one-part geopolymers are designed as the total chemical composition. The specimen C2 is designed as $\text{SiO}_2/\text{Al}_2\text{O}_3=2.5$ and $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}=1$ while the C3 is designed as $\text{SiO}_2/\text{Al}_2\text{O}_3=3.0$ and $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}=1$.

Table 8-1 Geopolymer mix design used in this chapter.

Group		Notation	Waste type	Precursor (g)			Activator [Na ⁺] (mol/L)	Sand (g)	w/b
				Waste	GGBS	SiO ₂ /Na ₂ O			
Two-part Geopolymer	FCC based	40F60G 8/1.0	FCC	160	240	1.0	8	1200	0.6
		40F60G 8/1.2	FCC	160	240	1.2	8	1200	0.6
		40F60G 6/1.0	FCC	160	240	1.0	6	1200	0.6
	CBA based	30C70G 10/1.2	Raw CBA	120	280	1.2	10	1200	0.6
		30fC70G 10/1.2	Alkali-fused CBA with 25% NaOH	120	280	1.2	10	1200	0.6

Group		Notation	Waste type	Precursor (g)		Activator (g)		Sand (g)	w/b
				Waste	GGBS	Sodium silicate	Sodium carbonate		
One-part Geopolymer	AS based	C2	AS burnt at 800 °C	66.3	265.3	66.3	52.0	1500	0.5
		C3	AS burnt at 800 °C	64.0	255.9	102.3	27.8	1500	0.5
	OBA based	40A60G	OBA	200	300	0	0	1000	0.5
		40A60G 4Cs	OBA	200	300	0	20	1000	0.5
		40A60G 10C	OBA	200	300	0	50	1000	0.5
		40A60G 10Cs	OBA	200	300	0	50	1000	0.5
	CBA based	30C70G 10C	Raw CBA	120	280	0	40	1200	0.5
		30C70G 5C10S	Raw CBA	120	280	40	20	1200	0.5
		30fC70G 4C	Alkali-fused CBA with 25% NaOH	120	280	0	16	1200	0.6
		30fC70G 5C10S	Alkali-fused CBA with 25% NaOH	120	280	40	20	1200	0.6
		30fC70G 5C20S	Alkali-fused CBA with 25% NaOH	120	280	80	20	1200	0.6
		50ffC50G 4C	Alkali-fused CBA with 50% NaOH	200	200	0	16	1200	0.6

The compressive strength of selected geopolymers before and after wet-dry cycling is presented in Table 8-2. Different groups of geopolymers showed distinct responses to the wet-dry cycles.

Specimens 30fC70G 10/1.2, C2, C3, 40A60G10C, 30fC70G5C10S and 50ffC50G4P exhibit significant strength reductions of over 35%. Conversely, specimens 40F60G 8/1.0, 30C70G 10/1.2 and 30fC70G5C20S showed intermediate strength reductions while the strength of specimens 40F60G 8/1.2, 40F60G 6/1.0, 40A60G, 40A60G 4Cs, 30C70G10C and 30fC70G4C improved. Notably, specimens 40A60G and 30C70G10C exhibit a significant strength increase of over 50%.

The results indicate that compressive strength reduction is related to the sodium dosage in the geopolymer system. For instance, increasing the sodium concentration from 6 mol/L to 8 mol/L shifts strength from a 25.58% increase (at 6 mol/L) to a 6.16% decrease. Furthermore, a two-part geopolymer made with raw CBA showed only a 2.88% compressive strength reduction, whereas a two-part geopolymer made with 25% alkali-fused geopolymer recorded a 68.47% strength reduction. The significant Na^+ introduced in the system during alkali fusion can be blamed for this strength drop. Similar trends are observed when comparing 40A60G vs. 40A60G4Cs vs. 40A60G10C and 30fC70G4C vs. 30fC70G5C10S.

Additionally, silicate dosage played a positive role in the resistance to wet-dry cycles. Increasing the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio from 1.0 to 1.2 reversed the strength reduction trend. Raising the silicate dosage from 10% to 20% in one-part geopolymer lowers strength reduction from 38.26% to 11.45%.

Table 8-2 Strength change of geopolymer samples after wet-dry cycles (SD= Standard Deviation).

			Compressive strength			
Group		Notation	Before (MPa)	After (MPa)	SD	Strength Change
Two-part Geopolymer	FCC based	40F60G 8/1.0	48.38	45.40	3.06	-6.16%
		40F60G 8/1.2	51.47	55.90	1.98	8.61%
		40F60G 6/1.0	47.96	60.23	2.25	25.58%
	CBA based	30C70G 10/1.2	29.83	28.97	2.76	-2.88%
		30fC70G 10/1.2	46.47	14.65	0.07	-68.47%
One-part Geopolymer	AS based	C2	66.50	30.30	1.41	-54.44%
		C3	65.90	35.50	2.36	-46.13%
	OBA based	40A60G	15.43	27.90	0.62	80.82%
		40A60G 4Cs	22.25	23.57	1.25	5.93%
		40A60G 10C	36.84	22.13	1.06	-39.93%
	CBA based	30C70G10C	30.70	53.50	0.57	74.27%
		30fC70G4C	36.35	36.85	1.34	1.38%
		30fC70G5C10S	52.80	32.60	2.35	-38.26%
		30fC70G5C20S	58.33	51.65	1.06	-11.45%
		50ffC50G4C	42.98	16.55	0.49	-61.49%

The chemical and mineral composition of the geopolymers play a role in durability. C-A-S-H gel and certain calcium salts like calcite and gaylussite can decompose when the concentration of calcium ions in the external environment is low (Yang et al., 2023). This leads to increased porosity and a decline in mechanical properties. Wet-dry cycling facilitates dissolution, hydrolysis, ion transport and diffusion which can damage the geopolymer. The soluble salt content, particularly sodium and calcium salts

which dissolve and re-crystallize during wet-drying episodes can induce microcracking and cement decomposition.

Physically, repeated wetting and drying cause expansion and contraction that lead to the formation of microcracks. Microcracks can accumulate over cycles progressively weakening the structure. Ghosh et al. (2019) report that FA-based geopolymer exhibited approximately a 25% strength reduction after wet-dry cycling, despite showing no visual deterioration on the surface. They attributed the strength loss to the repeated expulsion of moisture from the pores and the cyclic expansion and contraction. Yahya et al. (2024) note that Friedel's salt, ettringite, mirabilite and thenardite can form during wet-dry cycling causing delamination and spalling.

On the other hand, the availability of water may continue the geopolymerization process, thereby enhancing the performance of geopolymers. Autogenous healing of Portland cement materials under wet-dry cycling has been widely reported (Snoeck et al., 2014; Su et al., 2020; Y. Yang et al., 2009). The hydration of unhydrated cement particles and the crystallization of calcite can promote the healing of microcracks in PC-based concrete and restore mechanical performance. A similar mechanism can be applied to geopolymer materials (Alshaaer, 2020; Ulugöl et al., 2021; Ozen et al., 2024). Geopolymers made with FA and metakaolin have demonstrated excellent strain-hardening behaviour after 10 wet-dry cycles, with amorphous aluminosilicate gels observed as the reaction product of autogenous healing.

8.2 SULPHATE ATTACK

The prevalent sulphate environment on the surface of the earth, coupled to seasonal fluctuations of the water table or tidal action in oceans create dry-wet cycles that can lead to considerable damage in structures. During the wet phase of the cycle, when the water level rises, SO_4^{2-} ions penetrate concrete and react with calcium and aluminate phases to produce expansive products such as calcite and gypsum. During the dry phase, as the water level falls, sulphate crystals precipitate within the pore spaces of the structural material as the internal solution evaporates. The accumulation of these crystals leads to volume expansion, causing cracking and physical erosion (Hewlett & Liska, 2019).

The deterioration of concrete and reduction in structural durability due to sulphate attack is a significant concern. The damage to concrete exposed to alternating wet and dry environments is more severe and complex than in conditions of constant sulphate brine immersion. The cyclic exposure intensifies the damage mechanisms, making the assessment and mitigation of sulphate-induced deterioration critical for maintaining the integrity and longevity of concrete structures in such environments (Hewlett & Liska, 2019).

The weight loss and changes in the mechanical performance of various geopolymers after sulphate attack are detailed in Table 8-3. Most geopolymers experienced slight weight loss except for the two-part geopolymer made with raw CBA and one-part CBA-based geopolymers. Although most geopolymers retained their original shape after the sulphate attack cycles, the geopolymer made with AS suffered severe damage, with significant surface peeling and weight losses of 18.62% and 12.96%, respectively. These specimens were too damaged to undergo compressive strength testing post-attack.

Among other groups, the specimens 30fC70G 10/1.2, 40A60G 4Cs, 40A60G 10C, 40A60G 10Cs, 30fC70G5C10S and 50ffC50G4C show significant strength reduction of over 35%. The specimen 30fC70G5C20S exhibited a slight strength reduction while others demonstrate enhanced mechanical

performance after sulphate attack. Notably, the specimens 40A60G and 30C70G5C10S exhibit remarkable sulphate resistance, with an increase in compressive strength of over 50%.

Table 8-3 Strength Change of Geopolymer Samples after sulphate attack (SD= Standard Deviation).

Group	Notation		Weight loss	SD	Compressive strength			
					Before (MPa)	After (MPa)	SD	Strength change
Two-part Geopolymer	FCC based	40F60G 8/1.0	-2.55%	0.44%	48.38	57.12	1.80	18.07%
		40F60G 8/1.2	-2.81%	0.35%	51.47	59.65	0.78	15.89%
		40F60G 6/1.0	-1.96%	1.66%	47.96	65.25	0.49	36.05%
	CBA based	30C70G 10/1.2	2.00%	0.08%	29.83	43.97	1.48	47.40%
		30fC70G 10/1.2	-2.22%	0.29%	46.47	14.25	0.81	-69.34%
One-part Geopolymer	AS based	C2	-18.62%	3.14%	66.50	-	-	-
		C3	-12.96%	0.02%	65.90	-	-	-
	OBA based	40A60G	-1.66%	3.16%	15.43	23.37	1.45	51.46%
		40A60G 4Cs	-0.96%	1.46%	22.25	14.33	3.19	-35.60%
		40A60G 10C	-5.80%	0.78%	36.84	18.39	3.77	-50.08%
		40A60G 10Cs	-3.15%	0.67%	43.94	12.80	1.20	-70.87%
	CBA based	30C70G10C	0.82%	1.64%	30.70	32.16	2.93	4.76%
		30C70G4C10S	2.11%	0.59%	24.89	45.47	3.59	82.68%
		30fC70G4C	3.31%	0.25%	36.35	37.85	0.96	4.13%
		30fC70G4C10S	2.78%	0.38%	52.80	24.80	3.66	-53.03%
		30fC70G4C20S	4.10%	0.46%	58.33	58.05	1.48	-0.48%
		50ffC50G4C	3.29%	1.55%	42.98	21.68	0.58	-49.56%

As aforementioned, sulphate can react with the original geopolymer mineral components adversely affecting durability. The mineral composition of FCC-based geopolymer before and after sulphate attack appears in Figure 8-1. After sulphate attack, slight mineralogical changes were observed. In the 40F60G 8/1.2 specimen, the mineral composition became more amorphous, and the original crystal phase disappeared. In the 40F60G 10/1.2 specimens, a new crystal phase, gypsum, formed from the reaction between sulphate and calcium from GGBS or gels.

The photographs of FCC-based geopolymer specimens appear in Figure 8-2. No significant expansion or peeling was observed on the sample surface, but minor damage showed at some corners. The dense and compact microstructure contributed to the excellent sulphate resistance.

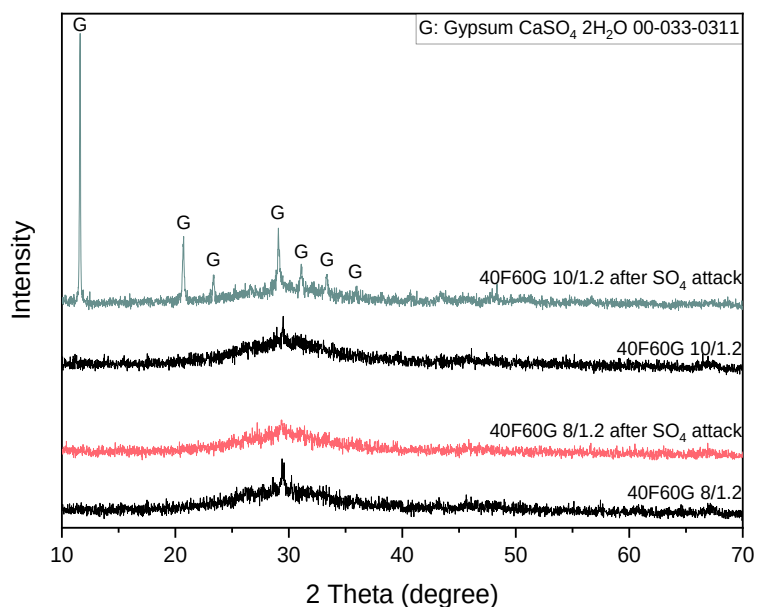


Figure 8-1 Mineral composition of FCC-based geopolymer before and after sulphate attack.



(a) 40F60G 8/1.2

(b) 40F60G 6/1.0

Figure 8-2 Photographs of FCC-based geopolymers after sulphate attack.

The mineral composition of CBA-based two-part geopolymers before and after sulphate attack is presented in Figure 8-3. The results evidence no alteration of mineral composition in the specimens after sulphate attack. However, a small amount of gypsum appears in specimen 30fC70G 10/1.2 after sulphate attack. The expansion and peeling at the edges shown in Figure 8-4 and the strength reduction can be attributed to the crystallization of gypsum. On the contrary, specimen 30C70G 10/1.2 remains in shape after the sulphate attack. The distinct responses to sulphate attack are likely related to the sodium content of the geopolymer. The alkali-fusion process involves the inclusion of significant sodium in the geopolymer. Excessive sodium exists in forms such as sodium carbonate (Na_2CO_3) or gaylussite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2$) due to carbonation. These soluble sodium salts likely dissolve during cycling, increasing

porosity and creating conditions for salt generation. This process further exacerbates weight loss and reduces mechanical properties.

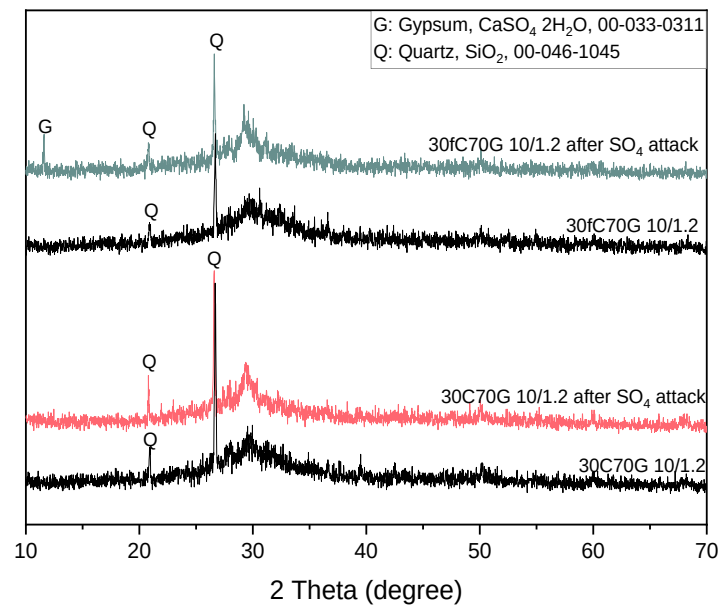


Figure 8-3 Mineral composition of two-part CBA geopolymers before and after sulphate attack.



Figure 8-4 Photographs of CBA-based two-part geopolymers after sulphate attack.

The damage to the microstructure of the geopolymers and the presence of secondary phases due to alteration were investigated with SEM/EDX analyses. The micrographs of two-part CBA geopolymers appear in Figure 8-5. The matrix of raw CBA-based geopolymer maintained its dense and compact nature after the sulphate attack; and the cycling did not result in the decomposition of the cementing phase. However, after cycling, abundant needle-shaped and cubic crystals appeared on the surface of

the geopolymer. The growth of these crystals causes expansion which may lead to cracking, but these secondary products can also fill microcracks and decrease porosity, leading to the improvement of mechanical performance (Wang et al., 2020). In comparison to the raw CBA geopolymer, the geopolymer made with alkali-fused CBA suffered more severe damage and contains more salts. The matrix is more porous and tends to flake and crack (Figure 8-5) agreeing with the results above.

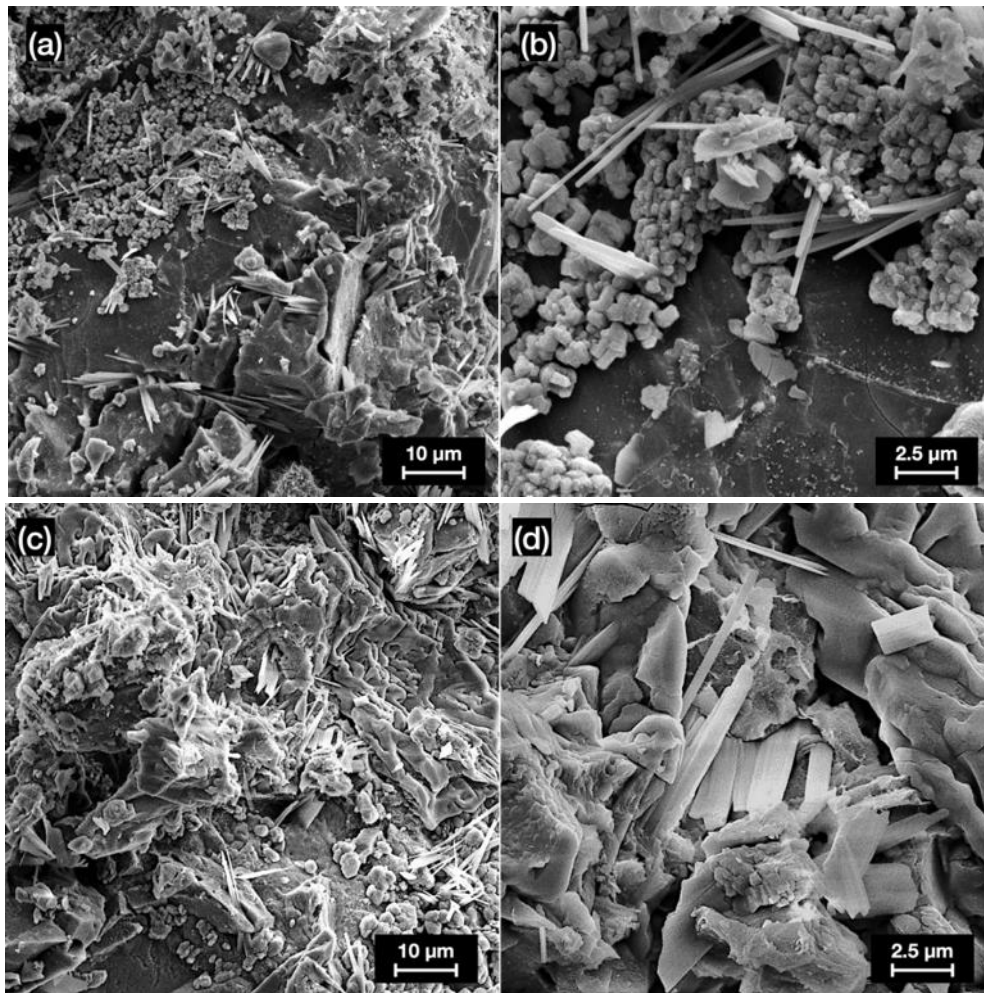


Figure 8-5 Micrographs of (a) & (b) raw CBA geopolymer (c) & (d) alkali-fused CBA, two-part geopolymer after SO_4^{2-} attack.

The mineral change of AS-based, one-part geopolymer due to sulphate attack is shown Figure 8-6. Gaylussite turned into calcite. Gaylussite has been considered a transition phase formed during the activation process of slags (Dung et al., 2019). It can turn into more stable phases such as calcite and hydrotalcite during geopolymerisation (Yuan et al., 2017). The phase transition in the geopolymers may be due to the availability of heat and water during cycling rather than to the sulphate attack. Ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$) was not detected in any of the sulphate attacked specimens. Secondary ettringite can result from the combination of alien SO_4^{2-} with calcium and aluminium from the geopolymer. It has been detected in one-part calcium-carbide geopolymer resulting in expansion (Yang et al., 2022).

However, a significant weight loss was observed in one-part AS geopolymer. This was likely due to the high sodium content in the geopolymer, with sodium activators (sodium silicate and sodium carbonate)

used at 35-40% of the precursor, as shown in Table 8-1. AS geopolymers already exhibited significant strength loss during wet-dry cycling due to increased porosity. Sulfate attack further exacerbated this condition by forming salts in the pores, leading to expansion and substantial weight loss.

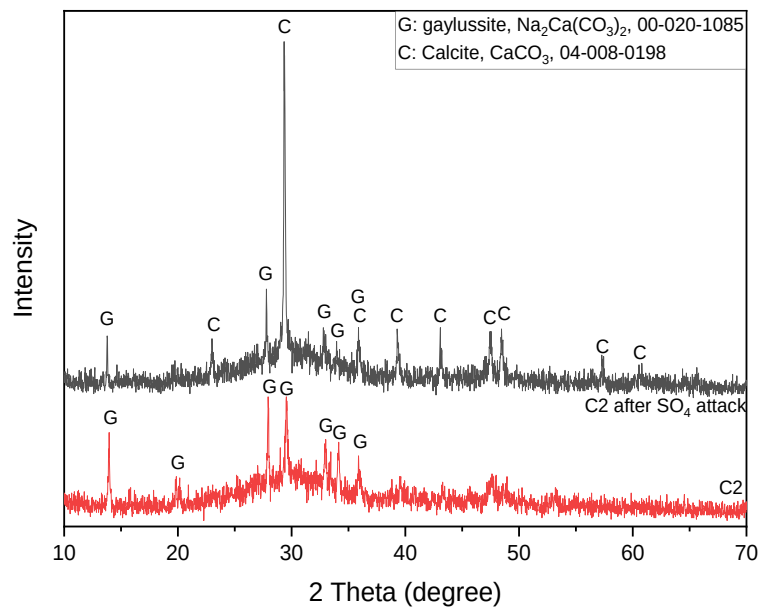


Figure 8-6 Mineral composition of AS based one-part geopolymer (C2 in Table 8-2) before and after sulphate attack.

The OBA one-part geopolymer exhibited minimal weight loss, within 6%, after sulphate attack as shown in Table 8-3 and Figure 8-7. Specimen 40A60G showed an increase in compressive strength from 15.43 MPa to 23.37 MPa after sulphate attack, similar to the results from wet-dry cycling. In this specimen, OBA alone acted as the activator, minimizing the concentration of soluble ions (e.g., Na^+ and K^+) in the geopolymer, thereby reducing the impact of sulphate attack. Additionally, the availability of water and thermal curing during the cycling process contributed to further strength development.

However, when sodium carbonate was added as an auxiliary activator, the extra sodium ions adversely affected the durability of the OBA geopolymer. The addition of 4% to 10% sodium carbonate reduced the compressive strength by 35.06% to 70.87%. While specimen 40A60G4Cs showed an increase in compressive strength during wet-dry cycling, it experienced a strength reduction of 35.06% after the sulphate attack.

The test results of the OBA one-part geopolymer confirmed previous analyses, indicating that soluble sodium content plays a significant role in the resistance of geopolymers to sulphate attack. Free or weakly bonded sodium ions can dissolve during cycling, leading to increased porosity. This increased porosity provides space for the formation of invasive sulphates. Repeated dissolution and recrystallization of the sulphate in the pores cause swelling and cracking of the matrix, facilitating further sulphate attack into the matrix.



Figure 8-7 Photographs of OBA-based, one-part geopolymers after sulphate attack (left: 40A60G4Cs, right: 40A60G10Cs).

However, all the CBA one-part geopolymers showed a weight increase after the sulphate attack. The photos of the CBA one-part geopolymer after the sulphate attack are presented in Figure 8-8.

The geopolymer made with raw CBA (denoted as C) demonstrated better resistance to sulphate attack than those made with alkali-fused CBA (denoted as fC and ffC). Notably, the compressive strength of specimen 30C70G5C10S increased by 82.68% after the sulphate attack, while the compressive strength of 30fC70G5C10S decreased by 53.03%. The sodium introduced by the alkali fusion process negatively impacted sulphate resistance.

However, the addition of sodium silicate improved the sulphate resistance of one-part geopolymers. By adding 20% sodium silicate, the compressive strength loss was limited to 0.48%. Compared to the 53.03% strength loss of specimen 30fC70G5C10S, the sulphate resistance was significantly enhanced. The extra silicate facilitated the formation of more cementing gels, densifying the matrix and thereby diminishing the solubilization of ions due to cycling.

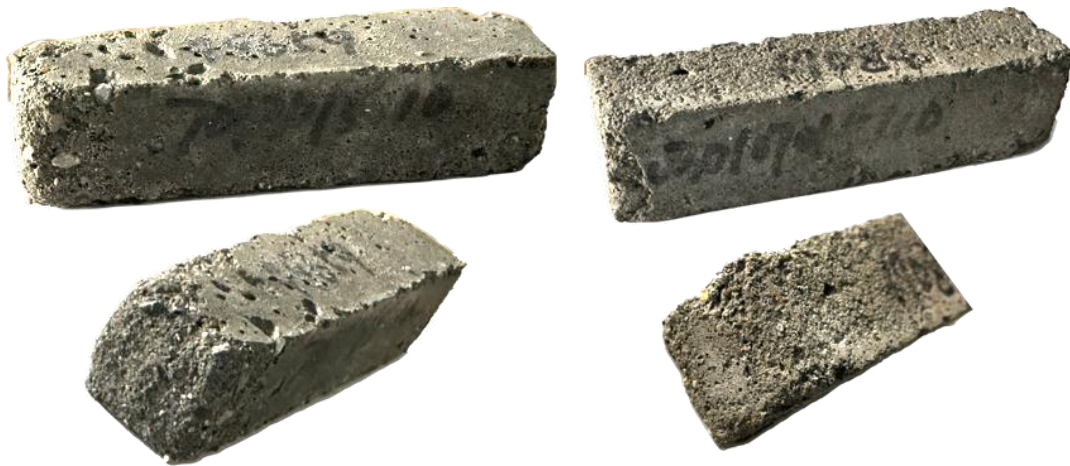


Figure 8-8 Photographs of CBA-based one-part geopolymers after sulphate attack (left: 30C70G5C10S, right: 30fC70G5C10S).

The mineral compositions of OBA and CBA, one-part geopolymers before and after sulphate attack are presented in Figure 8-9 and Figure 8-10 respectively. After the sulphate attack, no significant mineral alterations were detected. This indicates the amount of phase transformation and secondary salt formation caused by sulphate attack is minimum, under the detection limit of the XRD technique.

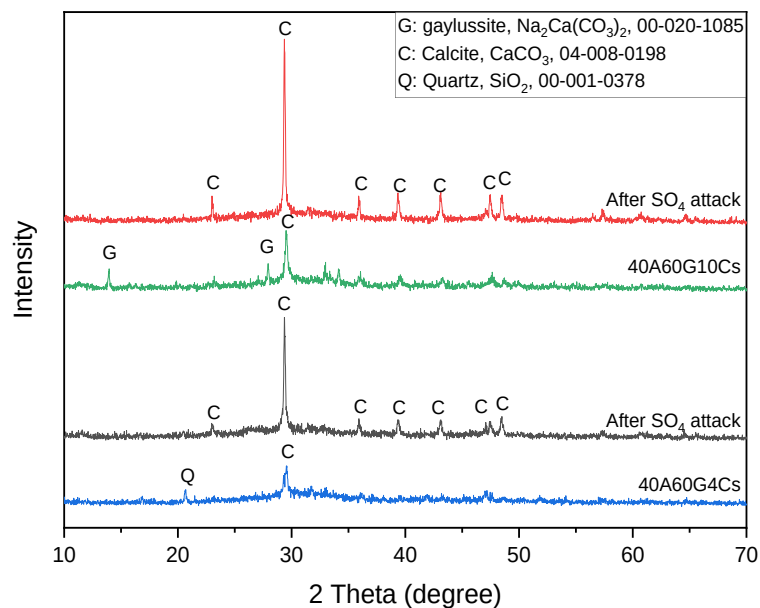


Figure 8-9 Mineral composition of OBA one-part geopolymer before and after sulphate attack.

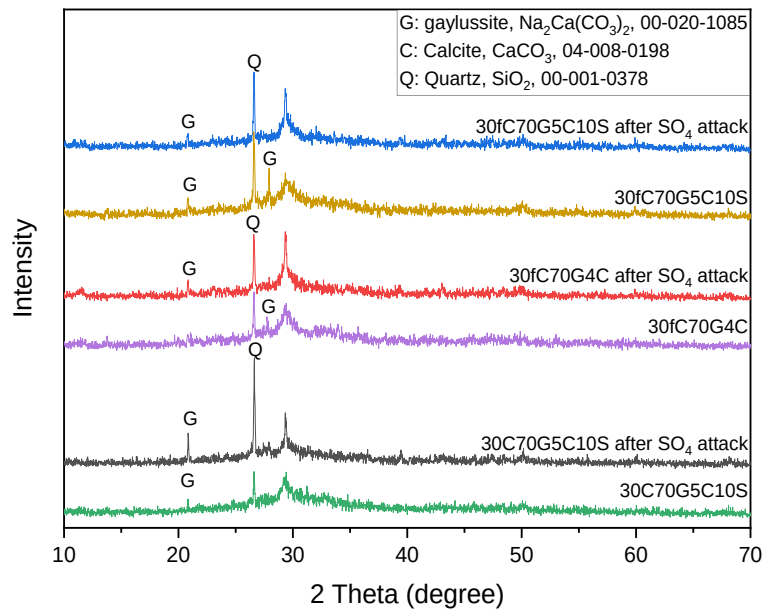


Figure 8-10 Mineral composition of CBA one-part geopolymer before and after sulphate attack.

From the results above, it seems that the damage caused by sulphate attack is of physical nature. Despite the chemical activity of the sulphate salt during cycling and the phase transition and residual gypsum occasionally noted in some geopolymers the sulphate does not react with the cementing phase in geopolymer agreeing with (Alyami et al., 2019).

The crystallization of sulphate salts within the pores and fractures is beneficial in the short-term, as the salts fill cracks and micro-pores, densifying the matrix and enhancing strength. However, repeated phase changes can cause cracking due to crystallization pressure in the pores and volume changes. Damage initiates on the surface of the specimens, with supersaturation and crystallization manifesting as scaling and flaking, as shown in the figures.

Additionally, the deterioration of geopolymer through scaling and flaking accelerates with increased sodium content. Sodium ions balance the charge due to the replacement of Al^{3+} by Si^{4+} during geopolymerisation (Duxson et al., 2007). Given their small atomic size, sodium ions can migrate through the moist gel network (Duxson et al., 2007). While this characteristic supports geopolymerisation, it also makes sodium ions more susceptible to loss during cycling. The loss of sodium salts increases porosity, further aggravating geopolymer deterioration.

8.3 HIGH-TEMPERATURE RESISTANCE

Although the chances of a fire occurring are small, it is still a major threat to building safety. Typically, concrete undergoes a general loss of strength and cracking when exposed to heat. Therefore, there is a need to study the high-temperature performance of building materials to assess their safety and reliability at high temperatures. The high-temperature resistance of the selected geopolymers appears

in Table 8-4. The percentage indicates the loss of compressive strength after calcination at that temperature relative to the strength without calcination.

Table 8-4 Mechanical performance of geopolymer after calcination (Percentage indicated the loss of strength).

Group	Notation	Compressive strength (Mpa)							
		0 °C	450 °C		600 °C		800 °C		
Two-part Geopolymer	FCC based	40F60G 8/1.0	48.38	26.77	-44.67%		23.27	-51.90%	
		40F60G 8/1.2	51.47	27.65	-46.28%		23.82	-53.72%	
		40F60G 6/1.2	45.73	35.5	-22.37%		24.23	-47.02%	
	CBA based	30C70G 10/1.2	29.83	19.21	-35.60%		9.44	-68.35%	
		30fC70G 10/1.2	46.47	11.13	-76.05%		8.38	-81.97%	
One-part Geopolymer	AS based	C2	66.5	15.07	-77.34%		11.5	-82.71%	
		C3	65.9	21.44	-67.47%		5.72	-91.32%	
	OBA based	40A60G	15.43	12.65	-18.02%		8.09	-47.57%	
		40A60G 4Cs	22.25	9.06	-59.28%		7.71	-65.35%	
		40A60G 10C	36.84	18.82	-48.91%		5.62	-84.74%	
		40A60G 10Cs	43.94	10.35	-76.45%		5.38	-87.76%	
	CBA based	30C70G10C	30.7	25.88	-15.70%		18.65	-39.25%	
		30C70G5C10S	24.89	19.49	-21.70%		14.34	-42.39%	
		30fC70G4C	36.35	26.69	-26.57%		15.99	-56.01%	
		30fC70G5C10S	52.8	21.01	-60.21%		12.84	-75.68%	
		50ffC50G4P	42.98	13.63	-68.29%		7.46	-82.64%	

FCC two-part geopolymer

FCC two-part geopolymers activated by various sodium silicate solutions exhibited different strength losses after calcination. The highest residual compressive strength of FCC two-part geopolymer after calcination at 450 °C was achieved with 40F60G 6/1.2, yielding 35.50 MPa. At 800 °C, the highest strength was achieved with 40F60G 8/1.2, yielding 16.33 MPa. Decreasing the silicate usage and reducing the Na⁺ concentration and the SiO₂/Na₂O ratio, facilitated thermal resistance at 450 °C but had a slight adverse effect on thermal resistance at 800 °C.

The mineral composition and FTIR spectra of the original and the calcined FCC-GGBS geopolymers are presented in Figure 8-11 and Figure 8-12 respectively. Calcination under 600 °C did not significantly alter the mineral composition of FCC-GGBS geopolymer but disrupted the atomic order, turning the originally amorphous structure into a crystalline one. The FTIR spectra results confirm this devitrification. The main bands, centred at around 960 cm⁻¹ and associated with the Si-O-Si(Al) anti-symmetric stretching vibrations, moved to a lower wavenumber and became broader with increasing calcination temperature, indicating the depolymerisation of the original structure. When the temperature reached 800°C, the original amorphous phases become crystalline transforming into gehlenite (Al₂SiO₇) and nepheline (NaAlSiO₄). The original hump corresponding to C-A-S-H disappears completely which is consistent with the dehydration of the geopolymer cementing hydrates and the subsequent crystallization of nepheline and gehlenite. These findings agree with Shi et al. (2020) who obtained gehlenite and nepheline from the crystallization of C-A-S-H and N-A-S-H gel respectively. Volume changes due to phase transition may be a cause for the strength loss.

The original main band in the FTIR spectra moved to a higher wavenumber indicating increased cross-linking as crystallization proceeded. However, the main band splits into two sub-bands centred at 935 cm⁻¹ and 900 cm⁻¹. These two bands are assigned to Q² and Q¹ units which may be related to the

presence of gehlenite and nepheline. The bands centred at 855 cm^{-1} and 513 cm^{-1} are assigned to the Al–O bonds stretching vibration of AlO_4 tetrahedral and Al–O–Si bonds stretching vibration in gehlenite (Perná et al., 2018). The absorption band located at 460 cm^{-1} which is assigned to the blending vibration of Si–O–Si(Al), increased significantly after calcination due to the reorganisations of the internal structure of the aluminosilicate phases.

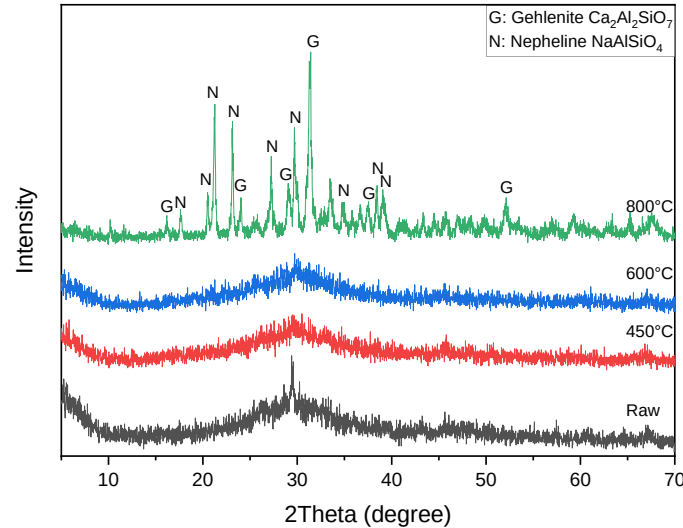


Figure 8-11 Mineral composition of raw and calcined FCC geopolymers (40F60G 8/1.2).

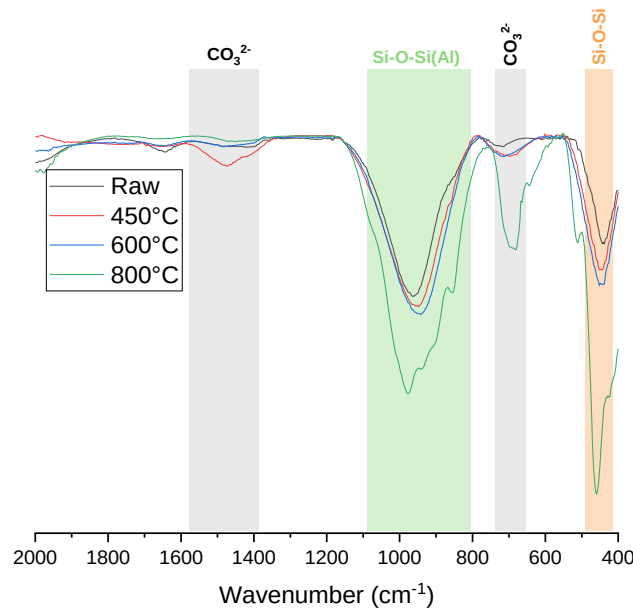


Figure 8-12 FTIR spectra of raw and calcined FCC-based geopolymers (40F60G 8/1.2).

The microstructure of the FCC-GGBS geopolymers exposed to high temperatures is presented in Figure 8-13. The SEM analyses revealed a significant change of microstructure after exposure to high temperatures. At 450°C , the originally dense and compact matrix turns loose and porous, showing shrinkage and cracking (Figure 8-13 a) agreeing with the reduction of mechanical strength. Newformed microcrystals appear on the gel surface due to the dehydration/depolymerization of the C(N)-A-S-H gel

(Figure 8-13 b). These microcrystals are likely the precursors of the aluminosilicate phases (gehlenite and nepheline) in which the gels transform on devitrification as shown in Figure 8-11.—At 800 °C separation at the interface between geopolymer binder and sand occurs (Figure 8-13 c). Further demolition of geopolymer gels ensues, and micro-pores emerge on the cracking gel indicating severe dehydration (Figure 8-13 d). This agrees with Kong & Sanjayan (2008) who found that the thermal contraction of geopolymer and thermal expansion of aggregate destroyed geopolymer mortar/concrete at high temperature. Kong & Sanjayan (2010) claim that aggregate <10 mm promotes spalling and extensive cracking in geopolymer concrete.

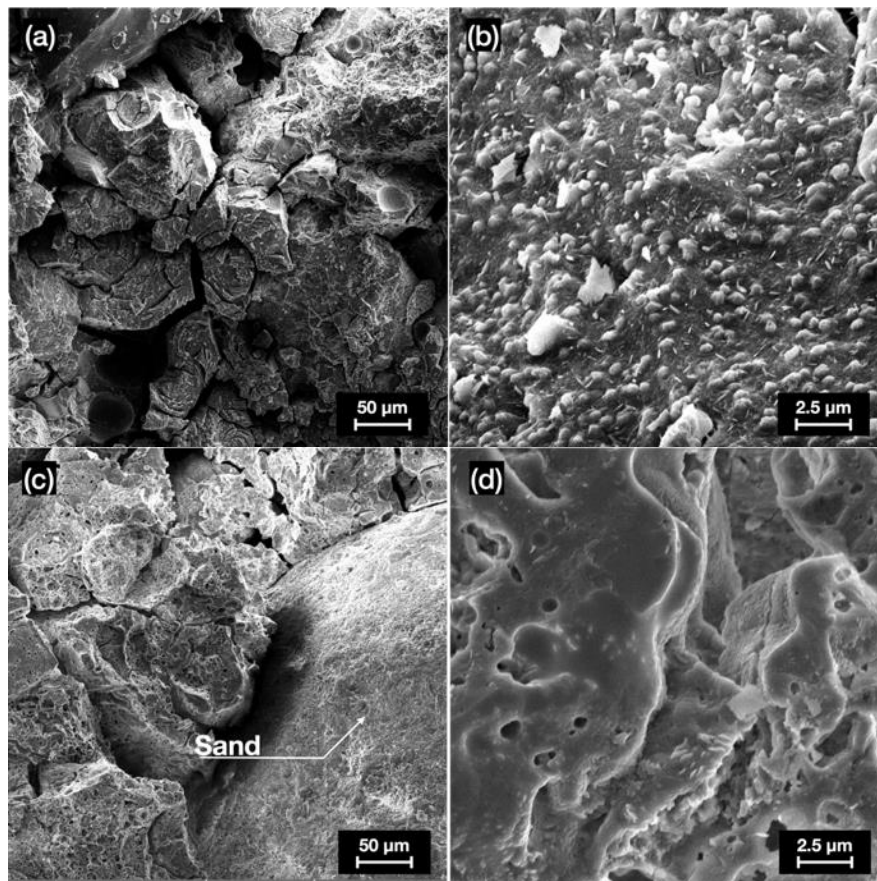


Figure 8-13 (a, b) Micrograph of FCC geopolymer (40F60G 8/1.2) calcined at 450 °C and (c, d) at 800 °C

CBA two-part geopolymer

According to Table 8-4, the two-part geopolymer made with raw CBA (denoted as C) demonstrated better thermal resistance at 450 °C than that made with alkali-fused CBA (denoted as fC). However, when calcined at higher temperatures, such as 600 and 800 °C, both geopolymers showed similar residual compressive strength.

The mineral composition and FTIR spectra of CBA two-part geopolymer are presented in Figure 8-14 - Figure 8-17. Decomposition of amorphous cementing gel was observed with increasing calcination temperature, as indicated by the subsidence of the hump centered at 30° 2 θ in Figure 8-14. Starting from 600 °C, crystalline combeite and gehlenite appeared, and further increasing the calcination temperature promoted their crystallization. A similar pattern was found in the alkali-fused CBA geopolymer (Figure 8-16), but with more prominent peak intensities.

The results evidence that the crystalline product formed after high-temperature calcination is clearly determined by the chemical composition of the starting amorphous phase. As aforementioned, gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) is a crystalline product of C-A-S-H, and the crystalline product of N-A-S-H is nepheline (NaAlSiO_4). However, due to the low aluminium content in the CBA geopolymer, combeite ($\text{Na}_4\text{Ca}_3\text{Si}_6\text{O}_{18}$) formed instead. This agrees with previous authors not combeite formed from the amorphous phase at around 700 °C (Dupuy et al., 2018). It is a silicate with a six-membered ring structure, where the rings are held together by Na and Ca, both in 6-coordination (Alventosa & White, 2024).

The FTIR spectra of calcined CBA-based geopolymer revealed the decomposition of carbonate and crystallization of silicates. The main absorption band located between 800 and 1200 cm^{-1} gradually splits from a single symmetric broad band into three absorption bands located at 920, 1000, and 1050 cm^{-1} after calcination. This indicates that the structure becomes more ordered after heating to very high temperatures, agreeing with the appearance of crystalline silicates determined with XRD.

30C70G 10/1.2

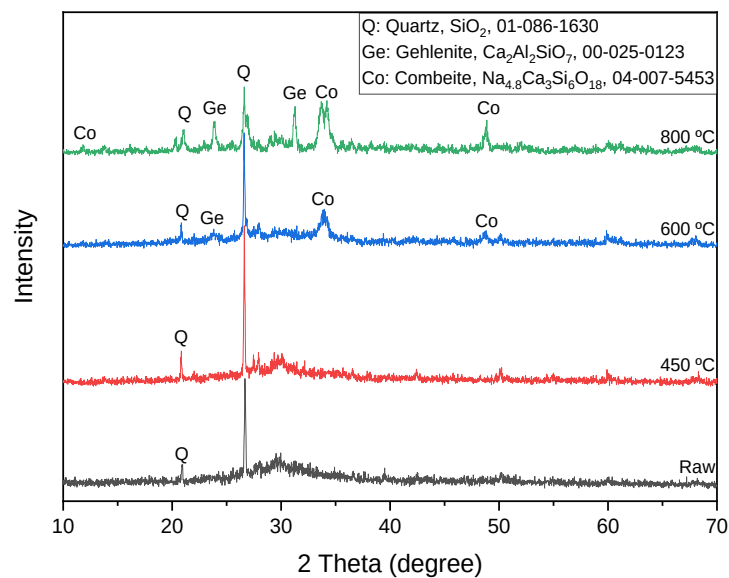


Figure 8-14 Mineral composition of raw and calcined CBA two-part geopolymers (30C70G 10/1.2).

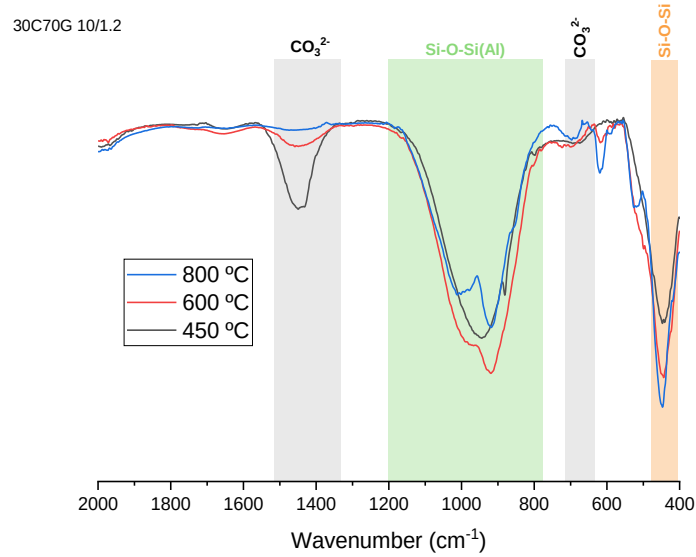


Figure 8-15 FTIR spectra of raw and calcined CBA, two-part geopolymers (30C70G 10/1.2).

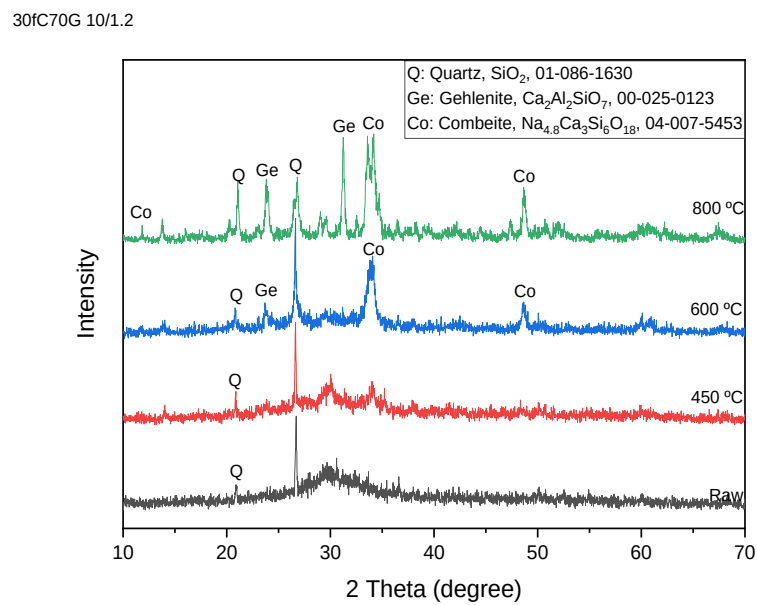


Figure 8-16 Mineral composition of raw and calcined, alkali-fused CBA, two-part geopolymers (30fC70G 10/1.2).

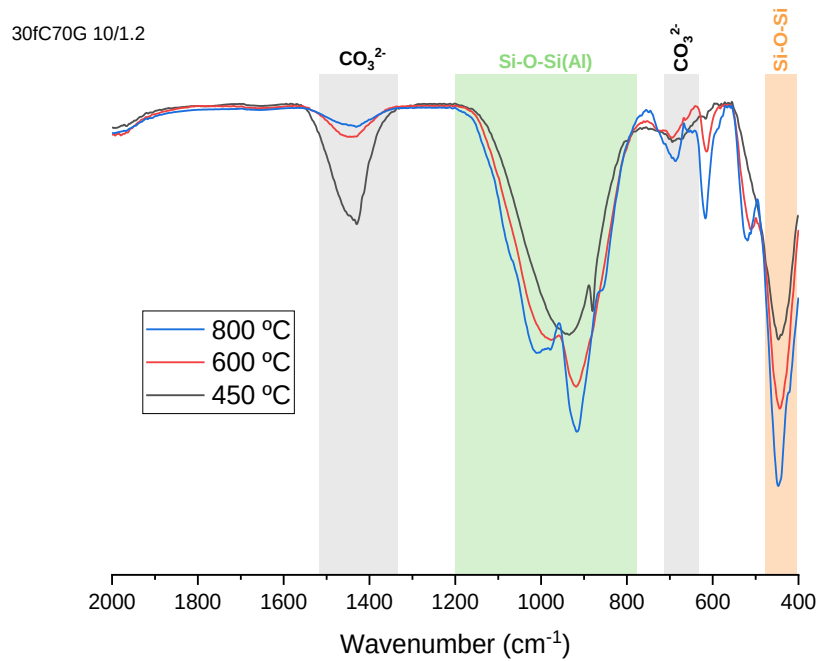


Figure 8-17 FTIR spectra of alkali-fused CBA, two-part geopolymers (30fC70G 10/1.2) calcined at increasing temperature.

The micrographs of CBA two-part geopolymer after calcination are presented in Figure 8-18. Cracks in the matrix appear in the alkali-fused CBA geopolymer at 450 °C and increase at 800°C. Alkali-fusing the CBA seems to lower the resistance of the CBA geopolymer to high temperatures. Increasing the temperature turns the matrix loose and porous. At 450 °C, crystals interspersed in the originally amorphous matrix can be observed in the higher magnification micrographs in Figure 8-18. At this stage, some amorphous cementing gels are still visible despite the precipitation of many crystals. However, when the calcination temperature raised to 800 °C, the originally dense amorphous structure became completely crystallized and fragmented into granules, indicating a gradual loss of cementing capacity.

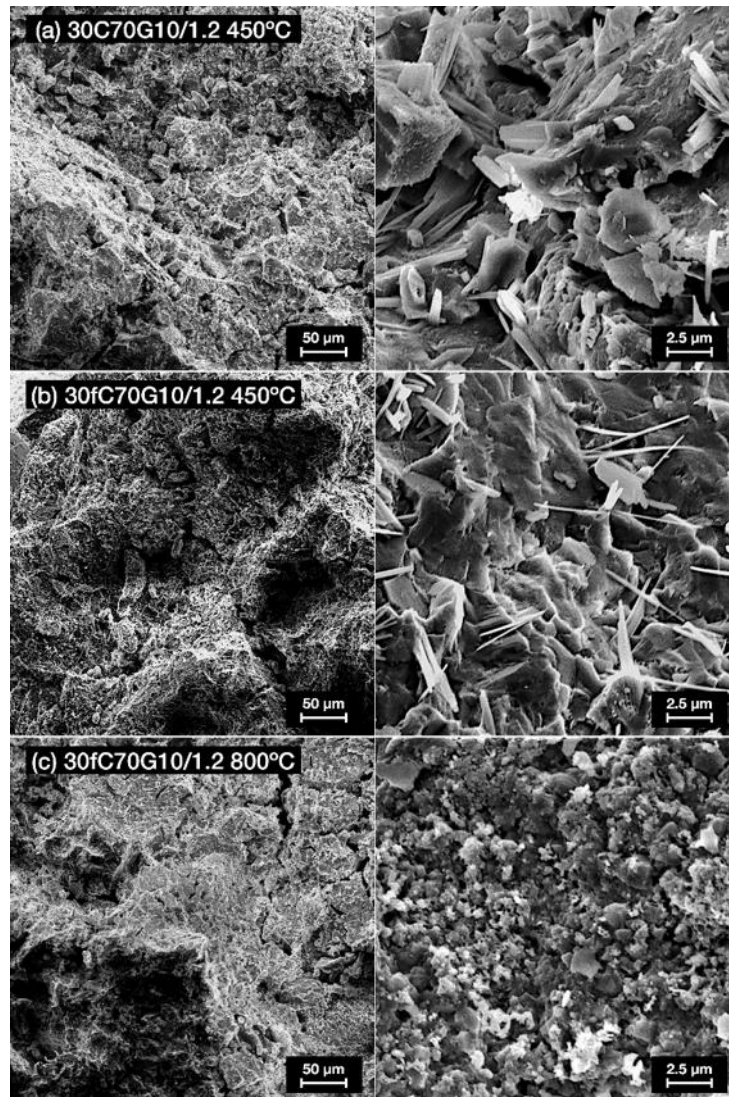


Figure 8-18 Micrographs of CBA two-part geopolymer after calcination (a): 30C70G 10/1.2 at 450 °C, (b): 30fC70G 10/1.2 at 450 °C, (c): 30fC70G 10/1.2 at 800 °C.

AS one-part geopolymer

The major mechanical strength loss of AS one-part geopolymer occurred after calcination at 450 °C. Specimen C2, with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 2.5, and specimen C3, with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 3.0, were analyzed. The composition of the activator affects the resistance to high temperature. Increasing the silicate and decreasing the carbonate content slightly improved thermal resistance at 450 °C but lowered the resistance to higher temperatures.

The mineral composition and FTIR spectra of AS, one-part geopolymer with increasing temperature are presented in Figure 8-19 and Figure 8-20. The AS geopolymer experienced first the decomposition of carbonate and amorphous content, followed by the precipitation of crystalline phases at 800 °C. Merwinite, gehlenite and some sodium aluminium silicate become the main crystal phases when the AS geopolymer is calcined at 800 °C. The formation of merwinite is due to the high GGBS content in the geopolymer which contributes significant Mg. The sodium aluminium silicate phase likely represents

the crystalline form of N-A-S-H gel. A small amount of calcite was also detected, possibly due to the carbonation of the specimens during the cooling process.

The main FTIR band, located between 800 and 1200 cm^{-1} , became more prominent after calcination at 800 °C. This trend aligns with the formation of crystalline phases detected by XRD. Calcination, especially above 800 °C, promoted the conversion of amorphous content to long-range ordered crystalline structures.

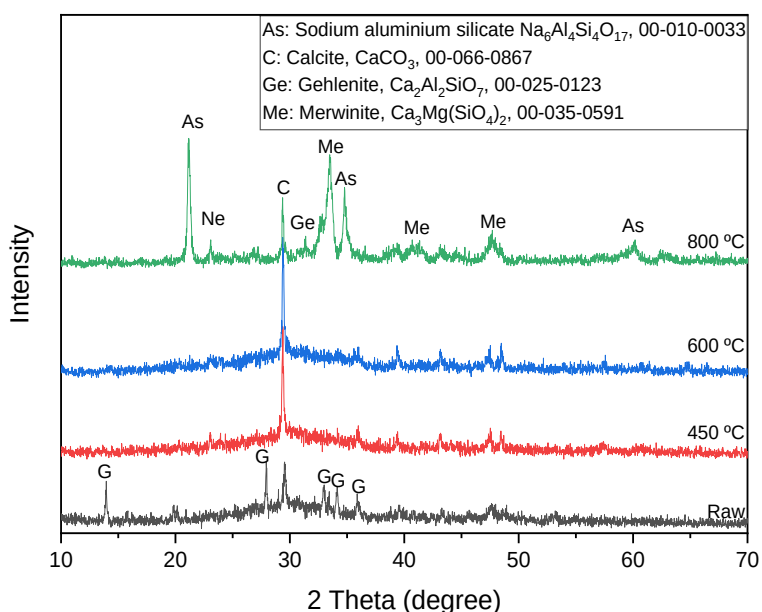


Figure 8-19 Mineral composition of raw and calcined, one-part AS geopolymers (C2).

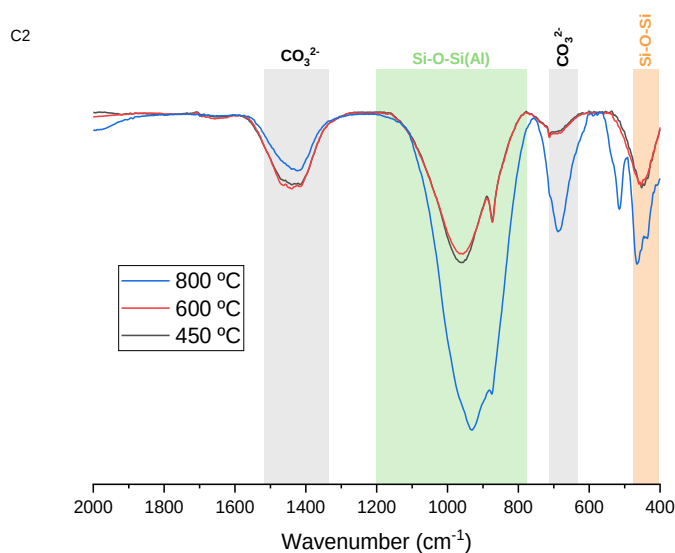


Figure 8-20 FTIR spectra of calcined, one-part AS geopolymers (C2).

The micrographs of C2 after calcination at 600 °C and 800 °C are presented in Figure 8-21. Even though the 600 °C calcined C2 still maintained its amorphous nature, the micrographs revealed that the matrix had become porous and relatively loose compared to the dense uncalcined matrix. At higher magnification, the geopolymer structure shows granular, incompletely crystallized particles which indicate the destruction of geopolymer cement at high temperatures. The specimens calcined at 800 °C became more porous and looser. The original granular particles appeared dense due to sintering.

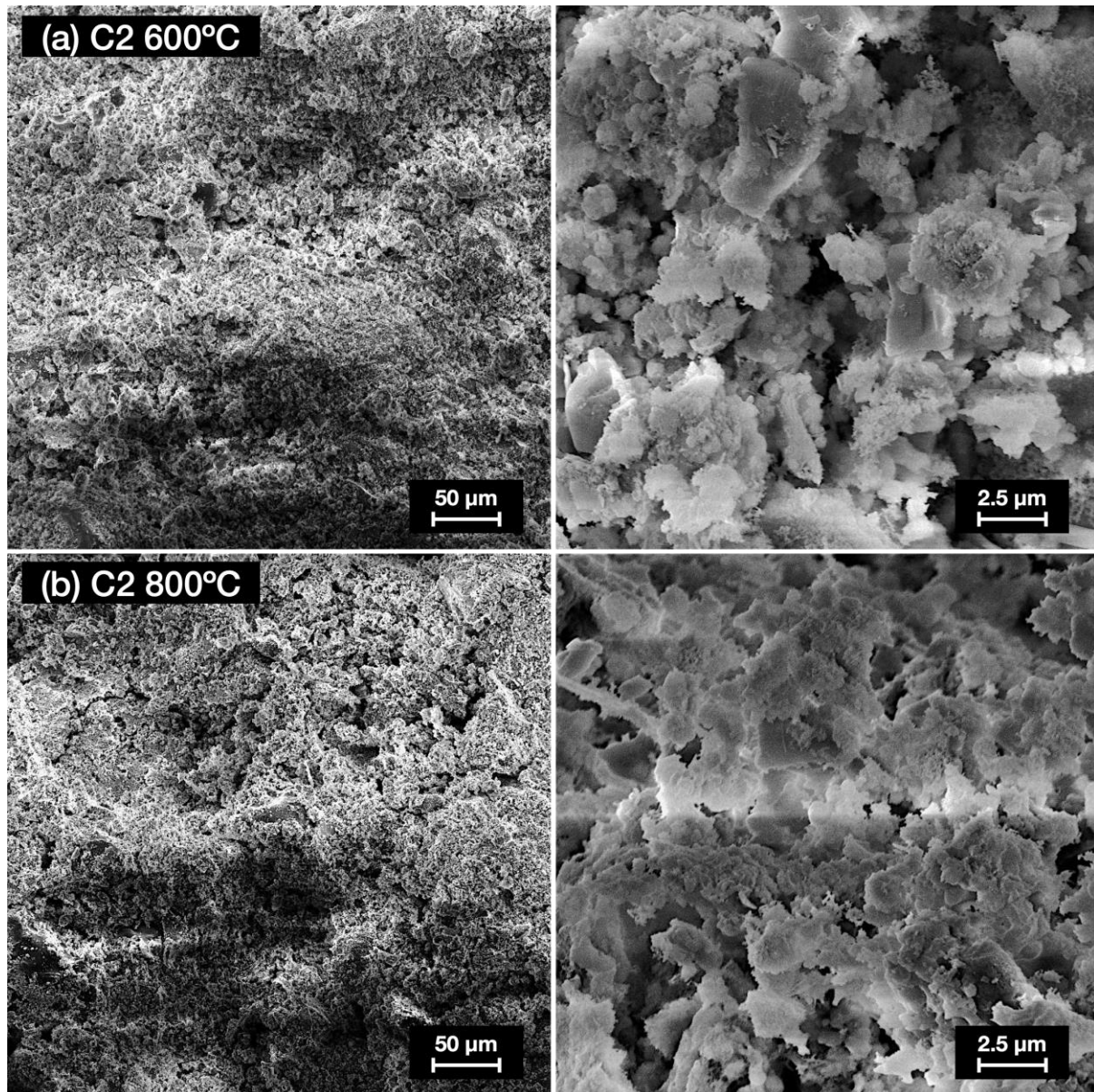


Figure 8-21 Micrographs of AS-slag geopolymer (C2) after calcination at 600 °C and 800 °C

OBA one-part geopolymer

Even with a low initial compressive strength (15 MPa), specimen 40A60G demonstrated high thermal resistance at 450°C, losing 18% of its initial strength - Table 8-4. The results also indicate that adding

pre-dissolved sodium carbonate (Cs) as an activator lowers the thermal resistance of the OBA geopolymers.

The mineral composition and FTIR spectra of OBA one-part geopolymer calcined at increasing temperature are presented in Figure 8-22 and Figure 8-23 respectively. Carbonate decomposition was observed at 450 °C. Upon further increasing the calcination temperature to 600 °C, crystals of gehlenite, merwinite and kalsilite appear. Gehlenite is the crystalline form of C-A-S-H, while the Mg provided by the GGBS in the geopolymer forms merwinite crystals. Kalsilite has been detected in potassium-based geopolymers after high-temperature calcination (Gomes et al., 2020). It is presumed to be the crystalline form of K-A-S-H. More pronounced crystalline peaks were observed at 800 °C. The changing pattern of the FTIR spectra of OBA geopolymer with increasing temperature is similar to that of one-part AS geopolymer, with progressive carbonate decomposition and an increase in Si-O-Si(Al) ordering as the temperature rises.

Using carbonate as an auxiliary activator promotes the formation of more abundant carbonates such as calcite and gaylussite. These salts can fill pores and densify the matrix, enhancing mechanical performance, but at high temperatures, their decomposition leads to significant strength reduction.

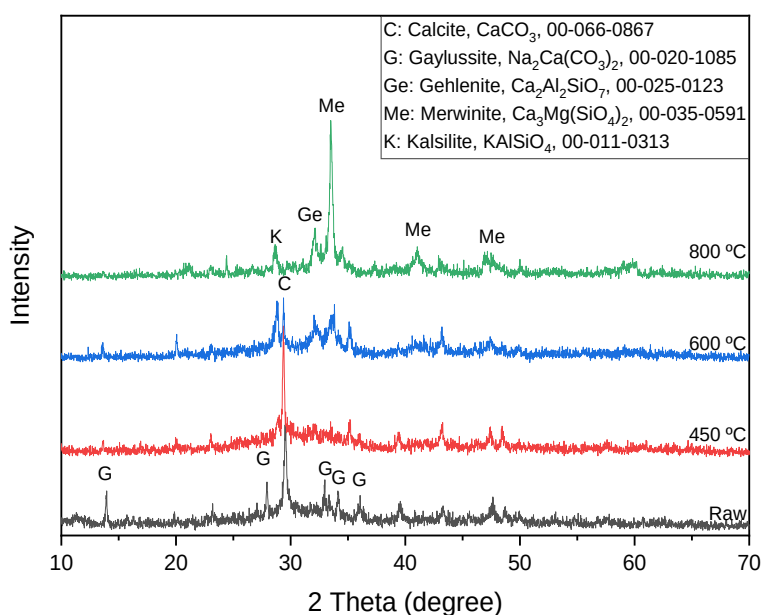


Figure 8-22 Mineral composition of raw and calcined OBA one-part geopolymer (40A60G 10Cs).

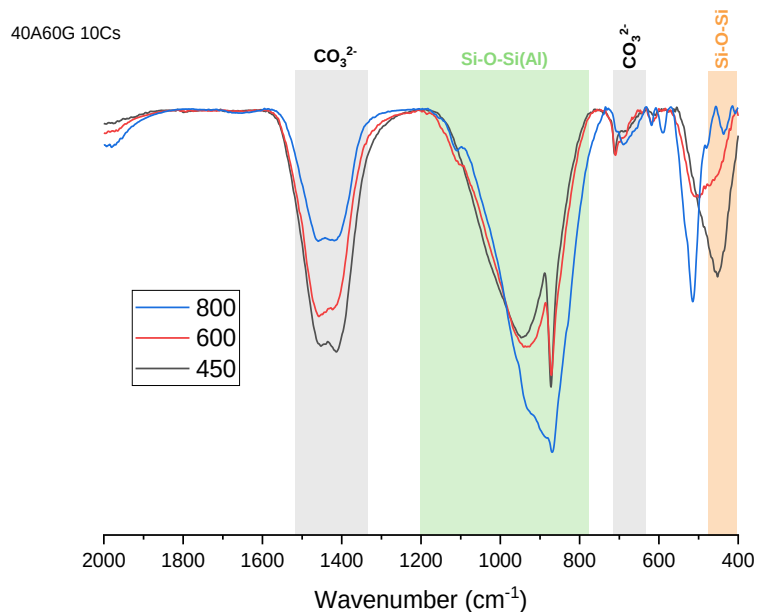


Figure 8-23 FTIR spectra of calcined OBA one-part geopolymer (40A60G 10Cs).

CBA one-part geopolymer

According to the results in Table 8-4, the sodium content has an adverse effect on the thermal resistance of one-part CBA geopolymer. Specimens made with raw CBA (denoted as C) showed better thermal resistance than those made with alkali-fused CBA (denoted as fC) which have greater Na content due to the fusion process. The geopolymers made with alkali-fused CBA show higher strength losses after calcination than their raw CBA counterparts (table 8-4). Specimen 30C70G10C exhibited a strength reduction of 15.70%, while specimen 30fC70G4C showed a higher reduction of 26.57% after calcination at 450 °C.

Increasing the Na content in the activator also reduced the thermal resistance of the geopolymer. After calcination at 450 °C, 30fC70G4C (activated with 4% Na carbonate) showed a strength reduction of 26.57% but 30fC70G5C10S (5% Na carbonate and 10% Na silicate) experienced a superior strength reduction of 60.21%. Additionally, the geopolymer made with raw CBA demonstrated sound thermal resistance with strength reduction of around 15-21% at 450°C and 40% at 600 °C.

The mineral composition and FTIR spectra of one-part CBA geopolymer are presented in Figure 8-24 and Figure 8-25 respectively. A similar variation pattern with increasing temperature was found in the one-part and the two-part CBA geopolymer. With increasing temperature, the amorphous microstructure decomposed as indicated by the disappearance of the XRD hump centred at ~30 °C 2θ. Subsequently, crystalline phases gehlenite and combeite newformed, starting from 600 °C and continuing up to 800 °C. The results in Figure 8-24 suggest that raising the silicate content (adding more silicate activator) promotes crystallization at lower temperature. The type of crystals formed was determined by the chemical composition of the initial amorphous content, agreeing with the results above. The FTIR spectra further confirmed the crystallization process. At high temperatures, the broad band located between 800 cm⁻¹ and 1200 cm⁻¹ split into two overlapping bands, indicating an increase in the long-range order of the microstructure.

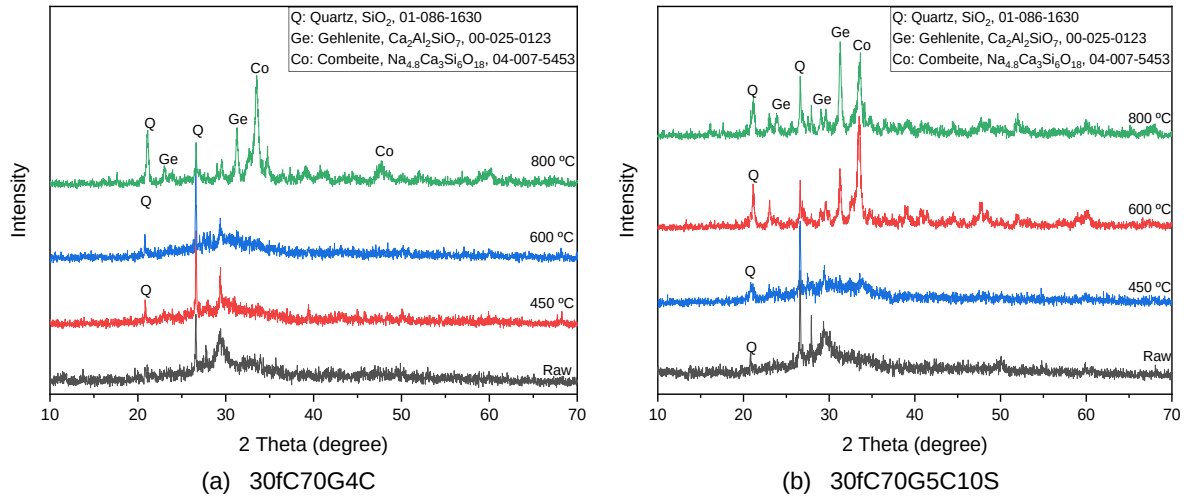


Figure 8-24 Mineral composition of raw and calcined, one-part CBA geopolymers.

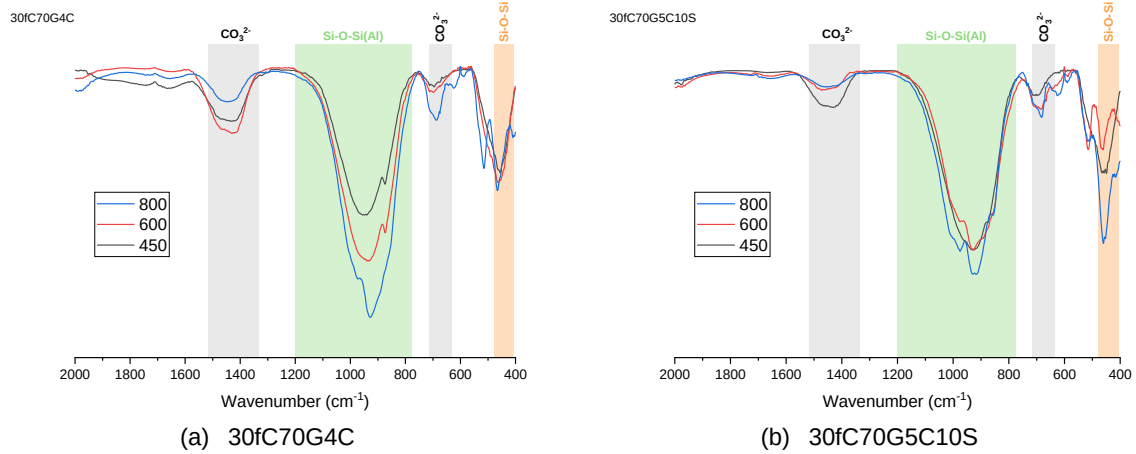


Figure 8-25 FTIR spectra of calcined, one-part CBA geopolymers.

The micrographs of one-part CBA geopolymer appear in Figure 8-26 and Figure 8-27. After calcination at 600 °C, the initially dense and compact microstructure became porous and loose. In the 30fC70G4C sample (Figure 8-26), the originally amorphous cement transformed into a highly porous and heterogeneous structure characterized by numerous fissures and voids. Semi-crystalline particles are loosely bound together, resulting in an overall sponge-like texture. When the specimen was calcined at 800 °C, the microstructure became denser due to sintering. However, the cracking of the geopolymer matrix was exacerbated by the effects of crystallization and dehydration.

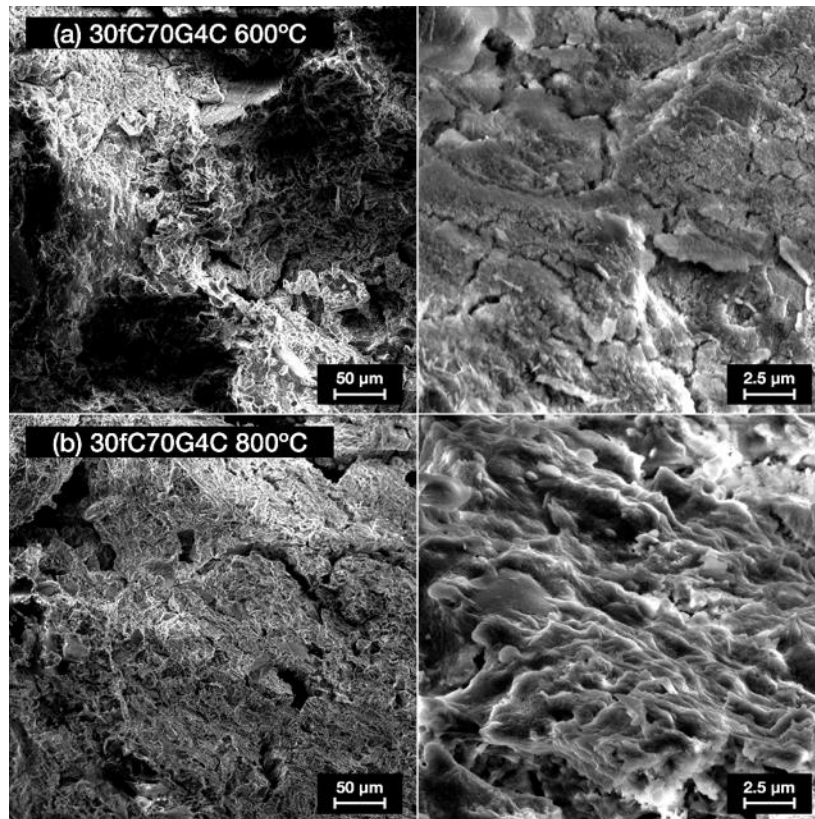


Figure 8-26 Micrographs of one-part CBA geopolymer 30fC70G4C after exposure to high temperature.

The introduction of silicate accelerates the crystallization of the geopolymer cement: raising the silicate content in the activator promotes crystallization at lower temperatures agreeing with the XRD results in Figure 8-24. In the 30fC70G5C10S (10% silicate) sample (Figure 8-27), newly formed crystals were clearly observed. This crystallization made the matrix denser but increased the number of pores. Further increasing the calcination temperature to 800 °C converted the amorphous content into a dense, compact solid but the sintering at high temperature increased the pore volume.

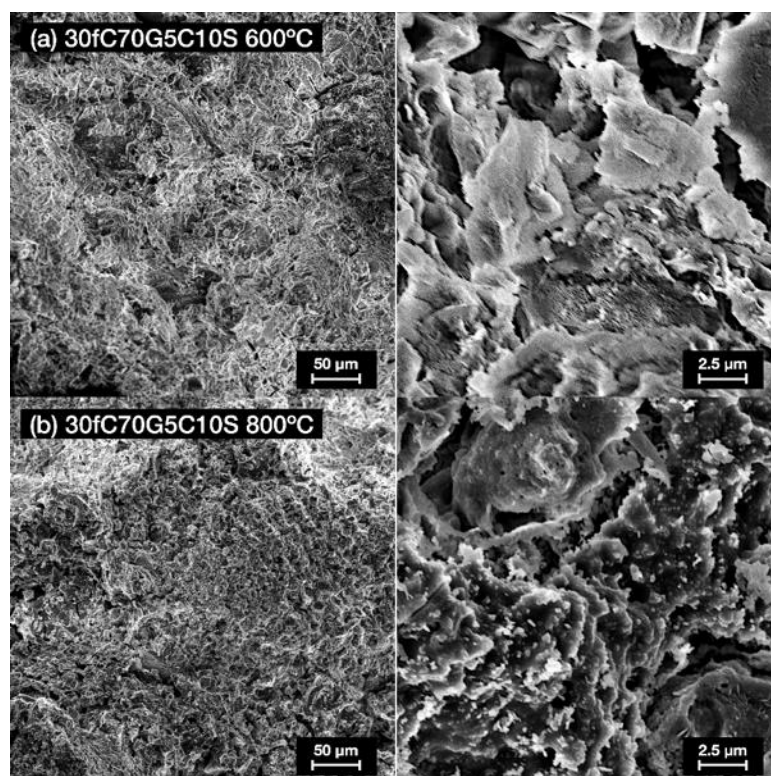


Figure 8-27 Micrographs of one-part CBA geopolymer 30fC70G5C10S after high temperature exposure.

8.4 SUMMARY

The resistance of geopolymers to hygrothermal changes, sulphate attack and high temperatures was investigated.

There is no significant difference in the durability of two-part and one-part geopolymers. With a proper activator, both two-part and one-part geopolymers display good durability. High initial strength does not necessarily indicate good durability. For example, AS-based geopolymers yielded a compressive strength of around 65 MPa but showed poor durability in wet-dry cycles and sulphate attack tests.

Experimental results indicate that high soluble sodium content can significantly detract from geopolymer durability. Excess sodium, not involved in charge neutralization, remains in a free state. During wet-dry cycling, these sodium ions dissolve, increasing porosity and causing strength reduction. This process facilitates further water and sulphate intrusion, increasing cracking and strength loss. Conversely, at low sodium dosages, an increase in mechanical strength after cycling was observed. This improvement is likely due to further polymerization taking place during cycling and to the filling of microcracks by new-formed crystals, resulting in a denser matrix. Furthermore, raising the sodium silicate activator content facilitated the formation of additional cementing gels which also improved durability.

High-temperature calcination reduced the mechanical performance of the geopolymers. The compressive strength decreases to 10-20 MPa after calcination at 450 °C and to 3-6 MPa when burning at 800°C. FCC-based geopolymers showed the best refractory properties, maintaining a residual compressive strength of nearly 30 MPa after calcination at 450 °C.

XRD and FTIR analysis revealed that the initial amorphous geopolymer cement decomposes and turns into crystalline silicates as temperature increases. Amorphous structures remain at 450 °C, with crystallization starting at 600 °C. At 800 °C, geopolymers become highly crystalline. The transition temperature from amorphous to crystalline phases is influenced by the silicate content, with higher silicate content leading to earlier crystallization.

The type of crystalline phase is determined by the chemical composition of the geopolymer system. N-A-S-H gel crystallizes as nepheline, C-A-S-H as gehlenite, K-A-S-H as kalsilite and systems with low aluminium content crystallize as combeite. High proportions of GGBS lead to the crystallization of magnesium as merwinite.

SEM analyses of heated geopolymers indicate that shrinkage cracking due to heat dehydration, phase conversion and separation from aggregates are the primary reasons for strength reduction. At 450-600 °C, the geopolymer matrix becomes loose and porous. At 800 °C, sintering and crystallization cause re-densification, but shrinkage due to dehydration results in increased porosity and a sharp decrease in strength.

These findings provide insights into the durability and long-term performance of geopolymers under various environmental conditions, and emphasize the complex relationships between chemical composition, activation methods and weathering agents.

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Chapter 9: Environmental Impact of Geopolymers Made with Waste

9.1 GOAL AND SCOPE OF THIS ANALYSIS

The main objective of this analysis is to assess the environmental impact of geopolymers (two-part geopolymer -TG- and one-part geopolymer - OPG) made with AS, FCC, CBA and OBA as alternative binders to conventional Portland cement materials. A cradle-to-gate approach was used in this section. Figure 9-1 presents the system boundaries for geopolymer binder production for the standard case scenario. The calculations for the environmental analysis refer to 1 m³ of mortar and 1 kg of binder.

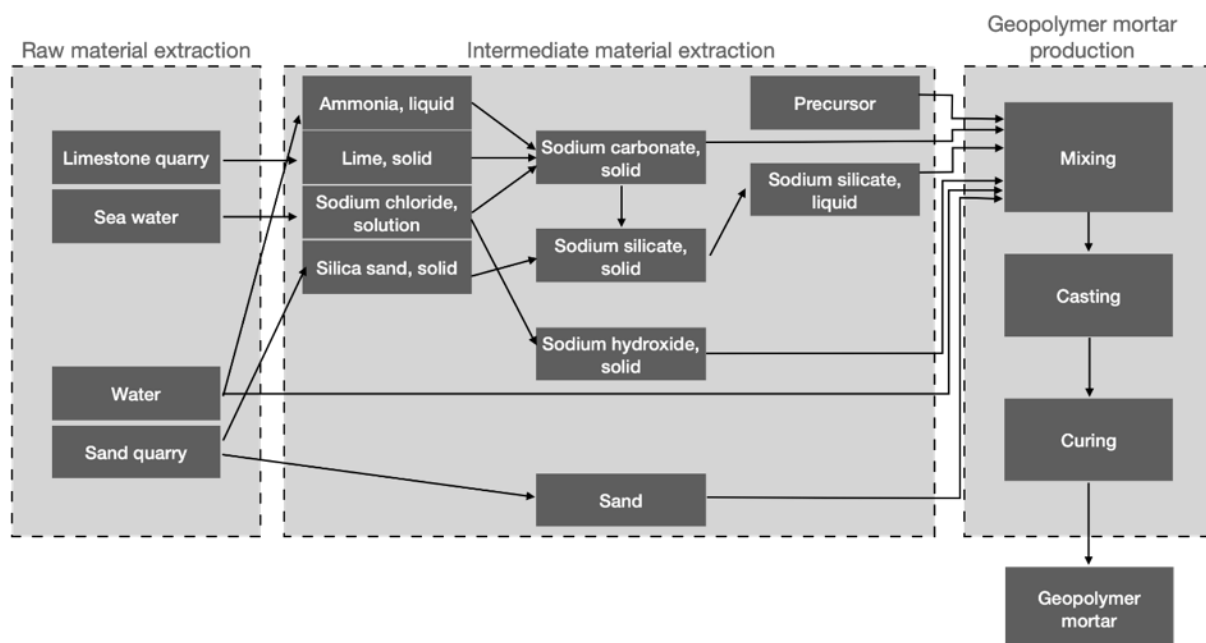


Figure 9-1 System boundaries for geopolymer binder production.

9.2 ACTIVATORS

9.2.1 Sodium Carbonate

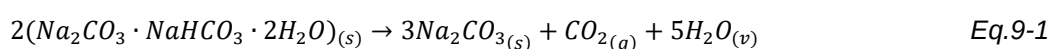
Sodium carbonate, Na_2CO_3 is also known as soda ash. It can be produced from natural minerals such as trona ($\text{Na}_3\text{HCO}_3\text{CO}_3 \cdot 2\text{H}_2\text{O}$) and natural soda ash or manufactured from several chemical processes.

Mining: The largest known deposit on earth is the Green River Formation in Wyoming which contains bedded trona deposits over an area of approximately 3400 km² (Eugster & Surdam, 1973). Estimates are that the deposit contains over 10000 x 10⁶ metric tons of trona, sufficient to satisfy world demand

for over 2000 years (Bradley & Eugster, 1969). The vast reserves make mining in North America more economical than chemical synthetic production.

Two processes are used to recover sodium carbonate from trona: the monohydrate process and the sesquicarbonate process, with the monohydrate process being the most prevalent (Muraoka, 1985). In the monohydrate process, trona is ground and calcined at 150–300 °C to produce crude soda ash (Eq. 1), which is then dissolved in hot water. The resulting hot liquor undergoes filtration and evaporative crystallization at 40–100 °C to produce sodium carbonate monohydrate.

The sodium carbonate monohydrate crystals from the crystallizers are concentrated in hydroclones and dewatered using centrifuges to achieve a free moisture content between 2 and 6%. The centrifuge cake is then sent to dryers where the product is calcined at 150 °C to form anhydrous soda ash (Eq. 9-1). Finally, the soda ash is screened and prepared for shipment.



The LCA data of Trona mining was obtained from the EPD of sodium carbonate (Semtrio Sustainability Consulting, 2017) which is presented in Table 9-1.

Table 9-1 Material and energy consumption of sodium carbonate production by mining Trona.

Non-renewable Resources	
Trona	946 kg
Gravel	4.17 kg
Uranium	21.9 MJ
Coal	7.20 kg
Oil, Crude	3.09 kg
Renewable Resource	
Biomass	56.2 MJ
Wind	2.55 MJ
Hydropower	28 MJ
Water	1 m ³
Potential Environmental Impacts	
Global Warming Potential (GWP)	26.1 kg CO ₂ eq.
Acidification Potential	0.128 kg SO ₂ eq.
Abiotic depletion potential for non-fossil resources	3.20x10 ⁻⁵ kg Sb eq.
Resource depletion	247 MJ eq.

Solvay Process: The Solvay process, developed in 1861 by Belgian industrial chemist Ernest Solvay, is a method for manufacturing sodium carbonate (Thieme, 2000). The first plant using this process was built in 1863 (Bertrams et al., 2013). Although the chemistry of the Solvay process is complex compared to the extraction of sodium carbonate from natural sources. The Solvay method is efficient and requires reactants widely available.

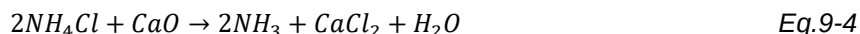
In the Solvay process, sodium chloride, ammonia, water and carbon dioxide are first reacted to form sodium bicarbonate and ammonium chloride (Eq.9-2).



The resulting sodium bicarbonate is then converted to sodium carbonate by heating at 175-225 °C, releasing water and carbon dioxide (Eq. 9-3).



Ammonia is regenerated by treating ammonium chloride by-products with lime (calcium oxide) left over from carbon dioxide generation (Eq. 9-4).

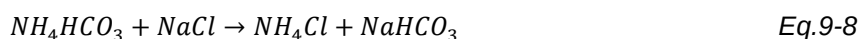


The Solvay method is efficient in recovering ammonia, consuming only brine and limestone with calcium chloride being its only waste product. The LCA data of sodium carbonate production by the Solvay process is presented in Table 9-2.

Table 9-2 Material and energy consumption of sodium carbonate production by the Solvay process.

Input	
Lime	420.03 kg
Sodium chloride	537.53 kg
Electricity, medium voltage	14.33 kWh
Water	38.04 m ³
Output	
Inert waste	89.59 kg
Potential Environmental Impacts	
Global Warming Potential (including land use and biogenic carbon)	435.21 kg CO ₂ eq.
Acidification Potential	4.27 kg SO ₂ eq.
Abiotic depletion potential for non-fossil Resources	1.19x10 ⁻² kg Sb eq.
Resource depletion	4194.51 MJ eq.

Solvay Process Vs Hou's Process: Developed in the 1930s by Chinese chemist Hou Debang, this process involves the production of sodium bicarbonate (Ahlgqvist, 1935). In this method, carbon dioxide is pumped into a saturated solution of sodium chloride and ammonia to produce sodium bicarbonate through the following reactions:



Because of its low solubility, the sodium bicarbonate is collected as a precipitate and then heated to 80 °C (176 °F) or 95 °C (203 °F) to obtain pure sodium carbonate, like in the final step of the Solvay method. The Hou process, when combined with the Haber process, offers better atom economy by eliminating the production of calcium chloride, as ammonia no longer needs to be regenerated. Additionally, the ammonium chloride by-product can be sold as a fertiliser.

The LCA data of sodium carbonate production by HOU's process is presented in Table 9-3.

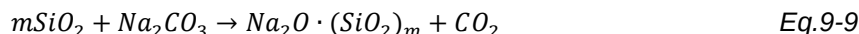
Table 9-3 Material and energy consumption of sodium carbonate production by HOU's process.

Input	
Ammonia, anhydrous, liquid	152.84 kg
Sodium carbonate, liquid	197.78 kg
Sodium chloride, powder	521.43 kg
Electricity, medium voltage	301.46 kWh
Heat	1810.59 MJ
Water	239.68 m ³
Potential Environmental Impacts	
Global Warming Potential (including land use and biogenic carbon)	1191.05 kg CO ₂ eq.
Acidification Potential	4.42 kg SO ₂ eq.
Abiotic depletion potential for non-fossil Resources	1.46x10 ⁻³ kg Sb eq.
Resource depletion	13641.02 MJ eq.

9.2.2 Sodium Silicate

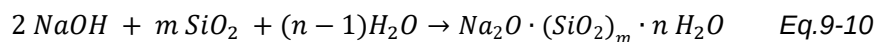
Sodium silicate is a generic name for chemical compounds with the formula $Na_2O \cdot (SiO_2)_m$. These compounds are typically available as a white powder or in an aqueous solution. There are two methods for sodium silicate production: the furnace process and the hydrothermal process (Schweiker, 1978).

The furnace process involves a high temperature (1400°C) reaction between quartz (SiO₂) and sodium carbonate (Na₂CO₃).



The reaction takes place in special furnaces where carbon dioxide (CO₂) is formed and released in the gaseous state while anhydrous sodium silicate ($Na_2O \cdot (SiO_2)_m$) is produced in the molten state in a magma. The liquid magma is then rapidly cooled and broken into pieces. To produce a liquid silicate solution, the glassy sodium silicate is hydrated and subsequently dissolved in water.

The hydrothermal process involves the chemical reaction of quartz with caustic soda in an aqueous solution to produce sodium silicate.



The reaction takes place in special reactors under high pressure and high temperature, resulting in the direct formation of sodium silicate in the hydrated state and in aqueous solution.

For solid sodium silicate, the furnace process is used by default for production. The LCA data of sodium silicate production by furnace process is presented in Table 9-4.

Table 9-4 Material and energy consumption of sodium silicate production by the furnace process.

Input	
Silica sand	772.00 kg
Soda ash, light	400.00 kg
Electricity, medium voltage	11.47 kWh
Water	1.4 m ³
Heat	4460 MJ
Potential Environmental Impacts	
Global Warming Potential (including land use and biogenic carbon)	790.72 kg CO ₂ eq.
Acidification Potential	4.46kg SO ₂ eq.
Abiotic depletion potential for non-fossil Resources	1.26x10 ⁻² kg Sb eq.
Resource depletion	6557.27 MJ eq.

Sodium silicate solutions at 37% and 48% concentrations are commonly used in chemistry. For a 37% sodium silicate solution, the furnace process is preferred for production. An extra dissolution process is required. The LCA data of 37 % sodium silicate production by the furnace process is presented in Table 9-5.

Table 9-5 Material and energy consumption of 37% sodium silicate production by the furnace process.

Input	
Sodium silicate, solid	1010.00 kg
Electricity, medium voltage	7.57 kWh
Water	2.24 m ³
Heat	996 MJ
Potential Environmental Impacts	
Global Warming Potential (including land use and biogenic carbon)	966.21 kg CO ₂ eq.
Acidification Potential	4.77kg SO ₂ eq.
Abiotic depletion potential for non-fossil Resources	2.06x10 ⁻³ kg Sb eq.
Resource depletion	9886.71 MJ eq.

For 48% sodium silicate solution, the hydrothermal process is preferred for production. The LCA data of 48% sodium silicate production by hydrothermal process is presented in Table 9-6.

Table 9-6 Material and energy consumption of 48% sodium silicate production by hydrothermal process.

Input	
Silica sand	676.00 kg
Sodium hydroxide, solid	435.00 kg
Electricity, medium voltage	30.73 kWh
Water	0.87 m ³
Heat	794.64 MJ
Potential Environmental Impacts	
Global Warming Potential (including land use and biogenic carbon)	810.87 kg CO ₂ eq.
Acidification Potential	3.87 kg SO ₂ eq.
Abiotic depletion potential for non-fossil Resources	1.30x10 ⁻³ kg Sb eq.
Resource depletion	10303.87 MJ eq.

9.2.3 Sodium Hydroxide

Industrially, sodium hydroxide is produced as a 50% solution with a variant of the electrolytic chlor-alkali process which also produces chlorine gas (Du et al., 2018). Solid sodium hydroxide is obtained from this solution by evaporating the water.

The electrolytic chlor-alkali process has several variations, including the membrane cell, diaphragm cell, and mercury cell processes (Seko, 1976). The mercury cell process is a significant source of mercury releases to the environment (Raldúa et al., 2007). The industry has witnessed a decline in global mercury use as mercury cell facilities age, and many facilities have been encouraged to close or convert to non-mercury processes.

In the membrane cell process, a membrane—such as those made from Nafion, Flemion or Aciplex—is used to prevent the reaction between chlorine and hydroxide ions. The LCA data of sodium hydroxide production by membrane cell is presented in Table 9-7.

Table 9-7 Material and energy consumption of sodium hydroxide production by membrane cell.

Input	
Sodium chloride, solid	773.96 kg
Electricity, medium voltage	1313.52 kWh
Water	45.07 m ³
Potential Environmental Impacts	
Global Warming Potential (including land use and biogenic carbon)	733.17 kg CO ₂ eq.
Acidification Potential	3.69 kg SO ₂ eq.
Abiotic depletion potential for non-fossil Resources	1.13x10 ⁻² kg Sb eq.
Resource depletion	13861.89 MJ eq.

In the diaphragm cell process, a permeable diaphragm made of asbestos fibres prevents the reaction of the caustic soda with the chlorine. The LCA data of sodium hydroxide production by diaphragm cell is presented in

Table 9-8.

Table 9-8 Material and energy consumption of sodium hydroxide production by diaphragm cell.

Input	
Sodium chloride, solid	773.96 kg
Electricity, medium voltage	1583.29 kWh
Water	129.10 m ³
Potential Environmental Impacts	
Global Warming Potential (including land use and biogenic carbon)	1462.49 kg CO ₂ eq.
Acidification Potential	6.56 kg SO ₂ eq.
Abiotic depletion potential for non-fossil Resources	1.15x10 ⁻² kg Sb eq.
Resource depletion	17613.92 MJ eq.

9.3 WASTES

9.3.1 GGBS

Ground granulated blast-furnace slag (GGBS) is obtained by grounding the granulated blast-furnace slag (GBS) produced when quenching molten iron slag, which is a by-product of iron and steel making in blast furnaces using water or steam.

In blast furnace ironmaking, iron ore, coke and limestone are loaded into the blast furnace in layers. The coke is burned at high temperatures to produce carbon monoxide and heat. The carbon monoxide rises to the top of the blast furnace where it reacts with the iron oxides in the iron ore to produce iron and carbon dioxide. Iron ore can be reduced to iron by reacting directly with the coke. Limestone decomposes into calcium oxide (CaO) which reacts with impurities in the iron ore (e.g. silica) to produce slag (Geerdes et al., 2020).

The resulting slag has a low melting point and can be kept in a liquid state in the blast furnace, making it easy to separate from the molten iron. The resulting molten iron (pig iron) is deposited at the bottom of the blast furnace due to its high density, while the slag floats above the molten iron. The molten iron and slag are discharged from the blast furnace through separate iron and slag outlets. Slow cooling of the slag results in the formation of a non-reactive, crystalline material consisting of a combination of Ca-Al-Mg silicates. For the slag to become reactive, it needs to be cooled quickly (quenched) to below 800°C to prevent the crystallisation of merwinite and melilite. To cool and break the slag, a granulation process can be used in which the molten slag is subjected to a pressurised water or air jet. To obtain suitable reactivity, the fragments are ground to the same fineness as Portland cement (Snellings et al., 2012). The blast furnace produces 200 to 300 kg of slag for every tonne of pig iron produced (Crossin, 2015).

The embodied carbon and environmental impact of GGBS are controversial because they vary depending on different allocation methods in LCA methodology. Previous studies assumed that GGBS was a kind of waste, therefore the carbon footprint of GGBS only included the emissions associated with processing and transport but excluded emissions associated with blast furnace operations. However, according to the European Union directive Article 5 (EU, 2024) :

Member States shall take appropriate measures to ensure that a substance or object resulting from a production process the primary aim of which is not the production of that substance or object is considered not to be waste, but to be a by-product if the following conditions are met:

(a) further use of the substance or object is certain;

(b) the substance or object can be used directly without any further processing other than normal industrial practice;

(c) the substance or object is produced as an integral part of a production process; and

(d) further use is lawful, i.e. the substance or object fulfils all relevant product, environmental and health protection requirements for the specific use and will not lead to overall adverse environmental or human health impacts.

Therefore, according to EU regulations the GGBS should be considered a by-product rather than a waste. The economic value of GGBS in the Irish and UK markets has surpassed that of Portland cement and therefore GGBS production should share the material and energy consumption from blast furnace ironmaking and the corresponding environmental burden. The material and energy consumption of GGBS production appears in Table 9-9. To produce one tonne of steel, 0.24 kg of GGBS is generated as a by-product.

Table 9-9 Material and energy consumption of GGBS production (adapted form Chen et al., 2010).

	1 kg pig iron	1kg granulated blast-furnace slag (GBS) Granulation + dewatering	1kg Ground granulated blast-furnace slag (GGBS) Drying + (grinding) + stock
Input			
Raw materials			
Sinter (kg)	1.05		
Pellets (kg)	0.40		
Lump ore (kg)	0.15		
Water (m ³)		0.01	
Energy			
Hard coal (kg)	0.49		
Electricity (kWh)	0.10	2.15x10 ⁻³	0.07
Gaz (MJ)			3.16x10 ⁻¹
Fuel (m ³)			1.14x10 ⁻⁶
Transport			
Boat (tkm)	1.50		
Train (tkm)	0.25	3.0x10 ⁻³	
Truck (tkm)	0.01		5.3x10 ⁻³
Output			
Waste			
Boues (kg)	2.5x10 ⁻²		1.5x10 ⁻³
Wastewater (m ³)	1.81x10 ⁻³	0.003	
Ashes (kg)	1.28x10 ⁻²		
Air emission			
Heat (MJ)	0.49		
Ashes (kg)	3.2x10 ⁻⁵	8.32x10 ⁻⁶	1.29x10 ⁻⁴
CO ₂	0.849		
Products			
Slag for crystallisation (kg)	0.1		
Slag for granulation (kg)	0.24		

The environmental impacts of a by-product are calculated by Eq 9-11.

$$I_{by-product} = C \times I_{primary process} + I_{secondary process} \quad Eq. 9-11$$

Where the $I_{by-product}$ refers to the environmental impacts of the by-product (GGBS in this case), $I_{primary process}$ refers to the environmental impacts of the primary product production (production of steel in this case) and the $I_{secondary process}$ refers to the further process of the by-product (quenching, grinding and drying of GGBS in this case).

C is an allocation coefficient, which is used to allocate the proportion of environmental impacts between the main product and the by-products. Two different allocation methods have been considered: allocation by the mass ratio and allocation by the economic value ratio between the primary product and the by-product.

The mass allocation coefficient C_m was calculated by Eq. 9-12.

$$C_m = \frac{m_{by-product}}{m_{primary product} + m_{by-product}} \quad Eq. 9-12$$

Where $m_{primary product}$ and $m_{by-product}$ refers to the masses of the primary product (steel in this case) and by-product (GGBS in this case) in a standard production process, respectively.

The economic allocation coefficient C_e was calculated by Eq. 9-13.

$$C_e = \frac{P_{by-product}}{P_{primary product} + P_{by-product}} \quad Eq. 9-13$$

Where $p_{primary product}$ and $P_{by-product}$ refers to the per unit price of the primary product (steel in this case) and by-product (GGBS in this case) in a standard production process, respectively.

Considering the latest 2024 data, the price of crude steel in Europe varies but has been reported to average around USD 756 per metric ton in March (FocusEconomics, 2024) whereas the price of GGBS in Europe was around USD 57 per metric ton during the first quarter of 2024 (chemanalyst, 2024). The allocation percentages are calculated in Table 9-10.

Table 9-10 Allocation coefficient of GGBS for two different allocation methods.

Product	Mass produced	Market price	Allocation by mass value	Allocation by economic value
Steel	1 kg	USD 756/t	80.6%	92.99%
GGBS	0.24 kg	USD 57/t	19.4%	7.01%

Based on the different allocation methods, the LCA data of GGBS is presented in Table 9-11.

Table 9-11 Environmental impacts of GGBS by different allocation methods.

	No allocation	Allocation by mass value	Allocation by economic value
Global Warming Potential (including land use and biogenic carbon)	18.8 kg CO ₂ eq.	1390 kg CO ₂ eq.	454.1 kg CO ₂ eq.
Acidification Potential	0.385 kg SO ₂ eq.	5.39 kg SO ₂ eq.	2.61 kg SO ₂ eq.
Abiotic depletion potential for non-fossil Resources	3.20x10 ⁻¹ kg Sb eq.	13.4 kg Sb eq.	4.75 kg Sb eq.
Resource depletion	1580 MJ eq.	22200 MJ eq.	10789 MJ eq.

9.3.2 FCC

As aforementioned, FCC is a spent catalyst regularly discharged during the fluid cracking process used for refining crude oil. Currently, there is no established further use for FCC, so it is considered a waste rather than a by-product.

Therefore, the material and energy consumption, as well as carbon emissions associated with FCC only refer to processing and transportation. Assuming local production and use as received, the global warming potential and other environmental impact factors are considered negligible.

9.3.3 AS

Alum sludge (AS) is an inevitable waste generated during the drinking water purification process. Due to the lack of established further uses, AS is considered a waste rather than a by-product.

In this study, the AS was dried, calcined at 800 °C and ground for 2 hours. Evaluating the energy consumption of calcination at an industrial level can be challenging. Therefore, a model built for the life cycle assessment (LCA) of metakaolin was used to evaluate the environmental impact of the AS calcination process, as the calcination temperature of metakaolin (650 °C – 850 °C) is close to that of AS. According to Tasiopoulou et al. (2023), the CO₂ emissions from calcination at 800 °C range from 130 kg to 240 kg per tonne of metakaolin, depending on the energy sources. Huang et al. (2024) provide an evaluation of carbon emissions for calcined AS, reporting 151 kg CO₂ eq. per tonne of AS. However, their assessment considered the energy consumption of grinding and calcination but neglected the carbon emissions from the oxidation of organic matter in AS during calcination. As seen in the characterization chapter (Section 4.2), the weight loss of AS between 105 °C and 550 °C is approximately 54.6%, which can be roughly attributed to organic content. The organic content in AS is natural organic matter with an average carbon content of 50%-60% (Zhang et al., 2017). Given that the loss on ignition (LOI) of AS is 65.5%, producing one kilogram of calcined AS consumes 2.90 kg of raw AS and releases 2.90 kg of carbon dioxide from organic matter. The calculation of carbon emission factor of calcined AS is presented in Table 9-12. The total carbon emission factor of calcined AS is 4.41 kg CO₂ eq. /kg.

Table 9-12 Global warming potential calculation of calcined AS.

	1 kg calcined AS
Raw AS	2.90 kg
Organic matter	1.58 kg
Carbon content	0.79 kg
Carbon footprint due to the release of organic matter	2.90 kg CO ₂ eq. /kg
Grinding + Calcination	1.51 kg CO ₂ eq. /kg
Carbon emission factor	4.41 kg CO ₂ eq. /kg

9.3.4 OBA

As aforementioned the OBA is not responsible for any carbon emissions as the carbon dioxide produced by burning the biomass equals the amount of CO₂ fixed during the biomass' growth through photosynthesis. The biochar (C), unburned biomass (C_xH_yO_z)_n and carbonate (M₂CO₃) in the OBA afford a carbon sequestration capacity. Figure 9-2 illustrates the OBA's carbon footprint by depicting the processes and components that must be considered to evaluate its environmental impact.

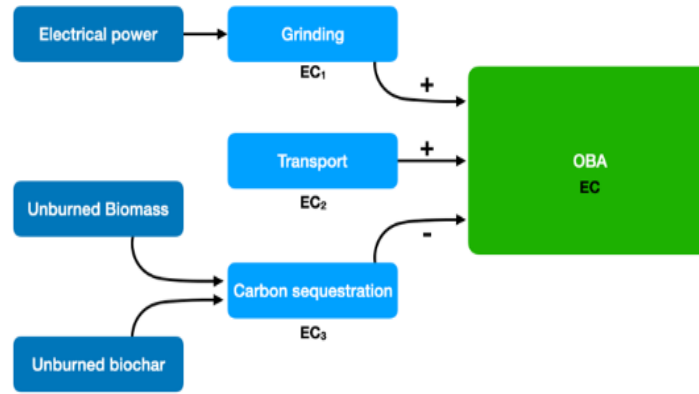


Figure 9-2 Outline of the carbon footprint of OBA.

As explained above, to obtain a uniform powder, the ash was ground in a ball mill for two hours. The carbon emission factor of the grinding process (EC_1) can be calculated using Eq. 9-14, taking into consideration the greenhouse gas emission intensity of electricity generation (I_{GHG}) in the EU-27, which is conservatively estimated to be 0.265 kg CO₂e/kWh (European Environment Agency, 2023). The grinding process is carried out in a ball mill (Ortoalresa ML 007) driven by municipal electricity. The ball mill used had a power of 0.15kW and was capable of processing 3kg of OBA at a time, with a processing time of 2 hours.

$$EC_1 = I_{GHG} \times P \times T / Capacity \quad Eq. 9-14$$

Where:

P = Power consumption of the ball mill (0.15 kW)

T = Processing time (2 hours)

I_{GHG} = Greenhouse gas emission intensity of electricity generation (0.265 kg CO₂e/kWh)

Capacity = OBA processed in a single batch (3 kg)

Considering that the cement is produced locally, carbon emissions due to transport are negligible. The carbon content in the matrix due to unburned biochar and biomass sequestration was calculated with the modified LOI test. The total carbon (TC) in OBA is 16.61 w/w%. The carbon emission factor of carbon sequestration (EC_2) can be calculated with Eq. 9-15.

$$EC_2 = -TC \times \frac{M_{CO_2}}{M_C} \quad Eq. 9-15$$

Where:

TC = Total carbon content in OBA (Δm_3 recorded in the modified LOI test)

M_C = Relative molecular mass of carbon (12.01 g/mol)

M_{CO_2} = Relative molecular mass of CO₂ (44.01 g/mol)

According to the above, the emission factor of the OBA is calculated in Table 9-13. The carbon emission factor calculated as -0.3251 kg CO₂ eq. /kg, show a notable capacity to sequester carbon. This agrees with López et al. (2018) who report a theoretical carbon sequestration capacity of 0.312 kg CO₂/kg, for olive cake bottom ash, calculated using its chemical composition.

Table 9-13 Calculation of the carbon emissions of the OBA.

Activity	Emission Factor	Unit
Grinding	0.0265	<i>kg CO₂ eq./kg</i>
Transportation	-	-
Carbon sequestration	-0.3507	<i>kg CO₂ eq./kg</i>
Total	-0.3251	<i>kg CO₂ eq./kg</i>

9.3.5 CBA

The CBA is also a waste from power generation. Therefore, the impacts of material, energy use and carbon emission of power generation are excluded from the calculation. The only processing that the CBA and the OBA have in common is grinding for 2h. Therefore, the carbon emission factor of CBA is 0.0265 *kg CO₂ eq./kg* as calculated by Eq.9-13.

The alkali-fusion process involves the use of 25% sodium hydroxide and burning at 600 °C. The carbon emission of calcination is assumed as 105 kg to 178 kg CO₂ eq. per tonne of CBA. An average value of 142 kg per tonne was used in this study.

The environmental impacts of CBA are presented in Table 9-14.

Table 9-14 Environmental impacts of alkali fused CBA.

	Mass	Global Warming Potential kg CO ₂ eq.	Acidification Potential kg SO ₂ eq.	Abiotic depletion potential for non-fossil resources kg Sb eq.	Resource depletion MJ
Input					
Raw CBA	800 kg	26.5			
Sodium hydroxide	200 kg	733.17	3.69	1.13x10 ⁻²	13861.89
Heat		1462.49	6.56	1.15x10 ⁻²	17613.92
		141.5			
Output					
Alkali-fused CBA	1000 kg	309.33	0.74	2.26x10 ⁻³	2772.34
		455.20	1.31	2.3x10 ⁻³	3522.78

9.4 AGGREGATE

The sand used was either natural or crushed. The environmental impacts of natural sand and crushed limestone sand are presented in Table 9-15.

Table 9-15 Environmental impacts of sand.

	Natural sand	Limestone sand
Source	EPDItaly, 2020	Rouwette, 2022
Global Warming Potential (including land use and biogenic carbon)	2.67 kg CO ₂ eq.	11.3 kg CO ₂ eq.

Acidification Potential	1.99x10 ⁻² kg SO ₂ eq.	4.43x10 ⁻² kg SO ₂ eq.
Abiotic depletion potential for non-fossil Resources	1.67x10 ⁻⁶ kg Sb eq.	8.90x10 ⁻⁷ kg Sb eq.
Resource depletion	32.8 MJ eq.	124 MJ eq.

9.5 ACTIVITY

The abiotic depletion potential for non-fossil resources, global warming potential and resource depletion per cubic meter of concrete mixed and cast were assumed as 5.50×10^{-07} Sb kg eq, 4.65 kg CO₂ eq and 67.81 MJ, respectively (Ali et al., 2022).

The geopolymers are cured at ambient temperature; therefore, the environmental impact of this process is negligible.

Given that these values are insignificant in terms of environmental impact compared to the production of raw materials for geopolymer, the carbon emissions and environmental impacts of these activities were not included in the calculations to simplify the analysis.

9.6 LCA CALCULATION

9.6.1 Global Warming Potential

The global warming potentials of selected geopolymer mortars are calculated in Table 9-16.

The optimized geopolymer formulations from the previous chapters are studied in this chapter. The names of each geopolymer follow the previous customary usage: F = FCC, C = CBA, fC = alkali-fused CBA with 25% NaOH, ffC = alkali-fused CBA with 50% NaOH, A = OBA, G = GGBS, S = sodium silicate, C = sodium carbonate, Cs = pre-solubilized sodium carbonate. Numbers before the letters indicate percentages, and numbers with slashes indicate components of the activator solution. The AS one-part geopolymers are designed as the total chemical composition. The specimen C2 is designed as SiO₂/Al₂O₃=2.5 and Al₂O₃/Na₂O=1 while the C3 is designed as SiO₂/Al₂O₃=3.0 and Al₂O₃/Na₂O=1.

Table 9-16 The global warming potential calculation of selected geopolymer mortars (kg CO² eq./m³ mortars).

	Precursor	GGBS			Sand		Sodium silicate			Sodium carbonate			Sodium hydroxide	
		No allocation	Allocation by Mass	Allocation by Economy	Natural	Limestone	Furnace Process	37%	48%	Mining	Solvay	Hou	Membrane	Diaphragm
40F60G 8/1.0	0.00	4.60	339.84	111.02	3.26	13.81		0.16	0.13				31.25	62.34
40F60G 8/1.2	0.00	4.69	346.69	113.26	3.33	14.09		0.19	0.16				26.55	52.95
40F60G 6/1.0	0.00	4.76	352.04	115.01	3.38	14.31		0.12	0.10				24.29	48.46
30C70G 10/1.2	3.17	5.25	388.06	126.78	3.19	13.52		0.23	0.20				31.84	63.52
30fC70G 10/1.2	35.82	5.08	375.60	122.70	3.09	13.09		0.23	0.20				30.82	61.48
C2	343.33	5.85	432.86	141.41	3.12	13.20	61.56			1.59	26.58	72.74	0.00	0.00
C3	356.76	6.08	449.80	146.94	3.24	13.71	102.35			0.92	15.33	41.96	0.00	0.00
40A60G	-56.10	4.87	359.79	117.54	3.46	14.62	0.00			0.00	0.00	0.00	0.00	0.00
40A60G 4Cs	-53.79	4.67	344.98	112.70	3.31	14.02	0.00			0.43	7.20	19.71	0.00	0.00
40A60G 10C	-56.27	4.88	360.86	117.89	3.47	14.67	0.00			1.13	18.83	51.53	0.00	0.00
30C70G10C	3.29	5.45	403.20	131.72	3.32	14.05	0.00			1.08	18.03	49.36	0.00	0.00
30C70G5C10s	3.28	5.43	401.49	131.16	3.31	13.99	32.63			0.54	8.98	24.57	0.00	0.00
30fC70G4C	38.40	5.45	402.67	131.55	3.31	14.03	0.00			0.43	7.20	19.72	0.00	0.00
30fC70G5C10S	37.71	5.35	395.39	129.17	3.25	13.78	32.13			0.53	8.84	24.20	0.00	0.00
30fC70G5C20S	36.30	5.15	380.58	124.33	3.13	13.26	61.86			0.51	8.51	23.29	0.00	0.00

The GWP of the resulting geopolymer can vary significantly due to differences in the production process of the activator and the allocation method of GGBS. The production of sodium carbonate using the Solvay process has a GWP 16.67 times higher than that of naturally mined sodium carbonate. Additionally, sodium hydroxide produced using a membrane cell has half the GWP of sodium hydroxide produced using a diaphragm cell. The GWP of GGBS allocated by mass is 74 times higher than if it were not involved in allocation.

Figure 9-3 gives the optimum case of geopolymer production where GGBS is treated as waste without allocating any carbon emissions from the blast furnace operation, using natural sand, the furnace process and 48% sodium silicate, naturally mined sodium carbonate and sodium hydroxide produced by membrane cell.

In this scenario, except for the AS geopolymer, the GWPs of other geopolymer groups are below 150 kg CO₂ eq./m³. Due to the carbon negativity of OBA, OBA-based geopolymer has a negative carbon footprint. The release of organic matter from AS significantly contributed to the carbon emissions of AS geopolymers, amounting to 415-469 kg CO₂ eq./m³ and accounting for approximately 76-82% of the total carbon emissions. In other groups, the main contributor to carbon emissions is sodium silicate, accounting for about 40-60% of the total emissions, depending on the amount used. In contrast, naturally mined sodium carbonate contributes only about 1% of carbon emissions, demonstrating that it is an extremely environmentally friendly activator.

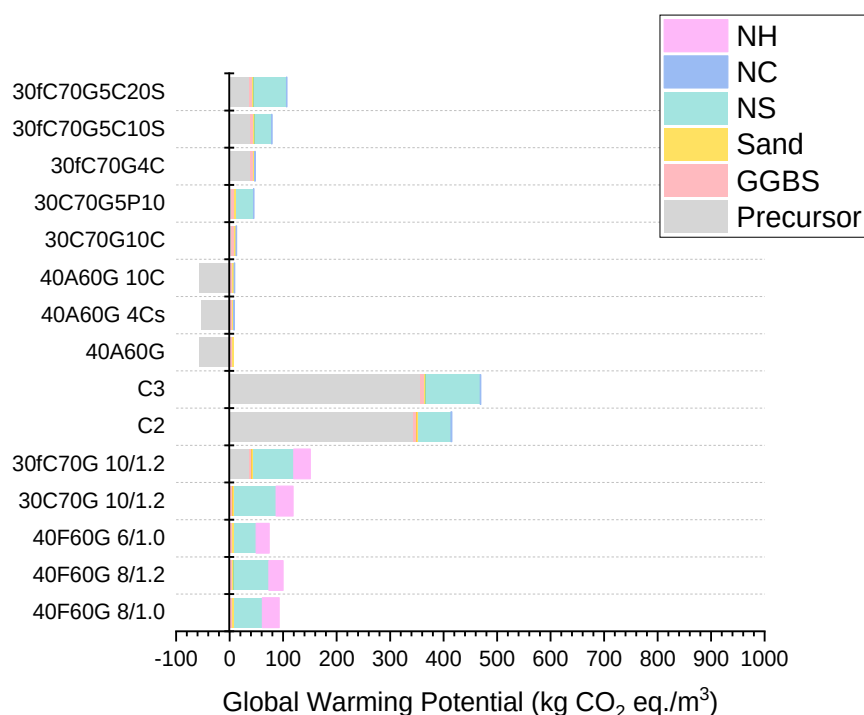


Figure 9-3 GWP calculation Scenario I: Lowest potential.

(GGBS: no allocation; Sand: Natural; NS: Furnace process (solid), 48% solution; NC: Mining; NH: Membrane)

On the contrary, Figure 9-4 illustrates the most unfavourable scenario for geopolymer production including the carbon emissions from GGBS by mass ratio of production, crushed limestone sand, sodium carbonate produced using the furnace process and 37% sodium silicate, sodium carbonate produced using the Hou's process and sodium hydroxide produced using diaphragm cells.

When the carbon emissions of GGBS are allocated by mass, GGBS contributes over 45% of the total carbon emissions. Consequently, the total carbon emissions from geopolymers will increase to 300-900 kg CO₂ eq./m³ while the carbon emissions of AS geopolymers rise (from c.415-469) to 923-964 kg CO₂ eq./m³, an amount much higher than in the optimal scenario. The carbon emissions caused by sodium hydroxide double due to differences in the production processes contributing to extra carbon emission of around 30 kg CO₂ eq./m³. Switching from natural sand to crushed limestone sand increases around 10 kg CO₂ eq./m³ carbon emissions but it does not become a major source of carbon emissions for geopolymer production.

Furthermore, since the other product of Hou's process, ammonium chloride is also commercially valuable, the carbon emissions calculated for sodium carbonate produced by Hou's process are inflated. As further allocation issues, such as the allocation between sodium carbonate and ammonium chloride, are involved and are beyond the scope of this study, they are not analyzed further here.

Apart from the carbon emissions caused by the Hou's process, the carbon emissions from activator production can be reduced by approximately 30% through optimizing the production process.

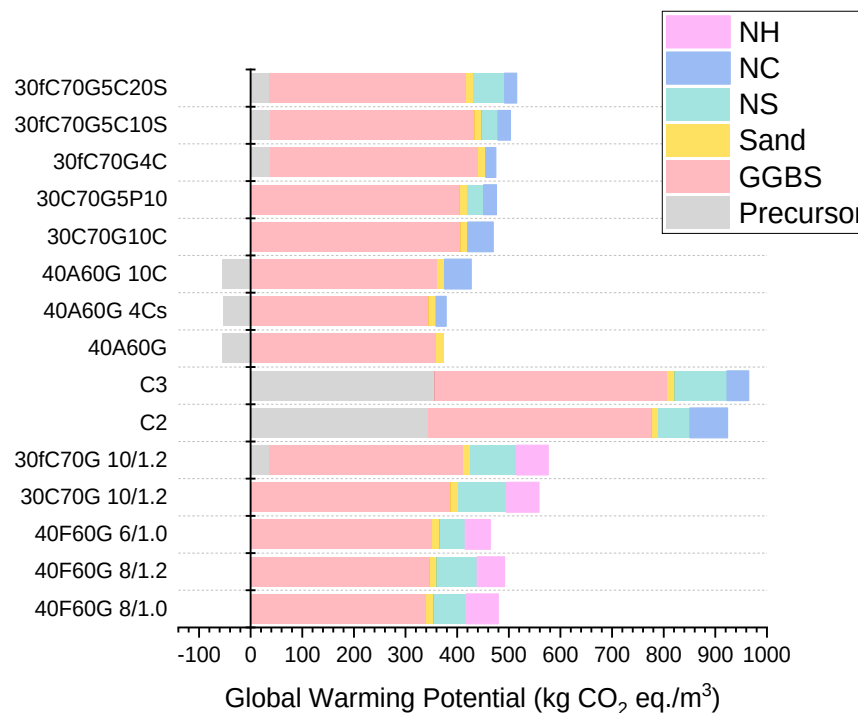


Figure 9-4 GWP calculation Scenario II: Highest potential

(GGBS: allocation by mass; Sand: Limestone; NS: Furnace process (solid), 37% solution; NC: HOU's; NH: Diaphragm)

Figure 9-5 gives a more reasonable scenario between the two scenarios above, where the carbon emissions from GGBS are allocated according to their economic value and the values are artificial sand, furnace process and 37% sodium silicate, sodium carbonate produced by the Solvay process, and sodium hydroxide produced by the Membrane cells. This scenario uses more common as well as more advanced production processes.

In this scenario, the carbon emissions of the geopolymer are below 300 kg CO₂ eq./m³, except for the AS-based geopolymer, which has nearly 650 kg CO₂ eq./m³. GGBS contributes about 50% of the total carbon emissions of the geopolymer, while sodium silicate accounts for 15-35% of the carbon emissions, making it the main source of carbon emissions besides the calcined AS and GGBS. Sodium carbonate and sand, on the other hand, account for only 1% of the carbon emissions.

For two-part geopolymers, a moderate reduction in the activator concentration and the SiO₂/Na₂O ratio within the strength allowance would significantly reduce the carbon emissions. For example, the carbon emissions of FCC-based geopolymer activated with a 6/1.0 solution are 12.4% lower than those of geopolymer activated with an 8/1.2 solution.

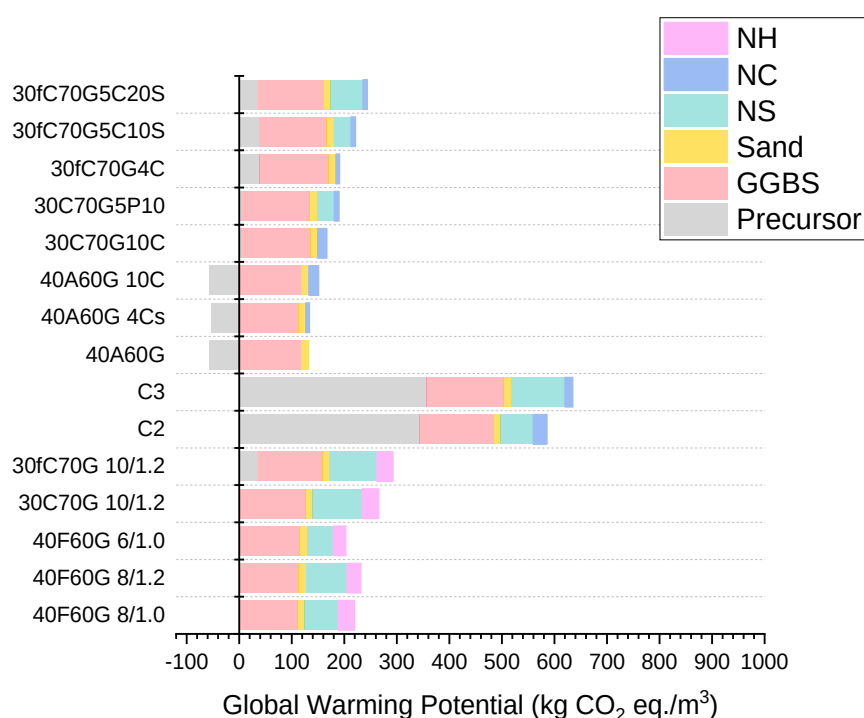


Figure 9-5 GWP calculation Scenario III: Reasonable potential.

(GGBS: allocation by economic; Sand: Limestone; NS: Furnace process (solid), 37% solution; NC: Solvay; NH: Membrane)

To better illustrate the carbon emissions of geopolymer, Figure 9-6 compares the carbon emissions of 1 kg of geopolymer with 1 kg of CEM I and CEM II A/L.

With the exception of AS-based geopolymer, all groups showed a significant reduction in carbon emissions compared to Portland Cement products. When compared to CEM I, the reduction in carbon emissions of geopolymers ranges from 30% to 80%, with FCC-based geopolymer shows a reduction of approximately 48%, OBA-based geopolymer shows a reduction of about 80%, and CBA-based geopolymer shows a reduction of about 43%. Conversely, AS-based geopolymer has a carbon footprint approximately 42% higher than CEM I.

Compared to CEM II A/L, FCC geopolymer reduces carbon emissions by 43%, OBA geopolymer reduces carbon emissions by 78%, CBA geopolymer reduces carbon emissions by 38%, and AS geopolymer increases carbon emissions by 56%.

In contrast, under appropriate activation conditions, the carbon emissions of two-part geopolymers are slightly higher than those of one-part geopolymers. However, this difference is not very significant and depends on the type and amount of activator used for one-part geopolymers.

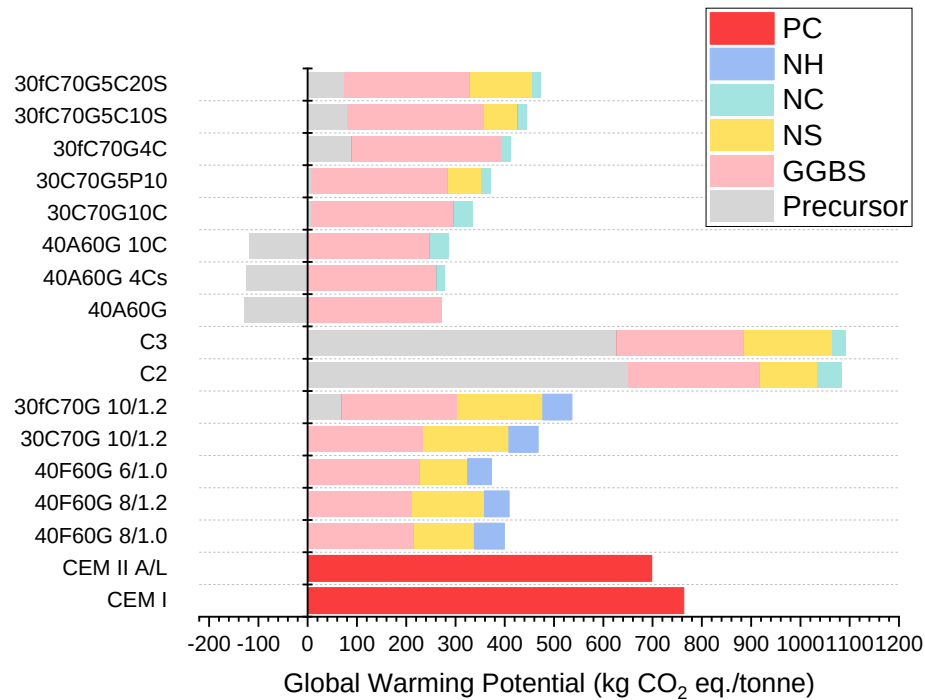


Figure 9-6 GWP calculation Scenario IV: per tonne binder.

(GGBS: allocation by economic; Sand: Limestone; NS: Furnace process (solid), 37% solution; NC: Solvay; NH: Membrane)

Meshram & Kumar (2022) conducted a life cycle assessment of FA/GGBS-based two-part geopolymer in the Indian context. They reported a GWP of 267 kg CO₂ eq. for FA/GGBS-based geopolymer, which is 70% lower than that of PC materials. This value is comparable to Scenario III in this study. They considered the GWP of GGBS to be 37.1 kg CO₂ eq./tonne, aligning closely with the no-allocation scenario in this study. However, they reported the GWP of sodium silicate as 1390 kg CO₂ eq./tonne, which corresponds to the diaphragm cell production scenario. Upgrading to a membrane cell can reduce the carbon footprint of sodium hydroxide production by nearly half, significantly enhancing the sustainability of geopolymer production.

Munir et al. (2023) indicate that the environmental impact of waste processing and curing is less than 1%, which is consistent with our findings. Except for precursors with high organic matter content, the environmental impact from precursors is negligible. However, specific processes for some precursors, such as high-temperature calcination and alkali-fusion, can overshadow the low-carbon nature of geopolymer production. For instance, some precursors such as AS and OBA release a considerable amount of CO₂ during the calcination process requiring additional attention.

Geopolymer technology presents an opportunity to utilize the carbon sequestration ability of precursors. For example, low-carbon or even carbon-negative materials can be prepared using the sequestered carbon in OBA. However, the organic matter in AS cannot be directly utilized as it would significantly hinder geopolymerization. Therefore, more research is needed to fully use this carbon to develop lower-carbon or even carbon-negative materials.

9.6.2 Acidification Potential

The acidification potential (AP) of geopolymer is presented in Figure 9-7. Acidification potential is a measure of the emissions that contribute to the acidifying effect on the environment, including sulphur dioxide (SO₂), nitrogen oxides (NO_x), nitric oxide (NO), nitrogen dioxide (N₂O) and a variety of other substances (Brough & Jouhara, 2020; Dincer & Abu-Rayash, 2020). Acidification can harm natural organisms such as fish and trees, as well as cause damage to buildings and other structures (Murphy et al., 2013).

The acidification potential is primarily attributed to the production of GGBS and sodium silicate, which account for more than 50% and 20-30% of the total acidification potential, respectively. The direct source of these emissions is the combustion of fossil fuels used in the manufacturing process. The standard method for controlling these emissions involves capturing the flue gases and treating them with technologies that are capable of achieving the required level of clean-up as mandated by regulations (Birat, 2020).

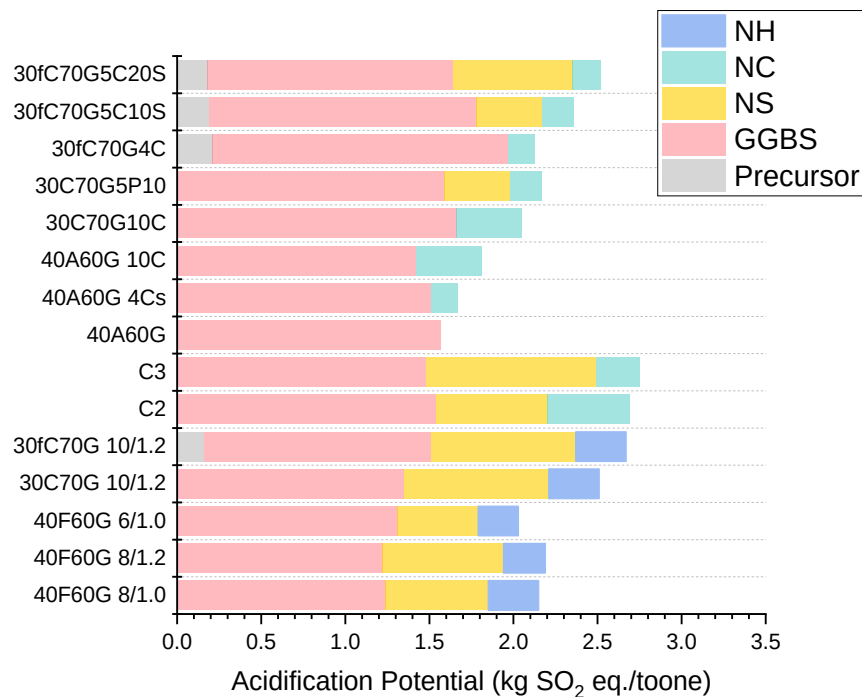


Figure 9-7 Acidification potential calculation: per tonne binder.

(GGBS: allocation by economic; Sand: Limestone; NS: Furnace process (solid), 37% solution; NC: Solvay; NH: Membrane)

9.6.3 Abiotic Depletion Potential

Abiotic depletion potential (ADP) refers to the amount of non-renewable resources used. The steel production represented behind GGBS gives GGBS an extremely high ADP and accounts

for a major portion of geopolymer production. When GGBS is removed, the production of activators is a major contributor to ADP, especially sodium hydroxide and sodium carbonate, both of which consume large amounts of natural resources for their production. However, overall, the ADP from activator production is still extremely low.

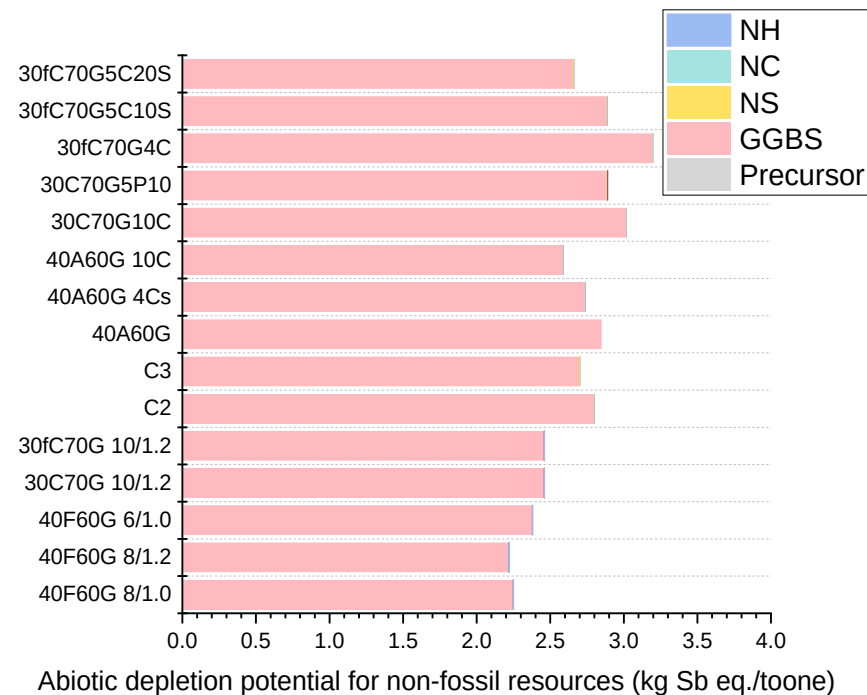


Figure 9-8 Abiotic depletion potential for non-fossil resources calculation: per tonne binder.

(GGBS: allocation by economic; Sand: Limestone; NS: Furnace process (solid), 37% solution; NC: Solvay; NH: Membrane)

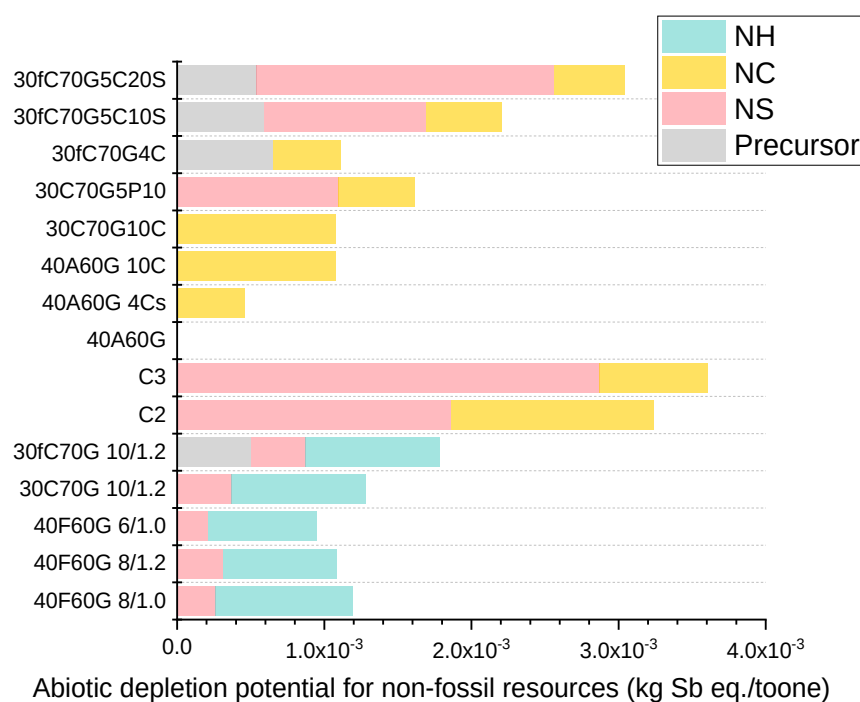


Figure 9-9 Abiotic depletion potential for non-fossil resources calculation without GGBS: per tonne binder.

(Sand: Limestone; NS: Furnace process (solid), 37% solution; NC: Solvay; NH: Membrane)

9.6.4 Resource Depletion

The resource depletion (RD) of geopolymer mortars is presented in Figure 9-10. GGBS and the underlying steel industry are the main contributors to resource depletion, accounting for over 60%. The next largest contributors are sodium silicate (NS) and sodium hydroxide (NH), with NS contributing about 7-20% and NH contributing 12-15%.

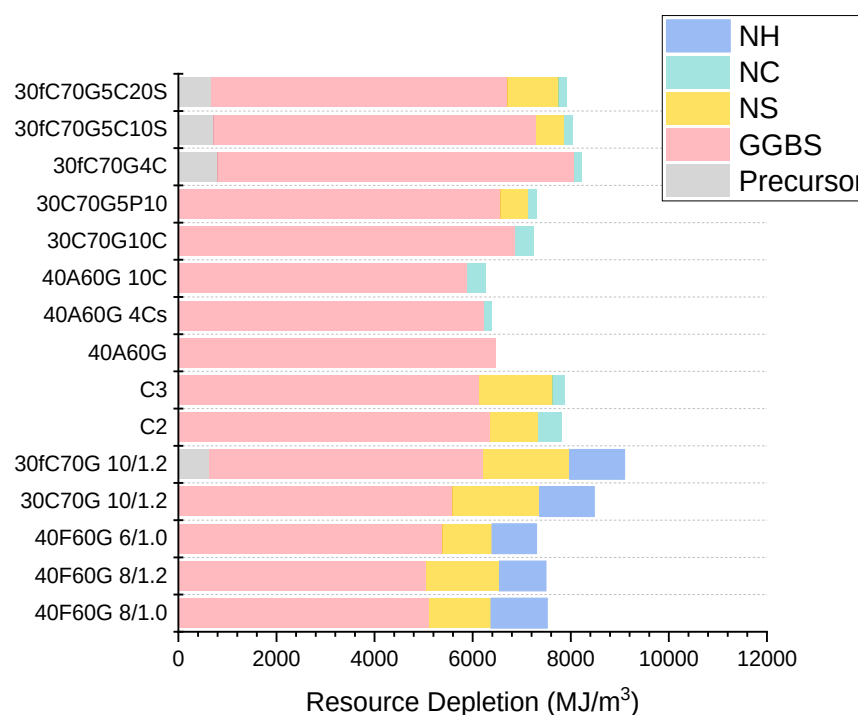


Figure 9-10 Resource depletion calculation: per tonne binder.

(GGBS: allocation by economic; Sand: Limestone; NS: Furnace process (solid), 37% solution; NC: Solvay; NH: Membrane)

9.7 SUMMARY

A life cycle assessment (LCA) of geopolymer mortars and binders has been conducted to illustrate the environmental impact of geopolymer production.

The results of the LCA demonstrate that allocation methods, the production process of the activator, and the treatment of precursors can significantly influence the environmental impact of geopolymers. The production of sodium carbonate using the Solvay process has a global warming potential (GWP) 16.67 times higher than that of naturally mined sodium carbonate, while the GWP of sodium hydroxide produced using a membrane cell is half that of sodium hydroxide produced using a diaphragm cell. Consequently, the environmental impacts of the same geopolymer production may vary dramatically in different regions and under different production scenarios. By optimizing the production of activators to a more environmentally friendly process, the carbon emissions associated with activator production in geopolymer fabrication can be reduced by approximately 30%.

Precursors treatments such as high-temperature calcination and alkali-fusion can significantly increase the environmental impact of geopolymer production. In precursors containing high organic content like AS, calcination releases their stored carbon, resulting in significant carbon emissions. Therefore, the carbon emissions per unit of AS geopolymer can be up to 42% higher than those of CEM I. On the contrary, precursors with carbon sequestration properties allow to develop low-carbon or even carbon-negative geopolymers. For example, the carbon sequestered by OBA reduces carbon emissions by nearly 130 kg CO₂ eq. per tonne of OBA geopolymer binder. Using raw AS in geopolymer technology is challenging because its high

organic matter hinders geopolymerization. More research is needed on high-carbon precursors to further reduce the environmental impact of their geopolymers.

Regarding other environmental impacts, the steel industry associated with GGBS production is the most significant contributor, followed by the production of sodium silicate and sodium hydroxide. Optimizing activation and using low-carbon emission activators instead of high carbon emission ones (e.g. using sodium carbonate instead of sodium hydroxide) are viable ways to further reduce the environmental impact of geopolymers.

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Chapter 10: Conclusions

In this study, four types of solid waste were characterized and subsequently used as precursors to develop geopolymers. The durability and environmental impacts of the geopolymers were evaluated. Based on the experimental results in previous sections, the main conclusions are summarized as follows.

Spent fluid cracking catalyst (FCC):

The spent fluid catalytic cracking catalyst (FCC) is semi-crystalline, with faujasite as the primary crystalline component. It predominantly consists of SiO_2 and Al_2O_3 , making up over 90%. The chemical and mineralogical properties of FCC suggest potential as a precursor for developing geopolymers. Reactivity assessments indicate high reactivity, and treatments like calcination, oxidation, and acid etching did not alter the structure and reactivity of FCC. However, alkali fusion with 15% NaOH turned FCC amorphous, decomposing faujasite entirely and increasing reactivity but also raising carbon emissions. Due to its inherent reactivity, raw FCC was chosen for geopolymer development.

Two-part geopolymers were developed using FCC and GGBS/FA with sodium silicate solution as the activator. FCC geopolymers exhibited excellent mechanical performances, especially when blended with GGBS, which is highly reactive and contributes Ca and Si to the geopolymerization process. The FCC-GGBS system showed robust performance, producing geopolymers with compressive strength of 45-57 MPa at 28 days when using a sodium silicate activator of Na^+ concentration from 6 to 10 mol/L and $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 1.0 to 1.4. The FCC-GGBS geopolymer matrix is dense and rich in Si, Al, Na, and Ca, with C(N)-A-S-H gel contributing to its mechanical strength. Conversely, the FCC-FA system is more sensitive to activator composition, with the optimal being $[\text{Na}^+] = 8.0$ mol/L, $\text{SiO}_2/\text{Na}_2\text{O} = 1.2$ and deviations reducing performance.

The FCC-GGBS geopolymer exhibited excellent durability, with mechanical performance significantly improving after cyclic testing. Additionally, it demonstrated high residual strength at elevated temperatures, maintaining a compressive strength of 23 MPa after calcination at 600°C.

Alum sludge (AS):

Chemical analysis of AS reveals high organic matter and aluminum content. AS is entirely amorphous suggesting high reactivity, but organic matter inhibits pozzolanic reactions and geopolymerization, requiring further treatment.

AS calcined at 450-1000°C was characterized, showing that calcination removes organic matter and disrupts the original microstructure through dehydroxylation, creating highly reactive transitional phases. Reactivity assessments indicated that AS calcined at 600°C exhibited the highest reactivity but cause flash setting, making the AS-containing paste difficult to handle. Further calcination at 800°C slightly reduces AS reactivity while avoiding flash setting, making 800°C-calcined AS suitable for geopolymer development.

AS was mixed with GGBS and activated with sodium carbonate and sodium silicate to develop one-part geopolymers. The optimal formulation, $\text{Na}_2\text{O}/\text{SiO}_2=1.0$ and $\text{SiO}_2/\text{Al}_2\text{O}_3=2.5$, achieved a compressive strength of 66.50 MPa. Deviations from this ratio significantly reduced mechanical performance.

The geopolymer has a dense matrix with gaylussite and calcite as main crystalline phases. FTIR spectra showed rich Si-O-Si(Al) bonds, indicating C(N)-A-S-H gels.

Achieving an optimal formulation required high activator dosage: 15.7% sodium carbonate and 20% sodium silicate. The high Na that this activator implies adversely affected durability. Cyclic testing showed significant strength reductions after wet-dry cycles and sulfate attack, with strength decreasing by 54% to 30.30 MPa after wet-dry cycles and significant mass loss after sulfate attack. This degradation is primarily due to salt crystallization and dissolution, exacerbated by high Na content.

High-temperature tests indicated that AS geopolymers maintain an amorphous structure at 600°C. Above 800°C, the amorphous cements become crystalline silicates gehlenite, sodium aluminum silicate and merwinite, resulting in a highly porous and loose structure.

Crop biomass ash (CBA):

CBA is highly crystalline due to controlled high-temperature combustion, and despite its high SiO_2 content (68.40%), its crystalline nature results in low reactivity. To enhance reactivity, an alkali fusion method was used, mixing CBA with 15-75% NaOH and calcining at 600°C for 2 hours. XRD and FTIR analyses indicated that alkali fusion effectively transformed quartz and albite into soluble silicates, increasing CBA reactivity.

Raw and 25% NaOH alkali-fused CBA were used to develop geopolymer binders using two-part and one-part techniques. The geopolymers are strong, the raw CBA geopolymers are weaker due to the lower reactivity of the raw CBA. However, two-part geopolymers consisting of 30% raw CBA and 70% GGBS, activated with $[\text{Na}^+] = 10 \text{ mol/L}$ and $\text{SiO}_2/\text{Na}_2\text{O} = 1.2$, achieved 29.83 MPa compressive strength. Alkali fusing the CBA increased strength: alkali-fused CBA geopolymers with the same activator reached 46.47 MPa, demonstrating the effectiveness of alkali fusion.

One-part geopolymers (30% raw CBA and 70% GGBS) achieved 30.70 MPa and 46.09 MPa compressive strength when activated with sodium carbonate and sodium carbonate+sodium silicate respectively. Alkali-fusion of CBA further improved the compressive strength of carbonate-activated one-part geopolymers to 58.33 MPa.

A properly activated alkali-fused CBA-based geopolymer matrix is dense and homogeneous, correlating with its excellent mechanical properties. The matrix is predominantly amorphous with few gaylussite crystals. FTIR spectra indicated the geopolymer matrix primarily comprises SiQ^2 and SiQ^1 structures.

Durability tests revealed that raw CBA geopolymers exhibit superior resistance to wet-dry cycles and sulfate attack. However, the high Na content introduced by alkali-fused CBA geopolymers is the primary factor in the reduction of durability.

Olive-pits bottom ash (OBA):

Olive-pits bottom ash (OBA) has a distinctive chemical composition, with K_2O content at 23.0% and CaO content at 19.95%. It also exhibits a high loss on ignition (LOI), indicating a significant amount of unburned carbon.

The unique chemical composition of OBA, with high alkali content, suggests potential as a low-carbon activator. When OBA is used as the only activator, the compressive strength of OBA-GGBS geopolymers reached 15.43 MPa. Incorporating sodium carbonate as an auxiliary activator raised compressive strength to 43.94 MPa. The presence of C(K)-A-S-H cements was determined in OBA-GGBS geopolymers, and the dense matrix indicated that GGBS was effectively activated by OBA.

The OBA-activated geopolymer showed a sound resistance to the wet-dry cycle and sulphate attack due to its low sodium content. The addition of sodium carbonate as auxiliary activator has a negative effect on durability due to the inclusion of sodium.

Life cycle assessments of geopolymer fabrication:

Life cycle assessments were conducted to demonstrate the environmental impacts of geopolymer production.

The LCA results demonstrate that environmental impact allocation methods, the production process of the activator, and the treatment of precursors significantly influence the environmental impact of geopolymers. By adopting the most environmentally friendly production process for activators, carbon emissions of activators can be reduced by around 30% compared to the most unfavorable process. As GGBS is considered a by-product rather than waste, its production contributes over 50% of the total carbon emission to geopolymer fabrication.

In general, precursor production accounts for minimal carbon emissions, under 2%. However, using treatments such as calcination and alkali-fusion increase carbon emissions. Especially when using wastes with high carbon content, calcination causes significant carbon emissions due to the release of carbon. Conversely, if calcination can be avoided, carbon can be sequestered into the geopolymer leading to the production of carbon-negative materials.

The geopolymer formulations developed in this thesis, except for the AS geopolymer, exhibit lower carbon emissions than Portland cement, with reductions ranging from 30-81% compared to CEM I and 23-79% compared to CEM II A/L.

In summary, the four types of solid waste—FCC, AS, CBA, and OBA—demonstrate potential as precursors/activators for developing geopolymers with excellent mechanical properties and sustainability. This research extensively investigated and summarized the processing and activation methods for each type of waste. The wastes represent a wide range of compositions and structures from semi-crystalline zeolites (FCC), to entirely amorphous wastes (AS), highly crystalline structures (CBA), and high-alkali content waste (OBA). Therefore, the findings provide valuable insights and reference material for the development and utilization of various other waste types with similar structures.

However, the scope of this PhD study leaves several research questions open for further investigation. The research primarily utilizes GGBS and FA as silica sources in the development of geopolymers, with a focus on high-calcium systems. Given the anticipated decline in GGBS and FA production due to industrial advancements and economic restructuring, the reliance on these materials limits the broader applicability of the findings in the future. Future studies should explore alternative silica sources, such as metakaolin, silica fume, and rice husk ash, to provide valuable insights for industrial applications.

Additionally, the development of one-part geopolymers in this study was confined to high-calcium systems. While low-calcium systems offer distinct advantages, they typically require a highly alkaline activator and thermal curing to facilitate setting and hardening, presenting challenges to the development of one-part low-calcium geopolymers. This study's limited exploration of low-calcium systems represents a constraint, which encourages further investigation in future research.

For durability testing, time and equipment constraints limited the assessment of long-term strength development and carbonation resistance. These parameters are critical for evaluating the durability and safety of geopolymers. Carbonation, in particular, poses significant concerns for long-term stability. To advance the use of geopolymers in practical applications, future research should focus on long-term strength measurements and assessing changes in strength and mineral composition following carbonation exposure.

Moreover, while this study briefly discussed the potential heavy metal content in the selected waste materials, additional leaching tests of the resulting geopolymers are necessary to address public and industrial concerns regarding their environmental safety. These tests should be prioritized in future research.

Appendices

Appendix A

PATENTS AND PAPERS PUBLISHED IN JOURNALS AND CONFERENCES

Patent under review

- [1] A method of producing a composition comprising calcium aluminate
- [2] A binding composition and method for producing the binding composition.

Published journal paper

- [1] Lei, Z., Pavia, S., & Wang, X. (2024). Alkali-fusion as an effective method for activating low-reactivity silicate wastes: A comparative study. *Construction and Building Materials*, 449, 138504.
- [2] Lei, Z., & Pavia, S. (2024). Biomass ash (BA) waste as an activator to produce carbon-negative cement. *CEMENT*, 100112.
- [3] Lei, Z., & Pavia, S. (2024). Geopolymer based on biomass ash from agricultural residues. *Construction and Building Materials*, 441, 137471.
- [4] Lei, Z., & Pavia, S. (2024). Pozzolanic activity of FCC catalyst waste slag (CWS) for cement and geopolymer production. *Cleaner Engineering and Technology*, 100758.
- [5] Lei, Z., Pavia, S., & Wang, X. (2024). Biomass ash waste from agricultural residues: Characterisation, reactivity and potential to develop one-part geopolymer cement. *Construction and Building Materials*, 431, 136544
- [6] Lei, Z., & Pavia, S. (2023). Potential of spent fluid cracking catalyst (FCC) waste for low-carbon cement production. Effect of treatments to enhance reactivity. *CEMENT*, 100081.
- [7] Peng, G. F., Zhang, G., Lei, Z. H., Ding, H., Jiang, Y. H., Niu, X. J., & Fan, Y. C. (2023). Verification of mechanism for effect of silane coupling agent modification of polyethylene (PE) fiber's surface on strain-hardening behavior of high-strength cementitious composites. *Journal of Building Engineering*, 67, 105870.
- [8] Lei, Z., & Pavia, S. (2023). Reactivity of raw, pyroprocessed and GGBS-blended alum sludge (AS) waste for sustainable cement production. *Journal of Building Engineering*, 65, 105787.
- [9] Alelweet, O., Pavia, S., & Lei, Z. (2021). Pozzolanic and Cementing Activity of Raw and Pyro-Processed Saudi Arabian Red Mud (RM) Waste. *Recent Progress in Materials*, 3(4), 1-19.

Conference paper

- [10] Lei, Z., & Pavia, S. (2023). Appraisal of alum sludge waste for low-carbon, calcium aluminate cement production, CEES 2023, Funchal, Portugal
- [11] Lei, Z., & Pavia, S. (2022). Effect of the early dissolution of Al-phases in reactive industrial wastes, on the setting times and rheology of sustainable binders, CERI Conference 2022, Dublin, Ireland