



University of Sheffield

The Effect of Strontium and Caesium Salts on the Kinetics and Mechanisms of Geopolymer Cement Formation

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Abstract

Strontium-90 and caesium-137 are two problematic fission products arising from nuclear power. These are categorised as intermediate level waste (ILW); the current technology for the safe containment and disposal of ILW is through encapsulation in Portland cement (PC) and ground granulated blast furnace slag (GGBFS) grouts. However, interactions between PC and the Sr and Cs means that alternative grouts may be needed for their safe encapsulation. Geopolymers (GP) have received significant interest due to favourable properties and potential to chemically immobilise cations. This thesis investigates the interactions of metakaolin-based, potassium-activated geopolymers with various salts of Sr and Cs. Metakaolin and potassium silicate reacted to form a geopolymer cement with a nominal formulation of $\text{Si/Al} = 1.5$, $\text{K/Al} = 1$, and $\text{H}_2\text{O/K}_2\text{O} = 11$. Incorporation of both Sr and Cs salts caused distinct changes to the kinetics of the geopolymer polycondensation reaction, depending on the solubility of the salt. The mechanisms for the change in kinetics fall into three categories: interactions with the metakaolin surface, reactions with the potassium silicate, or the filler effect caused by solid particles of insoluble Sr salts. Despite the change to the kinetics, the incorporation of the salts does not cause a significant change in geopolymer nanostructure, and does not prevent formation of a hardened monolith after 24 hours. The main binding phase is a K-A-S-H gel, although some of the potassium is displaced by the Sr^{2+} and Cs^+ , and in one case the presence of a crystalline Cs-A-S-H phase is detected. Sr is present in multiple forms within the geopolymer sample, including within a pseudo-zeolitic framework consistent with its incorporation as the charge balancing cation in the K-A-S-H gel. This thesis concludes that geopolymer cements show promise for incorporating Sr and Cs salts, and furthers their use case for long-term disposal of radioactive waste.

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1 Chapter 1: Introduction and Literature Review

1.1 Nuclear Power

1.1.1 Global Overview

Nuclear fission, the fundamental source of nuclear power generation, has been a vital tool for energy generation globally for 65 years, stemming from the commissioning of the first MAGNOX reactor at Calder Hall in 1956 [1]. Since then, 31 countries have adopted nuclear power as a form of energy production, with further countries, such as Denmark and Italy, relying on imported nuclear power to meet the demand for electricity [2]. In the near future, this value is destined to grow as more countries look for fossil fuel alternatives to provide a low carbon, stable baseline power source for their diversifying energy portfolios. Nuclear fission is currently responsible for providing around 9% of the global electricity demand [3].

The UK itself currently operates 10 nuclear reactors at 5 locations which generate approximately 13.9% of the national requirement [4]. However, government plans outline that this is expected to increase to 25% by 2050, providing 24 GW of electricity [5]. The construction of 2 new generation power plants is currently underway at Hinckley Point in Somerset, with aims to connect these to the grid in 2027 and 2028 respectively. Although, over recent years, the use of renewables such as wind and solar power have risen to take up the majority share of the current electrical generation within the UK, they are closely followed by the use of natural gas, a fossil fuel, demonstrating that change is vital to reduce the carbon footprint of the UK energy industry to align with goals set out in the Paris agreement [4].

1.1.2 Advantages of Nuclear Power

In the majority of industrialised countries, the electrical baseload is provided by the combustion of fossil fuels such as coal and natural gas. However, it is well-known that this practice is a key contributor to the global emissions of carbon dioxide [6]. Therefore, many countries are seeking alternative sources of clean electricity production to meet this value; two of the most promising options are renewable energy sources, such as wind and solar power, and nuclear fission. The low associated CO₂ emissions of nuclear fission means that it can provide the same service as fossil fuel fired power stations whilst still contributing towards lowering the carbon footprint.

Nuclear fission has the advantage over renewables in the sense that it can be operated continuously; many renewable energy sources are intermittent, only operating when certain weather conditions are met. This also means that many of the current renewable electricity sources are climate specific, whereas nuclear energy can be operated anywhere, providing there is access to cooling water and sufficient area. Most importantly, nuclear fission is capable of fulfilling a countries baseline needs single-handedly due to it being an incredibly energy dense fuel source, with the fission of 1g of fuel producing the same energy as burning 3 tons of coal. Although nuclear fission is not technically a renewable energy source,

it is currently seen as sustainable due to the large quantity of uranium available. It is estimated that, at present consumption rates, uranium resources will last for more than 100 years, with the possibility that sourcing uranium from seawater and the introduction of fast reactors could make supplies last for thousands of years, making nuclear power pseudo-renewable [7].

1.1.3 Nuclear Fuel Cycle

Nuclear fission is the act of a particle splitting either spontaneously or due to the impact of a foreign particle [8]. Upon splitting, energy, and in most cases one or more neutrons, is released from the particle and two products remain. The neutron(s) produced from this reaction can then go on to initiate further fission reactions. This is known as a chain reaction and allows the fission to be self-sustaining [9].

In order to achieve a suitable mass of fissile material within the uranium-based fuel rods of most thermal nuclear reactors, the natural uranium must be enriched in uranium-235. Natural uranium is approximately 99.27% uranium-238, which is not fissile, and 0.71% uranium-235, which is [10]. Therefore, the fuel goes through an enrichment process which increases the relative amount of uranium-235 to between 3-5%. Uranium-235 is a radioactive isotope of uranium and undergoes fission easily due to its large fission cross-section, meaning a relatively low energy neutron will be enough to split the atom [11]. Moreover, this isotope can easily maintain its fission through a chain reaction, as each fission reaction releases on average 2-3 neutrons which are able to migrate and cause another uranium-235 atom to undergo fission [12, 13]. Furthermore, a number of the fission products produced by the decay of uranium-235 are unstable themselves and move towards a more stable configuration by decaying further, emitting radiation. In most cases, this is via beta decay, where a neutron within the atom splits into a proton and an electron, with the electron being ejected from the nucleus at high speeds [12, 14]. The unstable daughter nucleus that forms due to this decay can then emit a neutron, leading to the delayed neutrons that are so important in controlling the rate at which a nuclear reactor operates [13].

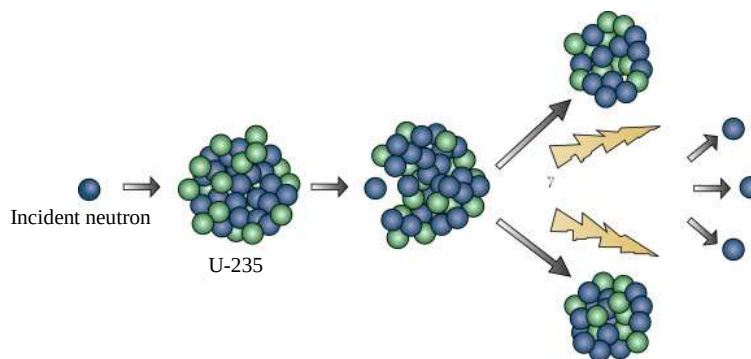


Figure 1-1: The splitting (fission) of a uranium-235 atom due to a collision with the incident neutron. Adapted from [15].

After an operating cycle of around 3 years, the concentration of uranium-235 within the fuel rod has dropped to a point where an interaction with a neutron is less probable [12]. At this point, the fuel rod

is considered spent and must be removed from the reactor, even though it contains approximately 96% uranium [16]. However, the majority of the remaining uranium is the more common uranium-238 isotope which is not susceptible to fission. In the spent fuel rod, only 0.5% of the material is fissile (0.23% uranium-235, 0.27% plutonium-239 and plutonium-241) [17], compared to the 3-5% of fissile material in fresh fuel [18, 19].

Upon leaving the reactor core, the spent fuel is still highly radioactive and produces significant amounts of heat [16]. To ensure that safe handling and appropriate disposal can be carried out on what is now radioactive waste, the spent fuel must spend a period of between 10 and 20 years in a specially designed cooling pond. This will contain the waste whilst the most radioactive isotopes decay away, reducing its activity and temperature [20, 21]. After this period, stable isotopes, very long-lived radioactive isotopes, and small quantities of the short-lived radioactive isotopes are all that remain within the waste [20]. In an open fuel cycle, this waste is left in the cooling pond, ready for transferal to a suitable geological depository [21]. However, in a closed fuel cycle, the waste is removed from the pond and transferred to a suitable reprocessing facility in order to recycle the useful uranium, and plutonium, that resides within the spent fuel [21, 22].

1.1.4 Spent Fuel Reprocessing

The reprocessing of spent nuclear fuel is the process of recovering the valuable plutonium and uranium isotopes, along with other useful actinides (i.e. thorium), from spent fuel liquors via solvent extraction processes [22-24]. The need for reprocessing is a contentious issue, with the majority of studies showing that reprocessing to create mixed oxide (MOX) fuels is not viable in the current economic climate [25]. However, many reprocessing plants operate around the world and the THERMAL Oxide Reprocessing Plant (THORP) at Sellafield, UK operated successfully up until its close in 2018 [26]. The implementation of nuclear fuel reprocessing is not currently advantageous in terms of fuel regeneration, however, there is the prospect of the worldwide commercial use of fast neutron reactors in the next few decades which will allow depleted uranium to be used as a fuel source [7, 25]. This will mean that the accumulation of uranium within spent fuel that is currently considered as waste will become another fuel resource, providing it is separated from the non-useful fission products that also reside within spent fuel via reprocessing. This will lessen the volume of uranium that is required to be mined, reducing the risk to both the environment and people's health [27].

1.2 Nuclear Waste

1.2.1 Generation of Waste

Nuclear waste is generated at every stage of the nuclear fuel cycle, from the initial mining of the uranium to the eventual reprocessing of the spent nuclear fuel and decommissioning of nuclear reactors. Any waste that is generated in the sector is separated into four different categories.

1.2.1.1 Categories of Waste

1.2.1.1.1 High Level Waste

High level waste (HLW) is the most problematic group of waste that is generated within a nuclear reactor. It is the only category of waste that is heat producing, containing some of the most active radioisotopes. HLW has an activity that exceeds 4 gigabecquerels per tonne of alpha activity or 12 gigabecquerels per tonne of beta/gamma activity [28]. The quantity by volume of HLW is the lowest of all the waste categories in the UK and consists mainly of the liquid by-product of the spent fuel reprocessing route [29]. The preferred disposal route for this waste is through the use of borosilicate glass vitrification [28]. Glass has been found to be very structurally flexible, adapting to bond many of the HLW constituents atomistically [30]. Further information can be found in Section 1.5.2.

1.2.1.1.2 Intermediate Level Waste

Intermediate level waste (ILW) differs only from HLW in the sense that its radioactivity does not lead to the generation of heat. ILW also has an activity that exceeds 4 gigabecquerels per tonne of alpha activity or 12 gigabecquerels per tonne of beta/gamma activity [28]. The UK currently holds a reasonable amount of ILW, contributing to ~5.5% of the total waste by volume as of 2022 [29, 31]. This waste category includes fuel cladding and reactor components from decommissioned reactors [29]. The preferred disposal route for this waste type is encapsulation within a cement grout stored in a steel drum [28]. Cementitious wasteforms are used due to their minimal cost and low processing temperature [32]. Further information on this can be found in Section 1.5.4.

1.2.1.1.3 Low Level Waste

Low level waste (LLW) is waste that does not reach the threshold activity that dictates whether waste can be classified as ILW or HLW. This waste category is responsible for a considerable volume of nuclear waste at approximately 35% and comprises mainly of rubble and soil from the dismantling and decommissioning of nuclear facilities [29]. A large proportion of the UK's LLW is disposed of at the Low-Level Waste Repository at Drigg, Cumbria, where it is grouted into a metal container using cement and stored in concrete lined vaults [33].

1.2.1.1.4 Very Low Level Waste

Very low level waste (VLLW) is a sub-category of LLW that is subject to further activity limits. Waste that falls into this category can be disposed of as standard waste, or in some cases must be disposed of at specialised landfill sites [29].

The volume of all of the categories of waste, excluding HLW, are predicted to increase in the future as shown by Table 1-1. Therefore, it is imperative that suitable waste packages are designed and implemented in a timely manner to correspond with the growing volume of waste being generated by the sector.

Table 1-1: The volumes of the four categories of nuclear waste as reported in 2019. The projected future generation of waste is also included. Adapted from [29].

Sample	Volume (m ³)		
	Reported at 1 April 2022	Packaged Volume	Estimated Future Arisings
HLW	1,670	1,470	Net decrease
ILW	249,000	496,000	148,000
LLW	1,580,000	1,340,000	1,550,000
VLLW	2,750,000	2,610,000	2,750,000
Total	4,580,000	4,450,000	4,448,000

1.3 Strontium-90

Strontium-90 is one of the most troublesome radioisotopes formed as a product of the fission of uranium-235. Strontium is one of the primary sources of heat generation in radioactive waste, generating 0.95 watts per gram of thermal energy [34]. This energy is transmitted through the electrons liberated by the beta decay of strontium-90 into yttrium-90, and then the further beta decay of yttrium-90 into zirconium-90 which is stable.

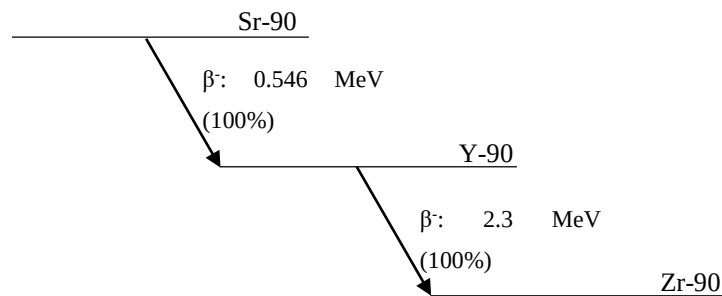


Figure 1-2: The decay of strontium-90 to zirconium-90.

The half-life of Sr-90 is 28.82 years, far shorter than the half-lives of numerous other fission products [35, 36]. Therefore, using the ten half-life rule [37, 38], Sr-90 will have decayed to background levels of radiation after approximately 290 years. This comparatively short half-life means that the generation of a suitable cement-based wasteform is more attainable than alternative waste conditioning approaches.

Strontium can be found in spent nuclear fuel as a direct fission product of U-235, but is also present in treated radioactive waste, nuclear reactor cooling water and, more importantly, in the environment surrounding the sites of nuclear disasters [39]. This is prominent when considering the contaminated cooling water that still remains within the Fukushima Daiichi nuclear power plant [40].

1.4 Caesium-137

Caesium-137 (Cs-137) also poses a serious problem in radioactive waste. Moreover, nuclear waste is not the only source of Cs-137 on the Earth's surface and in its atmosphere; substantial nuclear weapons testing during the arms race in the 1960's led to elevated levels of Cs-137 which can still be detected today [41]. This is possible due to the half-life of Cs-137 being 30.17 years, slightly longer than that of Sr-90 [36]. Cs-137 decays to stable barium-137 (Ba-137) through beta decay. However, it can also decay via a beta decay to a short-lived metastable Ba-137m isotope, which later decays by a high energy gamma emission to the stable Ba-137 isotope as seen in Figure 1-3. The accompanying energies for this type of decay are 512 keV for the beta decay of Cs-137 and 663 keV for the gamma decay of Ba-137m [42].

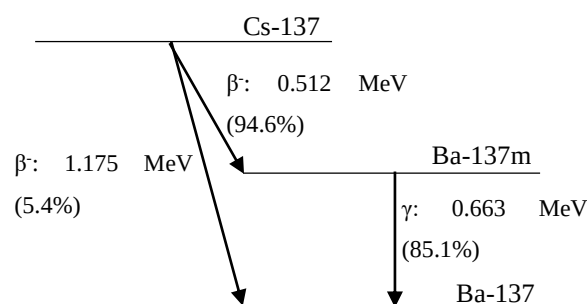


Figure 1-3: The decay of caesium-137 to barium-137.

Cs-137 is far more chemically reactive than most of its fellow fission products, many of which are transition metals. As an electropositive element, Cs-137 readily reacts with water, resulting in a waste containing stream that can be difficult to contain and process [43]. It can be found in the cooling water of nuclear reactors, and is present in the contained water at the Fukushima Daiichi plant [44]. The comparatively short half-life of Cs-137 means that the generation of a suitable cement-based wasteform is more attainable than alternative waste conditioning approaches.

1.5 Disposal Pathways for Radioactive Waste

1.5.1 Geological Disposal

The scientific consensus, and UK Government policy, within the nuclear industry is that a deep mined, multi-barrier geological disposal facility (GDF), as shown in Figure 1-4, is likely to be the best solution for the long-term storage of nuclear waste [45]. The coupling of both natural and man-made barriers offers a comprehensive strategy to contain waste that could be active for potentially thousands of years.



Figure 1-4: An example of a proposed multi-barrier system for a GDF.

The white paper produced by the UK government in 2018 outlines the route that the UK is following to determine a suitable location for a future GDF [46]. As shown in Table 1-1, the UK's waste inventory, which includes all four categories of waste, stands at 4,850,000m³ as of April 2022, with a further 4 million m³ projected to be created in the lifetime of the nuclear fuel cycle. Regardless of the fact that the majority of this waste is classified as VLLW which will eventually be disposed of in municipal waste sites, the large quantities of waste that must be stored and disposed of safely means that strategies to contain and store this waste are becoming more important as time passes.

Figure 1-4 shows that the use of multiple 'barriers' are proposed to mitigate the risk of release of radioactive waste. Each barrier's primary objective is to prevent the movement of groundwater. The first barrier, which will be focused on in this PhD thesis, is a specially engineered wasteform that is specific to its contents. The design of this wasteform is intended to prevent the leaching of radioisotopes into groundwater for potentially thousands of years and will be discussed in more detail below. To provide further protection from groundwater, the wasteforms are entrapped within a durable container that resists corrosion. The buffer backfill provides further resistance between the radionuclide and any surrounding groundwater before the natural barrier of chosen geology puts a distance of between 200 and 1000m between the radioisotopes and civilisation.

1.5.2 Vitrification

One of the options for the specially engineered wasteform is the use of glass in a vitrification process. The vitrification of nuclear waste involves the encapsulation and/or immobilisation of liquid HLW, most commonly within a borosilicate or phosphate glass matrix [37, 47]. This is achieved by combining molten glass, at temperatures greater than 1050°C, with the liquid waste stream, resulting in the formation of a solid glass wasteform which incorporates the waste into both its macro- and microstructure [37, 47, 48]. The chemical composition of the glass forming additives can be altered to ensure that the properties of the resulting vitreous wasteform are acceptable, with the use of glass composite materials (GCM) for partitioned phases becoming increasingly popular [48, 49].

Vitrification allows for a high waste loading, typically 20-35% and can remain stable despite the intense radioactive environment [37].

However, vitrification requires a significant amount of energy input to reach the required operating temperatures [50]. These high temperatures are also the reason for the loss of volatile elements [51]. This generates secondary waste streams which must then be captured and disposed of, meaning that multiple wasteforms are required for what was once a singular waste stream. Moreover, the high temperatures are particularly detrimental to the retention of Cs within the waste stream, as this radioisotope is very volatile and is released into the environment in the off gases of the process [52, 53].

Further disadvantages of vitrification include the fracturing of the wasteform, undesirable separation of the numerous phases found within the glass and the low solubility of some elements within the resulting glass material [51, 54]. Moreover, with the closure of THORP in 2018, the production of highly active liquor (HAL) has ceased, and so the use of vitrification is significantly less than it once was.

1.5.3 Ceramics

The use of crystalline ceramics to contain HLW has shown promising signs of becoming a key component in nuclear waste management [55, 56]. The need for more diverse wasteforms arises from the cacophony of differing waste streams provided by the nuclear industry, be it volatile elements, which are problematic for vitrification, or legacy wastes from the early years of nuclear testing and power generation [37, 57]. Natural analogues of common ceramics have proven that they are capable of containing radioisotopes for millions of years, and the aim for ceramics in the nuclear industry is to reproduce the properties of these analogues in immobilising matrixes [37, 58]. Furthermore, new approaches to radioactive waste management aim to create materials that are stable within potential disposal environments and ceramics, such as syn-roc, meet this criteria [37, 59].

However, a significant disadvantage to ceramics when compared to glassy wasteforms is the inability to contain various different radionuclides; they are only capable of containing certain isotopes on very specific sites within their structure [37]. Furthermore, these materials are still very much in the research and development phase of their use case, although the importance of these materials has risen in the recent past, with the government announcing the disposal of plutonium (Pu) stockpiles which are expected to be immobilised through the use of ceramic wasteforms [60, 61].

1.5.4 Cementation

Cement has been used to encapsulate and immobilise both low-level and intermediate-level nuclear waste for many decades at Sellafield due to its widespread availability, minimal cost, uncomplicated processing, technical and practical understanding of the material, simple remote handling processes and ease of adaptability for various waste streams [62, 63].

Cement is capable of containing both solid and liquid waste streams, including complex geometries [64]. The form in which the cement is added to the waste is dependent on the waste stream; complex geometries may require infiltration by a liquid grout whereas liquid waste streams will benefit from the addition of a powdered cement which will be activated by the waste itself [64].

Most commonly, cementation is carried out using Portland cement (PC), or PC combined with various additives such as blast furnace slag or fly ash [38, 65]. However, many novel cementitious systems have been proposed with varying success including, but not limited to, geopolymers, phosphate cements and calcium sulphoaluminate cements [63, 64, 66-70].

The major disadvantage concerning cementation is the increase in volume observed after hydration [71]. This is prevalent when considering the eventual disposal of the wasteform in a GDF, where storage space is limited. Encapsulating reactive metals has also proven problematic for historical cements base around PC, however, some of the aforementioned novel cementitious systems, such as geopolymers, are capable of combatting this [71, 72].

1.6 Cementation of Radioactive Waste

1.6.1 Overview

The use of cement as an encapsulant for radioactive waste has been operational in the UK since the 1980's after numerous investigations into potential wasteform candidates [73, 74]. Its primary use has been for the encapsulation of ILW, mainly within a blend of PC and supplementary cementitious materials (SCMs) such as blast furnace slag (BFS) and pulverized fly ash (PFS) [64]. The wasteforms are tailored for differing waste streams by altering the ratio of SCM:PC and also the type of SCM that is used [28]. The addition of the SCMs are an effort to improve the chemical and thermal properties of the resultant grout, especially aimed at lowering the heat of hydration of the PC [75, 76].

To prevent nuclear waste from escaping from its confines into the natural environment, two methods have been utilised; the physical encapsulation and/or chemical immobilisation of the waste. Physical encapsulation involves the introduction of a physical barrier between the waste and the environment, whereas the chemical immobilisation of waste aims to integrate the radionuclides into the structure of the wasteform to provide a chemical bond preventing release [55]. The main objective for the use of cementitious wasteforms has historically been for the encapsulation of the waste. However, more recently, an interest in the chemical immobilisation of radionuclides within cements has arisen [67, 77]. Alternative cements, such as geopolymers, are being investigated to meet this objective and provide further options for a 'toolbox' of cementitious wasteforms [78, 79].

1.6.2 Portland Cement

1.6.2.1 Overview

Portland cement was first patented back in 1824 by Joseph Aspdin, who marketed it as an alternative to Portland stone from which he derived its name [80, 81]. It is produced from the high temperature processing (approximately 1450°C) of limestone and various clays in a rotary kiln which forms the cement clinker [82]. The PC is produced by adding gypsum to the clinker before grinding to a fine powder. The addition of gypsum is necessary to control the early stage setting and strength gain upon the addition of water [80].

The clinker itself is composed of four main phases, all of which react with water to form hydrate phases that precipitate out of solution to dominate the structure of the resulting grout [83]. These phases can be found in Table 1-2 along with their chemical notation (often referred to as ‘cement chemist notation’). The use of such notation is common practice in the cements industry, due to the simplification of the oxide phases [64, 83]. Also present in the clinker, in much smaller amounts, are impurities from the fuel used to heat the kiln along with some clinker sulphates (sodium, potassium and calcium) [84, 85].

Table 1-2: Phase names, formulae and compositions for the ideal Portland cement clinker [86].

Phase Name	Formula	Chemical Notation	Typical Content (%)
Alite	$3\text{CaO}\cdot\text{SiO}_2$	C_3S	50-65
Belite	$2\text{CaO}\cdot\text{SiO}_2$	C_2S	15-25
Aluminate	$3\text{CaO}\cdot\text{Al}_2\text{O}_3$	C_3A	5-15
Ferrite	$4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$	C_4AF	5-15

When water is mixed with PC (the clinker and added gypsum), the clinker phases experience a dissolution reaction, and the reaction water becomes supersaturated with the individual phases; This allows the clinker phases to precipitate from solution, reacting to form the solid hydrate phases that are commonly associated with PC grouts. The hydration of the cement is controlled by the kinetics of formation of these phases and the available space for them to precipitate into [87].

When mixing with water, the addition of the gypsum slows down the immediate reaction of the C_3A phase, which can lead to flash setting [88]. The C_3S phase is the most abundant phase in the clinker and, correspondingly, has the greatest effect on the early stage strength of the grout [83]. C_2S , however, does not contribute as much to the early stage strength due to its comparatively slower reaction rate, instead influencing later stage strength development. The reaction of the C_4AF phase is also thought to be slow,

especially in the presence of gypsum [87]. The reaction water that has not been chemically bound into the structure remains within the hydrate assemblage, and is available for later stage reactions, all of which require water. This water, termed the pore water, leads to lower permeability by the end of the curing process as the remaining ions are able to react to fill the pores within which the water resides [89]. The presence and availability of water are essential throughout the hydration process, and altering the humidity and water content during curing can have a significant effect on the final properties of the grout.

1.6.2.2 Hydration

PC is a hydraulic cement, meaning that it gains its strength and properties due to the reaction it has with water. Therefore, the hydration of cement is incredibly important when considering the characteristics that will be present after the hardening process. Four distinct reaction phases are responsible for the strength of the final cement product: the initial period, the induction period, the accelerating period and the decelerating period. These are presented by the isothermal calorimetry curve shown in Figure 1-5.

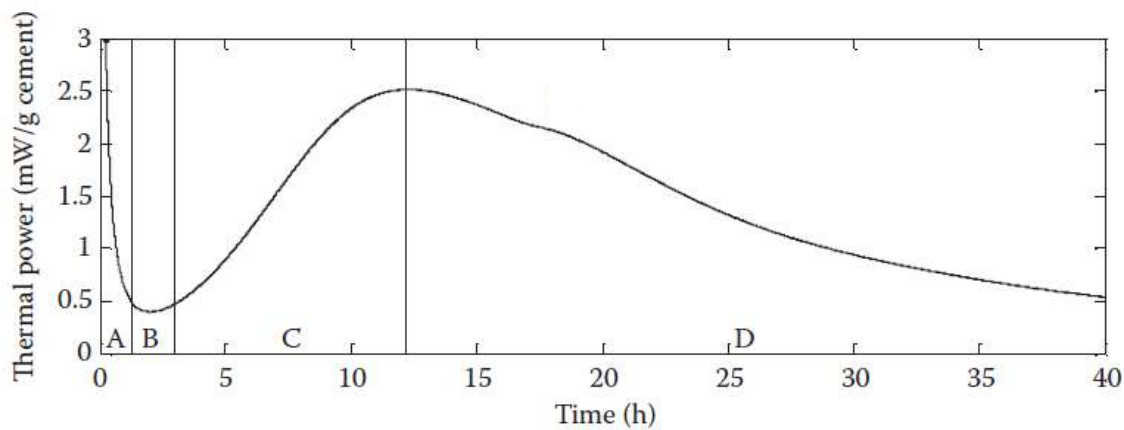


Figure 1-5: The reaction phases that accompany the hydration of PC as shown by isothermal calorimetry. The four phases displayed correspond to different points of the reaction: (A) initial period, (B) induction period, (C) accelerating period and (D) decelerating. Adapted from [90].

Upon the introduction of water to the ground cement powder, the gypsum and some of the clinker sulphates immediately dissolve into the water, creating a highly alkaline solution [91, 92]. The mixing of the powder with the water leads to the reaction of the aluminates phase, which forms an aluminate-rich gel. The gel reacts with the sulphates in solution to form early crystals of ettringite. The formation of ettringite changes once all of the sulphate in solution is depleted and, as the sulphur continues to be consumed, the ettringite breaks down into a more stable monosulphate phase [92]. This phase can then undergo a hydration reaction to form AFm phases which contain less calcium sulphate [80].

The initial reaction soon halts, giving rise to the dormant period in which the cement can be moulded and pressed into shape. By the end of this period, the cement will have become too stiff to be sculpted

or worked. The accelerating period marks the beginning of the reactions involving alite (Equation 1-1) and belite (Equation 1-2), the silica containing phases. It is these reactions which lead to the formation of calcium silicate hydrate (C-S-H) and calcium hydroxide (portlandite), the two hydration phases that form the bulk of the hydrated Portland cement assemblage.

Equation 1-1: Alite reaction.



Equation 1-2: Belite reaction.



The accelerating period is the longest lasting of the hydration phases where much of the reaction occurs. The strength of the cement continues to grow from this point onwards in its life cycle, with 70-80% hydration being reached after 28 days [65]. As the reaction proceeds, the reacting particles diminish in size, slowing the reaction due to a decrease in the available surface area and leading to the deceleration period, where the reaction slows as more of the reactants are consumed [65].

1.6.2.2.1 Calcium Silicate Hydrate

The C-S-H phase is the principal hydration product and strength giving phase in hydrated PC and composes over 60% by volume of the final hydrate assemblage [93]. The content of water, silicon and calcium in this phase is highly variable and is responsible for the final structure of the phase. This, accompanied by its disordered and poorly crystalline nature, make the structure of C-S-H hard to determine. However, natural analogues such as tobermorite and jennite have been used to describe the structure of C-S-H dependent on its calcium content. It is thought that for systems with a higher calcium content and, therefore, a greater Ca/Si ratio (typically >1.5), the structure may resemble that of a disordered jennite-like phase, although this remains unproven. Conversely, with low calcium systems, typically when SCMs are added to the blend, the resultant structure is thought to resemble that of tobermorite [94, 95].

The chemical environments of the silicate tetrahedra that form the basis of the C-S-H phase are often described using Q terminology. This terminology is exemplified in Figure 1-6 and is usually given in the form $\text{Q}^n(\text{mAl})$. In this form, Q notates the Si tetrahedra, n describes the number of other tetrahedra it is bonded to and m dictates how many of these tetrahedra are Al.

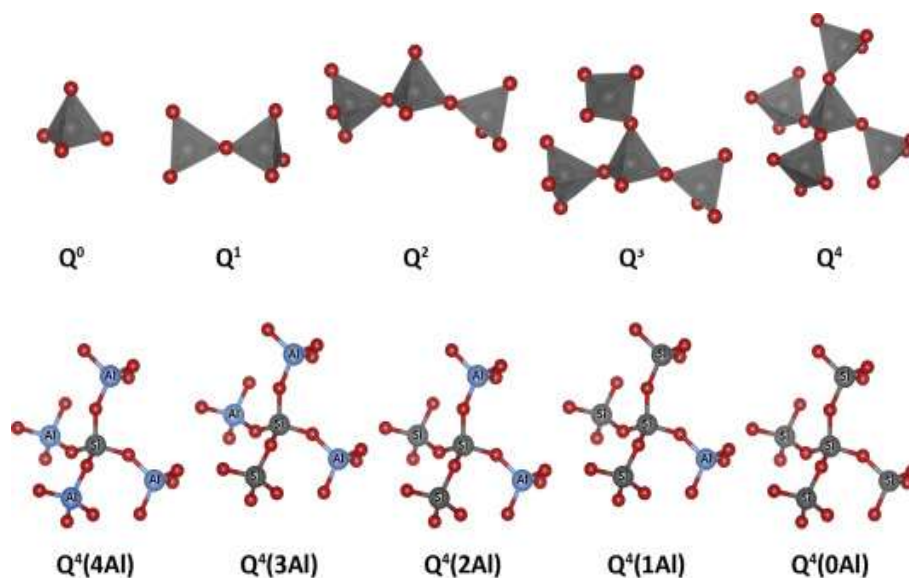


Figure 1-6: The Q terminology used to describe the chemical environments of silicate and aluminate tetrahedra. Adapted from [96].

The C-S-H structure is comprised of layers of silicate tetrahedra chains and calcium oxide as displayed in Figure 1-7. The Si tetrahedra form chains with a repeating kinked pattern, where every third tetrahedra is oriented such that it is not in contact with the CaO layer, but instead occupies the interlayer space. This produces the easily recognisable dreierketten unit associated with the phase, as is shown in Figure 1-7 [95]. The chain length, which determines the overall structure of the phase, is dictated by the Ca/Si ratio previously discussed; The lower the ratio, the longer the mean chain length [95]. The space between the layers of silicate chains allows for the penetration of the pore water, which leads to ion exchange and allows for charge balancing via alkali cations [96, 97].

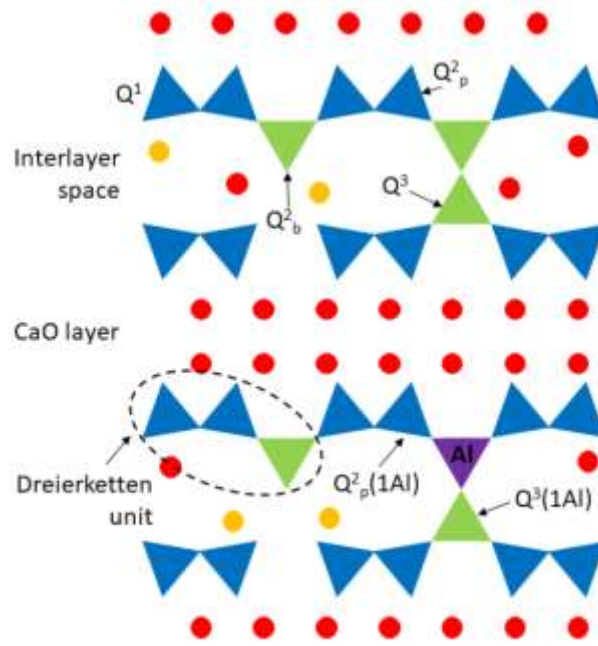


Figure 1-7: A schematic structure of C-S-H. The blue and green triangles represent the paired and bridging Si tetrahedra respectively, the purple triangle represents the possible substitution of Al tetrahedra, the red circles represent Ca and the yellow circles represent the charge balancing cation. Adapted from [98, 99].

1.6.2.2.2 Portlandite

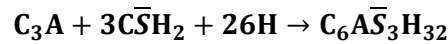
Portlandite is a crystalline calcium hydroxide ($\text{Ca}(\text{OH})_2$) formed from the reactions of alite and belite (Equation 1-1 and Equation 1-2 respectively) with a lattice structure that comprises of between 20 and 30% of the total mass of hydration products [80, 100]. This phase does not add significant strength to the cement and its primary role is to act as the primary buffer for the high pH of the pore water within Portland cement due to its high relative solubility in comparison to the other hydration products [83, 100]. The buffering of the pH protects reinforcing steel, among other materials, from corrosion due to carbonation [100, 101].

1.6.2.2.3 AFt and AFm Phases

The use of the terms AFt (Aluminate Ferrite tri (-sulphate, -hydroxide, etc.) hydrate) and AFm (Aluminate Ferrite mono (-sulphate, -hydroxide, etc.) hydrate) was first suggested by in 1961 to separate the phases with a higher sulphate content from those with lower sulphate content [102, 103]. Both of these phase types are calcium aluminates, where the crystal structures formed incorporate either a tri- (AFt) or mono- (AFm) substitution of anions [99].

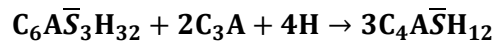
Ettringite is the most prominent, and first formed, of the AFt phases. It is produced during the hydration of the aluminate phase in the sulphate rich environment provided by the dissolution of gypsum (Equation 1-3) [102].

Equation 1-3: Ettringite formation..



Ettringite precipitates as rod-like crystals and expands to fill a large proportion of the space within the hydrate assemblage. However, as the sulphate concentration diminishes, the ettringite begins to break down into more stable AFm type phases, such as monosulphate (Equation 1-4) [80].

Equation 1-4: The breakdown of ettringite.



Although the phases are designated as ferrite phases, the formation of iron-containing ettringite and other iron-containing phases of this type are not commonly observed in cement systems due to their relatively slow formation kinetics when compared to the aluminium-containing phases [104].

Compounds of the AFm type are structurally similar to hydrocalumite, which is similar to the layered lattice of portlandite [105]. The difference in AFm structures is that every third divalent Ca atom is exchanged for a trivalent cation, which is more than often Al but can also be Fe. The introduction of this extra positive charge leads to a charge imbalance in the structure, resulting in the introduction of anions into the interlayer [99]. The identity of this charge balancing anion is primarily decided by the composition of the cement, but foreign additions to the cement can alter the service environment which, in turn, can alter the anions present [105, 106]. The most common AFm phases identified in hydrated PC are monocarboaluminate, hemicarboaluminate and monosulfoaluminate.

1.6.2.3 Encapsulating Sr-90 and Cs-137

The interactions of strontium and caesium with the phase assemblage of hydrated PC has been heavily researched [107-109]. PC mainly acts as an encapsulant to the wastes, physically trapping the radionuclides within the binder, allowing the C-S-H phase to continue to react and form in the space surrounding them. However, the chemical environment and formulation of the PC paste does allow for limited immobilisation routes that include, but are not limited to, chemisorption, atomic substitution and precipitation [110].

The majority of the studies involving specific phases of the cement paste have focused heavily on the reaction of radionuclides with the C-S-H phase [111, 112]. Strontium is capable of substituting the calcium cations that are present in the C-S-H phase, but it is also capable of substituting Ca in other hydrate phases [113].

The high pH of the pore solution provides a driver for the precipitation of insoluble salts of Sr. The pH is controlled by the portlandite phase, meaning that the control and inclusion of the portlandite phase is important for radionuclide retention [99]. The caesium cations prefer to remain in the pore solution of

the cement due to its high solubility [109]. This results in the cations not being sufficiently chemically bound within the structure which leads to high leach rates and an unsatisfactory level of containment [99]. Reactive metals, such as Cs, are of particular concern within PC based grouts due to their reactivity with water. The resultant corrosion of the metals leads to the production of hydrogen gas [79].

Moreover, the inclusion of HLW such as Cs-137 and Sr-90 can potentially lead to the radiolysis of the pore water of the PC. The production of hydrogen gas can lead to cracking and breakdown of the hydrate assemblage, reducing its durability and, moreover, its ability to contain the wasteform [79]. Further to this, the beta decay that is associated with the decay of the two radionuclides is capable of causing atomic displacements, weakening the structure and changing local chemical environments [63].

The use of PC in the nuclear industry is heavily regulated; standardised formulations cannot be altered due to the nature of the work. The current standard involves blending PC with blast furnace slag (BFS), a SCM [114]. However, supplies of BFS within the UK are fast diminishing resulting in the need for importing [115]. Furthermore, changes in upstream manufacturing techniques have resulted in the clinker powders being much finer than when the standard was originally written, resulting in faster setting times which can cause issues, especially for irregular waste geometries.

The release of carbon dioxide (CO₂) from the production of PC is a contentious issue, especially when considering the current stigma round climate change. The manufacture of PC significantly contributes to the CO₂ emissions of the cement and concrete industry which, as a whole, amounts to 8% of the global emission of carbon dioxide [116].

1.6.3 Geopolymer Cement

1.6.3.1 Overview

The use of alkali-activated and geopolymer cement systems dates back to 1895, when a patent was awarded to J. Whiting for ‘cement based manufacturing’ [117]. The suggestion that this material would be suitable for use as a nuclear wasteform was first made in the 1980’s [118-120]. Geopolymer cements as they are now known, are a subset of the family of cements known as alkali-activated materials (AAM) as shown by Figure 1-8.

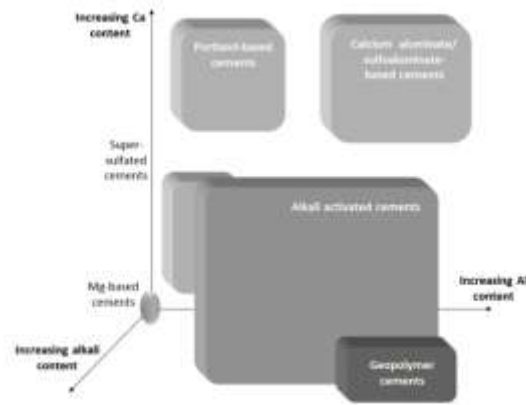


Figure 1-8: Traditional and non-traditional cements. Adapted from [121].

The term alkali-activated material covers a vast number of binder systems originating from the reaction of an alkali metal source with a silicate activator [121]. However, a geopolymer is a smaller subset within this term that describes binder systems with a chemical composition that is low in calcium and high in aluminium and alkali, leading to the formation of a highly inter-connected aluminosilicate binding phase. The low calcium content of geopolymer cements leads to the formation of a sodium or potassium, two of the more common alkali metals used, aluminium silicate hydrate ((N,K)-A-S-H) ((Na,K₂O)-Al₂O₃-SiO₂-H₂O) phase, which is the main binding phase of the geopolymer [118, 122]. The resulting gel is an amorphous, highly cross-linked, structurally disordered material [123].

1.6.3.2 Formation

Geopolymers cements are formed via a three-step reaction of an aluminosilicate precursor, usually naturally occurring clays such as metakaolin or industrial by-products such as fly ash, with a high pH alkali activating solution as shown in Figure 1-9.

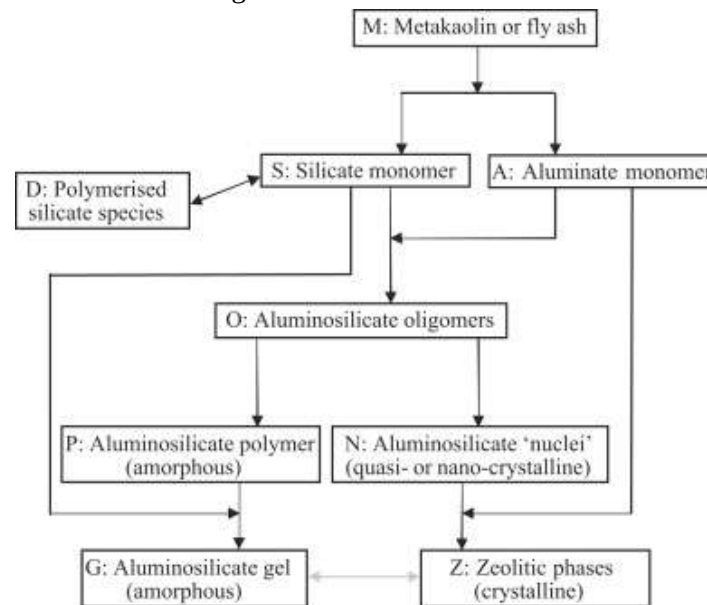


Figure 1-9: The reaction sequence leading to the formation of geopolymers, as proposed by Provis and van Deventer [124].

This results in the dissolution of the precursor, releasing the aluminate and silicate monomers which then react under the highly alkaline conditions to form polymeric Si-O-Al-O bonds, phase I as shown in Figure 1-10 [125]. It should be noted that the initials with this figure correlate to the phases displayed in Figure 1-9 above (i.e. S is equivalent to ‘Silicate monomer’). The separate oligomers undergo a further reaction to form the gel phase of the geopolymer, phase II. Over time, this phase will move to become more stable through transformation reactions, leading to the formation of pseudo-zeolitic, somewhat crystalline, aluminosilicate phases which is shown as phase III [126]. This reaction pathway follows Ostwald’s rule, which states that the least stable form of a polymorph will crystallise first, before the structure transforms into more stable phases [127].

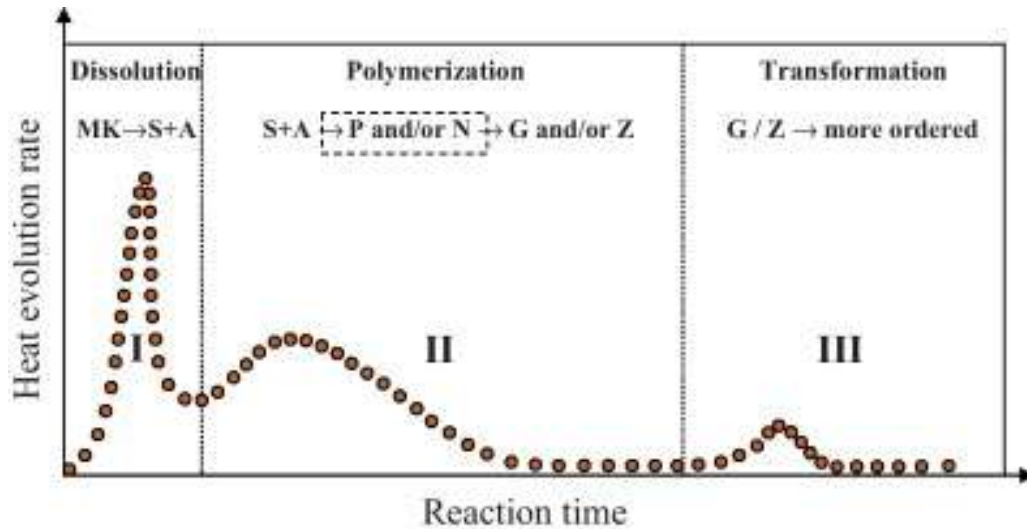


Figure 1-10: A schematic of the reaction process of a metakaolin based geopolymer activated by sodium hydroxide, where MK represents metakaolin, S represents silicate monomers, A represents aluminate monomers, P represents an amorphous aluminosilicate polymer, N represents a nano-crystalline aluminosilicate ‘nuclei’, G represents the aluminosilicate gel and Z represents crystalline zeolitic phases. Adapted from [128].

The fundamental binder structure in geopolymers is a structurally disordered, highly cross-linked aluminosilicate gel which, for potassium activated geopolymers, is the K-A-S-H gel [123]. Within this structure, the Si and Al exist in the tetrahedral co-ordination, and the chemical environments within which these tetrahedra lie is described by the Q terminology that is outlined in Section 1.6.2.2.1. The dissolution of the initial aluminosilicate precursor releases free Si and Al tetrahedra (SiO_4 and AlO_4^- respectively) through the breaking of Si-O-Si and Si-O-Al bonds within the original structure. Through the reordering of these components, chains of linked tetrahedra are able to precipitate into a three-dimensional, cross-linked structure where the Si and Al components are linked by bridging oxygen atoms [129]. The number of bonded Al tetrahedra, denoted as the m in the $\text{Q}^n(\text{mAl})$ notation, is dependent on the activator, with a silicate activator favouring low m values and a hydroxide activator favouring higher m values [130, 131]. The net negative charge of the structure, caused by the AlO_4^-

tetrahedra, allows for the charge balancing of cations, K^+ for potassium silicate-activated geopolymers as can be seen in Figure 1-11.

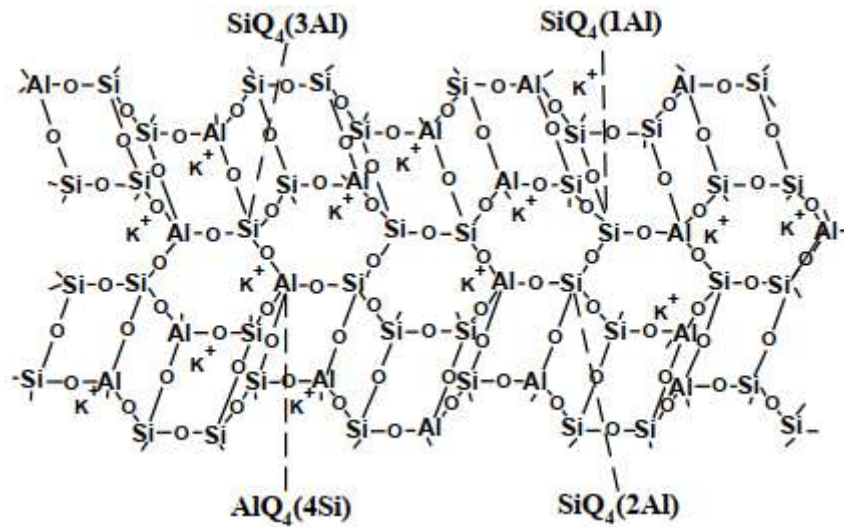


Figure 1-11: The proposed structure of a potassium activated geopolymer [132].

Although the structure is pseudo-zeolitic, it does not possess a regular and highly crystallised structure in the way that a zeolite does. Instead it is X-ray amorphous, with suggestions that it shows a chemical likeness to zeolites but becoming disordered on a scale no greater than several angstroms ($\text{\AA}$) [123, 133]. This is confirmed on length scales of up to 5-8 $\text{\AA}$ [134]. The use of a silicate activator over a hydroxide activator yields a much higher compressive strength and elastic modulus and a lower porosity in silicate-activated binder systems is achieved when the binder modulus (M_2O/Al_2O_3), where M represents the alkali within the activator, is between 1 and 2 [135].

1.6.3.2.1 Dissolution

The dissolution of the aluminosilicate precursor occurs via alkaline hydrolysis (the consumption of water) to release aluminate (AlO_4^-) and silicate (SiO_4) species into solution. As presented by Figure 1-9, this is likely to be in the form of monomeric species. The dissolution reaction is rapid at the high pH that is provided by the alkaline solution, which leads to the incorporation of the monomers into the aqueous phase and the production of a supersaturated aluminosilicate solution containing a complex mixture of silicate, aluminate and aluminosilicate [129, 136].

1.6.3.2.2 Polymerisation

The high concentration of the monomers in the aqueous phase results in the formation of a gel phase as the aluminosilicate oligomers form large networks [129]. The first phase of polymerisation involves a less stable Al-rich phase which evolves into the Si-rich phase within which the Si tetrahedra occupy differing chemical environments as described by $Q^n(mAl)$. Most commonly, the Si tetrahedra are in the form $Q^4(mAl)$, lending to the three-dimensional, highly cross-linked nature of the geopolymer gel

structure. The predominance of this chemical environment can be altered through the use of different activators and curing conditions [136].

The oligomers will immediately polymerise into one of two phases: small geopolymeric fragments or proto-zeolitic nuclei as shown by Figure 1-10. These two phases are incompletely cross-linked and thermodynamically metastable and will proceed to assemble into aluminosilicate inorganic polymer gels and partially crystallised phases [128].

Condensation reactions are responsible for the polymerisation of the gel phase. These reactions release the water that initially lead to the hydration and dissolution of the phases within the precursor. This water is now free to reside within the complex pore network of the gel assemblage, where the dominating alkaline presence leads to a high pH [123, 129].

1.6.3.2.3 Transformation

The reordering of the amorphous phase into more stable, final amorphous state occurs later in the polymerisation process [128, 137]. This transformation does not lead to an increase in the crystallinity of the system. It is possible that the aluminosilicate geopolymer gels, which are disordered, react to form proto-zeolitic structures which are too small to be detected via X-ray diffraction (XRD) spectroscopy [128].

1.6.3.3 Encapsulating Sr-90 and Cs-137

The ability of geopolymer cements to contain Sr and Cs ions has been studied extensively in the research [67, 138-140]. This is likely due to the chemical similarities between the common cations in the alkaline activators (K^+ and Na^+) and the alkaline earth Sr^{2+} ions and alkaline Cs^+ ions. The cations act to charge balance the negative charge from tetrahedral AlO_4^- in the geopolymer gel, and the chemical similarity allows the Sr^{2+} and Cs^+ cations to substitute into the structure, leading to the favoured chemical immobilisation; this has been reported in the literature [67, 141]. It is shown that the inclusion of Sr^{2+} and Cs^+ cations does not affect the integrity of the gel network and physicochemical properties that are dictated primarily by the local gel structure are likely to be unaffected. Kuenzel et al. report that the high pH of the system can lead to precipitation of Sr when the waste loading is too high, in the form of carbonate and hydroxide phases [142].

Walkley et al. showed that geopolymer gels activated by both sodium and potassium are capable of incorporating Sr into the structure [67]. In this work, the Sr is added at very low concentrations of an Sr/Al ratio of 0.00025 and is shown to displace some of the alkali cations used in the activating solution from the charge balancing sites, and this, in turn, leads to a reduction in the Si/Al ratio of the material. Moreover, when the materials were cured at a temperature of 80°C, the formation of a crystalline Sr containing phase is observed which has good implications for the immobilisation of the Sr within the geopolymer matrix.

Research regarding the encapsulation of ion exchange media contaminated with Sr and Cs has been carried out. Kuenzel et al. [142] found that the high pH of the alkaline activating solution causes the media (clinoptilolite, which is predominantly used in in the UK and in Kuenzel's work) to break down and release the Sr and Cs ions into solution. Interestingly, they also found that the Cs is released into the geopolymer solution prior to any dissolution of the clinoptilolite, suggesting that it may have only a weak structural bond to the Cs. It was posed that the Cs and Sr are incorporated into the geopolymer gel in place of the Na or K as the charge balancing cation. Furthermore, the leach rate of this Cs from the potassium-activated geopolymer itself was found to be higher than from a corresponding sodium-activated geopolymer. This has also been found in other studies, suggesting that sodium-based geopolymers are better at incorporating the Cs into the aluminosilicate gel structure [143]. Geopolymer cements have a more complex pore network in comparison to PC, leading to a reduction in the permeability and, consequently, the leach rate [77].

The rate of leaching of Sr and Cs ions in geopolymer cement systems has been shown to be lower than the corresponding leach rates of these ions in hydrated PC systems [144, 145]. This is promising when considering the long-term durability of the wasteform and its ability to contain the radionuclides for the required period of time. However, the leach rate of Sr is lower than that of Cs in potassium-activated geopolymer systems.

Minimal research regarding the individual effect of varying common salts of Cs and Sr can be found in the literature, moreover, there is very little literature that focuses on the effect on the chemical environment of the geopolymer when incorporating ion exchange media caused by these salts. One of the notable exceptions to this is published by Provis et al. [146]. This research outlines the effect of up to 5% by weight of nitrate, sulphate and hydroxide salts of Cs and Sr on sodium silicate-activated geopolymer systems. It was shown that strontium nitrate at high concentrations interferes significantly with the pore network development and strontium sulphate is converted gradually to carbonate salts by atmospheric carbonation. Caesium nitrate and sulphate have very similar effects, slightly retarding gel formation before significantly disrupting the gel structure. This disruption is posed to occur due to the presence of the anions of these salts in the pore water of the geopolymer sample; the large, negatively charged anions repel the negatively charged aluminosilicate gel structure which prevents the reactions required to close the pore structure over time. Despite the dissolution of the salts, there was only one sample that displayed evidence of any crystalline compounds, that being NaNO_3 in the system containing $(\text{SrNO}_3)_2$. Caesium hydroxide accelerates gel formation which leads to flash setting. Despite this, the soluble salts of Cs in this work appeared to lead to a good level of containment for the Cs, which agrees with the work by Kuenzel et al. discussed above suggesting that sodium-based systems show a greater ability to retain the Cs [142]. However, there is no research regarding the effect of the salts of either of these elements on potassium-activated geopolymer systems.

The carbon emissions of geopolymers are regarded to be far lower than those brought about by the production of PC. This value has been found to be up to 97% lower, however this depends heavily on numerous factors related to the production process, including transportation requirements and raw material composition [147].

The shrinkage of geopolymers, like other alkali-activated materials, is generally higher than that observed in PC [148]. This can increase the likelihood of cracking, which may decrease the durability of the wasteform, especially if the main mechanism of radionuclide retention is via physical encapsulation.

1.7 Analytical Approaches to Understand Cementitious Wasteforms

1.7.1 Reaction and Setting

1.7.1.1 Isothermal Conduction Calorimetry

1.7.1.1.1 Physical Basis

Isothermal conduction calorimetry (ICC) is used to monitor heat changes during chemical reactions such as phase changes, dissolution and hydration [149]. The heat produced by these reactions is recorded and then compared to an analogous reference sample with a similar heat capacity that is running in parallel [149].

1.7.1.1.2 Relevance to Cements

The polymerisation reaction of geopolymers (or hydration reaction in PC) is central to the formation of the material. This reaction is highly exothermic and can be tracked using the heat that is produced during the materials evolution [128]. Changes to the heat evolution upon the addition of further reactants, such as radionuclides, can be recorded. This data can be used to determine changes to the setting time of the geopolymer, and identify possible retardants or accelerants to the reaction. Furthermore, the initial dissolution of the metakaolin precursor into the aqueous activating solution is a pivotal event in the reaction process. Therefore, identifying changes to this reaction induced by the introduction of further reactants, i.e. radionuclides, will provide key information on the interactions between the radionuclide and the geopolymer reactants.

The heat generation for geopolymer formation is expected to happen at 3 general points of the geopolymerisation process, as outlined by Zhang et al. [128]. These 3 points correspond to the dissolution of the solid precursor, the polycondensation reaction of the aluminosilicate framework and the eventual transformation of the framework into a more ordered and thermodynamically stable configuration. These reactions are discussed in more detail by Duxson et al. in their state of the art report, a figure from which is shown in Figure 1-12 [129].

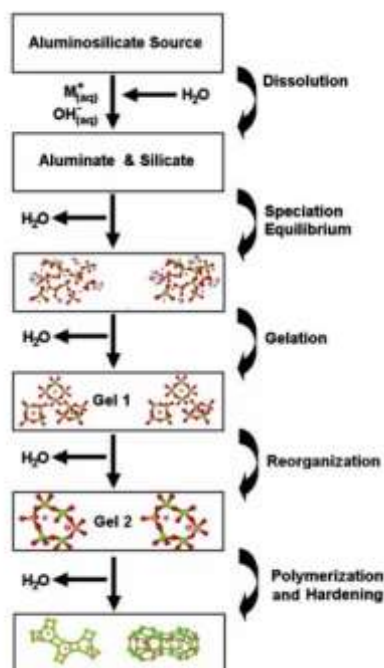


Figure 1-12: The reaction sequence leading to the formation of a solid geopolymer, as proposed by Duxson et al. [129].

The dissolution step is responsible for a large release of heat, as the high pH activating solution leads to the release of aluminate and silicate monomers through alkaline hydrolysis. This is followed by a series of reactions between these monomers that happen almost simultaneously, which lead to the formation of the solid geopolymer gel [150]. The third step discussed by Zhang et al. is not shown in Figure 1-12, and there is little evidence in literature that the reorganisation of the geopolymer gel does lead to a recorded heat release [128]. Regardless, this is likely to happen at time points beyond the scope of this work and so will not be considered here.

1.7.1.2 Diffuse Reflectance Infrared Fourier Transform Spectroscopy

1.7.1.2.1 Physical Basis

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) allows for the *in-situ* analysis of the structural formation of the geopolymer gel. This technique is a specific application of Fourier transform infrared (FTIR) spectroscopy which is discussed in Section 1.7.2.1, aimed mainly at the use of analysing the surface chemistry of solid samples. However, the use of DRIFTS does allow for the penetration of the bulk sample and does not rely solely on the information gleaned from the surface [151]. Much like FTIR, DRIFTS works by generating a beam of infrared radiation and firing this at the sample via a number of ellipsoidal mirrors. The diffuse reflection caused by the surface of the sample is guided towards the detector by further ellipsoidal mirrors, and in turn, a Fourier transform is applied to the signal collected which creates a DRIFTS spectrum. The infrared radiation that is absorbed by the sample is characteristic of the bonds that are present, and can be matched to known ranges for the bonds

that are expected within the sample. The optical diagram of the equipment used in this thesis is shown in Figure 1-13 for clarity.

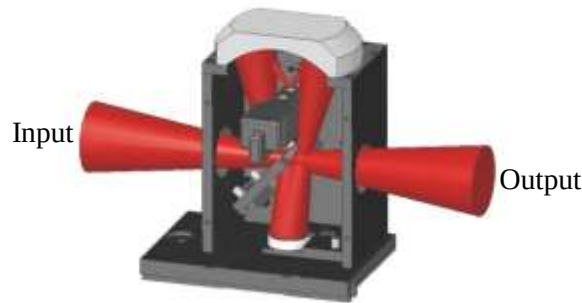


Figure 1-13: The optical diagram for the EasiDiff DRIFTS apparatus [152].

1.7.1.2.2 Relevance to Cements

DRIFTS has rarely been used to monitor the reaction progression of a cementitious material. In fact, the use of DRIFTS on cementitious materials as a whole is very novel, with only a small amount of research carried out using this technique. Hughes et al. were the first to use this technique on cements in 1995, carrying out a quantitative analysis on the phases found within a Portland cement sample [151]. Past this, diffuse reflectance IR spectroscopy has been shown to be effective when a quick and reliable measurement is needed, with Caggiani et al. suggesting that it could be an appropriate tool for the testing of geopolymer cements in an *in-situ* situation at the site of its application [153]. The use of DRIFTS is appropriate for monitoring the initial reaction of the geopolymer cement in this respect due to the ability to take multiple measurements within a short space of time on a constantly evolving sample [151, 154].

1.7.1.3 Zeta Potential

1.7.1.3.1 Physical Basis

The measurement of the zeta potential of a surface is reliant upon the electric double layer (EDL) that is formed around a particle with a charged surface [155]. As the name suggests, the EDL is comprised of two layers. For a negatively charged surface: the first layer of the EDL will be the layer of positively charged particles that are electrostatically attracted to the negative surface, termed the Stern layer. The second layer will be the negatively charged particles that are now drawn to this region of positive charge, and these negatively charged particles draw in more positively charged particles and so on. This layer is called the diffuse layer [156]. A schematic depicting this scenario can be seen in Figure 1-14 [157].

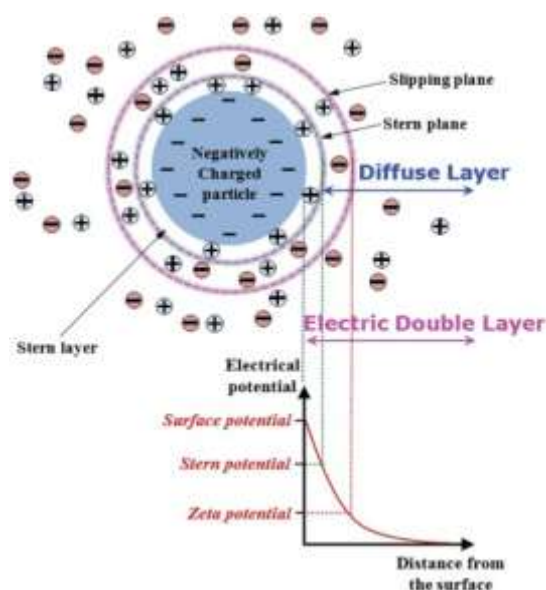


Figure 1-14: A schematic depicting the effect of a negatively charged particle on the surrounding solution. Adapted from Park and Seo [157].

From Figure 1-14, both the Stern layer and the diffuse layer can be seen. Mathematically, the diffuse layer can continue to infinity, although this is not seen experimentally [156]. Due to this, the introduction of the slipping plane gives a point at which the ions and particles within the bulk solution are no longer associated with the charged particle. Therefore, as shown by Figure 1-14, it is at this point that we can measure the zeta potential of the particle; as the particle and its associated EDL travel through the material due to the induced electrical charge of the apparatus (electrophoresis), the particle moves charged particles in the bulk solution, forming a voltage which can be measured [158]. It is not possible to measure the actual surface charge of the source particle, and so the use of zeta potential allows for the actual surface charge to be visualised.

1.7.1.3.2 Relevance to Cements

The surface charge of the particles within the reaction mixture will determine their interactions within the aqueous phase. For metakaolin based geopolymer materials, the surface charge of the metakaolin particles are very negative at the high pH of the system [159]. This negative charge leads to the electrostatic repulsion between the fine particles, preventing agglomeration which, in turn, maintains fluidity and also promotes dissolution, allowing for a more complete reaction. When further reactants are added to the mixture, such as radionuclides or solvent exchange media, the surface charge of these particles, or ions if reactant dissolves, may lead to an interaction between the additives and the metakaolin. This interaction could lead to multiple changes to the way in which the system reacts: the reaction could lead to a change to the rate of dissolution of the metakaolin, the reaction could change the fluidity of the mixture and the reaction could lead to a heterogeneous mixture. All of these possibilities, if not monitored, will lead to a change in the final material formed.

1.7.2 Microstructural and Phase Evolution

1.7.2.1 *Fourier Transform Infrared Spectroscopy*

1.7.2.1.1 Physical Basis

Fourier transform infrared (FTIR) spectroscopy operates by generating an infrared beam of multiple wavelengths and passing this through a sample. When passed through the sample, certain wavelengths of the infrared beam are absorbed whilst the remaining wavelengths continue to the detector. The signal detected is processed using a Fourier transform and the absorbed wavelengths are extracted to provide an FTIR spectrum. This spectrum plots the transmittance (%), which describes how much infrared radiation is transmitted by the sample, or the absorbance (%), the fraction of the infrared radiation which is absorbed, as a function of wavenumber [160].

Within each sample, each bonding environment absorbs radiation at a specific, characteristic wavelength. Therefore, the FTIR spectrum generated can be used to identify these bonding environments and therefore the resulting molecular structure of the sample [160].

1.7.2.1.2 Relevance to Cements

Geopolymer cements have a structure that is amorphous, highly cross-linked and structurally disordered. Therefore, techniques that identify crystalline phases, such as XRD, are unable to provide insight into the composition of the gel network. FTIR does not require long range order within a sample, and so can be used to identify individual bond environments in amorphous materials, which is ideal for cementitious materials [160].

1.7.2.2 *X-ray Diffraction*

1.7.2.2.1 Physical Basis

X-ray diffraction (XRD) is a technique that allows for crystalline phases within a sample to be identified due to the diffraction of incident X-rays by components of the crystal structure [161]. This occurs in accordance with Braggs law (eq.1).

Equation 1-5: Bragg's Law

$$n\lambda = 2d \sin\theta$$

In this equation, n represents an integer, λ represents the wavelength of the X-ray, d represents the spacing between the crystallographic planes and θ represents the incident angle of the original X-ray. This can be seen visually in Figure 1-15.

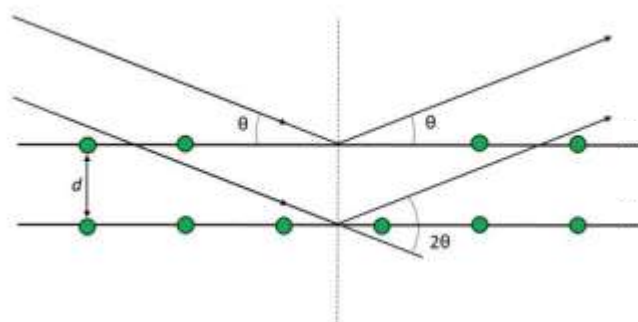


Figure 1-15: The derivation of Bragg's Law. Adapted from Kearney [162].

The constructive interference that occurs when the X-rays are in phase leads to the diffraction patterns that are used for the identification of crystalline phases within a sample. To do this, the measured diffraction patterns are compared to databases that contain a plethora of known diffraction patterns for crystalline phases [163].

1.7.2.2.2 Relevance to Cements

Geopolymer cements have a completely X-ray amorphous structure, but the use of XRD is possible to determine the formation of a geopolymer gel network [67, 164]. Geopolymers exhibit a broad diffuse scattering peak between approximately 20° and 40° 2θ , and it is the broad nature of this peak that suggests that the reaction product is crystallographically disordered [164, 165]. Furthermore, crystalline phases within the geopolymer gel can be distinguished by XRD; in many cases, these crystalline phases will be impurities within the solid precursor such as quartz or anatase, but crystalline reaction products, such as zeolitic phases and by-products can also be seen [166-168]. The presence of zeolitic phases are important when considering geopolymers for the application of nuclear waste disposal, providing a more secure binding site for the radionuclides. Likewise, the identification of by-products is important when investigating the effect of adding different radionuclides to the reaction mixture.

1.7.2.3 Solid-State Magic Angle Spinning Nuclear Magnetic Resonance

1.7.2.3.1 Physical Basis

Solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy provides a method of investigating the local chemical environments surrounding the nuclei of the chosen element. This technique is only capable of probing specific nuclei, that being those that have intrinsic magnetic moment brought about by an odd number of protons and neutrons within the nucleus, such as ^{29}Si , ^{27}Al and ^{39}K . In order to generate a meaningful spectrum, the sample containing the nuclei being investigated is placed within a strong magnetic field before being applied with a pulse of radiofrequency radiation which disturbs the plane of the spin of the nucleus. This alteration leads to the transition of the spin state to higher energy levels and, upon its relaxation back to its base spin state, it releases an electromagnetic signal of characteristic frequency. A Fourier transform is applied to this signal to

convert it to a NMR spectrum which displays the results in terms of either an observed (for nuclei with spin $> \frac{1}{2}$) or isotropic (for nuclei with spin $= \frac{1}{2}$) chemical shift (δ_{obs} or δ_{iso} respectively) [96, 169, 170].

In order to endure that the received spectrum is of the highest quality, notably with a high signal/noise ratio, magic angle spinning is employed. This involves spinning the sample around a fixed axis relative to the magnetic field at an angle of 54.74° , which is known as the magic angle [96]. This reduces the impact of dipolar interactions, anisotropy of the chemical shielding of the nuclei and quadripolar interactions on the line broadening of the spectrum [171].

1.7.2.3.2 Relevance to Cements

The use of MAS NMR can be used to probe the chemical environments of key components of the K-A-S-H gel of the geopolymer; This technique can probe the local structure surrounding silicon, aluminium and potassium [96, 172, 173]. Therefore, any changes to the local structure that may occur due to the incorporation of the added cations, such as Sr^{2+} or Cs^+ , can be observed. Moreover, the local environments of both strontium and caesium can be probed, illuminating any changes to the expected environment of these elements within the sample, which would be expected if they are to be immobilised within the geopolymer matrix [174]. Despite this possibility, the use of ^{87}Sr NMR has yet to be used to probe geopolymer samples in the literature and ^{133}Cs NMR is used very rarely.

Deconvolution of the ^{29}Si NMR is used to determine and quantify the level of cross-linking that occurs within the K-A-S-H gel, giving a numerical value for the number of $\text{Q}^4(4\text{Al})$ and $\text{Q}^4(3\text{Al})$ sites that comprise of the vast majority of silicon sites within the geopolymer [67].

1.7.2.4 *Electron Probe Microanalysis*

1.7.2.4.1 Physical Basis

Electron probe microanalysis (EPMA) allows for the spatial arrangement of the elements within a sample to be visualised. This is achieved by bombarding the sample using an accelerated and focused electron beam of a high enough energy to liberate X-rays from the sample. These X-rays are produced through the ejection of inner shell electrons from their orbit due to the inelastic collision between the ejected electron and the incident electron. This vacancy is filled by an electron from a higher energy shell, and the change in energy states here leads to the ejection of an X-ray of characteristic frequencies for each individual element [175]. The detection of these X-rays allows detailed chemical maps to be created of the samples surface [176].

1.7.2.4.2 Relevance to Cements

This technique has been previously used sparingly on cement based systems, most notably to measure the chloride ingress into a cement sample [177, 178]. The use of this technique on geopolymer samples is even more scarce, and have been carried out on fly ash based systems [179, 180]. This technique allows for individual phases within the geopolymer to be visually identified. Furthermore, it allows for

the distribution of these phases, including the K-A-S-H gel, to be investigated, determining whether the addition of further reactants disrupts the formation of this phase. Impurities within the gel can also be identified, be it anatase or quartz from the metakaolin, or further reaction products due to the addition of radionuclides.

1.7.2.5 *X-ray Absorption Spectroscopy*

1.7.2.5.1 Physical Basis

X-ray absorption spectroscopy (XAS) targets a particular element within the sample and elucidates information regarding the structural environment of the element in question. To achieve this, the sample is bombarded with X-rays, and, when these X-rays are high enough, a core electron is ejected from the atom through the photoelectric effect, whereby the X-ray collides with the electron and transfers its energy. At the point at which the energy of the incident X-ray scans across the binding energy, which is characteristic for each electron in each element, of one of the core electrons, the level of absorption sharply increases dramatically, and this is the phenomena that generates the absorption edge [181]. To examine the artefacts of the edge that are within the immediate vicinity of the edge, X-ray absorption near edge structure (XANES) is used, and for artefacts well above the energy of the absorption edge, extended X-ray absorption fine structure (EXAFS) is deployed [181].

1.7.2.5.2 Relevance to Cements

XAS is useful for geopolymers due to their X-ray amorphous structure; the use of XRD does not provide useful information on the actual structural layout of the K-A-S-H gel due to its amorphous nature, but XAS does not require an ordered crystalline structure to provide useful information [181]. Moreover, this technique allows for the key nanostructural information regarding bound radionuclides, such as Sr, to be investigated [182, 183]. This is key when determining the processes in which the radionuclide is bound to the structure, be it through chemical immobilisation or physical encapsulation.

1.8 *Aims and Objectives*

A review of the literature has shown that the disposal of Sr and Cs contaminated waste streams is suboptimal in the current state-of-the-art cementitious material of choice in the UK nuclear industry, PC. Geopolymer cements have been introduced as a viable alternative, showing promise for incorporating positively charged cations into their aluminosilicate gel framework structure. However, further research into these materials needs to be undertaken to justify their use case for this application. The research shows that geopolymer cements, based upon either metakaolin or fly ash and activated by a sodium-based alkali activator, have been extensively researched to this end. However, there is minimal research for geopolymers activated with potassium-based activators within this application, despite it being shown that the rheological properties of the material are more desirable for waste encapsulation applications when using a potassium-based activator compared to a sodium-based activator.

Moreover, much of the research into the incorporation of Sr and Cs waste streams has been carried out using only alkali activators based on hydroxide (OH^-) salts. Whilst this is an important baseline, it is unlikely that waste streams from legacy waste pools and nuclear disaster sites are simply going to contain the Sr and Cs in one species, considering their mobility and reactivity. Therefore, there is a distinct need for research into the incorporation of other salts of Sr and Cs, and the impact of the respective anions on the resultant reaction process and structure of the geopolymer.

Due to this, the key research gaps that are aimed to be filled in this thesis are as follows:

- Further research into potassium-activated geopolymer cements.
- A study into the effect of incorporating Sr and Cs compounds into geopolymer cements, with a key focus on understanding the interactions of both the Sr and Cs cations, and the anions in these compounds have with the geopolymer reaction mixture.

The over-arching research question that aims to be answered within this thesis is:

- Are the reaction kinetics and mechanisms of the formation of metakaolin-based, potassium silicate-activated geopolymer cements impacted due to the inclusion of Sr and Cs salts within the reaction mixture?

In order to answer this question, specific objectives must be met:

- Characterisation of the control geopolymer sample without the addition of any Sr or Cs over the first 28 days of reaction.
- Determination of the interactions of common Sr and Cs salts (the anions of which being NO_3^- , CO_3^{2-} , OH^- and SO_4^{2-}) with the raw precursor materials of the geopolymer.
- An analysis of whether these salt-precursor interactions impact the kinetics of the geopolymer formation.
- Determination of the local environment of the Sr and Cs in the geopolymer, to determine whether these cations are chemically bound within the K-A-S-H gel formed.
- Determination of the fate of the negatively charged anions of the salts that are incorporated into the geopolymer.

The decision to investigate the chosen anions stems from the conditions within which the radionuclides are likely to be found after nuclear disasters such as that seen in Fukushima Daiichi. Firstly, hydroxide salts are likely due to the mobility of Sr and Cs in aqueous solution. The use of strontium sulphate is due to this being the most common form of strontium found in nature. The investigation of both strontium and caesium carbonate, which will form when the aqueous cation reacts with the CO_2 in the air. Finally, the investigation into the nitrate salts stems from the industrial use of nitric acid within the

nuclear industry. When the aqueous radionuclides are dissolved within nitric acid, nitrate salts of the Sr and Cs are formed. The investigation into these anions, and their impact on geopolymer formation kinetics and mechanisms, is therefore paramount to determine the suitability of geopolymers to act as an appropriate wasteform for radioactive sludges containing Sr and Cs.

2 Chapter 2: Experimental Methods

2.1 Materials and Methods

2.1.1 Geopolymer Sample Production

2.1.1.1 Geopolymer Cements

The geopolymers in this study were produced by the reaction of metakaolin (MK) (MetaMax) with a potassium silicate activating solution. The X-ray Fluorescence (XRF) information for the metakaolin can be found in Table 2-1. The activating solution was made by reacting potassium hydroxide (AnalaR 99wt.%), deionized water and a potassium silicate solution (PQ-KS, 51.6% potassium silicate, with a solution modulus of $\text{SiO}_2/\text{K}_2\text{O}$ of 2.2, with the balance water, PQ-UK).

Table 2-1: Chemical composition, in wt. %, obtained by X-ray fluorescence (XRF) of the metakaolin provided by Metamax. The loss on ignition value was obtained at 1000 °C.

SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	Na_2O	Loss on Ignition
52.54	44.54	1.31	0.36	trace	0.15	0.63

Stoichiometry was designed to obtain an activating solution modulus $\text{SiO}_2/\text{K}_2\text{O} = 1$, an activator dose such that $\text{K}_2\text{O}/\text{Al}_2\text{O}_3 = 1$, and a water content molar ratio of $\text{H}_2\text{O}/\text{K}_2\text{O} = 11$.

For the Sr containing samples discussed in Chapter 3, the amount of strontium hydroxide octahydrate ($\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$) (Acros Organics, 98%), strontium carbonate (SrCO_3) (Sigma Aldrich, >99.9%), strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) (Alfa Aeser, 98%) and strontium sulphate (SrSO_4) (Alfa Aeser, Reagent Grade) added to the samples was determined by setting a constant Sr/Al molar ratio in the final geopolymer binder, as shown by Table 2-2. The $\text{H}_2\text{O}/\text{K}_2\text{O}$ ratio for the samples containing $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ take into account the water of crystallisation.

Table 2-2: The geopolymer samples loaded with Sr salts used in this work, with the corresponding anion and nominal Sr/Al, Si/Al, K/Al, $\text{H}_2\text{O}/\text{K}_2\text{O}$ and w/s molar ratios.

Sample	Anion	Sr/Al Ratio	Si/Al Ratio (Binder)	K/Al Ratio (Binder)	$\text{H}_2\text{O}/\text{K}_2\text{O}$ Ratio	w/s Ratio
KGP	-	-	1.5	1.0	11	0.55
OH_1	OH^-	0.025	1.5	1.0	11	0.55
OH_2	OH^-	0.050	1.5	1.0	11	0.55
OH_3	OH^-	0.075	1.5	1.0	11	0.54
OH_5	OH^-	0.125	1.5	1.0	11	0.54

CO ₃ _1	CO ₃ ²⁻	0.025	1.5	1.0	11	0.56
CO ₃ _2	CO ₃ ²⁻	0.050	1.5	1.0	11	0.57
CO ₃ _3	CO ₃ ²⁻	0.075	1.5	1.0	11	0.58
CO ₃ _5	CO ₃ ²⁻	0.125	1.5	1.0	11	0.60
NO ₃ _1	NO ₃ ⁻	0.025	1.5	1.0	11	0.56
NO ₃ _2	NO ₃ ⁻	0.050	1.5	1.0	11	0.58
NO ₃ _3	NO ₃ ⁻	0.075	1.5	1.0	11	0.59
NO ₃ _5	NO ₃ ⁻	0.125	1.5	1.0	11	0.62
SO ₄ _1	SO ₄ ²⁻	0.025	1.5	1.0	11	0.56
SO ₄ _2	SO ₄ ²⁻	0.050	1.5	1.0	11	0.57
SO ₄ _3	SO ₄ ²⁻	0.075	1.5	1.0	11	0.57
SO ₄ _5	SO ₄ ²⁻	0.125	1.5	1.0	11	0.60

For the Cs containing samples discussed in Chapter 4, the amount of caesium hydroxide (CsOH) (Thermoscientific, 96% (caesium carbonate <5%)), caesium carbonate (Cs₂CO₃) (FluoroChem, 99%), caesium nitrate (CsNO₃) (Thermoscientific, 99.8% (metals basis)) and caesium sulphate (Cs₂SO₄) (Thermoscientific, 99+%) added to the samples was determined by setting a constant Cs/Al molar ratio in the final geopolymer binder, as shown by Table 2-2.

Table 2-3: The geopolymer samples loaded with Cs salts used in this work, with the corresponding anion and nominal Cs/Al, Si/Al, K/Al, H₂O/K₂O and w/s ratios.

Sample	Anion	Cs/Al Ratio	Si/Al Ratio	K/Al Ratio	H ₂ O/K ₂ O Ratio	w/s Ratio
KGP	-	-	1.5	1.0	11	0.55
COH_1	OH ⁻	0.02	1.5	1.0	11	0.56
COH_2	OH ⁻	0.04	1.5	1.0	11	0.56
COH_3	OH ⁻	0.06	1.5	1.0	11	0.56
COH_5	OH ⁻	0.10	1.5	1.0	11	0.57
CCO ₃ _1	CO ₃ ²⁻	0.02	1.5	1.0	11	0.56
CCO ₃ _2	CO ₃ ²⁻	0.04	1.5	1.0	11	0.57
CCO ₃ _3	CO ₃ ²⁻	0.06	1.5	1.0	11	0.59
CCO ₃ _5	CO ₃ ²⁻	0.10	1.5	1.0	11	0.61
CNO ₃ _1	NO ₃ ⁻	0.02	1.5	1.0	11	0.56
CNO ₃ _2	NO ₃ ⁻	0.04	1.5	1.0	11	0.57
CNO ₃ _3	NO ₃ ⁻	0.06	1.5	1.0	11	0.57

CNO ₃ _5	NO ₃ ⁻	0.10	1.5	1.0	11	0.59
CSO ₄ _1	SO ₄ ²⁻	0.02	1.5	1.0	11	0.56
CSO ₄ _2	SO ₄ ²⁻	0.04	1.5	1.0	11	0.57
CSO ₄ _3	SO ₄ ²⁻	0.06	1.5	1.0	11	0.58
CSO ₄ _5	SO ₄ ²⁻	0.10	1.5	1.0	11	0.61

To produce the geopolymers containing the salts, the salt is mixed with the metakaolin powder before the introduction of the activating solution. The resulting mixture is mixed for 10 minutes before being stored in a sealed container at 20°C. At the desired curing times (3 and 28 days' post-reaction), a section of the geopolymer samples was removed from storage before being immersed in isopropanol to halt the alkali-activation reaction through the removal of loosely bound water.

For this work, one batch of each sample was prepared, meaning that all of the analysis techniques are carried out on samples from the same batch.

2.1.1.2 Assessment of the Effect of the Order-of-addition of Constituents in the Reaction Mixture

The production of a geopolymer binder can be considered as a recipe; A potassium hydroxide solution is first formed, followed by the addition of the potassium silicate before, finally, mixing with metakaolin. When done in an order not dictated as above, the final result can be far different to what was originally seen. To observe the effects of adding the salts of strontium and caesium at different points in the mixing process, 4 mixes were produced, in the order as shown by Table 2-4.

Table 2-4: The geopolymer mixes used in this experiment and the order-of-addition (OoA) of the raw components.

Stage of Addition	OoA #0	OoA #1	OoA #2	OoA #3
1.	Mix solid KOH with water	Mix salt with water	Mix solid KOH with water	Mix solid KOH with water
2.	Mix KOH solution with K-silicate	Mix salt solution with solid KOH	Mix salt with KOH solution	Mix KOH solution with K-silicate
3.	Mix Sr salt with MK	Mix KOH and salt solution with K-silicate	Mix KOH and salt solution with K-silicate	Mix silicate activating solution with salt
4.	Mix the salt and MK mixture with the silicate activating solution	Mix salt-loaded activating solution with MK	Mix salt-loaded activating solution with MK	Mix salt-loaded activating solution with MK

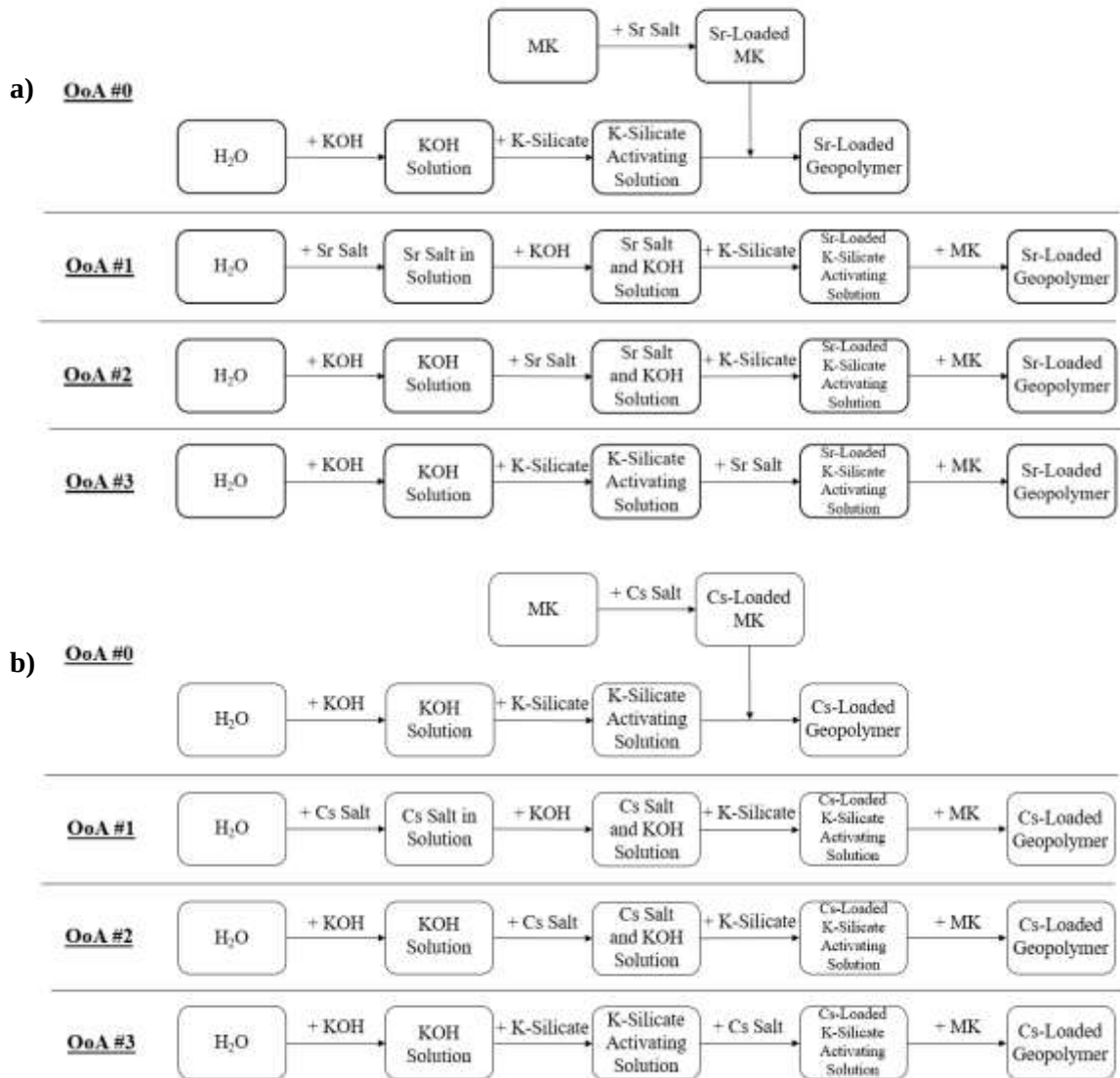


Figure 2-1: Schematic depicting the order-of-addition experiments a) with Strontium salts and b) with Caesium salts.

All of these mixes were produced using the corresponding salt sample (strontium hydroxide octahydrate, strontium carbonate, strontium nitrate, or strontium sulphate with an Sr/Al ratio of 0.125, or caesium hydroxide, caesium carbonate, caesium nitrate, or caesium sulphate with an Cs/Al ratio of 0.10). After each stage, the formulations were left to mix on a stirrer plate for at least 30 minutes per stage (longer for the dissolution of KOH into an aqueous solution due to it being a highly exothermic reaction to allow for cooling). Observations were made after each stage and, where solids were formed, Fourier-transform infrared spectroscopy analysis (Section 3.3.3) was performed to analyse the bonding environments within the solids. Upon the addition of the metakaolin to the silicate activating solution, isothermal conduction calorimetry (Section 3.3.1) was also carried out where possible to determine if there were any significant changes to the kinetics or mechanisms of reaction and gel polymerisation.

2.1.2 Sample Characterisation

2.1.2.1 *Fresh State*

2.1.2.1.1 Isothermal Conduction Calorimetry

Isothermal conduction calorimetry was utilized to examine the heat evolution during the reaction and, therefore, study the kinetics of the reaction between the activating solution and the metakaolin powder [149]. The geopolymer pastes were tested using a dual channel TAM Air isothermal conduction calorimeter from TA instruments at 20°C for a total of 7 days. Due to the initial geopolymer reaction mixture comprising of a large volume of water, water itself is used as the reference. 20g of each geopolymer was mixed within the glass ampoule using a vortex mixer to provide uniform mixing for two minutes before insertion into the calorimeter.

2.1.2.1.2 Zeta Potential

Zeta potential was used as a proxy for the measurement of the surface charge of the metakaolin particles in solution. 20g samples were used, each containing 2g of metakaolin and the corresponding mass of the salt required to reach the Sr/Al and Cs/Al ratios used in the entirety of this work, in a solution of potassium hydroxide (KOH) at pH 10 and pH 12. The zeta potential of the solutions were collected using a Stabino II system from Colloid Metrix. The samples were mixed via 10 inversions, and the readings were taken 30 seconds after the initial mixing. Error bars in the data show the standard deviation of 3 rounds of data collection.

2.1.2.1.3 Diffuse Reflectance Infrared Fourier Transform Spectroscopy

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) measurements were taken using a Thermo Fisher Nicolet iS5 FTIR spectrometer equipped with a Pike Technologies Easidiff diffuse reflectance accessory, scanning 64 iterations at a resolution of 16 cm⁻¹. The geopolymer samples were mixed using a vortex mixer for 2 minutes before being transferred to the spectrometer, where measurements were taken at a time point of 0 hours, every 15 minutes for the first 16 hours and then every hour until 24 hours post reaction.

2.1.2.2 *Hardened State*

2.1.2.2.1 Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectroscopy allows for the determination of the bonding environments in the samples, and hence provides information regarding the local structure of the geopolymer samples [160]. 2 mg of sample was mixed with 200 mg of KBr and pressed into a pellet prior to analysis. FTIR spectra were measured using a Perkin Elmer Frontier Mid FT-IR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector and KBr beam splitter optical system, scanning 16 iterations at a resolution of 4 cm⁻¹.

FTIR of the samples investigated in the ‘Order-of-addition’ experiments were probed using a Thermo Fisher Nicolet iS5 FTIR spectrometer equipped with a Specac Golden Gate Single Reflection Diamond ATR System, KBr optics, a diamond ATR crystal, and ZnSe lenses, scanning 64 iterations at a resolution of 16 cm⁻¹.

2.1.2.2.2 X-ray Diffraction

X-ray diffraction (XRD) data were obtained to examine the long range ordering and crystallinity of the reaction products in each sample. Data were obtained across a 2 θ range of 5°-70° using a Panalytical X'Pert³ Powder X-ray diffractometer with Cu K α radiation (1.54 Å), a nickel filter, a step size of 0.020° and a count time of 1 s/ step. Diffracted background intensity at low angles was reduced using an anti-scatter blade, and an incident beam divergence of 1.0 mm and a 2.5 ° Soller slit in the diffracted beam were used.

2.1.2.2.3 Solid State Nuclear Magnetic Resonance Spectroscopy

Solid state single pulse ²⁹Si and ²⁷Al magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were acquired on a Bruker Avance III HD 500 spectrometer at 11.7 T (B_0) using a 4.0 mm dual resonance CP/MAS probe, yielding a Larmor frequency of 99.35 MHz. A measured 60 s relaxation delay, a 5.5 μ s non-selective ($\pi/2$) excitation pulse, a total of 512 scans and spinning at 12.5 kHz were used to obtain the ²⁹Si MAS NMR spectra. ²⁷Al MAS NMR spectra were acquired using a 1.7 μ s non-selective ($\pi/2$) excitation pulse, a measured 10 s relaxation delay, a total of 128 scans and spinning at 12.5 kHz. The same instrument was used to perform the ²⁹Si cross-polarisation (CP) MAS NMR experiments, with the parameters differing only through an initial ¹H non-selective ($\pi/2$) pulse width of 2.5 μ s, a recycle delay of 1.25 s and Hartmann-Hahn contact periods of 2.0 ms. A nominal ¹H decoupling field strength of 80 kHz was employed during acquisition and 5120 scans were collected per experiment. The spectra were referenced against pure tetramethylsilane (TMS) at 0 ppm.

The deconvolution of the ²⁹Si MAS and ¹H-²⁹Si CP MAS NMR spectra was performed using Gaussian peak profiles. For both of the spectral deconvolutions of each resonance, the isotropic chemical shift (δ_{iso}) and peak full width at half maximum (FWHM) were maintained. Peak intensities were required to be consistent with the structural constraints described by the thermodynamics of a statistical distribution of Si and Al sites within a Q⁴ aluminosilicate network for (N,K)-A-S-H gel products.

High-field solid state ³⁹K MAS NMR data were acquired at 20.0 T (ν_0 = 39.67 MHz) using a Bruker Avance Neo 850 spectrometer with a Bruker 4.0 mm HX MAS probe which enabled a spinning rate of 14 kHz to be implemented. Pulse calibration and chemical shift referencing for all ³⁹K data were achieved using KCl_(s) (δ_{iso} = 47.8 ppm) as a secondary reference to the IUPAC primary reference of 0.1M KCl_(aq) (δ_{iso} = 0 ppm) [184]. A ‘non-selective’ $\pi/2$ pulse of 12 μ s was measured allowing for a ‘selective’ 4 μ s $\pi/2$ to be implemented. Spectra were acquired using a Hahn echo pulse sequence ($\pi/2$ –

$\tau - \pi - \text{acquire}$) using a measured relaxation delay of 0.1 s and acquiring a total of 480,000 scans per spectra.

High-field solid state ^{87}Sr MAS NMR data were acquired at 20.0 T ($\nu_0 = 36.843$ MHz) using a Bruker Avance Neo 850 spectrometer with a Bruker 4.0 mm HX MAS probe which enabled a spinning rate of 14 kHz to be implemented. Pulse calibration and chemical shift referencing for all ^{87}Sr data were achieved using the reference $\text{Sr}(\text{NO}_3)_2(\text{s})$ ($\delta_{\text{iso}} = -53.2$ ppm). Spectra were acquired using a Hahn echo pulse sequence ($\pi/2 - \tau - \pi - \text{acquire}$) with a ‘selective’ $3.25 \mu\text{s}$ $\pi/2$ pulse and a measured relaxation delay of 0.1 s, and acquiring a total of 839,680 scans per spectrum.

High-field solid state ^{133}Cs MAS NMR data were acquired at 20.0 T ($\nu_0 = 111.504$ MHz) using a Bruker Avance Neo 850 spectrometer with a Bruker 4.0 mm HX MAS probe which enabled a spinning rate of 12.5 kHz to be implemented. Pulse calibration and chemical shift referencing for all ^{133}Cs data were achieved using the reference $\text{CsNO}_3(\text{s})$ ($\delta_{\text{iso}} = 0$ ppm). Spectra were acquired using a Hahn echo pulse sequence ($\pi/2 - \tau - \pi - \text{acquire}$) with a ‘selective’ $3. \mu\text{s}$ $\pi/2$ pulse and a measured relaxation delay of 0.1 s, and acquiring a total of 12,288 scans per spectrum.

2.1.2.2.4 X-ray Adsorption Spectroscopy

XAS data were acquired on the bending magnet beamline B18 at Diamond Light Source, Harwell, UK. Beamline B18 utilises a Pt collimating mirror, a fixed-exit double crystal $\text{Si}(111)$ monochromator and a double toroidal focussing mirror. Sr K-edge XAS data were acquired on B18 in transmission mode using finely ground powder specimens dispersed in polyethylene glycol to achieve a thickness of two absorption lengths. Incident and transmitted beam intensities were measured using ionization chambers, filled with mixtures of He and Ar or N_2 , operated in a stable region of their I/V curve. Yttrium foil was measured to provide an absolute energy calibration; the first inflection point (in the first derivative) was defined to be 17133 eV. The yttrium foil was measured periodically to ensure that there was no energy drift over the course of the experiment. Data reduction and analysis was performed using the programmes Athena, Artemis and Hephaestus [185].

X-ray Absorption spectroscopy (XAS) was attempted on the geopolymer samples containing Cs, however, but data was unable to be collected at this beamline. A measurement of the L1 edge was attempted but the energy of the beamline was not great enough to generate a large enough edge step to analyse. There was also an attempt to measure the Cs L3 edge, but this was not possible due to the presence of titanium (Ti) within the samples. In this case, the edges for both of these elements are so close that they overlap, and a distinct edge for the Cs within the samples could not be separated from that of the Ti, making the data unusable. It is recommended that these experiments be performed at another beamline for these samples in the future.

2.1.2.2.5 EPMA

Electron probe micro-analysis (EPMA) was undertaken using a Jeol 8350F Plus Hyperprobe equipped with energy dispersive x-ray (EDX) and a wavelength dispersive x-ray (4 channel) system. The samples were analysed using beam conditions of an acceleration voltage of 10KV and a probe current of 10nA with a peak coating time of 40 seconds and a measurement of two background (upper and lower) positions for 20 seconds. The intensities of the characteristic x-rays generated by the elements of interest were measured according to their wavelengths by differing crystals, as follows: TAP for Si and Al, PETL for Sr, PETH for Ti and K. Elemental maps for the elements were obtained at 100x, 120x, and 1500x magnification.

3 Chapter 3: Geopolymer Cement: Potential Precursors and Baseline Properties

3.1 Introduction

The use of nuclear fission generates large quantities of waste; be it for power generation, accidental release or from medical uses, the volume of waste that must be safely separated and disposed of continues to grow [29]. The determination of the most suitable waste form material for each waste type is imperative to ensure that both the human race, and the environment, continue to thrive whilst utilising nuclear fission as an energy source. Furthermore, this waste form will need to remain stable for potentially thousands of years during its long-term storage in a geological disposal facility (GDF) which is the strategy that is to be implemented by the UK government [45].

The use of Portland cement (PC) as a means for encapsulating radionuclides has been, and still is, the preferred route of disposal for both Low-level waste (LLW) and intermediate level waste (ILW) [54]. However, the plethora of waste streams observed in the sector, accompanied by the length for which they must be contained, poses a significant challenge. The need for a ‘toolbox’ of cements which can be specifically engineered to the waste that needs disposing of is growing rapidly, and as such, research into novel cementitious alternatives to PC is being carried out on a grand scale [64, 67, 68, 70, 186]. One of these alternatives is the ‘geopolymer’ (GP) cement. Interest in geopolymers has been growing since its rise in the 1980’s due to its high chemical resistance and mechanical properties [187]. Moreover, the aluminosilicate framework that forms the geopolymer offers the potential for the chemical immobilisation of radionuclides due to their cation binding sites [67]. As a further advantage, fresh geopolymer pastes have shown desirable rheological performance which improves the migration of the paste around complex waste geometries, culminating in higher waste loadings [188].

Alkali-activated geopolymer cements are formed through the reaction of a solid aluminosilicate precursor with a high pH, alkaline solution [189]. In much of the literature, the choice of aluminosilicate material is between two common choices: metakaolin, a calcined kaolinite clay, or coal fly ash, a waste product of the combustion of coal as an energy source [67, 190-192]. On the other hand, the alkaline activating solution is more varied, being either a hydroxide or silicate of an alkaline metal, most commonly sodium (Na) or potassium (K) [128, 193, 194].

The reaction of these precursors leads to the formation of an alkaline aluminosilicate hydrate gel, commonly abbreviated as M-A-S-H gel, where M corresponds to the alkali used in the activating solution (Na or K). This gel has long range structural disorder and comprises of highly cross-linked aluminate and silicate tetrahedra, where Si exists in $Q^4(mAl)$ chemical coordination, where $1 \leq m \leq 4$ as a result of the Si/Al ratio of the gel matrix. In this matrix, Al exists in $q^4(4Si)$ chemical environments and the net negative charge of the AlO_4^- tetrahedra introduce the charge balancing cation binding sites discussed above.

Studies have been carried out to investigate the capability of geopolymers to safely contain common elements found in radioactive waste. Much of the research is focused upon Sr and Cs due to both their relatively short half-lives and incompatibility with PC [67, 174, 195, 196]. Moreover, research into the incorporation of common ion-exchange resins loaded with Sr and Cs have shown that geopolymers are capable of incorporating these materials into the waste form [142, 197, 198]. It is thought that the positively charged cations of these radioisotopes are capable of displacing the charge balancing alkali cation, be it Na^+ or K^+ , from its position with the M-A-S-H gel, therefore, becoming immobilised by its chemical bond to the alkali aluminosilicate gel framework structure [67, 199].

This chapter begins by discussing the choice of reactants that forms the basis of the work completed in the entirety of this PhD. The differences between coal fly ash and metakaolin, and then potassium and sodium based activating solutions will be outlined before the selection of a metakaolin based, potassium silicate activated geopolymer will be presented. Isothermal conduction calorimetry and diffuse reflectance infrared Fourier transform spectroscopy are used to investigate the fresh state development of the K-A-S-H gel. Fourier transform infrared spectroscopy and solid state NMR probing ^{29}Si , ^{27}Al and ^{39}K are used to establish a baseline for the nanostructure of the K-A-S-H gel after 3 and 28 days of reaction to allow for distinct differences to be discussed later on in this PhD work.

3.2 Material Selection

The raw materials used for the manufacture of the geopolymer make a considerable difference to the structure, and resulting chemical properties of the geopolymer gels. The raw materials can be split into two sub groups, solid precursor and alkali activator.

3.2.1 Solid Precursor

Traditionally, there are two primary choices for the solid precursor for geopolymers: fly ash and metakaolin. Both of these materials are aluminosilicate materials, and so meet the basic requirements needed to react to form a geopolymer cement. However, the material must also have a low calcium content to classify the final material as a geopolymer compared to an alkali-activated cementitious material. The classification of these materials is shown in Figure 1-8.

Within this section, the two materials will be briefly introduced before direct comparisons regarding their individual advantages and disadvantages will be discussed.

3.2.1.1 Coal Fly Ash

3.2.1.1.1 Material Background

Coal fly ash is a by-product of the fossil fuel industry, originating from coal-fired power stations [200]. It has been favoured for use in geopolymers due to its high concentration of silica and alumina, along with its relative historical availability. The main components of fly ash are silica (SiO_2) and alumina (Al_2O_3), two of the key materials needed for the formation of a geopolymer. However, the fly ash also

contains ferric oxide (Fe_2O_3) and calcium oxide (CaO), albeit in far less significant quantities, but the composition, and therefore quality, of the fly ash varies greatly depending on the source, as shown in the literature [201-204]. For fly-ash based geopolymers, materials containing a lower percentage of CaO are preferred to prevent the rate of reaction to form the geopolymer gel from being negatively impacted [205].

3.2.1.1.2 Advantages of Coal Fly Ash

The use of fly ash as the solid precursor for the geopolymer cement has its advantages; the resulting geopolymer is mechanically stronger and has increased durability when compared to its metakaolin-based counterpart [129]. The consistently round particle shape results in better rheological qualities during the mixing phase. Moreover, the calcined nature of this material leads to an increased compressive strength of the final geopolymer [206]. The use of fly ash in the binder leads to significantly less water being required in the activation [207]. The resulting structure is also more tightly bound, and the partial replacement of metakaolin by fly ash can lead to a decrease in porosity within the final material [207, 208].

3.2.1.1.3 Disadvantages of Coal Fly Ash

The composition of the fly ash is shown to be inconsistent and does not always guarantee high reactivity [209, 210]. The stockpile of fly ash is quickly diminishing, and, with the reduction in the number of operating coal-fired power stations, fly ash sources will be limited in the future [211, 212]. Therefore, irrespective of its mechanical advantages, the use of fly ash is becoming less relevant, and research into its main competitor, metakaolin, is growing [67, 192, 212]. The microstructure of the fly ash results in the need for post reaction temperature treatment being required in a lot of use cases [208, 213].

3.2.1.2 Metakaolin

3.2.1.2.1 Material Background

Metakaolin is a product of the calcination of kaolin, a natural clay, at temperatures between 500-900°C [214]. The calcination removes structural OH groups from the material, and causes the structural reorganisation of Al sites, with a decrease in the number of octahedral sites and an increase in pentahedral and tetrahedral coordinated sites [215, 216]. Kaolin clay is an abundant natural resource and, consequently, the metakaolin produced from kaolin clay obtained from a single source exhibits consistent chemical and physical characteristics [217]. The chemical and physical properties of the metakaolin do alter dependent on where the original clay is sourced; for example, clay sourced from Africa will have a slightly different composition to clay sourced from Europe [212, 218, 219]. The main components of the metakaolin are silica (SiO_2) and alumina (Al_2O_3), which gives rise to its classification as an aluminosilicate material [220]. The other constituents consist of impurities such as quartz (SiO_2) and anatase (TiO_2), small percentages of combustible organic components, as well as small quantities of ferric oxide (Fe_2O_3) [219, 221, 222].

3.2.1.2.2 Advantages of Metakaolin

The purity of the mined kaolinite clay leads to consistency in the product and the high concentration of alumina and silica leads to increased reactivity [212]. Moreover, the amorphous nanostructure of the metakaolin means that it is very reactive when mixed with an alkaline activating solution [214, 223]. The use of metakaolin as the solid precursor can also lead to increased early strength of the material due to its higher pozzolanic activity accompanied by the filling effect of its fine particles [224, 225]. These very same fine particles also promote reactivity, as the large surface area increases the rate of dissolution [212, 226]. The geopolymers that result through the use of metakaolin as the solid precursor are highly durable to carbonation and alkali-silica attack [227]

3.2.1.2.3 Disadvantages of Metakaolin

The plate-like particles of metakaolin leads to a fresh geopolymer paste that has poorer rheological performance, and hence requires more water to reach a similar viscosity to a fly ash based system [209]. Metakaolin based geopolymers exhibit pore networks that result in a lower density microstructure [207, 228]. This reduction in density results in a lower mechanical strength of the material containing metakaolin when compared to fly ash [208, 228].

3.2.2 Activating Solution

In order for the raw solid precursor to become a geopolymer gel, it must be chemically activated by a liquid ‘activating solution’. This solution provides a highly alkaline environment in which the solid precursor can dissolve. The pH of the system determines the rate at which the solid precursor can dissolve and initiate the reaction process. Therefore, a higher pH is preferred to increase the level of dissolution in the early stages of the reaction process [194].

The activator can be split into two sections: the alkaline metal component and the corresponding anionic group. The most common activators are hydroxides and silicates of sodium (Na) and potassium (K) [118]. The inherent difference between these elements, brought about mainly by their atomic sizes, leads to changes in the way that the activating solution reacts with the solid precursors. Similarly, the use of silicates alongside the hydroxides within the activator promotes the compressive strength of the resultant material, as well as reducing alkali saturation within the pore networks of the material [229, 230].

3.2.2.1 Sodium-based Activators

Activating solutions containing sodium as the alkali metal have been subject to the large majority of studies carried out on geopolymer cements [128, 231-234]. The positives for using either sodium silicate, commonly referred to as waterglass, or sodium hydroxide as activators are clear; firstly, in the context of nuclear waste immobilization, the use of sodium activators allows for the incorporation of positive cations such as Sr and Cs into the structure as charge balancing cations [67, 235, 236]. Walkley et al. also showed that using sodium as the alkali metal in the activator leads to a greater degree of

displacement of the alkali metal for positive cations when compared to potassium based activators [67]. The cations of sodium that are present within the activating solution are smaller than the corresponding potassium cations and have a lower bond affinity to the geopolymeric structure meaning that they are more prolific at migrating throughout the network that is formed in the paste. On top of this, sodium has a higher charge density than potassium and these properties can lead to a greater degree of crystallisation to form pseudo-zeolitic structures [193, 230].

However, sodium is shown to have a weaker interaction with the gel network than its potassium counterparts, leading to a reduced propagation of the gel structure resulting from the faster setting times of the material [237]. Sodium based geopolymers have been shown to have a lower overall density when compared to potassium based materials which will lead to poorer mechanical performance of the material [238]. The silica modulus, $\text{SiO}_2/\text{Na}_2\text{O}$, of the sodium silicate activating solution provides potential issues for its use as the activator; the use of this activator leads to the risk of spontaneous crystallization of the solution at silica modulus' (<1) close to that of the optimum silica modulus (~ 1.5) for the formation of geopolymers [239].

3.2.2.2 Potassium-based Activators

There has been less historical research carried out on geopolymers using potassium silicate and hydroxide as the activator, however, more recently research into these materials has started to grow, although in some cases, this is as a mixed activator with sodium [67, 192, 193, 240, 241]. Potassium based activators lead to a solution with higher alkalinity [242]. The higher alkalinity, and subsequent higher pH, lead to a faster rate of dissolution, and therefore a greater extent of reaction with regard to the solid precursor. This reduces the amount of unreacted solid precursor within the final sample. To add to this, the reaction kinetics for potassium based activators are slower, and this leads to a further increase to the extent of reaction, as the setting times, this being the time between the initial dissolution and the hardening of the paste, are slightly longer allowing for greater mobilisation of the components in solution [237]. The use of potassium activating solutions also lead to a paste that has a lower viscosity than those of sodium based materials [192, 243, 244]. This property is particularly important when considering the application of geopolymer cements for nuclear waste disposal, as the lower viscosity is imperative for complete infill of complex waste geometries. The use of potassium silicate also leads to materials that are more microstructurally consistent than sodium silicate due to their increased homogeneity brought about by the lower percentage of unreacted solid precursor, which is further beneficial for the nuclear application [245, 246].

However, there are some downfalls with the use of potassium based activators. Firstly, it has been shown that for some systems, such as those in the study by Walkley et al., sodium activators are capable of forming zeolitic phases with the cations in the radioactive waste stream, chemically immobilising them [67]. There is yet to be any research that shows that potassium zeolitic phases are formed in

geopolymer systems, providing a gap to be explored in this work. Also, when using potassium hydroxide as an activator with fly ash as a solid precursor, large voids are formed which reduces the density of the material and leads to increased leaching [247].

3.2.3 Raw Materials for This Work

The advantages and disadvantages of each of the activators and the solid precursors were considered prior to selection. For this work, it was decided that metakaolin would be used as the solid precursor and a potassium silicate based solution would be used for the liquid activating solution. The main driving force for the use of metakaolin was the ability to increase reaction and ensure that the vast majority of the material actually reacts to form the geopolymer gel phase. Moreover, the fact that it is available in such vast quantities when compared to the diminishing reserves of fly ash may result in this research being more applicable for future systems. The use of potassium silicate was selected primarily due to its enhanced rheological properties when compared to sodium. This will also help to combat the poorer rheology of metakaolin based materials when compared to fly ash based materials, further justifying the selection of metakaolin. Furthermore, the advantages of potassium silicate for use in the nuclear industry are more fitting for the industrial application of this work; at the required silica modulus, potassium silicate is far more stable than sodium silicate, which is prone to spontaneous crystallisation, and this possibility will lead to it being unable to pass vital safety tests that are required for use in the nuclear industry [192, 239]. In addition, the rheological advantages of K based geopolymer systems over Na based systems is fitting for this work as the key waste type being targeted is sludge waste, primarily found around the site of nuclear disaster such as Fukushima Daiichi. The need for the wasteform to mould to the complex geometries posed by this waste type lends itself towards the use of K based systems.

The metakaolin used in this work is termed MetaMax and is provided by Lawrence Industries (UK), which complies with the pozzolan definition set out within BS EN 197-1 (2019) [248]. The XRF data for this material can be seen in Table 3-1.

Table 3-1: Chemical composition, in wt. %, obtained by X-ray fluorescence (XRF) of the metakaolin provided by Metamax. The loss on ignition value was obtained at 1000 °C.

SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	Na ₂ O	Loss on Ignition
52.54	44.54	1.31	0.36	trace	0.15	0.63

As can be seen, the calcium content, shown by the CaO, is minimal in this material, which is required for the formation of a geopolymer cement by definition. Moreover, the wt.% of silica and alumina show

that these materials comprise of over 95% of the total composition which will provide the building blocks for the formation of the aluminosilicate gel network.

The potassium silicate activating solution was designed for this work to meet the ratios shown in Table 3-2.

Table 3-2: Relevant silica modulus ($\text{SiO}_2/\text{K}_2\text{O}$), water modulus ($\text{H}_2\text{O}/\text{K}_2\text{O}$) and $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of the liquid activating solution.

Ratio	$\text{SiO}_2/\text{K}_2\text{O}$	$\text{H}_2\text{O}/\text{K}_2\text{O}$	$\text{K}_2\text{O}/\text{Al}_2\text{O}_3$
Potassium Silicate Activating Solution	1	11	1

The properties of the activating solution here were designed based on the work of Geddes in their thesis where extensive work was carried out to determine this formulation envelope [192].

3.2.4 Geopolymer Synthesis

The raw materials, that being the solid metakaolin precursor and the aqueous K-silicate activator, are added simultaneously. They are added as such that the properties of the binder reach the ratios that are shown in Table 3-3.

Table 3-3: The nominal Si/Al, K/Al, $\text{H}_2\text{O}/\text{K}_2\text{O}$ and w/s molar ratios for the geopolymer sample used in this work.

Si/Al Ratio (Binder)	K/Al Ratio (Binder)	$\text{H}_2\text{O}/\text{K}_2\text{O}$ Ratio	w/s Ratio
1.5	1.0	11	0.55

The mixture is then mixed at high shear using a Heidolph RZR2020 overhead stirrer at 1800 RPM for 10 minutes. This choice was made after the work on the mixing techniques of geopolymers performed by Geddes within their thesis [192]. When comparing the effects of the mixing speed between 650, 1300 and 2000 RPM, it was shown that for a MetaMax based metakaolin system with a slightly higher $\text{H}_2\text{O}/\text{K}_2\text{O}$ ratio, a higher mixing speed for 10 minutes provides a greater extent of reaction, as measured

by the cumulative heat flow of the reaction mixture over the first 5 days. The lower water content of the samples used in this work further support using a higher mixing rate, as the viscosity of the mix is likely to be lower and will require greater torque to mix effectively.

After the mixing process, the geopolymer is sealed within a container and stored in an environmental chamber at 20°C. In this work, the geopolymer samples are examined at two time points, 3 and 28 days after the initial mixing of the samples. At these two designated time points, the sample is removed from the environmental chamber and a section of it is hand ground and immersed in isopropanol, removing any loosely bound water to prevent any further reaction. The ground sample is then used in the analysis techniques discussed in the next section. In all sections of this work, the geopolymer mix described here will be referred to as KGP.

3.3 Sample Characterisation

3.3.1 Isothermal Conduction Calorimetry

Isothermal conduction calorimetry (ICC) was utilized to examine the heat evolution during the reaction and, therefore, study the kinetics of the reaction between the activating solution and the metakaolin powder [149]. The geopolymer pastes were tested using a dual channel TAM Air isothermal conduction calorimeter from TA instruments at 20°C for a total of 7 days. Due to the initial geopolymer reaction mixture comprising of a large volume of water, water itself is used as the reference. 20g of each geopolymer was mixed within the glass ampoule using a vortex mixer to provide uniform mixing for two minutes before insertion into the calorimeter.

3.3.2 Diffuse Reflectance Infrared Fourier Transform Spectroscopy

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) measurements were taken using a Thermo Fisher Nicolet iS5 FTIR spectrometer equipped with a Pike Technologies Easidiff diffuse reflectance accessory, scanning 64 iterations at a resolution of 16 cm⁻¹. The geopolymer samples were mixed using a vortex mixer for 2 minutes before being transferred to the spectrometer, where measurements were taken at a time point of 0 hours, every 15 minutes for the first 16 hours and then every hour until 24 hours post reaction.

3.3.3 Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectroscopy allows for the determination of the bonding environments in the samples, and hence provides information regarding the local structure of the geopolymer samples [160]. 2 mg of sample was mixed with 200 mg of KBr and pressed into a pellet prior to analysis. FTIR spectra were measured using a Perkin Elmer Frontier Mid FT-IR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector and KBr beam splitter optical system, scanning 16 iterations at a resolution of 4 cm⁻¹.

3.3.4 Solid State Nuclear Magnetic Resonance Spectroscopy

Solid state single pulse ^{29}Si and ^{27}Al magic angle spinning (MAS) NMR spectra were acquired on a Bruker Avance III HD 500 spectrometer at 11.7 T (B_0) using a 4.0 mm dual resonance CP/MAS probe, yielding a Larmor frequency of 99.35 MHz. A measured 60 s relaxation delay, a 5.5 μs non-selective ($\pi/2$) excitation pulse, a total of 512 scans and spinning at 12.5 kHz were used to obtain the ^{29}Si MAS NMR spectra. ^{27}Al MAS NMR spectra were acquired using a 1.7 μs non-selective ($\pi/2$) excitation pulse, a measured 10 s relaxation delay, a total of 128 scans and spinning at 12.5 kHz. The same instrument was used to perform the ^{29}Si cross-polarisation (CP) MAS NMR experiments, with the parameters differing only through an initial ^1H non-selective ($\pi/2$) pulse width of 2.5 μs , a recycle delay of 1.25 s and Hartmann-Hahn contact periods of 2.0 ms. A nominal ^1H decoupling field strength of 80 kHz was employed during acquisition and 5120 scans were collected per experiment. The spectra were referenced against pure tetramethylsilane (TMS) at 0 ppm. CP-MAS data was collected to isolate the signal from the geopolymer gel from that of the unreacted metakaolin. This is discussed in more detail in Section 3.4.3.1.

The deconvolution of the ^{29}Si MAS and ^1H - ^{29}Si CP MAS NMR spectra was performed using Gaussian peak profiles. For both of the spectral deconvolutions of each resonance, the isotropic chemical shift (δ_{iso}) and peak full width at half maximum (FWHM) were maintained. Peak intensities were required to be consistent with the structural constraints described by the thermodynamics of a statistical distribution of Si and Al sites within a Q^4 aluminosilicate network for (N,K)-A-S-H gel products.

High-field solid state ^{39}K MAS NMR data were acquired at 20.0 T ($\nu_0 = 39.67$ MHz) using a Bruker Avance Neo 850 spectrometer with a Bruker 4.0 mm HX MAS probe which enabled a spinning rate of 14 kHz to be implemented. Pulse calibration and chemical shift referencing for all ^{39}K data were achieved using $\text{KCl}_{(\text{s})}$ ($\delta_{\text{iso}} = 47.8$ ppm) as a secondary reference to the IUPAC primary reference of 0.1M $\text{KCl}_{(\text{aq})}$ ($\delta_{\text{iso}} = 0$ ppm) [184]. A ‘non-selective’ $\pi/2$ pulse of 12 μs was measured allowing for a ‘selective’ 4 μs $\pi/2$ to be implemented. Spectra were acquired using a Hahn echo pulse sequence ($\pi/2 - \tau - \pi - \text{acquire}$) using a measured relaxation delay of 0.1 s and acquiring a total of 480,000 scans per spectra.

3.4 Results and Discussion

3.4.1 ICC

The use of ICC in this work allows for the level of reaction to be explored, and also the times at which the level of reaction is at its maximum. The different reactions that occur during the reaction between the metakaolin and the activating solution are exothermic, that being that they give off heat as a by-product of the reaction [249]. The amount of heat generated indicates the level of reaction at that point in time; a higher heat flow will show that there are more reactions occurring than at a lower heat flow.

Figure 3-1 displays the calorimetry curves produced by the reaction of the KGP geopolymers sample over the first 3 days of reaction.

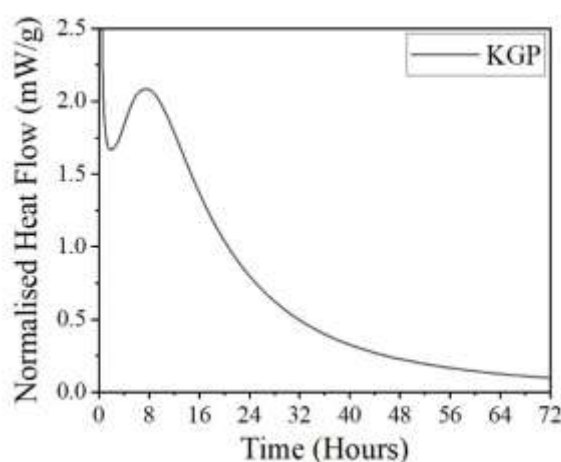


Figure 3-1: The normalised heat evolved during the reaction between metakaolin and the K-silicate activating solution over the first 3 days of reaction.

Figure 3-1 begins by showing a large, declining heat release at a time point of 0 hours. This is the remnants of the dissolution peak that would be seen if the entirety of the mixing process could be seen in the ICC data. Due to the sample being mixed outside of the calorimeter, the majority of the dissolution occurs before any measurements are able to be taken as the high pH leads to a rapid breaking of the bonds within the metakaolin [250, 251]. Therefore, by the time the sample is inputted into the calorimeter after 2 minutes of mixing, this reaction has proceeded past its maximum.

The second feature of this heat evolution curve is the singular peak that reaches its maximum within the first 12 hours of reaction. This peak corresponds to the secondary reaction point as discussed above and is a sign that the aluminate and silicate monomers within the solution are reacting to form a polymeric network, notably the geopolymeric K-A-S-H gel. This peak is broad and it is likely that the reaction steps shown in Figure 1-12 occur continuously as the remaining metakaolin continues to dissolve within the solution, increasing the concentration of silicate and aluminate monomers within the solution. This reaction reaches its maximum heat flow within the first day of the reaction, which suggests that the geopolymer will also set into a hardened monolith within this period. This is not an ideal setting time for the application of geopolymers as a nuclear wasteform packaging material, as it is expected that the material will have a final set greater than 24 hours post reaction [252].

3.4.2 FTIR & DRIFTS

Utilising FTIR allows local chemical environments to be probed to determine the bonds that are formed within the sample. When considering geopolymer systems, the main characterisation region is seen between 800 and 1300 cm^{-1} , encompassing the most intense peak caused by the stretching of the Si-O-T (where T=Si or Al) bond that is characteristic of geopolymer gels [129, 253-255]. Figure 3-2, shows

the FTIR spectra for the metakaolin precursor and the KGP sample after 3 and 28 days of reaction. The main change between the metakaolin spectra and that of the KGP samples is the shift of the main Si-O-T peak from 1085 cm^{-1} to 1000 cm^{-1} . This corresponds to the change in silica environment that occurs after the reaction to form the geopolymer, and this shift is also seen in the literature [256, 257]. The reasoning for this is the formation of the K-A-S-H gel, which contains highly cross-linked aluminosilicate structures, increasing the number of $Q^4(4Al)$ and $Q^4(3Al)$ silicon sites in comparison to the $Q^4(1Al)$ and $Q^4(0Al)$ sites seen more prominently in the metakaolin [67, 172]. This shift is further supported by the appearance of the shoulder at 860 cm^{-1} in the KGP samples which is a direct result of the asymmetric stretching of the Si-O-Al bonds introduced by the formation of the K-A-S-H gel [258, 259]. Despite the clear shift discussed between the metakaolin and the KGP samples suggesting that the metakaolin has reacted to form the K-A-S-H gel, the shoulder on the main peak in the spectra of the KGP samples at $\sim 1085\text{ cm}^{-1}$ suggests that some of the metakaolin has yet to react within the samples. This is more prominent in the KGP sample after 3 days, but is still present after 28 days of reaction. This indicates that the metakaolin continues to dissolve throughout the first 28 days of reaction, although it does not appear to have had a huge effect on the nanostructure of the gel, as the spectra for the KGP samples at both time points are comparable excluding the shoulder just discussed.

The FTIR spectra for the KGP samples display multiple peaks that are not present in the metakaolin spectra; firstly, the peak at 1650 cm^{-1} indicates that there is both chemically bound and free water found within the sample [260]. This is a result of the hydration of the sample, with the water being consumed from the activating solution through the dissolution of the metakaolin and then released again through the polycondensation reaction that forms the K-A-S-H gel [129]. The peak at 585 cm^{-1} is evidence of the vibrations within aluminosilicate rings consisting of TO_4 tetrahedra [261]. The low intensity peak at 700 cm^{-1} is thought to be caused by the pseudo-lattice vibrations of small aluminosilicate rings, which were previously observed in synthetic geopolymer gels by Walkley et al. [67, 262].

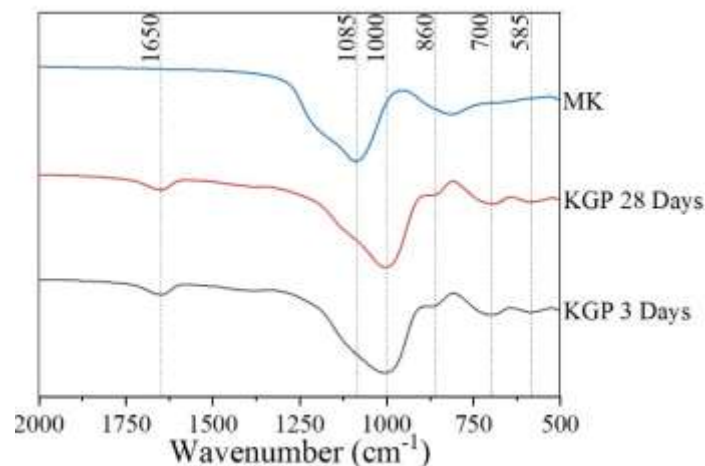


Figure 3-2: The FTIR spectra generated by the KGP sample after the first 3 and 28 days of reaction and the raw metakaolin precursor (MK).

Table 3-4: Characteristic stretching vibrational bands of metakaolin based geopolymer systems.

Wavenumber (cm ⁻¹)	Bonding	Reference
700	Asymmetric stretching (Si-O-Si and Al-O-Si)	[231]
800-810	Metakaolin bending vibrations (Al-O)	[263]
850-880	Si-O stretching and OH bending (Si-OH)	[258, 259]
950-980	Si-O stretching (Si-O-K)	[264]
1000-1060	Asymmetric stretching (Si-O-Si and Al-O-Si)	[129, 253, 265, 266]
1105-1160	Asymmetric stretching (Si-O-Si)	[264, 266]

DRIFTS can be performed on the samples in the early stages of reaction. In this case, the DRIFTS is essentially taking in-situ FTIR measurements, taking discrete measurements of the sample at prescribed time points. In the case of in-situ attenuated total reflectance (ATR) FTIR, this has been previously performed in the literature, but the use of DRIFTS on cementitious materials is a less common practice [154, 253, 267]. However, the use of DRIFTS allows for the structural and phase evolution of the exact same physical quantity of sample to be tracked throughout the entirety of the first 24 hours without any user interference. This is not possible with the ATR-FTIR equipment, as the corrosive nature of the activating solution can damage the ATR sample holder, meaning the sample needs to be removed after each measurement. For singular discrete measurements at certain time points, the use of ATR-FTIR as a widely used and well understood technique prevails, but for the continued measurements performed here, DRIFTS was selected as it has been shown that this technique can be used to provide quick and accurate results for the composition of samples [151, 154]. Other analysis techniques could be used to show the local structure of the K-A-S-H gel, most notably ²⁹Si MAS NMR, but this is not attainable for the speed and time-precision at which the measurements need to be taken [268].

The DRIFTS spectra displayed in Figure 3-3 show the bond evolution of peaks in the KGP sample over the first 8 hours of reaction. The wavenumber at which characteristic resonances occur in the DRIFTS spectra are directly comparable with the transmission data seen in the FTIR discussed above [154]. Therefore, it can be seen that the K-A-S-H gel begins to form almost immediately, with the peak centred around 1000 cm⁻¹ growing continuously over the first 8 hours of reaction. It is also worth noting that there is no clear resonance in the region that would be expected for the main Si-O-T peak for metakaolin. This suggests that the majority of the metakaolin has dissolved during the 2 minutes of mixing prior to the initial measurement. The shift of the Si-O-T peak to lower wavenumbers can also be seen in the spectra, synonymous with what is seen in the FTIR data between metakaolin and the KGP samples. This provides further evidence that the metakaolin continues to dissolve throughout the reaction. The presence of other peaks relating to the release of aluminate and silicate into solution, notably the bonds

at $\sim 585\text{ cm}^{-1}$ and 860 cm^{-1} . Overall, it is clear that the K-A-S-H gel is formed in large quantities by the 8-hour time point.

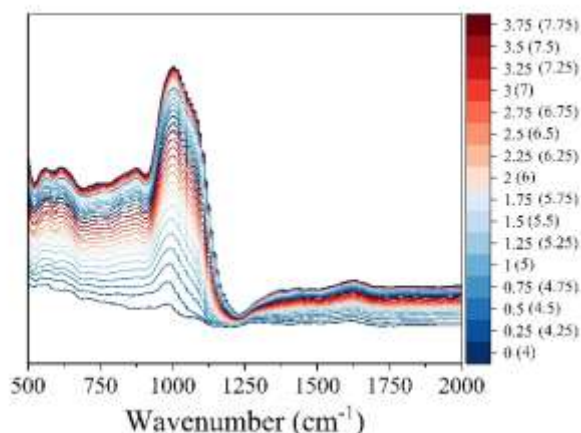


Figure 3-3: DRIFTS spectra for the KGP sample in the first 8 hours of reaction. The spectra are displayed in 15 minute intervals, beginning at $t=0$ as marked and progressing through the colour gradient, which repeats after 4 hours. Times are shown in hours.

The remaining time in the first 24 hours of reaction is shown by the spectra in Figure 3-4. The peaks that are present within the main characterisation region remain very similar, although they begin to drop in intensity. It is not clear why this happens but, as previously mentioned, DRIFTS is a relatively new analysis technique for cementitious materials. Therefore, further research is required to fully understand the phenomena that is seen here. It is most likely that the shrinkage of the cement is responsible for this drop; as the cement begins to harden, it shrinks, changing the distance between the surface of the sample and the detector [269, 270]. This occurs in this situation as the same sample is used throughout the measurement and, during this time, no changes are made to the apparatus and so the measurement distance does not change. This could also be due to the increase in the proportion of the band at $\sim 1400\text{cm}^{-1}$ reducing the height of the main peak relatively.

After 14 hours of reaction, another intense peak begins to grow at $\sim 1400\text{ cm}^{-1}$. The cause of this peak is likely to be the carbonation of the sample due to reaction with the CO_2 in the air [271]. The infrared beam used for the DRIFTS measurement must pass through the surface of the sample to reach the bulk material. Therefore, artefacts from the surface of the sample, notably the point where carbonation would occur, will always be included in the spectra. This phase is likely to be a potassium carbonate phase, due to the interaction of the K within the sample and CO_2 in the air.

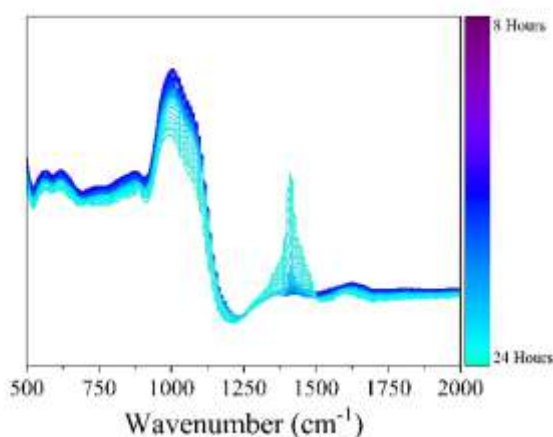


Figure 3-4: DRIFTS spectra for the KGP sample from 8 to 24 hours post initial reaction. The spectra are displayed in 15 minute intervals up until the 16-hour mark, at which the time progresses in whole hours, beginning at $t=8$ hours as marked and progressing through the colour gradient. Times are shown in hours.

3.4.3 SS MAS NMR

Utilising solid state magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy allows determination of the local chemical environment of silicon, aluminium and potassium sites within the geopolymer samples. Due to the amorphous and disordered nature of the geopolymer gel, the use of NMR can provide useful information regarding the nuclei surrounding the incident nuclei [96, 170].

3.4.3.1 ^1H - ^{29}Si CP MAS and ^{29}Si MAS NMR

^1H - ^{29}Si cross-polarisation (CP) MAS and ^{29}Si MAS NMR are used to distinguish between the various silicon environments found in geopolymer cements. The use of ^1H - ^{29}Si CP MAS allows for the nanostructure of the hydrated K-A-S-H gel to be investigated whilst disregarding anhydrous Si sites that represent unreacted metakaolin within the binder [272]. This distinction is possible through the preferential enhancement of the resonances of Si atoms in close proximity to surrounding protons, which is most commonly seen in phases that are in a hydrated state [273]. Figure 3-5 displays the ^1H - ^{29}Si CP MAS NMR and ^{29}Si MAS NMR spectra for the KGP sample after 3 and 28 days of reaction. The ^{29}Si MAS NMR spectra for the metakaolin precursor is also shown.

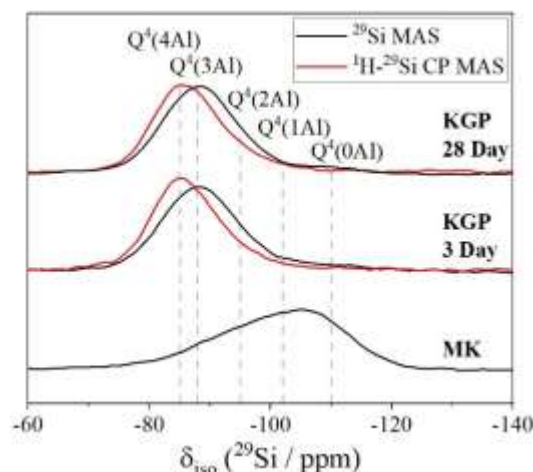


Figure 3-5: ^1H - ^{29}Si CP MAS and ^{29}Si MAS spectra for the KGP sample precursor at both 3 and 28 days after reaction and the unreacted metakaolin (MK).

By firstly considering the metakaolin, the ^{29}Si MAS NMR exhibits a broad resonance ranging from $\delta_{\text{iso}} = -80$ to -120 ppm. This suggests that the structure contains various Si sites which correlates well with spectra of this kind seen in previous work [67, 172, 274]. This resonance centres at $\delta_{\text{iso}} = -107$ ppm, showing that the structure is dominated by Si sites that are not connected to Al, that being $\text{Q}^4(1\text{Al})$ and $\text{Q}^4(0\text{Al})$ sites. However, the distribution over such a large range of chemical shifts suggests that the presence of Si exists in all $\text{Q}^4(m\text{Al})$ environments (where $0 \leq m \leq 4$).

On the other hand, the ^{29}Si MAS NMR spectra for the KGP sample at both time points suggest that the sample is dominated by Si sites that contain a high Al distribution, notably $\text{Q}^4(4\text{Al})$ and $\text{Q}^4(3\text{Al})$, centred at $\delta_{\text{iso}} = -88$ ppm. This supports the formation of a geopolymer, notably the hydrated K-A-S-H gel, which has a highly cross-linked aluminosilicate structure [172, 268, 274]. As is to be expected, the peak of the spectra shifts to higher δ_{iso} values between the ^{29}Si MAS NMR and ^1H - ^{29}Si CP MAS NMR spectra as the intensity supplied by the Si sites in the metakaolin are diminished. This spectra centres at $\delta_{\text{iso}} = -85$ ppm and indicates that the hydrated K-A-S-H gel itself is comprised of primarily $\text{Q}^4(4\text{Al})$ sites after both 3 and 28 days of reaction. The spectra observed here are similar to those seen in previous work, suggesting that the K-A-S-H gel is formed by a mixture of Si environments in the form of $\text{Q}^4(m\text{Al})$ sites, where $1 \leq m \leq 4$ [67]. The deconvolution of the NMR spectra allows the amount of each of the individual ^{29}Si sites to be quantified [172]. This deconvolution is shown numerically in Table 3-5 and visibly in Figure 3-6. The fitting residue for this deconvolution is presented in Appendix 1.

Table 3-5: Relative integral areas for the Si sites present within the K-A-S-H gel of the KGP sample both 3 and 28 days after initial reaction from the deconvoluted ^{29}Si MAS NMR spectra. The $Q^4(0\text{Al})$ site attributed to the unreacted metakaolin is disregarded for the quantification of the K-A-S-H gel.

	Relative Integral Area (%)				
Time point	$Q^4(4\text{Al})$	$Q^4(3\text{Al})$	$Q^4(2\text{Al})$	$Q^4(1\text{Al})$	Si/Al
3 Days	25	54	20	1	1.32
28 Days	28	44	26	2	1.34

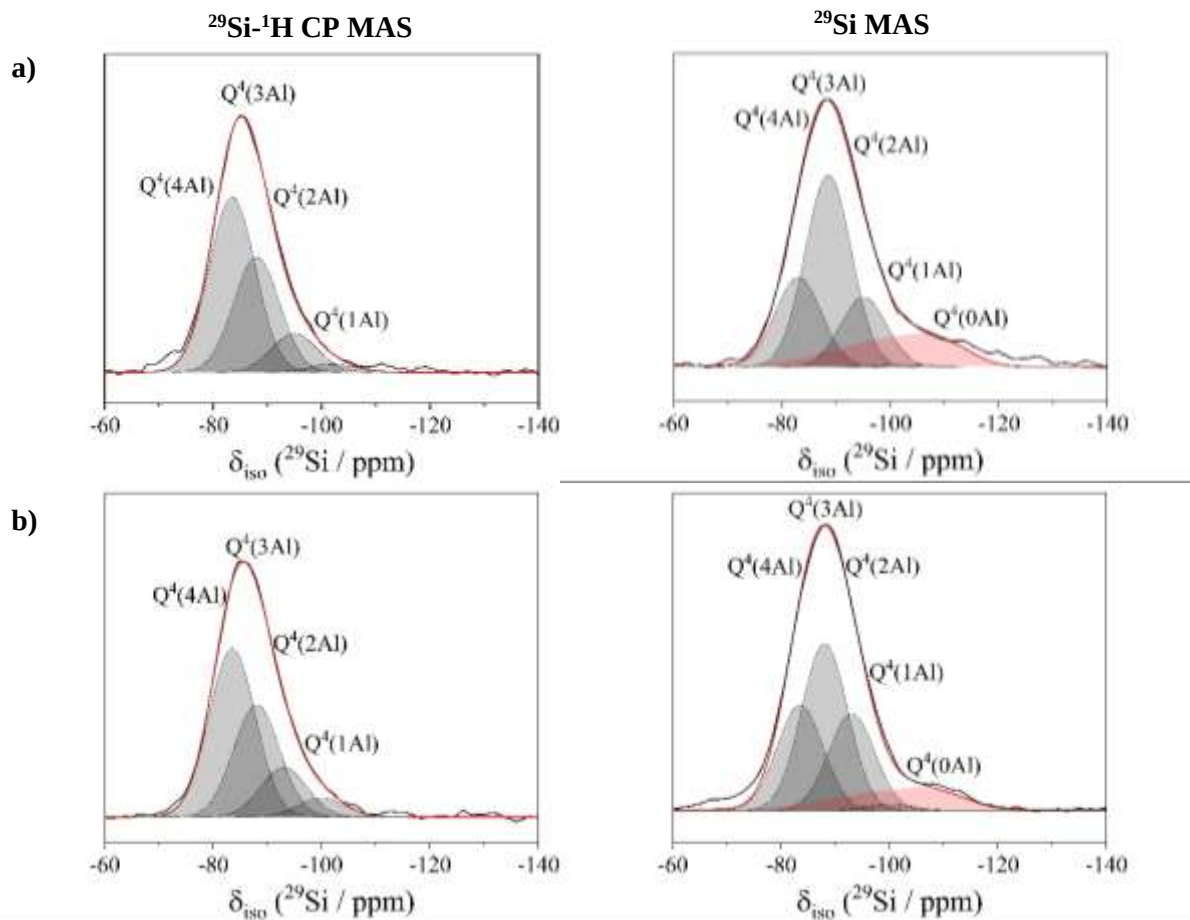


Figure 3-6: ^{29}Si - ^1H CP MAS and ^{29}Si MAS NMR spectra and the associated deconvolutions for the a) KGP sample after 3 days and b) KGP sample after 28 days. The ^{29}Si - ^1H CP MAS NMR data is shown in the left column and the ^{29}Si MAS NMR data is shown in the right column. For each spectrum, the raw data is shown as a solid black line and the model fit is shown as a solid red curve. The deconvolutions that represent each ^{29}Si site within the K-A-S-H gel are depicted as grey curves, whilst the deconvolutions that represent ^{29}Si sites within the unreacted metakaolin are shown in a faded red.

The deconvolution of the ^{29}Si MAS NMR spectra shows that the geopolymer sample as a whole is dominated by $Q^4(3\text{Al})$ sites, which agrees with the literature reporting on potassium activated

geopolymer gels [172, 275]. Between the 3- and 28-day time points, the percentage of Q⁴(3Al) sites decreases slightly and the percentage of Q⁴(4Al) sites increases. This could be due to the continued dissolution of the metakaolin, which releases more Al into solution, and the continued reaction of the metakaolin is shown by the decrease in the area of the faded red curve between the time points in Figure 3-6. This is also supported by the extents of reaction calculated by subtracting the total percentage of silicon sites present due to the unreacted metakaolin, and is shown in Table 3-6.

Table 3-6: The extent of reaction of the KGP sample both 3 and 28 days after initial reaction, calculated using the ²⁹Si MAS NMR spectra.

Time point	Extent of reaction (%)
3 Days	82.17
28 Days	88.00

The Si/Al ratios of the K-A-S-H gel of the samples are shown in Table 3-5. This ratio is calculated using Engelhardt's formula (Equation 3-1) [276].

Equation 3-1: Engelhardt's formula [276].

$$\frac{Si}{Al} = \frac{\sum_{m=1}^4 I_{AQ^4m(Al)}}{\sum_{m=1}^4 0.25 \times m \times I_{AQ^4m(Al)}}$$

In this equation, I_{AQ⁴(mAl)} represents the relative integral areas beneath the deconvoluted resonances in the ²⁹Si MAS NMR spectra. This equation can only be used under the assumption that Loewenstein's rule is followed, where Al-O-Al bonds are negligible [277]. Previous work has shown that this assumption is valid for geopolymer systems where Si/Al > 1 through the use of ¹⁷O 3QMAS NMR spectroscopy [278]. The nominal Si/Al ratios that the samples were designed with is Si/Al = 1.5, and so it is safe to assume that this assumption is valid in this case. The recorded actual Si/Al ratio of the samples is shown to be lower than this value, at 1.32 after 3 days and 1.34 after 28 days. This suggests that the incorporation of Al into the gel is higher than would be expected, suggesting an Al-rich gel. The increase in the ratio between the time points does show an increase in the amount of Si in the gel compared to the Al, and is most likely an artefact of the continued reaction of metakaolin to form a greater quantity of the K-A-S-H gel.

3.4.3.2 ²⁷Al MAS NMR

²⁷Al MAS NMR allows for the local chemical environments surrounding Al sites to be distinguished. The ²⁷Al MAS NMR spectra for the KGP sample both 3 and 28 days after the initial reaction are displayed in Figure 3-7.

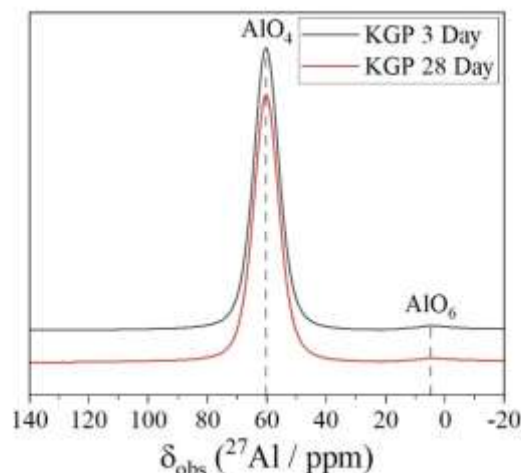


Figure 3-7: ^{27}Al MAS spectra for the KGP sample both 3 and 28 days after reaction.

Previous work shows that a ^{27}Al MAS NMR resonance for the metakaolin precursor contains 3 visible peaks corresponding to the 3 Al coordinations of tetrahedral (AlO_4), pentahedral (AlO_5) and octahedral (AlO_6) [67, 279-281]. As can be seen from Figure 3-7, the spectra for the KGP sample only contains 2 peaks, that of the tetrahedral and octahedral coordinations. Of these two peaks, the structure is clearly dominated by Al in tetrahedral coordination, which is encouraged by the large excess of alkali cations within the gels and gives rise to the negative charge that is then balanced by the cations in question. The peak centres at $\delta_{\text{obs}} = 60.5$ ppm and spans between 50 and 70 ppm. The spectra here agree with ^{27}Al MAS NMR spectra seen in the literature, with an intense peak for the tetrahedral coordination and a less intense peak for the octahedral coordination [67, 282, 283]. The tetrahedral Al sites are bonded to tetrahedral Si (SiO_4) sites within the disordered and highly cross-linked K-A-S-H gel as the energy penalty associated with Al-O-Al bonding promotes the existence of Al in the $q^4(4\text{Si})$ coordination [284, 285].

The small resonance observed at a $\delta_{\text{obs}} = 5$ ppm is attributed to the presence of octahedral Al sites (AlO_6) within the samples [274]. The intensity of this peak is negligible when compared to that of the tetrahedral Al peak, and suggests that the majority of the Al within the metakaolin has reacted as the octahedral peak corresponds exclusively to the Al found within the unreacted metakaolin [279].

Previous work from Duxson et al. suggests that geopolymer gels with an $\text{Si}/\text{Al} < 1.40$ display a further resonance at around 80 ppm, corresponding to pentahedral Al in the form of aqueous $\text{Al}(\text{OH})_4^-$ within the pore structure [279]. All of the samples here have an Si/Al ratio of 1.40 or less, but there is no evidence of any pentahedral Al within the samples here, due to the dehydration of the samples prior to testing. Therefore, the observed Si/Al ratio is true for the K-A-S-H gel.

3.4.3.3 ^{39}K MAS NMR

The use of ^{39}K MAS NMR probes the local environments of the potassium sites within the sample. In geopolymer gels activated by K-silicate, like the samples used in this work, the majority of K sites

within the sample are due to the K^+ ions acting as the charge balancing cation within the K-A-S-H gel [173]. The ^{39}K MAS NMR spectra for the KGP sample both 3 and 28 days after the initial reaction are displayed in Figure .

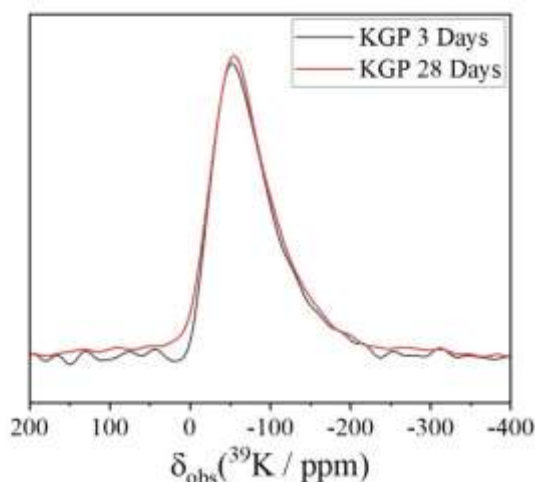


Figure 3-8: ^{39}K MAS NMR spectra for the KGP sample both 3 and 28 days after reaction.

The spectra at both time points are comparable, clearly displaying a singular broad peak that spans between $\delta_{\text{obs}} = 0$ and -200ppm . There is a slight shift between the two time points; after 3 days, the peak centres at $\delta_{\text{obs}} = -55\text{ppm}$ and shifts to $\delta_{\text{obs}} = -52\text{ppm}$ after 28 days of reaction. The very minimal shift suggests that there is little change between the chemical environments of the potassium in the sample between 3 and 28 days of reaction. This is likely because the potassium is acting as the charge balancing cation within the

When comparing ^{39}K NMR data to the literature, it is important to note that the positioning of the peaks is highly dependent on the strength of the magnetic field used within the instrument [286]. This is due to the strong quadrupolar interactions exhibited by the K atoms, which leads to the broad, asymmetric peak observed in the data. There is little literature surrounding the use of ^{39}K MAS NMR on geopolymer samples activated by a potassium silicate activator. However, Duxson et al showed that geopolymer samples similar to the ones used in this work display peaks of similar lineshape, although it must be noted that the peaks presented by Duxson et al. are far sharper than those seen here due to their observations of ^{39}K in species within the pore solution [173]. The broader peaks seen in this work are indicative of the potassium being bound tightly into a rigid solid phase, which is the K-A-S-H gel in the KGP sample. Geddes et al. show that for very chemically similar samples, the line shape of the peak is comparable to those seen in this work [183]. This provides good confidence that the samples here do indeed contain K^+ in charge balancing sites within the K-A-S-H gel.

3.5 Conclusions

The work presented here shows that the reaction to form a metakaolin based, potassium silicate activated geopolymer cement occurs almost completely within the first 3 days of reaction, as shown by the ICC data. A large proportion of this reaction occurs within the first 24 hours, and the main binding

phase of the geopolymer, the K-A-S-H gel, forms throughout this time period as seen in the DRIFTS data. The formation of a geopolymeric specimen is proven through the use of FTIR and solid state NMR, which show that the gel is dominated by silicon in the $Q^4(3Al)$ and $Q^4(4Al)$ tetrahedral coordinations, which is expected after the alkali activation of the metakaolin. Further confirmation is presented in the ^{27}Al and ^{39}K NMR data, which show that these elements are present in singular coordinations within the sample, consistent with what is expected in a K-A-S-H gel. The work discussed in this chapter will serve as a baseline that the remaining work in this thesis will be compared to, acting as the KGP control sample that will be discussed.

4 Chapter 4: The Effect of Strontium Salts on the Kinetics and Mechanisms of Geopolymer Cement Formation

4.1 Introduction

Cementation is ideal for the conditioning of ^{90}Sr containing wastes as a low cost, low temperature disposal route [62, 63, 113]. Geopolymers, an alkali activated aluminosilicate cement binder, have been considered as a viable substitute to Portland cement-based encapsulants. Geopolymers comprise a structurally disordered, highly cross-linked alkali aluminosilicate gel framework containing cation binding sites which possesses the potential to incorporate cations, such as Sr^{2+} , into the gel framework via ion exchange [96, 97]. This, as well as their desirable chemical, mechanical and thermal properties, has led to a significant level of interest surrounding geopolymers as a wasteform for the disposal of radioactive waste.

The most common alkali metals used to produce geopolymers are sodium and potassium, leading to the primary aluminosilicate hydrate gel network being abbreviated to (N,K)-A-S-H (sodium or potassium aluminosilicate hydrate). The nanostructure is described as pseudo-zeolitic; it is identical to that of a zeolite over short distances (no greater than several Å) [123, 133], yet over longer distances the alkali aluminosilicate gel exhibits extensive disorder, and is completely X-ray amorphous, contrasting with crystalline zeolites.

Previous work has focused on the interaction between sodium silicate-activated geopolymers and strontium containing wasteforms yet, potassium silicate-activated geopolymers have been shown to possess more preferential flow characteristics and rheological properties than an equivalent sodium activated geopolymer formulation [287-289].

The kinetics of reaction of the soluble alkali and silica constituents and the solid aluminosilicate precursor (typically metakaolin), and subsequent alkali aluminosilicate gel formation, dictate the initial setting period of the geopolymer [290, 291]. An understanding of these properties allows for the initial phase of reaction to be tailored to its application; for example, altering the speed of reaction to maintain fluidity which allows for better infill of complex waste types with tortuous pathways producing a lower porosity wasteform. The order in which the components of the geopolymer reaction mixture are added together can also significantly alter the early stage kinetics of reaction; there are varying observations in the literature about the speed at which the reaction occurs, and an understanding of the role of each constituent and its point of addition carries both scientific and industrial importance.

The understanding of the mechanisms involved in the formation of the K-A-S-H gel, the main binding phase in potassium-activated geopolymers, is fundamental when considering its suitability as a wasteform for the disposal of nuclear waste. The radionuclide binding capacity of the geopolymer is dictated by the nanostructure that develops during the formation of the K-A-S-H gel. The order in which the reactants are added can also alter the mechanisms of formation as the constituents available for

reaction change depending on this. An understanding of when to add each constituent to maximize the chemical immobilisation of the radionuclide is essential to develop a robust wasteform that will perform over the required period of time.

This work investigates the impact of incorporating various salts of non-radioactive isotopes of strontium (Sr) on the kinetics and mechanisms of reaction, and K-A-S-H gel formation of potassium silicate-activated geopolymers. The chemical environments created by the introduction of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, SrCO_3 , $\text{Sr}(\text{NO}_3)_2$ and SrSO_4 to the geopolymer reaction mixture simulate the potential interactions observed when complex waste streams resulting from e.g. cooling water, radioactive sludge/slurries, spent-ion exchange materials, etc., containing Sr are encapsulated/immobilised within a geopolymer wasteform. Isothermal conduction calorimetry (ICC) is used to monitor the heat evolution of the system, and zeta potential measurements are taken to determine the electrokinetic potential on the surface of the solid reactant particles, which can help to reveal the reaction mechanisms of any changes to the heat evolution. Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction are coupled with solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy probing the local environments of ^{27}Al , ^{29}Si , ^{39}K and ^{87}Sr , and X-ray adsorption near edge structure (XANES) to observe the any nanostructural changes caused by the presence of the Sr salts. These are visualised by the use of electron probe microanalysis (EPMA) imaging. The findings of this work provide an important overview of the early stage reactions within the geopolymer wasteforms, and suggest that these materials are suitable for the long-term immobilisation of radioactive waste streams containing ^{90}Sr .

4.2 Results and Discussion

4.2.1 Strontium Hydroxide

4.2.1.1 Fresh State

4.2.1.1.1 ICC

Figure 4-1 displays the calorimetry curves produced by the reaction of the K-geopolymers loaded with $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ over the first 3 days of reaction.

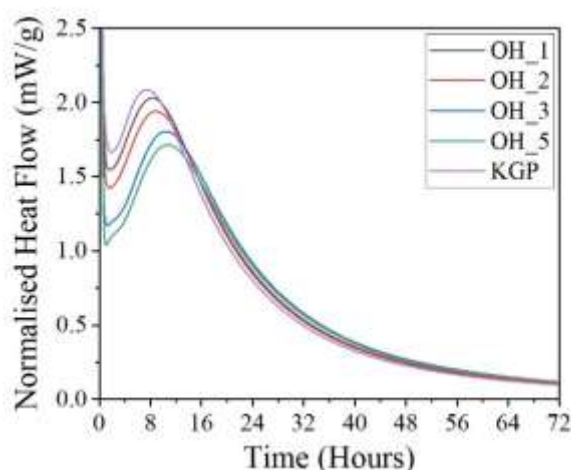


Figure 4-1: The effect on the heat evolution of reaction of loading K-activated metakaolin geopolymers with $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ over the first 3 days.

Each of the curves display a single broad peak within the first day of reaction. Previous work shows that the reaction process for geopolymers produces three distinct peaks in the calorimetry data [292]. Dissolution of the metakaolin as a result of the high pH of the activating solution is attributed to the appearance of the first peak, which usually occurs within the first few minutes of reaction. The method used in this work does not allow for this peak to be fully observed in its full state due to the initial mixing of the reaction mixture occurring outside of the calorimeter. Therefore, any sign of this first peak will be disregarded and all observations will be taken from the second peak, which is attributed to the heat produced from the formation of the aluminosilicate framework as observed in Figure 4-1. Finally, some systems exhibit a third peak which is attributed to the transformation of the aluminosilicate gel framework into more thermodynamically stable states [128]; this transformation happens toward the end of reaction, past the 3 day period investigated in this work, and is not always observed. As such, no evidence of this peak could be seen in any of the samples in this work.

Figure 4-1 shows that the addition of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ has a mild effect on the kinetics of the reaction process. Increasing the Sr/Al ratio increases the level of retardation of the reaction, as the maximum observed heat flow both decreases, and occurs later in the reaction. This can also be seen in Figure 4-3, which shows that the time of maximum heat evolution increases and the maximum heat evolution itself decreases with increasing Sr/Al ratio. All of the samples in this study had formed hardened monoliths by 24 hours after the initial reaction.

The solubility of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ is very low, and is not expected to fully dissolve into solution when combined with the activator [293]. Therefore, the effect of the addition of the salt on the kinetics will be partially due to the salt acting as a filler material within the gel phase. However, this ‘filler effect’ is not able to explain why there is an observed retardation of the reaction, meaning that multiple mechanisms are responsible for the changes that are seen in Figure 4-1.

A useful analogy to this is the use of quartz in the R^3 test method for the chemical reactivity of SCMs. In order to monitor the reactivity of varying supplementary cementitious materials (SCMs) such as ground granulated blast furnace slag (GGBFS) and pulverized fly ash (PFA), the R^3 test introduces the SCM into a pseudo-cementitious system composing of $\text{Ca}(\text{OH})_2$, calcite, alkali and sulphate to replicate ‘real’ PC without the PC clinker itself [294, 295]. Within this test, quartz is utilised as an inert material, meaning it does not react with the system and acts as a filler material within the structure [294, 296]. Upon the addition of quartz, a reduction in the heat evolved during the reaction is observed, much like that seen in Figure 4-1 upon the addition of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ [295]. Therefore, it could be suggested that the addition of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ to the geopolymer mix leads to the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ acting as a filler material and not partaking in the reaction.

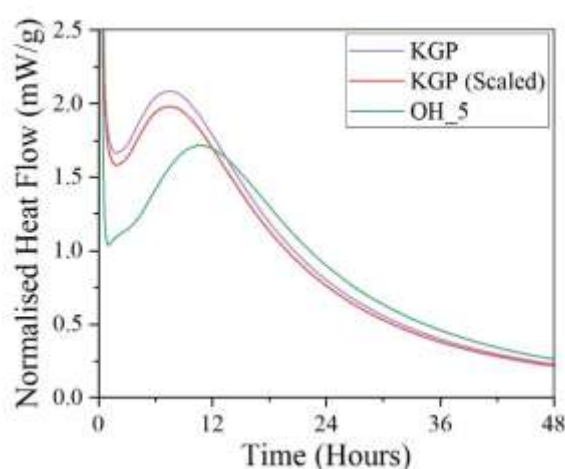


Figure 4-2: The heat evolution of the KGP and OH_5 samples compared to a scaled curve of the KGP sample.

Figure 4-2 shows the KGP and OH_5 samples seen in this work to a scaled version of the curve generated by the KGP sample, shown in red. This is calculated by normalising the heat evolution of the KGP sample by a mass that would be consistent with a OH_5 sample with the same mass of metakaolin and activating solution as the 20g KGP sample. This curve gives the normalized heat evolution of the situation that could be described as the ‘extreme case’ scenario, where none of the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ dissolves into the activating solution and remains as a solid, acting as a filler material. As can be seen, the curve for OH_5 is quite dissimilar to the scaled version of the KGP curve, suggesting that at least some of the salt dissolves into solution. This supports comments previously made in this section, that it is likely that the filler effect is being complimented by another effect caused by the slight dissolution of the salt and introduction of Sr^{2+} ions into the geopolymer mix.

Figure 4-3 shows that the relationships between Sr/Al ratio and both time and value of the maximum heat evolution of the visible peak in the data are approximately linear, although the effect begins to dampen between an Sr/Al ratio of 0.075 and 0.125. This suggests that the maximum retardation of reaction caused by $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ within this KGP formulation is reached around this region, as adding

more of the salt above an Sr/Al ratio of 0.075 has less of an effect on the kinetics of reaction when compared to the salt addition at a lower Sr/Al ratio.

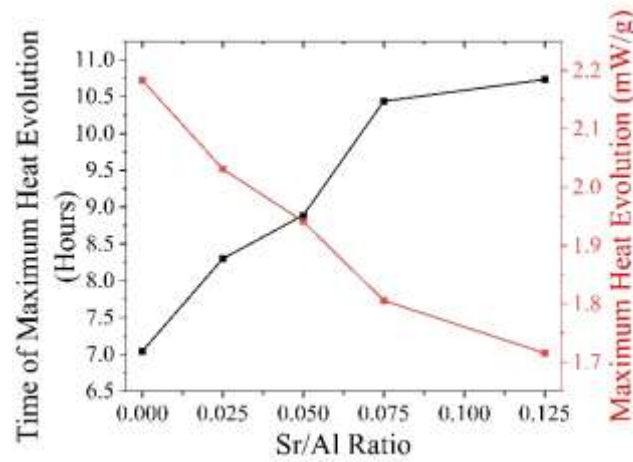


Figure 4-3: The relationship between Sr/Al ratio and the observed time of maximum heat evolution and the value of the maximum heat evolution.

Figure 4-4 shows the cumulative heat release of the systems over the first 6 days of reaction. The cumulative heat release is a measure of the thermal release due to the polymerisation reaction of the geopolymer, along with any further metakaolin dissolution that occurs after the introduction of the sample to the chamber. The heat release after 144 hours is equivalent to approximately 2/3 of the total heat release of the system for PC, and this can be assumed to be the same for geopolymer systems. Both geopolymer and PC systems undergo the majority of their reaction in the first few days after the initial mixing of the reactants. Heat release after the first week in both systems is mainly down to the reorganisation of the phases into more ordered and thermodynamically favourable configurations. Therefore, due to the similarity of the reaction profiles of the two cements, it is valid to assume that the heat release profiles will also be comparable. Using this assumption, the total heat release of the geopolymers containing strontium hydroxide will be no more than 330 J/g even in the case of the OH_1 sample, which shows the greatest cumulative heat release [297]. This is higher than the average heat release of the current nuclear standard, a Portland cement and GGBS blend, which is around 100 J/g but is within the guideline value of 180 J/g over the first 24 hours of reaction set by the current UK requirements for nuclear wastefoms [298, 299].

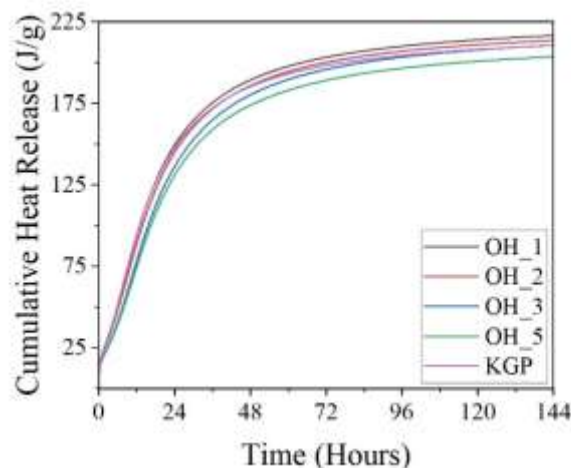


Figure 4-4: The cumulative heat release curves over the first 144 hours of reaction.

4.2.1.1.2 Zeta Potential

The zeta potential values obtained for the surface charge of the metakaolin in the presence of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ at different pHs is shown in Figure 4-5.

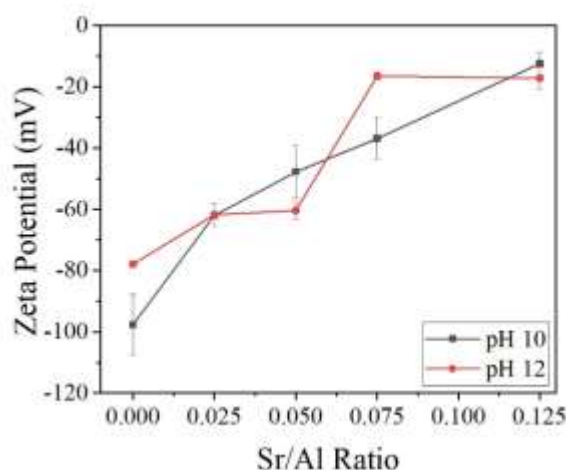


Figure 4-5: Comparing the effect of Sr/Al ratio, altered by the addition of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, on the zeta potential of metakaolin in a KOH solution at pH 10 and 12.

The zeta potential values for the metakaolin, the samples with an Sr/Al ratio of 0, become less negative as the pH increases from pH 10 to pH 12. This agrees with previous work in this area, where Derkani et al. showed that the dissolution of metakaolin occurs at a higher rate at a higher pH [159]. The net negative charge that is seen on the surface of the metakaolin is due to the deprotonation of surface hydroxyl groups in the alkaline environment [159]. As the pH increases, the number of sites that are deprotonated also increases, leading to a higher pH.

Derkani et al. also show that the introduction of divalent cations, such as the Sr^{2+} seen in this work, leads to an increase of the recorded zeta potential towards a value of 0 [159]. This is due to the cation adsorbing to the surface of the metakaolin particles. The zeta potential results here suggest that the solubility of the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ at these high pH's is not sensitive to the pH of the solution, as the

solution is already saturated with OH^- ions at these pH values, driving the equilibrium point towards the solid form in line with Le Châtelier's principle. The zeta potential trends do not drastically change between pH 10 and pH 12, reaching a value of around -12.4 mV at its greatest. This is due to the positively charged Sr^{2+} ions adsorbing to the surface of the metakaolin. It can be assumed that this would also be similar in the geopolymer systems themselves at the slightly higher pH seen in the real systems.

The presence of K^+ cations from the KOH solution will lead to an increase in the zeta potential, as these cations will also be drawn to the negative sites on the metakaolin surface. However, the concentration of K^+ ions is not altered between the Sr/Al ratios at either one of the pHs used here. Therefore, there will be the same number of K^+ cations when the zeta potential is at -97.7 mV (pH 10, Sr/Al ratio of 0) as when the zeta potential is -12.4 mV (pH 10, Sr/Al ratio of 0.125). Therefore, due to the difference in recorded values of zeta potential, it is clear that the main contributor to this change is the introduction of the Sr^{2+} cation. It is also likely that the Sr^{2+} interactions are dominating when compared to the OH^- ions as the introduction of the OH^- ions here are negligible when compared to the concentration of OH^- ions already present in solution.

The mechanism for the increase in zeta potential is unknown, however, it is posed that the shift in surface charge towards neutral promotes the agglomeration of the metakaolin particles in solution [300, 301]. This agglomeration results in a reduction to the total surface area of metakaolin available and, therefore, a reduction in the dissolution rate. Another potential mechanism for the reduced dissolution rate is the formation of a layer of Sr^{2+} particles on the surface of the metakaolin, producing a physical barrier that lowers the concentration gradient between the metakaolin and the surrounding solution. This mechanism is inspired by the dissolution of glass, as outlined in Frugier et al. [302]. Although the materials are different, the concept of a physical barrier to dissolution fits the work seen here, as the Sr^{2+} ions are drawn to the surface of the metakaolin. In reality, it could be either one of these mechanisms, or a combination of both, that leads to the reduced rate of dissolution seen by the OH samples in the ICC.

The zeta potential results seen in Figure 4-5 suggest that the delay in reaction seen in the ICC results are, in some part, due to the effect of the Sr^{2+} cations on the dissolution of the metakaolin. The reduced rate of dissolution leads to a lower concentration of silicon and aluminium particles within the solution, meaning that the reaction to form the geopolymer cannot occur until a later stage in the reaction. The effect is seen to increase as the Sr/Al ratio increases, which is exactly what can be seen in the ICC data. This effect on the surface charge of the metakaolin, coupled with the filler effect exhibited by the undissolved $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, leads to the changes to the heat flow of the reaction seen in the ICC.

4.2.1.1.3 DRIFTS

The DRIFTS spectra for the OH_5 sample in the first 4 hours of reaction can be seen in Figure 4-6.

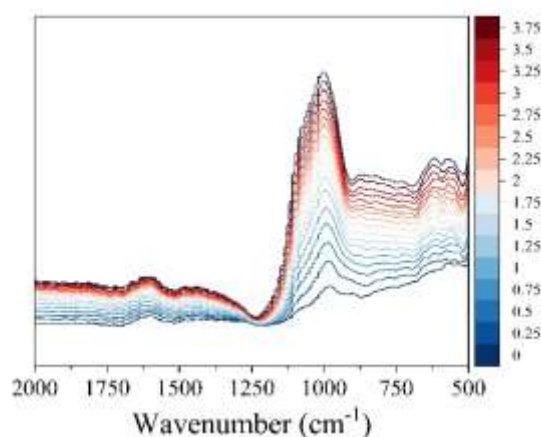


Figure 4-6: DRIFTS spectra for the OH_5 sample in the first 4 hours of reaction. The spectra are displayed in 15 minute intervals, beginning at $t=0$ as marked and progressing through the colour gradient. Times are shown in hours.

Over the first 4 hours of reaction, the Si-O-T peak, centred at $\sim 1000\text{ cm}^{-1}$, continuously grows, representing the reaction that forms the K-A-S-H gel beginning rapidly post mixing. This shows that the reaction occurs almost immediately after dissolution, as suggested by Duxson et al. in the state of the art review of 2007 [129]. Over time, this peak continues to grow as more of the metakaolin dissolves, increasing the concentration of aluminate monomers within the system and allowing for further reaction. The peak begins to broaden to higher wavenumbers as time progresses, suggesting that there is more than one Si-O-T environment present within the sample, indicative of the Si-O-Si and Si-O-Al environments present due to the bonding between silicate and aluminate tetrahedra within the gel. There are no other clear peaks present at this point in the reaction.

The spectra for the KGP sample over the first 4 hours of reaction is shown in Figure 4-7.

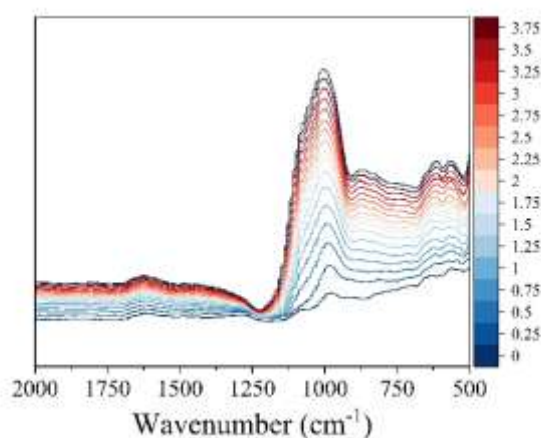


Figure 4-7: DRIFTS spectra for the KGP sample in the first 4 hours of reaction. The spectra are displayed in 15 minute intervals, beginning at $t=0$ as marked and progressing through the colour gradient. Times are shown in hours.

There is very little change between the OH_5 sample and the KGP control sample over the first 4 hours of reaction. The main Si-O-T peak follows a similar pattern, starting almost immediately after dissolution. This suggests that the addition of the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ has very little impact on the initial structural phase evolution with respect to the chemical formula of the K-A-S-H gel.

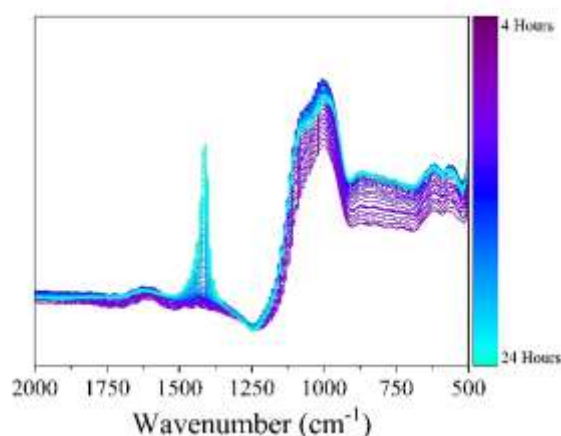


Figure 4-8: DRIFTS spectra for the OH_5 sample from 4 to 24 hours post initial reaction. The spectra are displayed in 15 minute intervals up until the 16-hour mark, at which the time progresses in whole hours, beginning at $t=4$ hours as marked and progressing through the colour gradient. Times are shown in hours.

The spectra for the OH_5 sample for the remainder of the first day of reaction (4 hours to 24 hours) is displayed in Figure 4-8. The Si-O-T peak continues to grow following the first 4 hours and the appearance of two distinct peaks becomes more apparent. The growth continues up until 9 hours post reaction; at this point, the intensity of the two peaks begins to drop. It is not clear why this happens, as, as previously mentioned, DRIFTS is a relatively new analysis technique for cement. Therefore, further research is required to fully understand the phenomena that is seen. It is most likely that the shrinkage of the cement is responsible for this drop; as the cement begins to harden, it shrinks, changing the distance between the surface of the sample and the detector [269, 270]. This occurs in this situation as the same sample is used throughout the measurement and, during this time, no changes are made to the apparatus and so the measurement distance does not change.

Also during this time, a second peak forms at approximately 1400 cm^{-1} . This begins around 11 hours after the initial reaction and continues to grow as the reaction progresses. The cause of this peak is likely to be the carbonation of the sample due to reaction with the CO_2 in the air. The infrared beam used for the DRIFTS measurement must pass through the surface of the sample to reach the bulk material. Therefore, artefacts from the surface of the sample, notably the point where carbonation would occur, will always be included in the spectra. Due to this, it is most likely that this peak is a reflection of the carbonation of Sr within the sample. This peak is also visible in the spectra for the KGP sample for the 4 to 24 hour period after initial reaction, as seen in Figure 4-9.

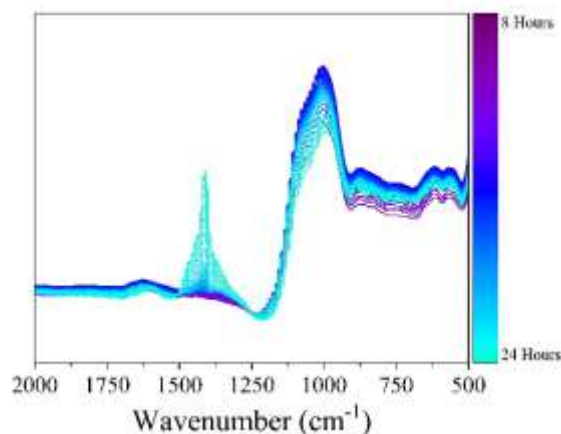


Figure 4-9: DRIFTS spectra for the KGP sample from 4 to 24 hours post initial reaction. The spectra are displayed in 15 minute intervals up until the 16-hour mark, at which the time progresses in whole hours, beginning at $t=4$ hours as marked and progressing through the colour gradient. Times are shown in hours.

The appearance of this peak comes at a later time point than is seen in the OH_5 sample, suggesting that the carbonation of K within the sample comes at a later point, which supports the fact that the presence of Sr is causing the carbonation in the OH_5 sample. Moreover, the intensity of this peak in the KGP sample is far lower, which signifies that less carbonation is occurring in this sample.

By comparing the Si-O-T peaks in the OH_5 and KGP samples, it can be seen that the presence of 2 peaks is far more prominent in the OH_5 sample. This is evidence for the inclusion of Sr into the structure of the geopolymer, displacing some of the K in the K-A-S-H gel from the charge-balancing cation sites. The incorporation of Sr into the gel leads to a reduction in the Si/Al ratio of the gel, essentially resulting in a greater number of Al sites in relation to the Si sites. This is seen in the OH_5 sample here, and can be ratified by the findings of the ^{29}Si MAS NMR seen in Section 3.4.3.1.

4.2.1.1.4 Order-of-addition Experiments

In order to determine whether the point at which the Sr salt is added to the mix impacts the performance of the geopolymer, order-of-addition experiments were performed as outlined in section 2.1.1.2.

4.2.1.1.4.1 Order-of-addition #1

1. The $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ does not dissolve in the water at this stage due to its low solubility [303].
2. The addition of the solid KOH, and the resultant heat production, did not change the state of the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$; it still does not dissolve in the solution.
3. The addition of the silicate stock solution led to a reaction within the solution. The formation of a ‘cloudy, white’ solid was observed within the solution. This solid did not lead to a hardened monolith, and there was still some liquid solution left. The FTIR spectra of this solid can be seen in Figure 4-10.

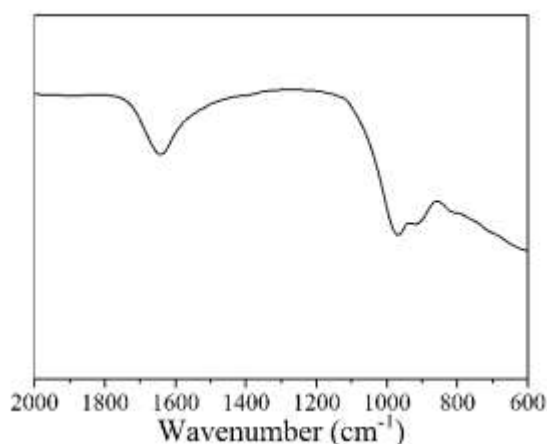


Figure 4-10: FTIR spectra of the white solid observed after stage 3 of the order-of-addition #1 experiment containing $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$.

4. The addition of the metakaolin did lead to the formation of what appeared to be a geopolymer. However, the dissolution was not complete and a proportion of the metakaolin remained undissolved as the solution reacted with the surface metakaolin and was too viscous to move through the rest of the container.

Figure 4-10 shows the FTIR spectra for the solid that forms after the addition of K-silicate to the KOH and $\text{Sr}(\text{OH})_2$ solution. The sharp peak at 1600 cm^{-1} indicates the presence of water. The peak at around 1000 cm^{-1} is indicative of the Si-O-Si bond introduced by the silicate.

There is also another peak present at $\sim 920\text{ cm}^{-1}$. This peak could be indicative of the lack of dissolution of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, as this is present in the FTIR spectra displayed by the raw compound, as shown in Figure 4-11.

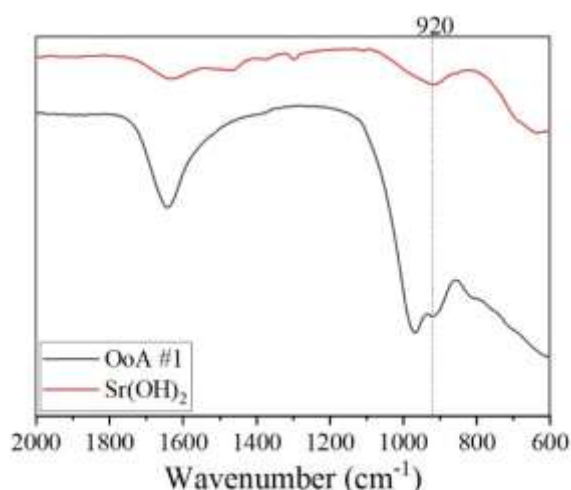


Figure 4-11: The FTIR spectra of the OoA #1 sample compared to pure $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$.

However, due to the lack of intensity of this peak in the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ spectra, this peak in the order-of-addition spectra could indicate the presence of a further silicate compound within the solid, or

potentially a secondary silicate site within the compound. This is further evidence for the formation of a strontium silicate compound in some form, whether it be pure strontium silicate or a potassium strontium silicate as discussed below.

There is the potential that this salt is a mixture of both potassium and strontium silicate. The introduction of the divalent Sr^{2+} cation and its subsequent displacement of the monovalent K^+ cation within the K-silicate structure could lead to the bridging of silicate chains and the precipitation of solid strontium silicate, as shown in Figure 4-12.

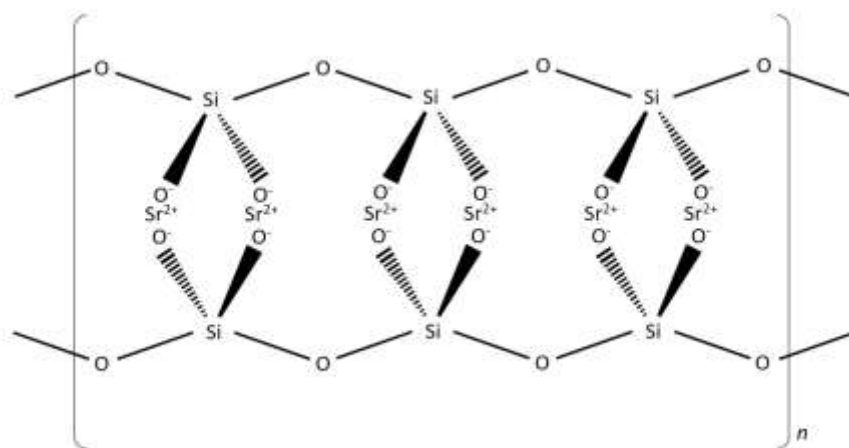


Figure 4-12: Proposed structure for a strontium silicate polymerised chain.

The Si NMR data shows that the OH_5 samples have an increased number of Si sites in $\text{Q}^4(2\text{Al})$ coordination, which supports the potential for this phase. Further discussion on this can be found in Section 4.2.1.2.3.1.

Another possibility is the precipitation of potassium strontium silicate. Glasser et al. showed that sodium strontium silicate has a crystalline structure, and also alluded to the potential for other cations to form crystal structures of a similar nature [304]. Table 4-1 shows the structures of the anions in this type of crystalline compound, as shown by Glasser et al., displaying the potential for potassium strontium silicate crystals to form.

Furthermore, the infra-red spectra for potassium strontium silicate compounds, in the forms $\text{K}_4\text{SrSi}_3\text{O}_9$ and $\text{K}_8\text{SrSi}_{10}\text{O}_{25}$, are both displayed by Gunawardane and Glasser [305]. The peaks seen at $\sim 1000\text{ cm}^{-1}$ and 900 cm^{-1} are comparable to what is shown in the literature. However, these peaks are closely associated with the silicate bonds and may not indicate the presence of Sr and K in the structure. The main differences within the spectra are seen at lower wavenumbers (below 500 cm^{-1}) which are not displayed in Figure 4-10. Future work may include the probing of the structure using infra-red at lower wavenumbers. However, it is continually noted by Gunawardane and Glasser that the preparation of potassium strontium silicate crystals is difficult, and so it is unlikely that this compound has formed in this work and it will not be considered further.

Table 4-1: Symmetries and anion structures of $M'_4M''T_3O_9$ compounds ($T=Si, Ge$), recreated from Glasser et al. [304]. The blank spaces represent areas for further research at the time of publishing, whereas the crossed box represents a compound that cannot be formulated.

$M'' =$ $M' =$						
		Ca	Sr	Ba	T =	
Na			Monoclinic 3-chains			Si
K	Cubic 12-rings			Ψ -cubic 6-chains?		Si
K				Monoclinic 6-chains		Ge

4.2.1.1.4.2 Order-of-addition #2

1. The addition of solid KOH to water leads to an exothermic dissolution reaction.
2. The addition of solid $Sr(OH)_2 \cdot 8H_2O$ did not result in dissolution of the salt. The salt remains as a solid in the KOH solution. No further observations are made.
3. The addition of the potassium silicate stock solution to the KOH solution and solid salt suspension did not result in the formation of the solid that was observed in OoA #1 after stage 3. The solid suspension of $Sr(OH)_2 \cdot 8H_2O$ salt remains within the solution, which was more viscous at this stage due to the K-silicate stock solution. The solution also went a cloudy white colour.
4. The addition of the metakaolin did lead to the formation of what appeared to be a geopolymer. However, the dissolution was not complete and a proportion of the metakaolin remained undissolved as the solution reacted with the surface metakaolin and was too viscous to move through the rest of the container. The Sr salt did not dissolve and so settled to the bottom of the

container as it was being added to the metakaolin. This meant that the Sr salt was simply added to the top of the mixture and was not uniformly added to the mix.

4.2.1.1.4.3 Order-of-addition #3

1. The addition of solid KOH to water leads to an exothermic dissolution reaction.
2. The addition of the K-silicate stock solution to the KOH solution resulted in a clear liquid mix.
3. The addition of solid $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ does not lead to the dissolution of the salt. The salt is suspended within the solution, which went a cloudy white, but not visibly viscous to a greater extent than expected.
4. The addition of the metakaolin did lead to the formation of what appeared to be a geopolymer. However, the dissolution was not complete and a proportion of the metakaolin remained undissolved as the solution reacted with the surface metakaolin and was too viscous to move through the rest of the container. The Sr salt did not dissolve and so settled to the bottom of the container as it was being added to the metakaolin. This meant that the Sr salt was simply added to the top of the mixture and was not uniformly added to the mix.

4.2.1.1.4.4 Order-of-addition ICC

Figure 4-13 shows the calorimetry curves generated by the order-of-addition samples compared to the control KGP sample over the first 3 days of reaction.

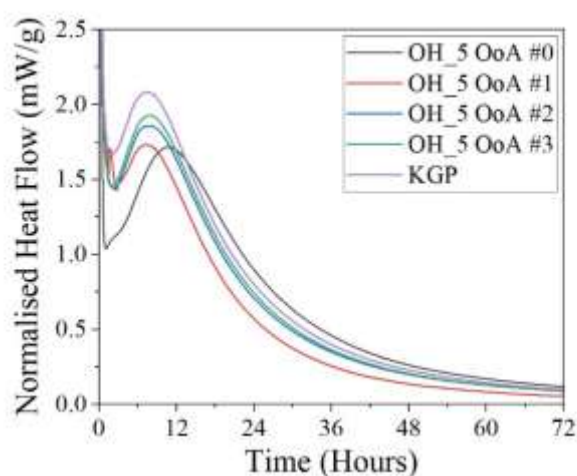


Figure 4-13: The effect on the heat evolution of the reaction of adding $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ at different stages to K-activated metakaolin geopolymers over the first 3 days.

As seen in the calorimetry curves in section 4.2.1.1.1, any addition of the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ salt leads to a reduction in the normalised heat flow output when compared to the KGP sample. The changes to kinetics caused by all of the addition methods does not appear to be significant; The method used in this work, OoA #0, appears to have the greatest impact, retarding the reaction as well as reducing the observed heat flow but this is only by 20%, from ~ 2.1 mW/g to ~ 1.75 mW/g. For OoA #2 and #3, the lack of retardation of the reaction is potentially explained by the lack of dissolution of the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ salt into the solution; upon the addition of the metakaolin, the salt settled at the bottom and did not fully

integrate into the geopolymer mix. Hence, the reaction occurs without the presence of the dissolved salt (as it remains in the solid phase), simulating the control sample. This would support the data, as the time of maximum heat evolution is the same for these samples and the KGP control. Moreover, the lack of complete reaction, signified by the lack of metakaolin dissolution outlined in sections 4.2.1.1.4.2 and 4.2.1.1.4.3, would explain the lower heat flow observed.

Much like the $\text{Sr}(\text{OH})_2$ OoA #0 experiment, the salt did not dissolve into solution for OoA experiments #2 and #3; A ‘gloopy’ solid was formed in OoA #1 but it cannot be confirmed as to whether the salt dissolves into the solution (suspected due to large OH peak in FTIR). The lack of dissolution meant that, once the mixing ceased, the solid salt settled at the bottom of its container, making complete transfer into the ICC ampoule very difficult. The lower heat flow observed for the OoA #1 experiment is explained by the lack of complete dissolution of the metakaolin into the silicate solution. The time of maximum heat flow is comparable to that of the control KGP sample, suggesting that the $\text{Sr}(\text{OH})_2$ was not incorporated into the geopolymer mix in sufficient quantities, much like OoA experiments #2 and #3. The lower heat flow value for OoA #1 is likely due to the lack of reaction caused by the viscous precipitated silicate solution which is unable to migrate through the metakaolin to trigger complete dissolution.

4.2.1.1.4.5 *Order-of-addition Conclusion*

The addition of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ to the activating solution at different stages had very differing effects on the properties of the solution; the salt did not dissolve in the water or the KOH solution and only caused the precipitation of a solid in one of the cases. Due to the solid still being present when the activating solution was mixed with the metakaolin in the other two cases, it could be argued that adding the salt at any point in the mix will have an equal effect, and no special considerations should be taken when incorporating $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ into a geopolymer mix. However, the slight retardation of the reaction caused by its inclusion suggests that, despite the effect being minimal, adding the salt after the initial dissolution of metakaolin within the K-silicate activating solution would be potentially better. However, this may not lead to a sufficient level of immobilisation of Sr via incorporation into the geopolymer gel structure and further experiments may be required to investigate this.

Despite this experiment suggesting that the method used in this work, OoA #0, has the greatest effect on the kinetics of reaction, the information gleaned is important when considering the effect of solids within the bulk wasteform. This method is the most suitable for identifying the effects of dissolved Sr content on the reaction mechanisms and kinetics of the geopolymer samples. Therefore, for all following analysis and discussion, OoA #0 has been used in this work.

4.2.1.2 Hardened State

4.2.1.2.1 FTIR

Figure 4-14 shows the FTIR spectra of the K-geopolymers loaded with $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ after the first 3 days of reaction.

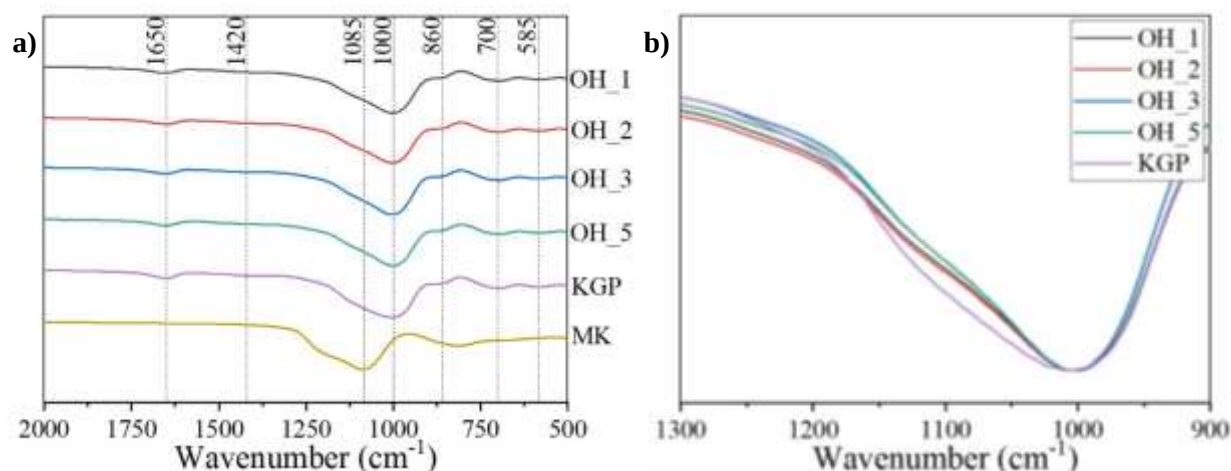


Figure 4-14: The FTIR spectra generated by loading K-activated metakaolin (MK) geopolymers with $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, the KGP control sample and the unreacted metakaolin after the first 3 days of reaction. Plot b) is focused on the 900-1300 cm^{-1} range of plot (excluding the metakaolin) a), and the lines are overlaid.

From Figure 4-14 a), for all samples, the bond vibrations that are responsible for the resonances seen are discussed in Section 3.4.2 and summarised in Table 3-4. The very low intensity band that can be seen centred at 1420 cm^{-1} is indicative of the carbonation of the samples due to exposure to air [271]. This carbonate compound could be potassium carbonate or strontium carbonate, or potentially a mixture of the two.

When comparing the geopolymer samples with varying Sr/Al ratios, only small differences are observed. The shoulder that represents the unreacted metakaolin, shown at $\sim 1100 \text{ cm}^{-1}$ in Figure 4-14 b), is slightly more intense in the KGP sample suggesting that the extent of dissolution is potentially increased by the addition of the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. The extra OH^- ions that are introduced by the inclusion of the salt result in a greater dissolution of the metakaolin. This is further aided by the hydrated state of the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, providing further OH^- ions from the bound water. This would increase the pH and, theoretically increase the speed of the reaction. Furthermore, this could lead to enhanced wetting of the metakaolin particles, providing a larger solid-fluid interface area for the dissolution reaction. However, this increase in dissolution does not lead to an increase in reaction and gel formation as seen in the ICC data, as a greater Sr/Al ratio, and therefore greater associated concentration of added OH^- ions, leads to a reduction in the maximum heat released during the reaction. Therefore, it is likely that the Sr causes the delay in reaction seen in the ICC data.

Walkley et al. (2020) showed that the incorporation of alkaline earth cations such as Sr results in a shift of the band attributed to the asymmetric stretching of the Si-O-T towards higher wavenumbers [67]. The lack of shift of this band suggests that the Sr is not significantly incorporated into the structure, which would further explain the lack of change in the spectra between samples.

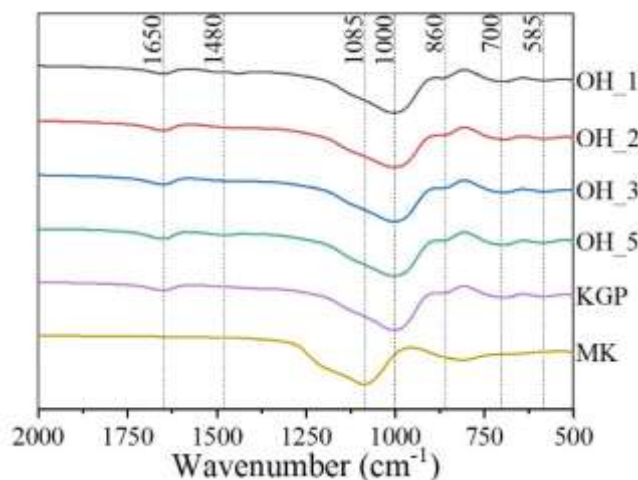


Figure 4-15: The FTIR spectra generated by loading K-activated metakaolin geopolymers with $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, the KGP control sample and the raw metakaolin after the first 28 days of reaction.

Figure 4-15 shows the FTIR spectra of the same samples after 28 days of reaction. As can be seen, many of the peaks present after 3 days of reaction are also present after 28 days, suggesting that the reaction products formed within the first 3 days of reaction are integral in developing the final nanostructure of the geopolymer. The main change that is observed is the shift of the carbonate bond from 1420 cm^{-1} after 3 days to 1480 cm^{-1} after 28 days.

Figure 4-15 also shows that there has been a decrease in the intensity of the shoulder attributed to the Si sites present within the unreacted metakaolin. This suggests that more of this metakaolin has reacted. Despite this, no new bonding sites are observed, and so it is clear that the metakaolin is reacting to form more of the reaction products that were seen after 3 days.

4.2.1.2.2 XRD

The X-ray diffraction spectra for the geopolymer samples containing $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ 3 days after initial reaction are shown in Figure 4-16.

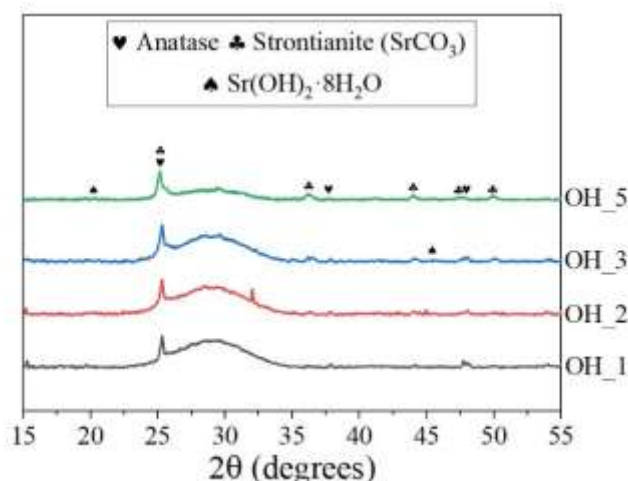


Figure 4-16: The X-ray diffraction spectra generated by loading K-activated metakaolin geopolymers with $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ after the first 3 days of reaction.

The XRD patterns for each sample are comparable, exhibiting a broad diffraction peak between 22° 2θ and 35° 2θ . This peak indicates the presence of an amorphous phase within the sample, notably the presence of the K-A-S-H gel [164].

The XRD patterns for the samples do indicate the presence of some crystalline phases within the hardened gel. The presence of anatase (TiO_2 , Powder Diffraction file (PDF) # 01-084-1286) is indicative of the unreacted metakaolin that remains within the structure, as supported by both the FTIR and NMR data.

The presence of strontium hydroxide octahydrate ($\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, PDF # 00-027-1438) in samples OH_3 and OH_5 is expected due to the low solubility of the salt. It is clear that some of the strontium is still in the form in which it was added to the geopolymer mix, and has not dissolved to be incorporated into the structure due to its low solubility. The diffraction peaks for this salt are not present in the spectra for samples OH_1 and OH_2. This could be due to the concentration being too small in the samples as, potentially, a greater percentage of the mass of the salt has dissolved into the activating solution resulting in a lower mass percentage of solid salt within the sample. The diffraction spectrum for the OH_2 sample shows that there is strontianite (SrCO_3 , PDF # 00-005-0418) present. This is most likely due to the carbonation of the geopolymer due to air, forming SrCO_3 crystals.

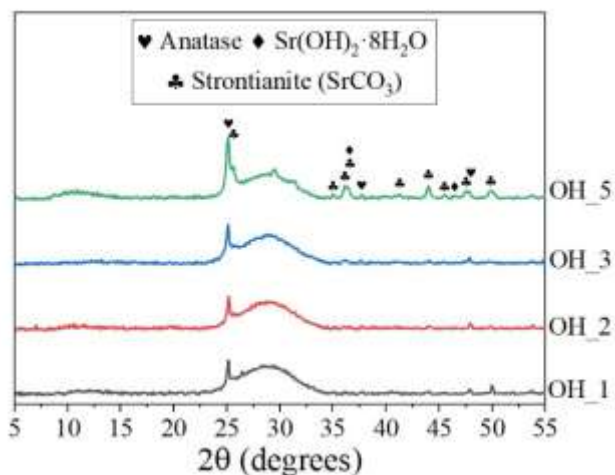


Figure 4-17: The X-ray diffraction spectra generated by loading K-activated metakoalin geopolymers with $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ after the first 28 days of reaction.

The XRD patterns after 28 days are shown in Figure 4-17. Much like the samples after 3 days, there is evidence of carbonation of the samples via the presence of strontianite. This is most prominent in OH_5 and is most likely due to the exposure of the samples to the carbon dioxide within the air. There is no evidence that an K_2CO_3 is present within the samples, suggesting that there is more Sr available to react with the air. Therefore, it is possible that the majority of the K within the sample is being utilised as the charge balancing cation within the geopolymer gel, and that the Sr is being encapsulated within the material. This also corroborates the assumption that the majority of the Sr has not dissolved into solution, and remains as solid $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ within the gel structure. Further evidence for this comes as the XRD patterns show that this phase exists within the sample.

4.2.1.2.3 NMR Spectroscopy

4.2.1.2.3.1 ^1H - ^{29}Si CP MAS and ^{29}Si MAS NMR

The ^1H - ^{29}Si CP MAS NMR and ^{29}Si MAS NMR spectra for the OH_5 and KGP samples both 3 and 28 days after the initial reaction are displayed in Figure 4-18.

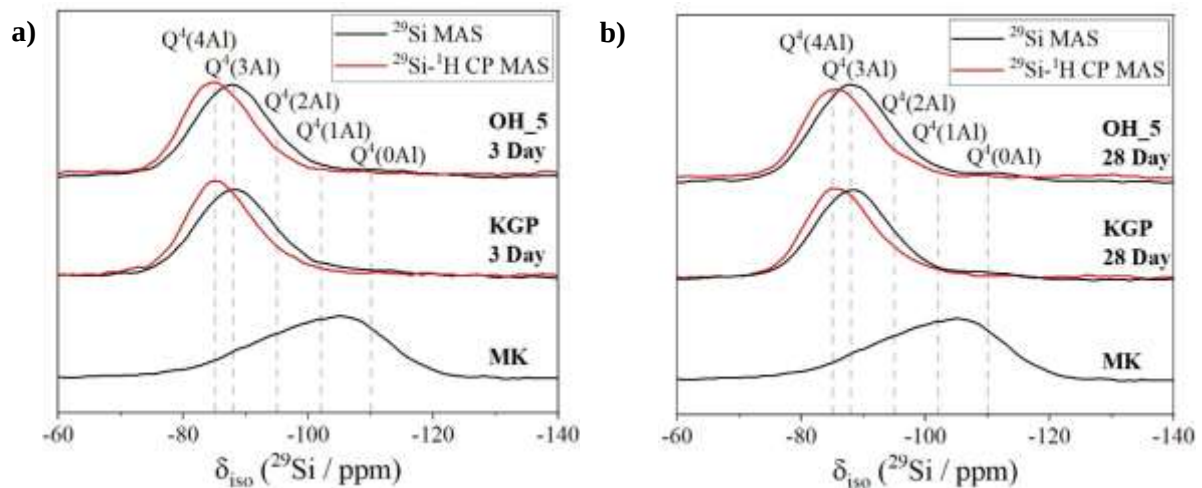


Figure 4-18: ^1H - ^{29}Si CP MAS and ^{29}Si MAS spectra for the OH_5, KGP samples and the unreacted metakaolin (MK) a) 3 days and b) 28 days after reaction.

The ^1H - ^{29}Si CP MAS spectra, shown in red in Figure 4-18, display a single broad peak at δ_{iso} between $\sim \delta_{\text{iso}} = -75$ and $\delta_{\text{iso}} = -110$ ppm. The maximum intensity is reached at $\sim \delta_{\text{iso}} = -85$ ppm, suggesting that the hydrated geopolymer gels are principally composed of $\text{Q}^4(4\text{Al})$ sites in all cases. The use of ^1H - ^{29}Si CP MAS allows for the nanostructure of the hydrated reaction products to be investigated whilst disregarding anhydrous Si sites that represent unreacted metakaolin within the binder. This distinction is possible through the preferential enhancement of the resonances of Si atoms in close proximity to surrounding protons, which is most commonly seen in phases that are in a hydrated state [273].

In contrast, the ^{29}Si MAS NMR spectra display the entire range of Si sites present within the sample, including those that are a result of Si sites within the unreacted metakaolin, most notably $\text{Q}^4(0\text{Al})$ sites. Due to this, the maximum peak intensity for all samples is recorded at a lower δ_{iso} of approximately $\delta_{\text{iso}} = -88/89$ ppm. The shift to lower δ_{iso} values is a result of the contribution to the spectra from the anhydrous Si sites present in the unreacted metakaolin, as shown in Figure 4-18, where the peaks for the $\text{Q}^4(1\text{Al})$ and $\text{Q}^4(0\text{Al})$ arise due to Si sites in the metakaolin. The spectra observed here are similar to those seen in previous work, suggesting that the K-A-S-H gel is formed by a mixture of Si environments in the form of $\text{Q}^4(m\text{Al})$ sites, where $1 \leq m \leq 4$ [67]. This is supported by Table 4-2, which shows the presence of each Si site as a percentage calculated from the ^{29}Si MAS NMR data.

Table 4-2: Relative integral areas for the Si sites present within the K-A-S-H gel of each sample both 3 and 28 days after initial reaction from the deconvoluted ^{29}Si MAS NMR spectra. The $\text{Q}^4(0\text{Al})$ site attributed to the unreacted metakaolin is disregarded for the quantification of the K-A-S-H gel.

Sample	Time point	Relative Integral Area (%)				Si/Al
		$\text{Q}^4(4\text{Al})$	$\text{Q}^4(3\text{Al})$	$\text{Q}^4(2\text{Al})$	$\text{Q}^4(1\text{Al})$	
KGP	3 Days	25	54	20	1	1.32
OH_5	3 Days	27	35	34	4	1.40

KGP	28 Days	28	44	26	2	1.34
OH_5	28 Days	31	32	30	7	1.39

The deconvolution of the NMR spectra allows the amount of each of the individual ^{29}Si sites to be quantified [172]. For the KGP samples, the ^{29}Si MAS NMR spectra in Figure 4-19 show that the gel structure is dominated by $\text{Q}^4(3\text{Al})$ sites, which is in line with data that is widely reported in the literature for potassium activated geopolymers [172]. The OH_5 samples move from a gel structure that is predominantly $\text{Q}^4(2\text{Al})$ and $\text{Q}^4(3\text{Al})$ sites after 3 days, to an increase in the number of $\text{Q}^4(4\text{Al})$ sites after 28 days. This is likely due to the increase in availability of Al to bind into the structure as the reaction progresses. Table 4-2 also shows the molar Si/Al ratio of the K-A-S-H gel, disregarding the Si sites that are attributed to the unreacted metakaolin. This ratio is calculated using Engelhardt's formula (Equation 3-1) [276].

The Si/Al ratio of the OH_5 samples after both 3 and 28 days are greater than that of the KGP sample suggesting that the incorporation of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ at such a high Sr/Al ratio slightly decreases the cation binding capability of the gel. This is contrary to what has been seen in previous work, with Walkley et al. showing that the Si/Al ratio for K-activated geopolymer systems containing Sr is less than the associated control geopolymer system [67]. However, this is using much lower concentrations of Sr within the structure, which would have less of an impact on the formation of the K-A-S-H phase. The greater relative percentage of Si in $\text{Q}^4(2\text{Al})$ configuration in the OH_5 samples when compared to the KGP samples could in fact be evidence of the presence of the strontium silicate phase discussed in Section 4.2.1.1.4.1. This would support the data seen in the order-of-addition experiments and provide evidence of the reaction between the Sr salt and the silicate activating solution.

The Al_2O_3 within the metakaolin dissolves preferentially when compared to the SiO_2 due to Al-O-Al bonds being weaker than Al-O-Si and Si-O-Si bonds [279]. The addition of the Sr could target this dissolution as it sorbs to the surface of the metakaolin, as discussed in Section 4.2.1.1.2, slowing the dissolution of the Al_2O_3 rather than that of the SiO_2 . Therefore, the increase in Si/Al ratio seen in this work can be linked to the retardation of the reaction seen in the ICC (Section 4.2.1.1.1), slowing the dissolution of the Al_2O_3 within the metakaolin when compared to the KGP sample, meaning that the number of Al atoms that are free to bind into the structure is reduced. This is compounded by the decrease in the Si/Al ratio that is observed for the OH_5 sample between 3 and 28 days, suggesting that the metakaolin continues to dissolve over the first 28 days of reaction as shown by the FTIR spectra in section 4.2.1.2.1. However, the deconvolution of the ^{29}Si MAS NMR suggests that the OH_5 sample has reacted to a greater extent after 3 days than the KGP sample. This does not agree with the data that is seen in the ICC, which suggests that the addition of the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ in the OH_5 sample reduces

both the rate and extent of reaction. This is also contrary to the zeta potential results which suggest that the Sr sorbs to the surface of the metakaolin and therefore reduces its rate of dissolution. This is due to the levels of error associated with this method of quantification; the designed model may fit the data well, but there is a chance that it is not completely representative of what is actually happening in the system. Table 4-3 quantifies this extent of reaction, calculated by subtracting the total percentage of silicon sites present due to the unreacted metakaolin, shown in light pink in Figure 4-19 for the OH_5 samples and Figure 3-6 for the KGP samples, from 100%.

Table 4-3: *The extent of reaction of the OH_5 and KGP samples both 3 and 28 days after initial reaction, calculated using the ^{29}Si MAS NMR spectra.*

Sample	Time point	Extent of reaction (%)
KGP	3 Days	82.17
OH_5	3 Days	87.28
KGP	28 Days	88.00
OH_5	28 Days	87.44

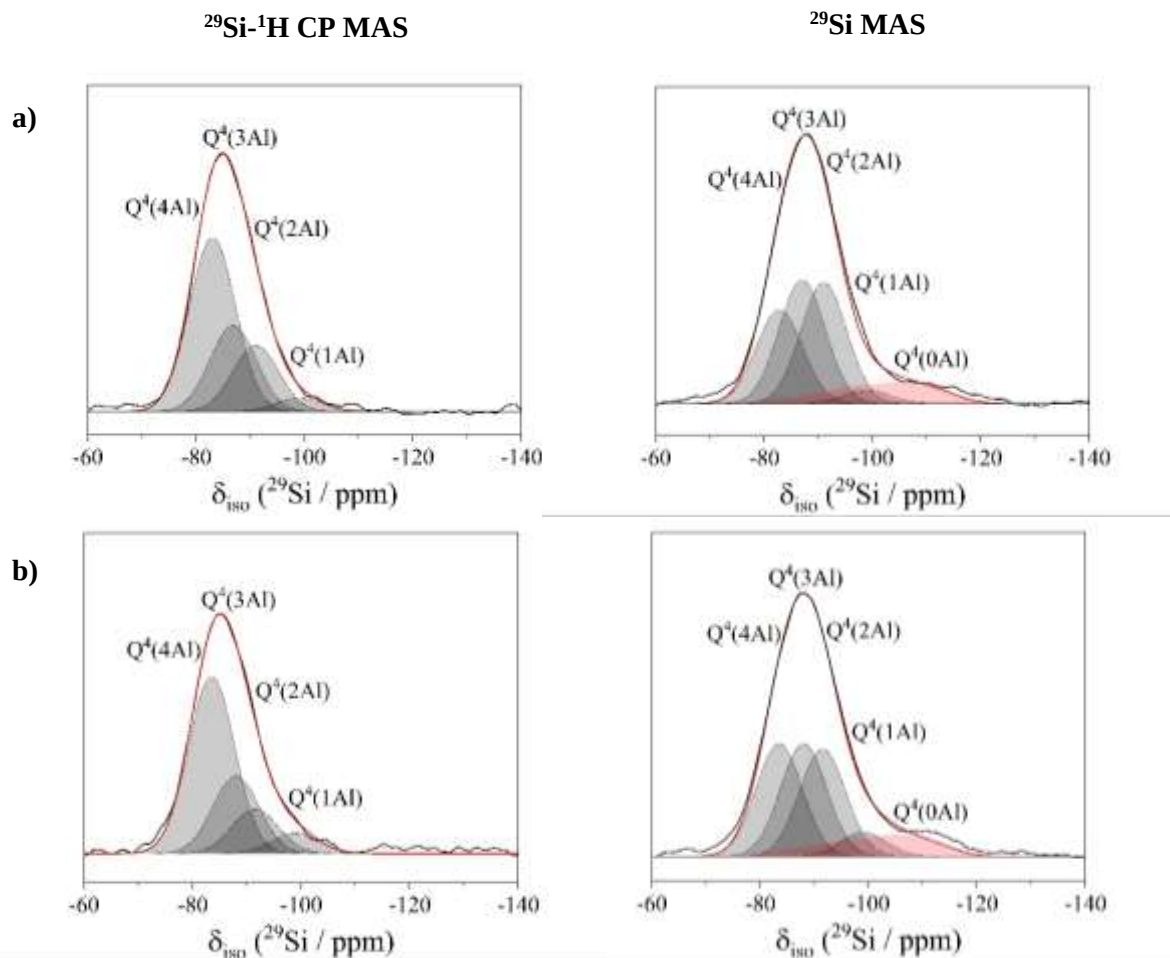


Figure 4-19: ^{29}Si - ^1H CP MAS and ^{29}Si MAS NMR spectra and the associated deconvolutions for the a) OH_5 sample after 3 days and b) OH_5 sample after 28 days. The ^{29}Si - ^1H CP MAS NMR data is shown in the left column and the ^{29}Si MAS NMR data is shown in the right column. For each spectrum, the raw data is shown as a solid black line and the model fit is shown as a solid red curve. The deconvolutions that represent each ^{29}Si site within the K-A-S-H gel are depicted as grey curves, whilst the deconvolutions that represent ^{29}Si sites within the unreacted metakaolin are shown in a faded red.

4.2.1.2.3.2 ^{27}Al MAS NMR

The ^{27}Al MAS NMR spectra for the OH_5 and KGP samples both 3 and 28 days after the initial reaction are displayed in Figure 4-20.

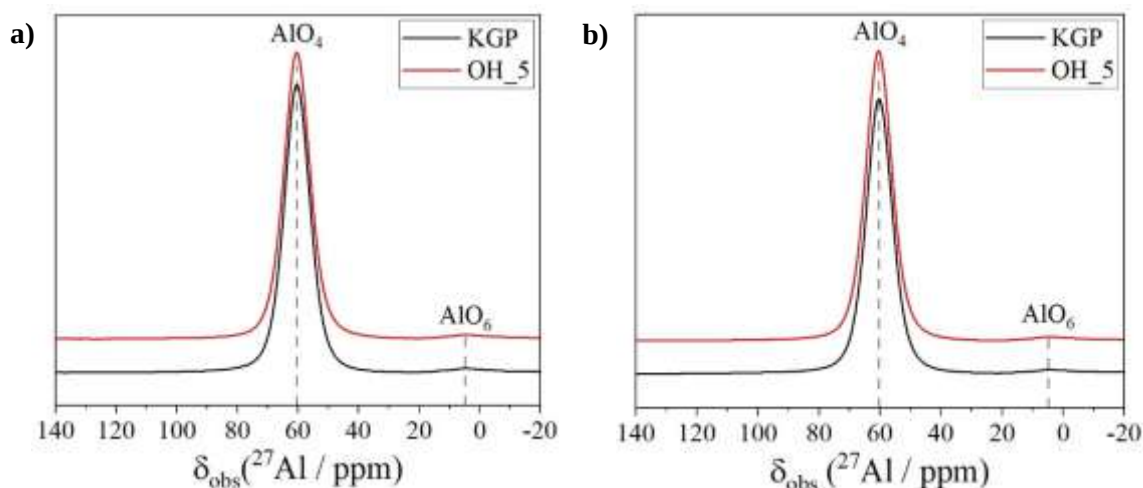


Figure 4-20: ^{27}Al MAS spectra for the OH_5 and KGP samples a) 3 days and b) 28 days after reaction.

Figure 4-20 shows that the ^{27}Al MAS NMR spectra for both the KGP and OH_5 samples display two distinct resonances. The most obvious resonance, centred at $\delta_{\text{obs}}=60.3$ ppm and spanning between $\sim \delta_{\text{obs}}=50$ ppm and $\delta_{\text{obs}}=70$ ppm is recognisable as the tetrahedral Al site (AlO_4^-) found in the K-A-S-H gel phase of the geopolymer [279, 306]. This coordination is promoted by the large excess of alkali cations within the gels and gives rise to the negative charge that is intricate to the use of geopolymers in the application of the disposal of radioactive Sr, and is introduced by the substitution of Al^{3+} ions for Si^{4+} as shown by Figure 4-21 [307]. This negative charge is balanced by cations: K^+ in the KGP sample and a combination of both K^+ and Sr^{2+} in the OH_5 sample [308]. The preference of Al to exist within the $\text{q}^4(4\text{Si})$ coordination is due to the energetic penalty associated with Al-O-Al bonding [284, 285].

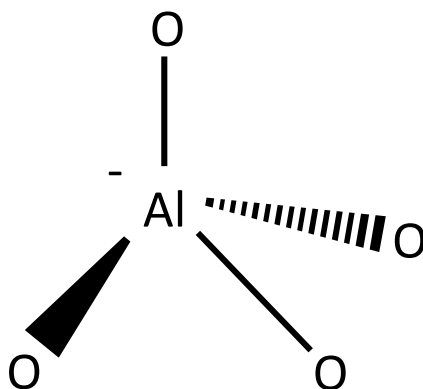


Figure 4-21: Al in tetrahedral coordination.

The small resonance observed at ~ 5 ppm is attributed to the presence of octahedral Al sites (AlO_6) within the samples [274]. The intensity of this peak is negligible when compared to that of the tetrahedral Al peak, and suggests that the majority of the Al within the metakaolin has reacted as the tetrahedral peak corresponds exclusively to the Al found within the unreacted metakaolin [279]. This is supported by the findings of both the ^{29}Si MAS and ^1H - ^{29}Si CP MAS which display the preferential dissolution of Al during the dissolution phase of the reaction.

As discussed, the spectra for both the KGP and OH_5 samples display Al within the samples in both the Al(IV) and Al(VI) species. Previous work from Duxson et al. suggests that geopolymer gels with an Si/Al < 1.40 display a further resonance at around 80 ppm, corresponding to Al(V) in the form of aqueous $\text{Al}(\text{OH})_4^-$ within the pore structure [279]. All of the samples here have an Si/Al ratio of 1.40 or less, but there is no evidence of any Al(V) within the samples here, due to the dehydration of the samples prior to testing. Therefore, the observed Si/Al ratio is true for the K-A-S-H gel.

4.2.1.2.3.3 ^{39}K MAS NMR

The ^{39}K MAS NMR spectra of the OH_5 sample and the KGP control sample can be seen in Figure 4-22 at the time points of both 3 and 28 days.

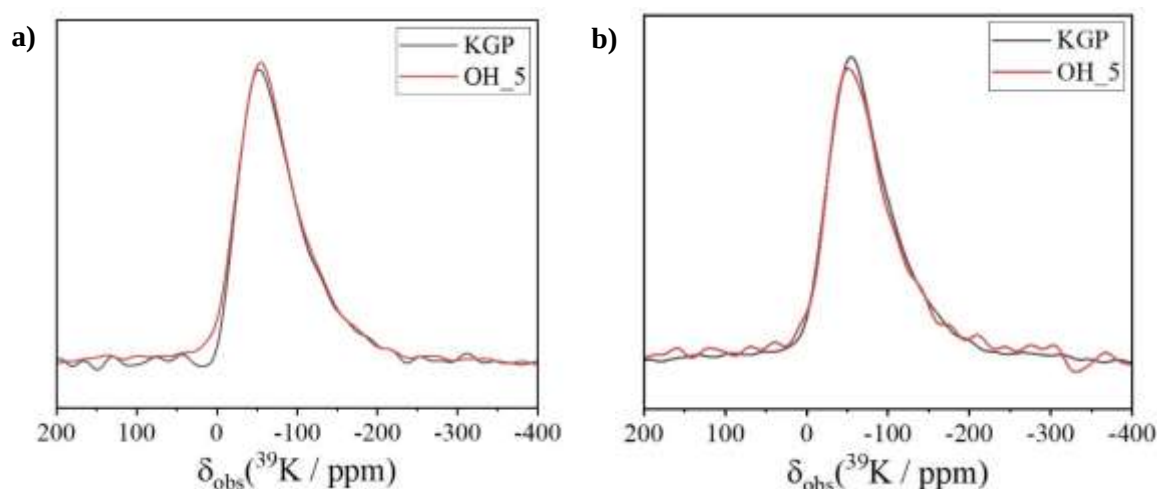


Figure 4-22: ^{39}K MAS NMR spectra for the OH_5 and KGP samples a) 3 days and b) 28 days after reaction.

Figure 4-22 shows that there is very little difference between the OH_5 samples and the KGP samples at both 3 and 28 days. Moreover, there is very little observable change between the OH_5 samples at 3 and 28 days. The peaks for all samples are observed between $\delta_{\text{obs}} = -50$ and $\delta_{\text{obs}} = -55$ ppm, and the line shape across the samples is comparable, suggesting little change to the chemical environments experienced by the K atoms within the sample. The presence of only a single peak suggests that there is only one K phase within the sample. In work by Geddes et al. undertaken on Na-based geopolymers, it was shown that the observed peak in ^{23}Na NMR data shifts upon the incorporation of Sr as a charge balancing cation into the geopolymer gel matrix [183]. This shift is also seen in the 28-day ^{39}K NMR data presented here, suggesting that some of the Sr is incorporated into the K-A-S-H gel in place of the K. The shift seen here, from $\sim \delta_{\text{obs}} = -55$ ppm in the KGP control sample to $\sim \delta_{\text{obs}} = -51$ ppm in the OH_5 sample is consistent with the shielding of K^+ cations due to the presence of Sr^{2+} in the charge balancing sites within close proximity to the K.

As discussed in Section 3.4.3.3, the comparison to literature should focus on the lineshape of the peaks. Therefore, it is possible to conclude that it is likely that some of the K^+ cations have substituted by Sr^{2+} cations as charge balancing cations within the geopolymer gel structure.

4.2.1.2.3.4 ^{87}Sr Solid-State NMR

The ^{87}Sr NMR spectra for the OH_5 sample after 3 days of reaction is shown in Figure 4-23. The data for the sample after 28 days could not be acquired and further attempts to acquire this should be made in the future.

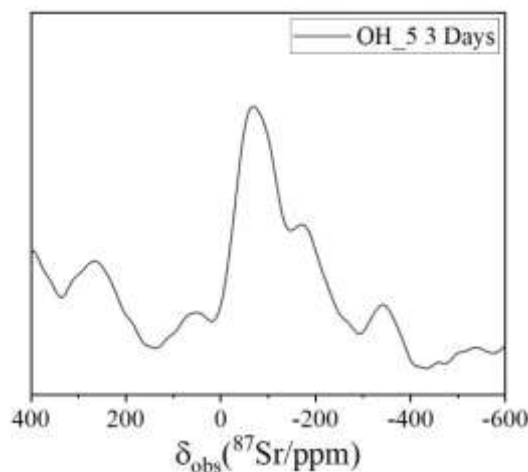


Figure 4-23: ^{87}Sr solid-state NMR spectra for the OH_5 sample after 3 days of reaction.

The spectrum here suggests that Sr is present in multiple chemical environments within the geopolymer sample, denoted by the presence of a clear peak at $\sim \delta_{\text{obs}} = -70\text{ppm}$ in the OH_5 sample after 3 days of reaction. Furthermore, the shoulder on this peak at lower δ_{obs} values, $\sim -173\text{ppm}$, suggests the presence of a further Sr chemical environment within the sample. The low solubility of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ in the activating solution, accompanied by other findings in this work such as the XRD data discussed above, suggest that one of these sites is likely to be that of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. This would leave the salt physically trapped, or encapsulated, within the pore structure of the geopolymer. The crystalline structure of $\text{Sr}(\text{OH})_2$ is tetragonal, where each Sr atom is cubically surrounded by 8 water molecules [309, 310]. The central Sr^{2+} ion is co-ordinated into the antiprism configuration by 8 oxygen (O) atoms from the H_2O molecules that make the salt hydrated [311]. These H_2O molecules form hydrogen bonds to maintain the crystallinity. If the Sr^{2+} cations in these samples are bonded into the geopolymer, it is likely that the formation of a pseudo-zeolite will occur, similar to that of brewsterite, a natural strontium containing zeolite [183]. This hypothesis is supported by the literature, suggesting that similar zeolitic phases form within geopolymer structures after the inclusion of different cations [312, 313]. The structure of this is very chemically similar to that of the crystalline $\text{Sr}(\text{OH})_2$, where each of the Sr atoms are bonded to four framework O atoms and five H_2O molecules [314, 315]. This slight difference in structure will explain the different resonances seen between the peaks, as the local chemical environment surrounding the Sr atoms will affect the NMR spectrum seen in Figure 4-23.

Although this is not clear evidence for the chemical immobilisation of Sr, it does not disprove the theory that the geopolymer is capable of binding the Sr within the aluminosilicate gel framework structure.

4.2.1.2.4 EPMA

The use of electron probe microanalysis (EPMA) allows for the chemical composition of the geopolymer gel to be spatially resolved and quantified [316]. In this work, it has been used to determine the distribution of Sr throughout the geopolymer matrix.

Figure 4-24 displays the EPMA images generated after probing the OH_5 sample 28 days post-reaction at a magnification of x100.

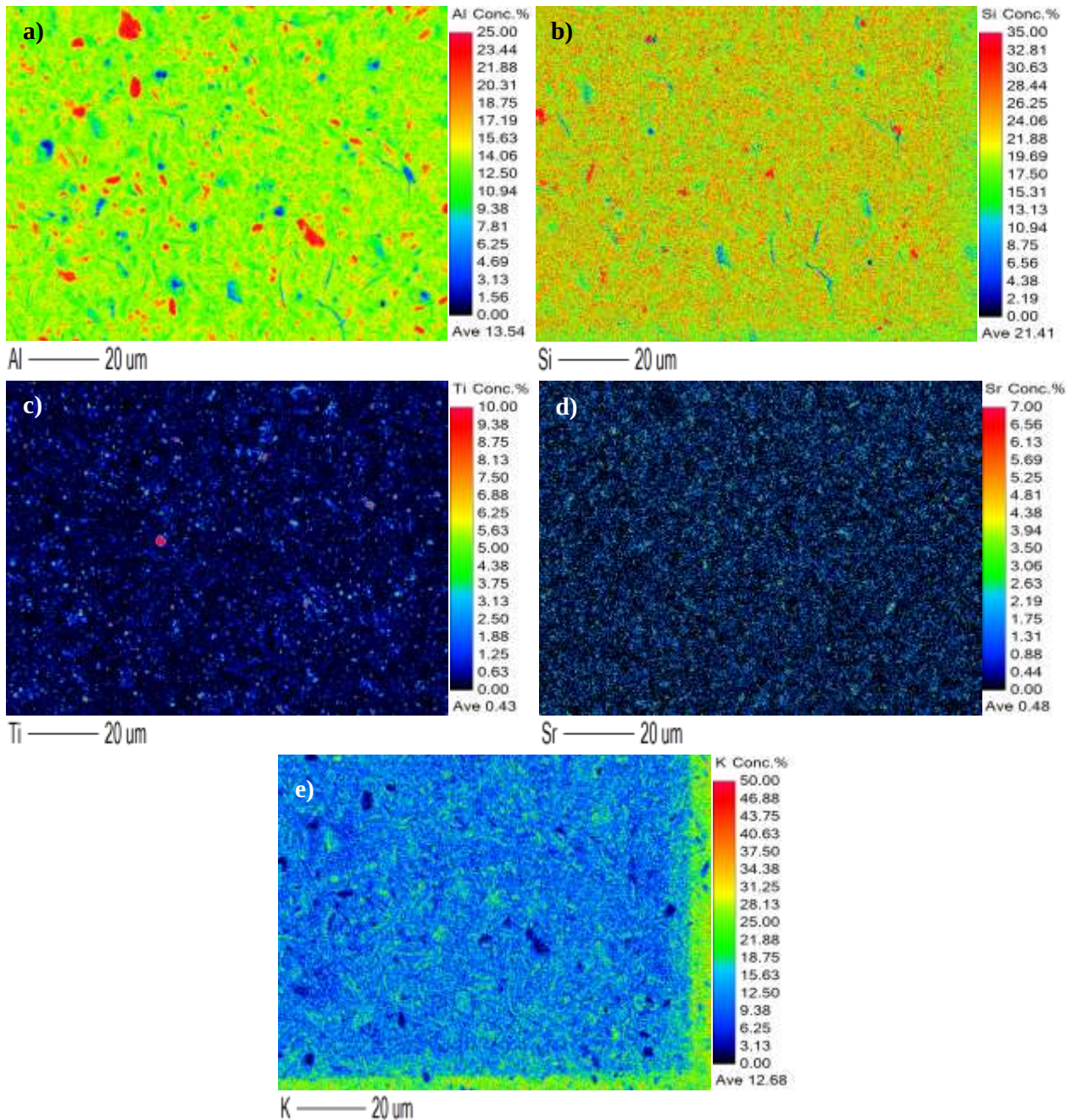


Figure 4-24: The EPMA images generated for the OH_5 sample after 28 days of reaction. The elements shown in each image are as follows: a) Aluminium, b) Silicon, c) Titanium, d) Strontium, and e) Potassium. The magnification factor is x100.

Images a) and b) show the aluminosilicate structure that comprises the majority of the geopolymer gel matrix. Image a) displays the porosity of the system through the dark blue regions, most of which are pores in the polished surface of the geopolymer. Notably, one of these dark blue regions aligns with the titanium (Ti) rich region seen in image c). This region is likely anatase (TiO_2), an impurity in the metakaolin that was shown to be present through the XRD seen in Section 4.2.1.2.2. The aluminium rich phases, outlined by the dark red regions in image a), are unreacted metakaolin, which aligns with some of the titanium rich phases seen in image c).

Image d) shows that the Sr within the system is relatively evenly distributed in small discrete particles throughout the gel matrix. This supports the hypothesis that the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ does not dissolve within the activating solution, and is instead acting as a filler material, becoming physically entombed within the gel matrix as discussed and exemplified in the ICC (Section 4.2.1.1.1). There are regions that have a slightly higher concentration of Sr, as shown by the green and red spots, however, these are likely due to the presence of slightly bigger pieces of the salt.

On the contrary, it can be argued that the distribution of the Sr as shown in image d) supports the hypothesis that Sr has displaced some of the charge balancing K^+ cations within the actual gel structure of the sample.

The potassium, much like the Sr, is present throughout the sample, most likely as charge balancing ions for the net negatively charged aluminium sites within the aluminosilicate matrix. The K poor regions, shown in dark blue, align with the Al rich regions seen in image a), which would fit the suggestion that these regions show unreacted metakaolin. However, there are not any K poor regions that align with the areas of higher concentration of Sr that are shown in image d). This could show that the K is not displaced by the Sr, but it could be argued that the Sr is in such low concentration that it is unlikely to effect the amount of K in any one area.

Figure 4-25 displays the EPMA images generated after probing the OH_5 sample 28 days post-reaction at a magnification of x1500. At the greater magnification shown in Figure 4-25, the presence of unreacted metakaolin is clearer, shown by the Al rich phases in red in image a). The aluminosilicate K-A-S-H phase is clearly visible in images a), b) and e), with the main constituent being Si with the greatest concentration. The distribution of K, as shown by image e), suggests that the majority of the cation binding sites are occupied by K^+ ions as opposed to the divalent Sr^{2+} ions. However, similarly to the images at x100 magnification, this could be due to the fact that Sr is present in such small concentrations that it is not clear as to whether it is acting as a charge balancing ion or whether it is physically encapsulated within the matrix. Furthermore, the spatial distribution of K and Al within the sample aligns, which is consistent with the presence of K-A-S-H phase. The dark red regions in image c) are further evidence for the presence of anatase within the structure, as shown by the XRD (Section 4.2.1.2.2).

The pores of the geopolymer are more visible at this magnification, and are represented by the dark blue regions in both image a) and b). In the top left, and bottom right, of these two images, a discrepancy can be seen in the pore network; The red, Si rich phases seen here, highlighted by the black boxes in image b), is evidence of a silicate containing contaminant, potentially silica fume, residing in the pores. This contaminant was likely picked up during the polishing process, as there is no evidence of this in any of the powder-based analysis techniques in this work. The contaminating grains can also be seen in Figure 4-26, highlighted again in the black box.

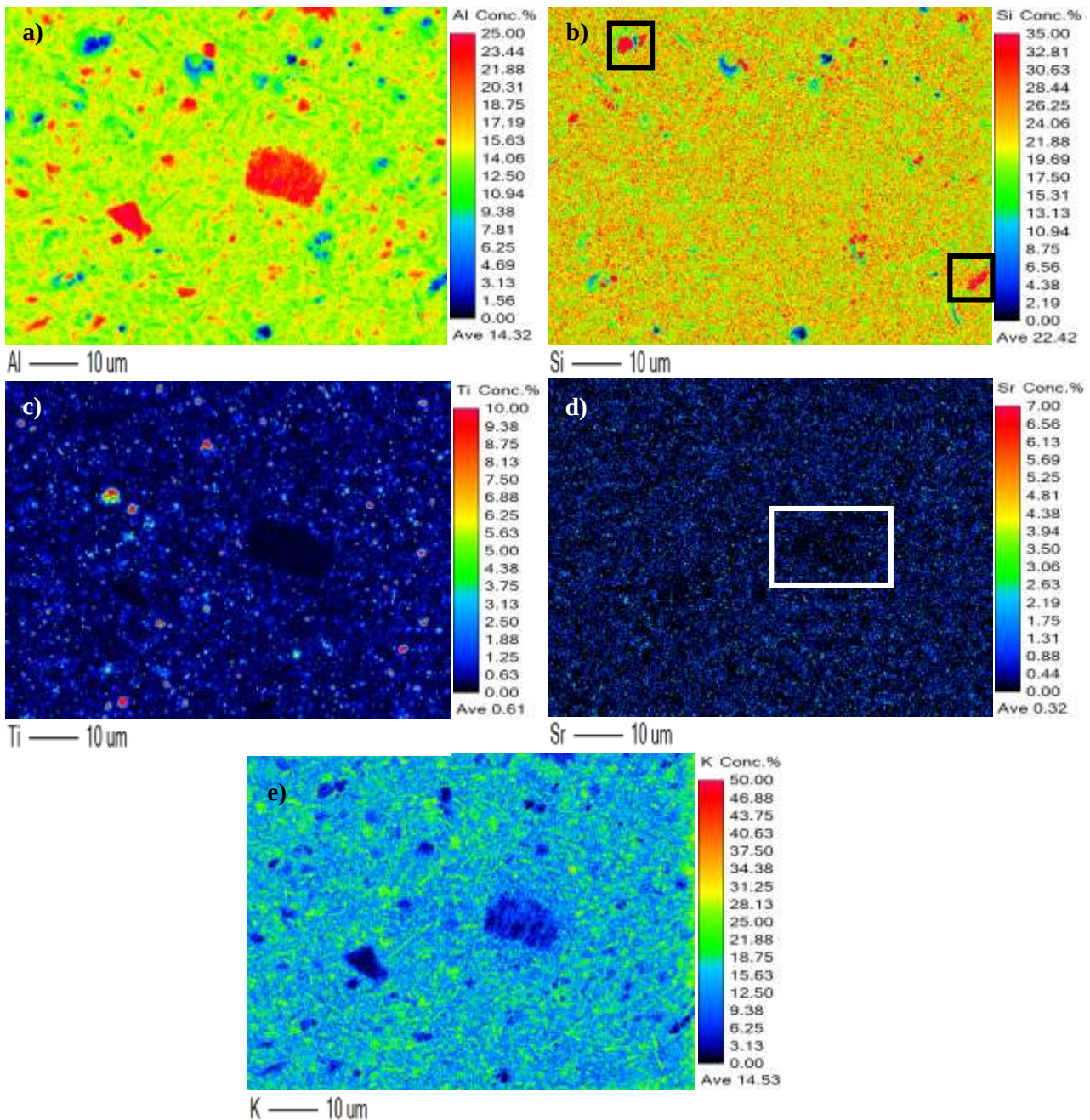


Figure 4-25: The EPMA images generated for the OH_5 sample after 28 days of reaction. The elements shown in each image are as follows: a) Aluminium, b) Silicon, c) Titanium, d) Strontium, and e) Potassium. The magnification factor is x1500.

In a similar manner to what can be seen at a magnification of x100, the Sr is scattered relatively uniformly throughout the sample as shown in image d). However, it can be seen that in the region where there is unreacted metakaolin, highlighted by the white box in image d), there is a small concentration of Sr. This supports the evidence that some of the Sr dissolves within the activating solution and is adsorbed to the surface of the metakaolin in the early stages of the geopolymer reaction, aligning with results seen in the zeta potential (Section 4.2.1.1.2). Therefore, it is very likely that the retardation of the reaction seen in the ICC (Section 4.2.1.1.1) is due to a combination of the filler effect had by the undissolved $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and the Sr that did dissolve adsorbing to the surface of the metakaolin, slowing the dissolution reaction. This phenomenon can also be seen in image e), suggesting that the K^+ cations from the activating solution undergo a very similar effect, adsorbing to the negatively charged surface of the metakaolin.

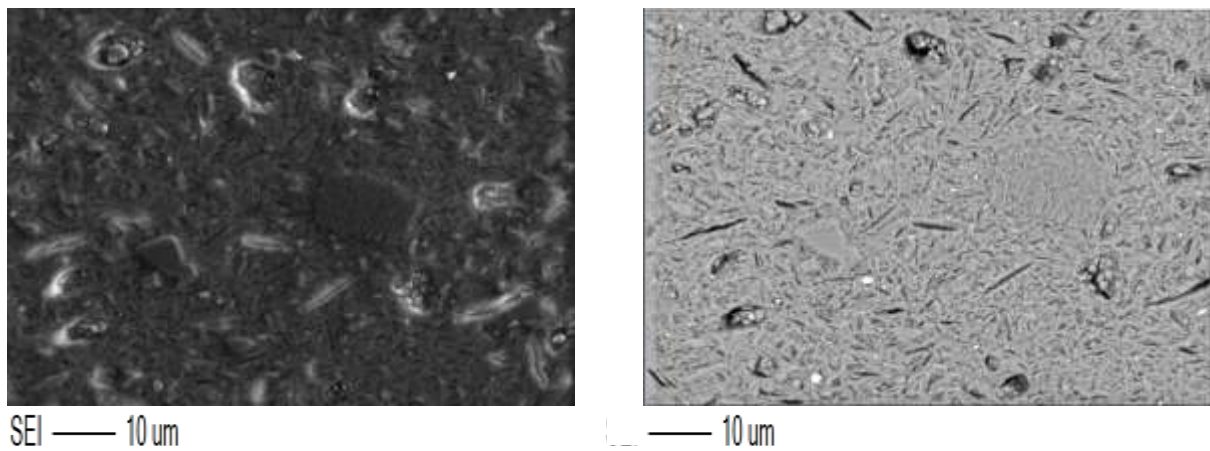


Figure 4-26: a) A secondary electron image and a b) backscattered electron image of the region observed in the EPMA images.

The two large regions of the Al-rich phase seen in Figure 4-25 can be seen in both the secondary electron (SEI) and backscattered electron (BEI) images displayed in Figure 4-26. From the SEI, these regions can be clearly distinguished from the surrounding K-A-S-H gel, suggesting that this phase is harder than that of the gel and has protruded during the polishing process. The BEI shows that the larger of the two particles displays clear striations; This is not consistent with metakaolin particles seen in other work, as these are usually visible plate-like particles [317]. However, it is possible that these particles are unreacted metakaolin orientated on a different plane to those seen in the literature. A scanning electron microscope (SEM) image of the metakaolin used in this work is shown in Figure 4-27.

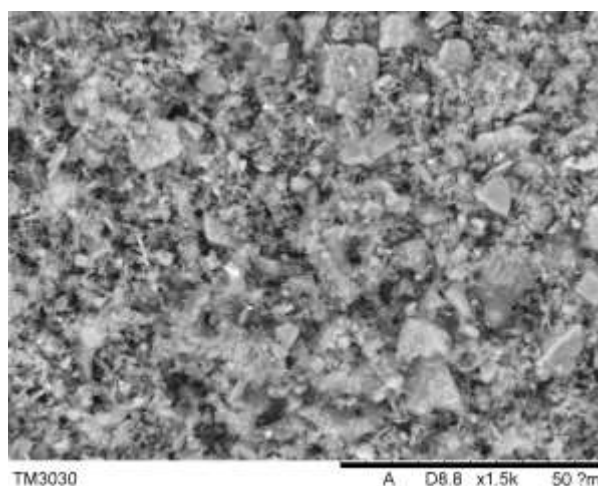


Figure 4-27: A scanning electron microscope image of the raw metakaolin used in this work at a magnification factor of $\times 1500$.

When comparing the shapes of the particles in this image to those seen in Figure 4-26, it is possible that the large particles seen within the structure could be unreacted metakaolin particles. Similar large, and straight edged particles can be seen in the SEM image, providing ratification for the hypothesis that these particles are unreacted metakaolin. The SEM image does not provide examples of striations on the particles, however, the striations could be caused by the presence of the K^+ and Sr^{2+} cations adsorbed to the surface of the metakaolin. The EPMA images show that there is a presence of both K and Sr in this region, with the K also present in what could be described as striations across this region. The presence of these two cations preventing the complete reaction of the metakaolin would support the evidence of the zeta potential measurements (Section 4.2.1.1.2), where the cations prevent the migration of the activating solution to the surface of the metakaolin particle.

However, it is not possible to be completely certain that this particle is an example of unreacted metakaolin. Firstly, it would be expected that there would be some evidence of anatase within the particle, which would be signalled by the presence of Ti in the EPMA, but this is not the case. Furthermore, there is not a clear change in the concentration of Si within this region; a higher concentration of Si would be expected for a particle of metakaolin.

4.2.1.2.5 X-ray Absorption Spectroscopy

4.2.1.2.5.1 X-ray Absorption Near-Edge Structure (XANES) Spectroscopy

The normalised spectra for the Sr K-edge XAS analysis of the OH_5 sample after 3 days of reaction compared to both the $Sr(OH)_2 \cdot 8H_2O$ reagent and the mineral brewsterite-Sr $((Sr,Ba)_2Al_4Si_{12}O_{32} \cdot 10H_2O)$ are shown in Figure 4-28 [315]. The 28 day OH_5 sample is not included here as the X-ray absorption measurement was unable to be taken. The use of XANES allows for the chemical state of the Sr with respect to the K-A-S-H gel to be probed, providing insight into the chemical immobilisation mechanisms and the capability of the geopolymer to bind the Sr through displacement of K in the cation binding sites of the gel.

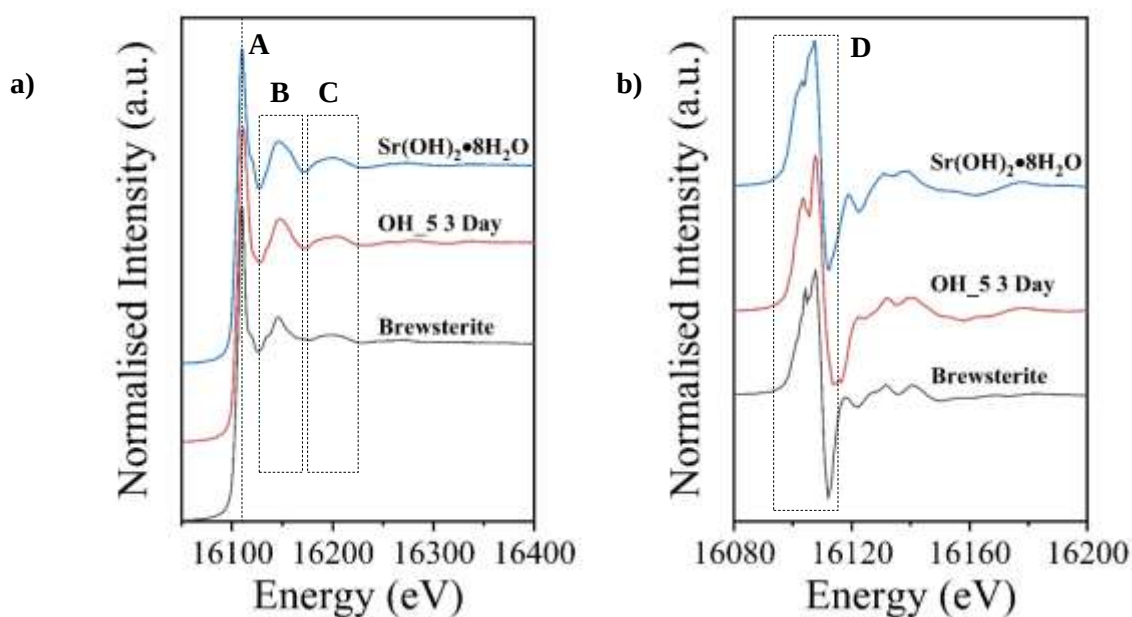


Figure 4-28: a) Normalised X-ray absorption spectra for the geopolymer samples loaded with $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ reactant used and the mineral brewsterite-Sr. b) The 1st derivative of these spectra.

The Sr K-edge is relatively featureless when compared to that of transition metals for example, but the highlighted regions in Figure 4-28 allow for some qualitative analysis between samples [318-320]. When inspecting feature A within Figure 4-28a), the maximum of the edge for the OH_5 sample after 3 days is at a slightly higher energy than that of both the brewsterite-Sr and the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, which share similar energies for this peak. Moreover, without the use of the 1st derivative plot, shown in Figure 4-28b), it is almost impossible to discern the presence of the doublet on the rising edge. This feature is highlighted by the box labelled D in Figure 4-28b), and is far more pronounced in the brewsterite-Sr mineral than in the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ reagent. Additionally, when comparing this to the OH_5 sample, the peak is more resembling of the brewsterite spectra than the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ salt, but still displays features of both, most notably the difference in maximums between the two peaks which is more resembling of the salt. To build upon this, referring back to Figure 4-28a), the OH_5 sample appears to exhibit further features of both the salt and Sr in a pseudo-zeolitic structural environment. When exploring the features above the absorption edge, it can be seen that within feature B, the OH_5 sample appears to have a small shoulder at ~ 16135 eV, which is at the same energy as that of the shoulder in the brewsterite spectra. However, this exact same peak follows a similar path to that of the corresponding peak in the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ spectra. Furthermore, feature C for the OH_5 sample appears to show features relating to both the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ reagent and the brewsterite, with the lower energy region of this area following a curve comparable to that of brewsterite and the higher energy region comparing to the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ reagent.

From this data, it is implied that the OH_5 sample contains Sr environments both in pseudo-zeolitic structural environments, i.e. incorporated as the charge balancing cation in the K-A-S-H gel, and also in the structural environment of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. This finding is supported by the Sr NMR data, which suggests that there are two Sr environments present within the sample. The EPMA data also alludes to this, and the XRD and order-of-addition experiments show that the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ does not completely dissolve within the activating solution.

4.2.1.3 Conclusions

Isothermal conduction calorimetry shows that introduction of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ at varying Sr/Al ratios affects the kinetics of formation of the geopolymer gel, with the relationship showing that as the Sr/Al ratio increases, the retardation of the reaction does the same. The mechanisms for this have been investigated using zeta potential, diffuse reflectance infrared Fourier transform spectroscopy, EPMA and order-of-addition experiments, with the conclusion being that some of the Sr dissolves into the system and adsorbs to the surface of the metakaolin particles, slowing the dissolution, whilst the remainder of the undissolved $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ acts as a filler material within the gel matrix. The DRIFTS shows that this does not change the overall structural evolution of the geopolymer in the early stages of reaction.

However, the dissolved Sr^{2+} cations do not significantly affect the resulting structure, the primary phase of which is shown to be a K-A-S-H gel through the use of FTIR spectroscopy, ^{29}Si MAS NMR and ^1H - ^{29}Si CP MAS NMR. This phase is comprised of Si and Al in tetrahedral coordination, with the Si mainly existing in $\text{Q}^4(4\text{Al})$ and $\text{Q}^4(3\text{Al})$ environments. The negative Al sites caused by Al^{3+} in tetrahedral coordination are charge balanced by K^+ , although, upon the introduction of Sr^{2+} cations, some of the K^+ is displaced in favour of the Sr^{2+} which is confirmed by the use of XANES. XRD shows that, with higher waste loadings, the crystalline structure of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ is observed within the sample. Therefore, it is shown that the geopolymer is capable of both immobilising the Sr that does dissolve, and then further encapsulating the remainder of the salt within the matrix. It is shown that the incorporation of the $\text{Sr}(\text{OH})_2$ leads to an increase in the Si/Al ratio, most likely due to the lower extent of reaction of the system compared to the KGP control sample.

The order-of-addition experiments displayed that the reaction of the strontium hydroxide with the silicate activating solution can lead to the production of a by-product that is potentially the cause for the retardation of the reaction seen in the ICC data. The identity of this by-product is thought to be a mixture of strontium and potassium silicate crystals, but future work is required to verify this.

This work shows that K-silicate activated geopolymers are capable of incorporating wastes containing $\text{Sr}(\text{OH})_2$ at high waste loadings of up to 5% by weight. However, in practice, the loadings are likely to be far lower due to activity limits per package on the wasteforms, owing to the radioactivity of the waste in question. Whilst this, and any impact of the radiation and resulting decay products, are not considered

in this work, it is important to note that they will likely have a notable effect on the performance of the geopolymer as a wasteform, and further work to determine how great this effect is will be crucial to determine the overall suitability of the wasteform.

Despite this, the findings of this work show that the incorporation of $\text{Sr}(\text{OH})_2$ containing waste has only a small effect on both the kinetics and mechanisms of formation of a metakaolin based, potassium silicate activated geopolymer system, and the proof that these materials are capable of chemically immobilising the Sr within the structure suggests that these systems show great promise as wasteforms for the long term immobilisation of radioactive waste streams containing ^{90}Sr in the form of $\text{Sr}(\text{OH})_2$.

4.2.2 Strontium Carbonate

4.2.2.1 Fresh State

4.2.2.1.1 ICC

Figure 4-29 displays the calorimetry curves produced by the formation of the K-geopolymers loaded with SrCO_3 over the first 3 days of reaction.

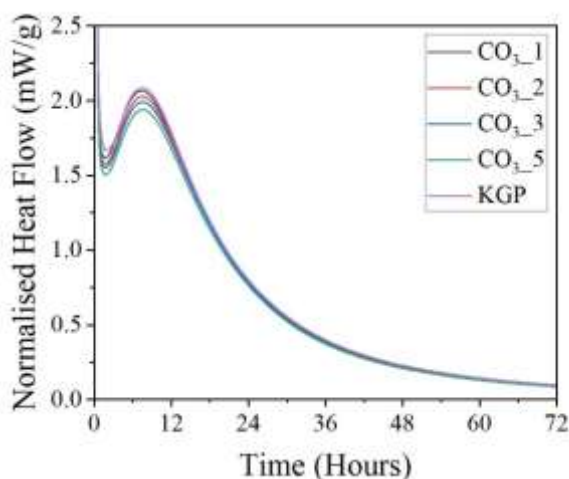


Figure 4-29: The effect on the heat evolution of reaction of loading K-activated metakaolin geopolymers with SrCO_3 over first 24 hours of reaction.

The heat evolved during the formation of the K-A-S-H gel is briefly discussed in Section 4.2.1.1.1 and is also applicable for the systems here. The peak seen in Figure 4-29 displays the heat evolved during the reaction phase of the geopolymer formation and is centred at around 7.5 hours after initial reaction. Figure 4-29 shows that the addition of SrCO_3 at all Sr/Al ratios has a negligible effect on the reaction. Both the maximum value of normalized heat flow, and the time of maximum heat flow appear to be negligibly changed by the addition of the salt. To emphasise this, the time of maximum heat evolution for the KGP control sample is approximately 7 hours, almost identical to that of all of the CO_3 containing samples, which have a maximum value of 7.5 hours. The CO_3_5 sample showed the greatest deviation from the control with respect to the maximum recorded heat flow, decreasing by around 11%. This is most likely due to SrCO_3 being an insoluble compound and so is unlikely to dissolve within the activating solution. Instead, the solid SrCO_3 particles are suspended within the binder, acting as a filling material and slightly retarding the reaction.

This hypothesis is further supported by Figure 4-30. This shows the KGP and CO_3_5 samples seen in this work to a scaled version of the curve generated by the KGP sample, shown in red. This is calculated by normalising the heat evolution of the KGP sample by a mass that would be consistent with a CO_3_5 sample with the same mass of metakaolin and activating solution as the 20g KGP sample. This curve gives the normalized heat evolution of the situation that could be described as the ‘extreme case’ scenario, where none of the SrCO_3 dissolves into the activating solution and remains as a solid, acting as a filler material. As can be seen from Figure 4-30, the CO_3_5 sample, shown in green, is not too

dissimilar from the scaled KGP curve. This suggests that the majority of the SrCO_3 does not dissolve in the CO_3_5 sample. However, it is clear that some of the salt does dissolve, exposed by the slight retardation of the reaction when compared to the KGP sample.

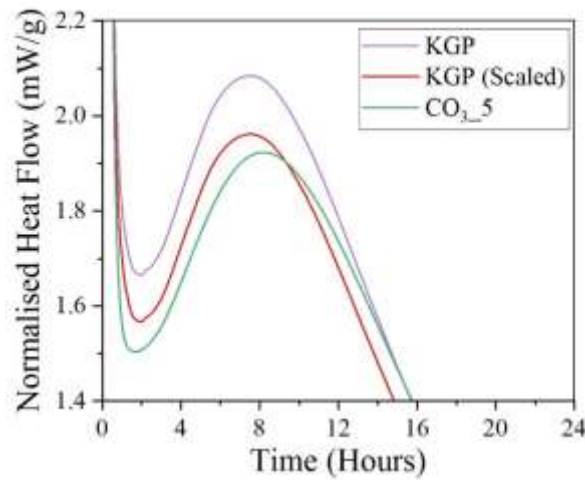


Figure 4-30: The heat evolution of the KGP and CO_3_5 samples compared to a scaled curve of the KGP sample.

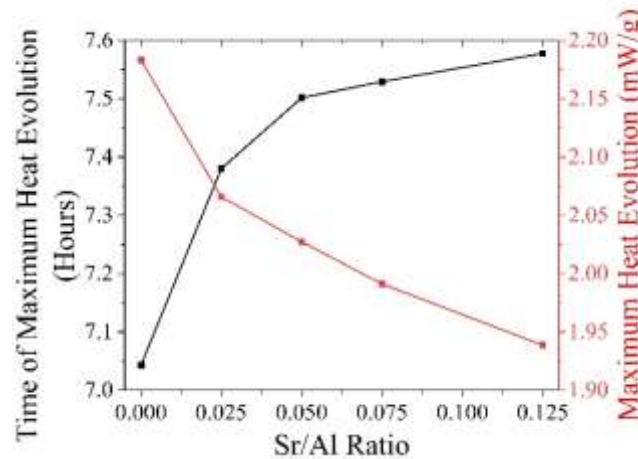


Figure 4-31: The relationship between Sr/Al ratio and the observed time of maximum heat evolution and the value of the maximum heat evolution.

Figure 4-31 shows that as the Sr/Al ratio of the geopolymer mix increases, so does the time at which the maximum heat evolution is reached. However, this effect diminishes as the Sr/Al ratio continues to increase, suggesting that, at some defined point, the effect of adding more SrCO_3 reaches its maximum. Therefore, the data suggests that the addition of the SrCO_3 has an impact on the extent of reaction within the system as opposed to retarding the reaction, as the time of maximum heat evolution is minimally impacted and the main change is the reduction in the value of the maximum heat evolution, although this is still an insubstantial change. This impact could be due to the addition of the SrCO_3 resulting in a smaller mass of both metakaolin and activating solution available to react and, therefore, produce heat through dissolution. The wt.% of the SrCO_3 salt in the CO_3_5 sample is 6.1%, and the maximum drop

in heat flow is observed for this sample drops by $\sim 11\%$ compared to the KGP control, suggesting that the decline in available reactive material could be the reason for the reduction in heat flow. Furthermore, it is likely that ‘wetting’ of the SrCO_3 molecules is occurring, with the activating solution becoming adhered to the surface of the salt, preventing it from commencing the dissolution reaction in the first instance. A combination of these two explanations is the likely cause of the decrease in heat flow, suggesting that no changes should be found in the structure of the resulting geopolymer matrices.

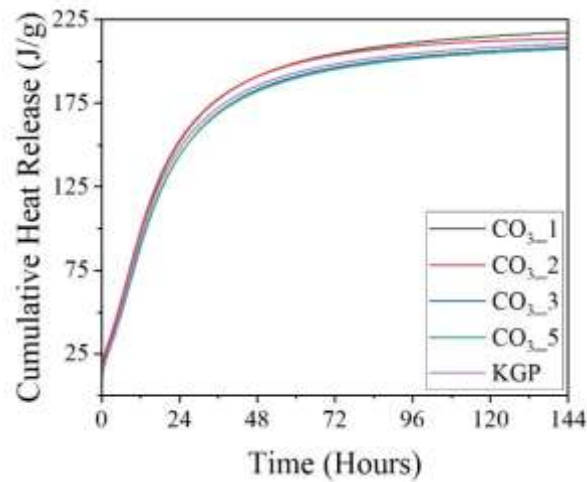


Figure 4-32: The cumulative heat release curves over the first 144 hours of reaction. Figure 4-32 shows the cumulative heat release of the systems over the first 6 days of reaction of the geopolymers containing SrCO_3 compared to the KGP control. As can be seen, the heat release of all of the samples is comparable, which is expected when considering the similar heat flows observed in Figure 4-29. As discussed in Section 4.2.1.1.1, the heat release after 144 hours corresponds to roughly $2/3$ of the total heat release of the system for PC, and if it assumed to be the same for geopolymer systems, the maximum total heat release for the SrCO_3 containing geopolymer samples will be around 325 J/g [297]. This is higher than the average heat release of the current nuclear standard, a Portland cement and GGBS blend, which is around 100 J/g but meets the guideline value of 180 J/g over the first 24 hours set by the current UK requirements for nuclear wastefoms [298, 299].

4.2.2.1.2 Zeta Potential

The zeta potential values obtained for the surface charge of the metakaolin in the presence of SrCO_3 at different pHs is shown in Figure 4-33.

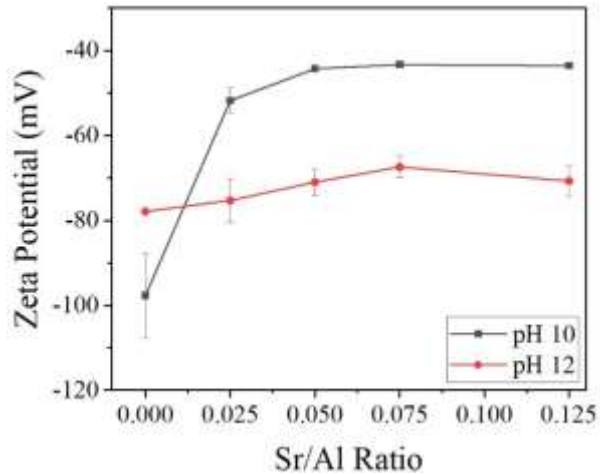


Figure 4-33: Comparing the effect of Sr/Al ratio, altered by the addition of SrCO_3 , on the zeta potential of metakaolin in a KOH solution at pH 10 and 12.

Figure 4-33 shows that increasing the pH has a clear effect on the surface charge of the metakaolin particles. As mentioned in Section 4.2.1.1.2, the addition of the divalent cation Sr^{2+} is causing the change in surface charge due to the electrostatic attraction to the negatively charged metakaolin. The magnitude of this change is directly related to both the pH, and the concentration of Sr^{2+} cations within the solution. This is shown in Figure 4-33, as the increase in the pH to pH 12 leads to a less significant change to the zeta potential than was seen at pH 10. This correlates with the reduced solubility of SrCO_3 at higher pH's, meaning that there are less Sr^{2+} ions available to interact with the surface of the metakaolin.

At pH 10, the introduction of the SrCO_3 causes the surface charge to increase towards 0. This is likely due to the interactions with the Sr^{2+} cations with the negatively charged surface of the metakaolin, as discussed in Section 4.2.1.1.2. However, this increase, when compared to metakaolin in solution without the presence of Sr, is not affected by the increasing Sr/Al ratio. This is due to the low solubility of the SrCO_3 , meaning that only a small amount of the salt dissolves, and the solution is saturated with the salt at the Sr/Al ratio of 0.025.

However, at pH 12, increasing the Sr/Al ratio does lead to a greater dissolution of the salt, as the zeta potential values recorded increase towards 0 as the Sr/Al ratio increases. However, this increase is still minimal, as the surface charge of the metakaolin remains very negative. When compared to the pH 10 data, the maximum increase toward 0 is far less; a 10% increase as opposed to a 55% increase. Therefore, it is likely that at the high pH of the geopolymer samples used in this work, around pH 14, the SrCO_3 will not dissolve in any great quantities and have negligible effect on surface charge of the metakaolin. This is supported by the data seen in the ICC, providing further evidence that the majority of the SrCO_3 does not dissolve into solution and simply acts as a filler within the geopolymer matrix. However, the ICC results do suggest that a small portion of the salt does dissolve, and it is likely that

the Sr that is introduced into solution adsorbs onto the surface of the metakaolin to produce the slight increase in zeta potential seen here.

4.2.2.1.3 DRIFTS

The DRIFTS spectra for the CO₃_5 sample in the first 4 hours of reaction can be seen in Figure 4-34.

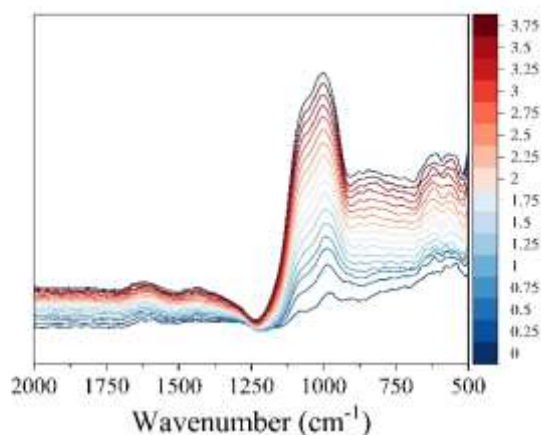


Figure 4-34: DRIFTS spectra for the CO₃_5 sample in the first 4 hours of reaction. The spectra are displayed in 15 minute intervals, beginning at $t=0$ as marked and progressing through the colour gradient. Times are shown in hours.

Over the first 4 hours of reaction, the only clear structural change comes in the formation of the K-A-S-H gel, signified by the growth of the peak attributed to the Si-O-T bond centred at $\sim 1000\text{ cm}^{-1}$ [253]. When compared to the spectra of the KGP control sample, shown in Figure 4-7, the only real difference is the shoulder on this peak at approximately 1200 cm^{-1} . It is possible that the Sr^{2+} in the solution, released from the small fraction of SrCO_3 that does dissolve, is having an impact on the Si/Al ratio of the resultant K-A-S-H gel phase, promoting the inclusion of Al tetrahedra into the network. This further Si-O-T environment, with the peak centre shifted to higher wavenumbers, could provide evidence that Sr is being incorporated into the K-A-S-H phase as a charge balancing cation, suggesting that some of the sites preferentially bind to Sr over K, considering its relative low concentration in solution.

With this change being the only noticeable difference between the two spectra, the inclusion of SrCO_3 does not appear to significantly alter the reaction progression or pathway over the first 4 hours post reaction. This is expected due to its low solubility and its inclusion as a ‘filler’ as discussed in section 4.2.2.1.1.

The spectra for the remaining time in the first day of reaction (4 to 24 hours) for the CO₃_5 sample is presented in Figure 4-35.

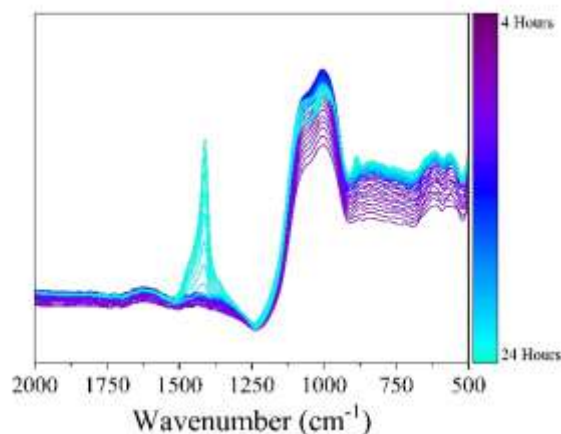


Figure 4-35: DRIFTS spectra for the CO₃_5 sample from 4 to 24 hours post initial reaction. The spectra are displayed in 15 minute intervals up until the 16-hour mark, at which the time progresses in whole hours, beginning at $t=4$ hours as marked and progressing through the colour gradient. Times are shown in hours.

The Si-O-T peaks continue to grow in intensity until the 8.5-hour mark. At this point, the intensities begin to decrease, but there are no changes in peak position or size relative to each other. This is most probably due the shrinkage of the geopolymer sample during the reaction [269, 270]. As the sample shrinks, the distance between the detector and the surface of the sample changes slightly, which could lead to the reduction in intensity seen here. This is supported by the fact that the peaks do not change relative position, and the whole spectra can be seen to reduce in intensity as opposed to just a singular characteristic peak. This is also seen in the spectra for the KGP control sample over the same time period, shown in Figure 4-9.

The anomaly to this reduction in intensity is the peak that appears at $\sim 1400\text{ cm}^{-1}$ on the spectra. This peak is due to the carbonation of the sample after reaction with the air. It could be argued that, due to there already being a carbonate compound in the system, this peak should be present in the spectra from the outset. However, as this technique obtains the majority of its dataset from the surface of the sample, it is possible that the SrCO₃ within the sample does not migrate to the surface and so is not detected. Upon the carbonation of the sample surface, the carbonate compounds formed are readily detected by the infrared waves and so appear on the spectra. The intensity of the carbonation peaks is slightly different, with the intensity being greater in the spectra for the CO₃_5 sample. This could be due to the increased availability of the K and Sr to carbonate, or the migration of the SrCO₃ towards the surface as the reaction progresses.

4.2.2.1.4 Order-of-addition Experiments

In order to determine whether the point at which the Sr is added to the mix impacts the performance of the geopolymer, order-of-addition experiments were performed as outlined in section 2.1.1.2.

4.2.2.1.4.1 Order-of-addition #1

1. The SrCO_3 does not dissolve in the water, However, it does turn the solution from a clear liquid into a white liquid. FTIR of this liquid was taken and can be seen in Figure 4-36.

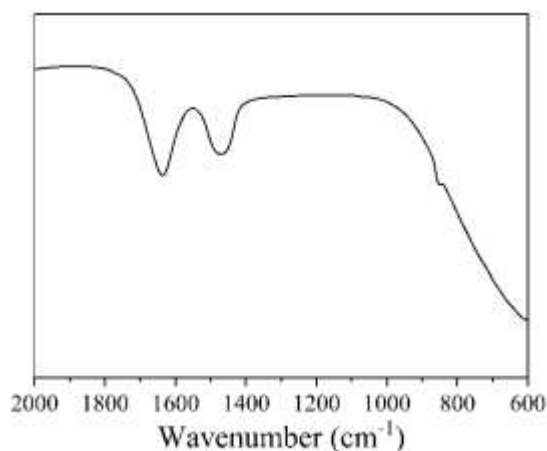


Figure 4-36: The FTIR spectra of the white solution observed after stage 1 of the order-of-addition #1 experiment containing SrCO_3 .

Unsurprisingly, the main component of this solution is water (shown by the peak at 1640 cm^{-1}), but the peaks for the strontium carbonate bonds can clearly be seen at $\sim 1480\text{ cm}^{-1}$ and there is also evidence of a peak at around 850 cm^{-1} . It is unlikely that any other compounds are formed, and that the SrCO_3 simply exists as a suspension within the water. This is clarified by Figure 4-37, where the spectra for the pure SrCO_3 is superimposed over the order-of-addition spectra seen in Figure 4-36. As can be seen, SrCO_3 is responsible for these peaks.

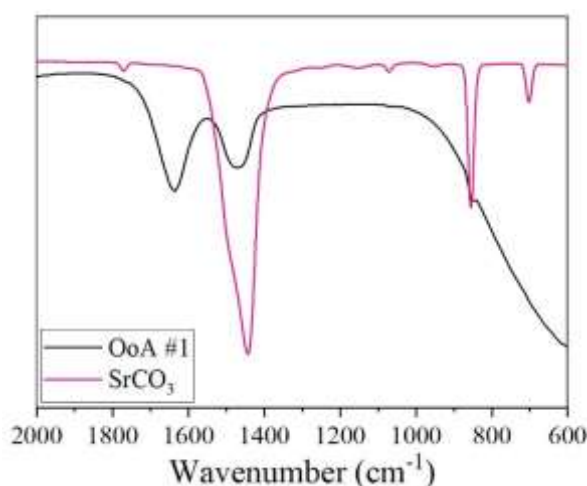


Figure 4-37: The FTIR spectra of the OoA #1 sample compared to pure SrCO_3 .

2. The addition of the solid KOH, and the resultant heat production, did not change the state of the solution, with the SrCO_3 still existing in a suspension.
3. The addition of the silicate stock solution still did not change the suspension. This further supports the hypothesis that the SrCO_3 does not dissolve into the activating solution in OoA #0.

4. The addition of the metakaolin did lead to the formation of what appeared to be a geopolymer. Upon pouring the activating solution (which was very fluid) containing the SrCO_3 into the metakaolin, it became clear that the mixture was a suspension of SrCO_3 within the activating solution. The suspension easily mixed with the metakaolin to form a geopolymer.

4.2.2.1.4.2 *Order-of-addition #2*

1. The addition of solid KOH to water leads to an exothermic dissolution reaction.
2. The addition of the SrCO_3 causes a white suspension to form, identical to that observed in OoA #1, stage 1, 2 and 3.
3. The addition of the silicate stock solution still did not change the suspension.
4. The addition of the metakaolin did lead to the formation of what appeared to be a geopolymer. Upon pouring the activating solution (which was very fluid) containing the SrCO_3 into the metakaolin, it became clear that the mixture was a suspension of SrCO_3 within the activating solution. The suspension easily mixed with the metakaolin to form a geopolymer.

4.2.2.1.4.3 *Order-of-addition #3*

1. The addition of solid KOH to water leads to an exothermic dissolution reaction.
2. The addition of the K-silicate stock solution to the KOH solution resulted in a clear liquid mix.
3. The addition of the SrCO_3 leads to the formation of a white suspension, similar to that observed in the other OoA experiments.
4. The addition of the metakaolin did lead to the formation of what appeared to be a geopolymer. Upon pouring the activating solution (which was very fluid) containing the SrCO_3 into the metakaolin, it became clear that the mixture was a suspension of SrCO_3 within the activating solution. The suspension easily mixed with the metakaolin to form a geopolymer.

4.2.2.1.4.4 *Order-of-addition ICC*

Figure 4-38 shows the calorimetry curves generated by the OoA samples compared to the control KGP sample over the first 3 days of reaction.

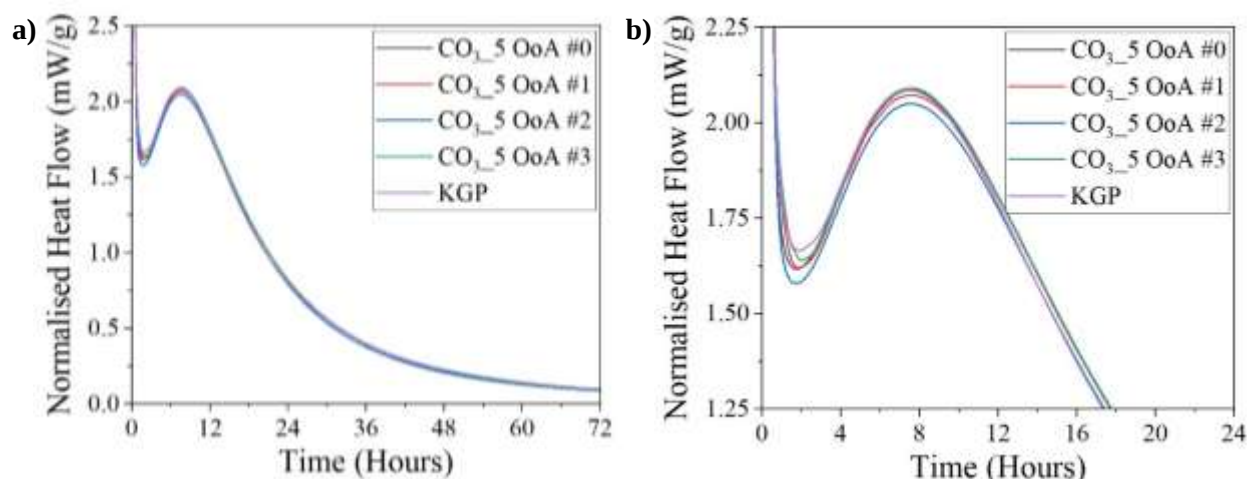


Figure 4-38: The effect on the heat evolution of the reaction of adding SrCO_3 at different stages to K-activated metakaolin geopolymers over the first 3 days of reaction. Plot b) is focused upon the first 24 hours of reaction.

As previously discussed in Section 4.2.2.1.1, the addition of SrCO_3 does not cause a significant change in the normalised heat flow observed during the first 3 days of reaction. Each of the samples exhibit a similar curve, with a maximum heat flow of approximately 2.1 mW/g. Moreover, the time at which this occurs is identical for all of the samples, including the KGP sample. This further suggests that the addition of the carbonate salt does not impact the reaction kinetics and, consequently, the mechanisms of reaction.

It is likely that the formation of the suspension seen in OoA #1, or similar, occurs in all cases, mainly due to the fact that the SrCO_3 is insoluble within the activating solution. Therefore, it is unsurprising that there are minimal changes seen between the experiments, as the lack of reactivity will result in the same outcome regardless of the order of addition.

4.2.2.1.4.5 Order-of-addition Conclusion

The addition of the SrCO_3 salt to the geopolymer at different stages of the process does not appear to have any effect on the ability of the geopolymer to encapsulate the salt. In all cases, the addition of the solid salt to the relevant liquid (water, KOH solution or the K-silicate activating solution) lead to the formation of a suspension of SrCO_3 within the liquid phase, as shown by the FTIR spectra displayed in Figure 4-36. This suspension did not prevent the formation of a geopolymer when the activating solution was combined with the metakaolin, and a solid geopolymer is formed in each case.

The ICC curves show that, regardless of at which point the SrCO_3 is added, the reaction kinetics are the same, suggesting that waste streams containing SrCO_3 can be added to the geopolymer mix at any point for similar results. Therefore, it is reasonable to use OoA #0 in this work to investigate the properties of the geopolymer during the formation phase of the material.

4.2.2.2 Hardened State

4.2.2.2.1 FTIR

Figure 4-39 displays the FTIR spectra generated by loading K-activated metakaolin geopolymers with SrCO_3 after the first 3 days of reaction.

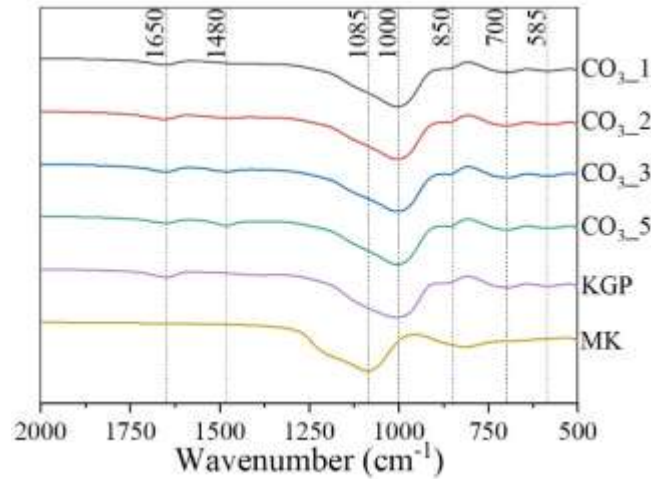


Figure 4-39: The FTIR spectra generated by loading K-activated metakaolin geopolymers with SrCO_3 , the KGP control sample and the raw metakaolin after the first 3 days of reaction.

For Figure 4-39, the bond vibrations that are responsible for the resonances seen are discussed in Section 3.4.2 and summarised in Table 3-4. The very low intensity band that can be seen centred at 1480 cm^{-1} is indicative of the carbonation of the samples due to exposure to air [271]. This carbonate compound is likely to be a mixture of potassium carbonate and strontium carbonate, as can be seen from Figure 4-41. Table 3-4 outlines the characteristic stretching bands for metakaolin based geopolymers.

Each of the spectra included within Figure 4-39 exhibit peaks at incredibly similar wavenumbers, with no single spectra exhibiting an anomalous peak, even when compared to the control KGP sample. Therefore, it appears that the addition of the SrCO_3 , even at the relatively high Sr/Al ratio of 0.125 in the case of sample CO_3_5 , has a negligible impact on the bonds formed within the geopolymer product observed at 3 days. This is most likely due to the insolubility of the SrCO_3 leading to a lack of dissolution within the activator, as SrCO_3 has a solubility limit of $0.00034\text{g}/100\text{g}$ of H_2O [303]. Although the K-silicate activating solution leads to a highly alkaline environment, this environment further decreases the solubility limit, as shown in Section 4.2.2.1.2. Therefore, the reactions happen as if the salt is not present. This is supported by the ICC results and the postulations made in Section 4.2.2.1.1 regarding the mechanisms for retardation.

Walkley et al. (2020) showed that the incorporation of alkaline earth cations such as Sr results in a shift of the band attributed to the asymmetric stretching of the Si-O-T towards higher wavenumbers [67]. The lack of shift of this band suggests that the Sr is not significantly incorporated into the structure, which would further explain the lack of change in the spectra between samples.

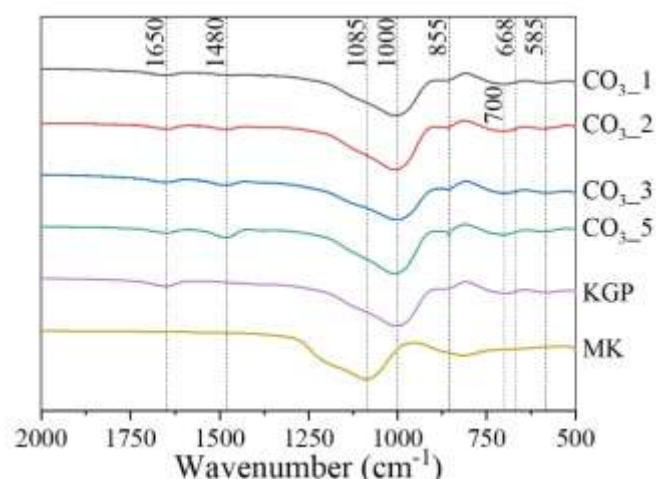


Figure 4-40: The FTIR spectra generated by loading K-activated metakaolin geopolymers with SrCO_3 , the KGP control sample and the raw metakaolin after the first 28 days of reaction.

The spectra after 28 days of reaction, shown in Figure 4-40, show very little change when compared to those after 3 days of reaction. The carbonate peaks at 1480 cm^{-1} are still prominent, suggesting that the SrCO_3 has not dissolved into its constituent ions. The only significant changes are the appearance of a sharp, yet not very intense, peak at 668 cm^{-1} and a change to the sharpness of the peak at $\sim 850\text{ cm}^{-1}$.

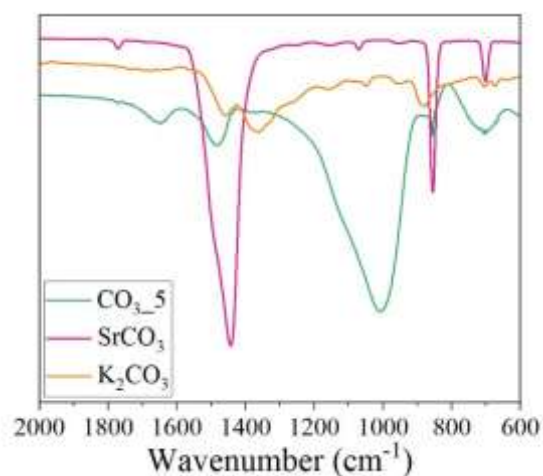


Figure 4-41: The FTIR spectra of the $\text{CO}_3\text{_5}$ sample after 28 days of reaction compared to pure SrCO_3 and K_2CO_3 .

As can be seen from Figure 4-41, the sharp peaks seen at 700 cm^{-1} and 855 cm^{-1} in Figure 4-40 are indicative of SrCO_3 present within the geopolymer matrix after 28 days of reaction. This is further confirmation that the SrCO_3 does not dissolve fully within the activating solution and resides in its solid form within the pores of the gel.

The peak at around 670 cm^{-1} in the $\text{CO}_3\text{_5}$ sample aligns with the resonance exhibited by the spectra for K_2CO_3 in Figure 4-41. Furthermore, the broad peak at $\sim 1480\text{ cm}^{-1}$ encompasses peaks from both the SrCO_3 and K_2CO_3 samples, suggesting that there is a mix of the two carbonates within the sample. This

could be due to at least a small quantity of the original SrCO_3 dissolving within the activating solution, suggesting that a quantity of Sr^{2+} ions exist within solution that could be immobilized by the cation binding sites within geopolymer matrix. However, it could also be due to carbonation of the K-A-S-H phase due to contact with air [321].

4.2.2.2.2 XRD

The X-ray diffraction spectra for the geopolymer samples containing SrCO_3 3 days after initial reaction are shown in Figure 4-42.

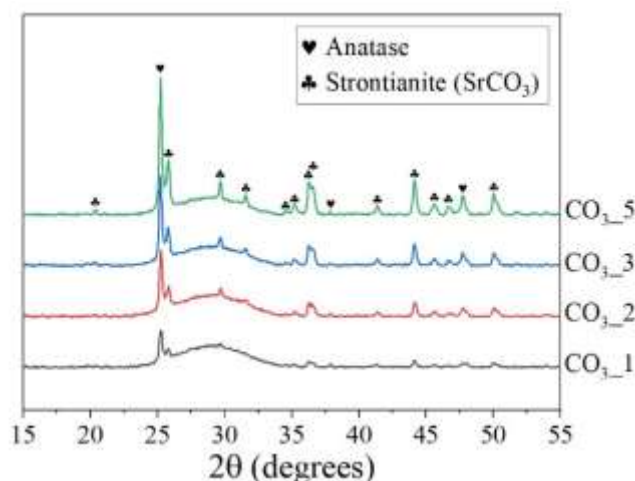


Figure 4-42: The X-ray diffraction spectra generated by loading K-activated metakaolin geopolymers with SrCO_3 after the first 3 days of reaction.

The XRD patterns for each sample are comparable, exhibiting a broad diffraction peak between 24° 2θ and 33° 2θ . This peak indicates the presence of an amorphous phase within the sample, notably the presence of the K-A-S-H gel [164].

The XRD patterns for the samples do indicate the presence of some crystalline phases within the hardened gel. The presence of anatase (TiO_2 , PDF # 01-084-1286) is indicative of the unreacted metakaolin that remains within the structure, as supported by both the FTIR and NMR data.

The diffraction peaks due to the crystalline strontianite phase (SrCO_3 , PDF # 00-005-0418) indicate that the addition of the SrCO_3 did not lead to its dissolution into within the activating solution. This is supported by the low solubility limits exhibited by the SrCO_3 , and also by the ICC data.

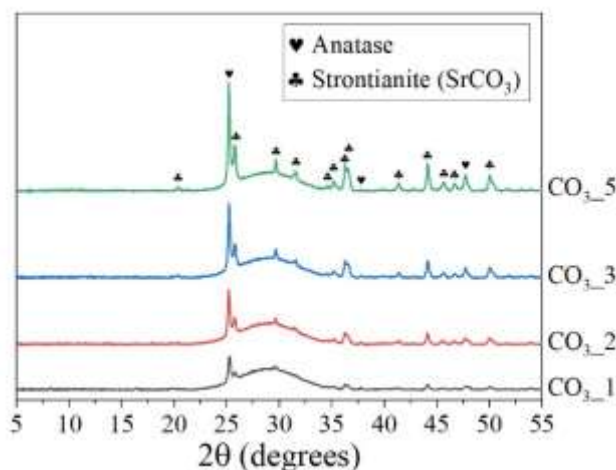


Figure 4-43: The X-ray diffraction spectra generated by loading K-activated metakaolin geopolymers with SrCO_3 after the first 28 days of reaction.

Much like the 3-day diffraction patterns, after 28 days the samples show the presence of both crystalline anatase and strontium carbonate. The presence of SrCO_3 is more obvious as the Sr/Al ratio increases, shown by the intensity of the peaks. This is as expected as there is an increasing amount of the salt within the samples.

4.2.2.2.3 NMR

4.2.2.2.3.1 ^1H - ^{29}Si CP MAS and ^{29}Si MAS NMR

The ^1H - ^{29}Si CP MAS and ^{29}Si MAS NMR spectra for the CO_3_5 and KGP samples both 3 and 28 days after the initial reaction are displayed in Figure 4-44.

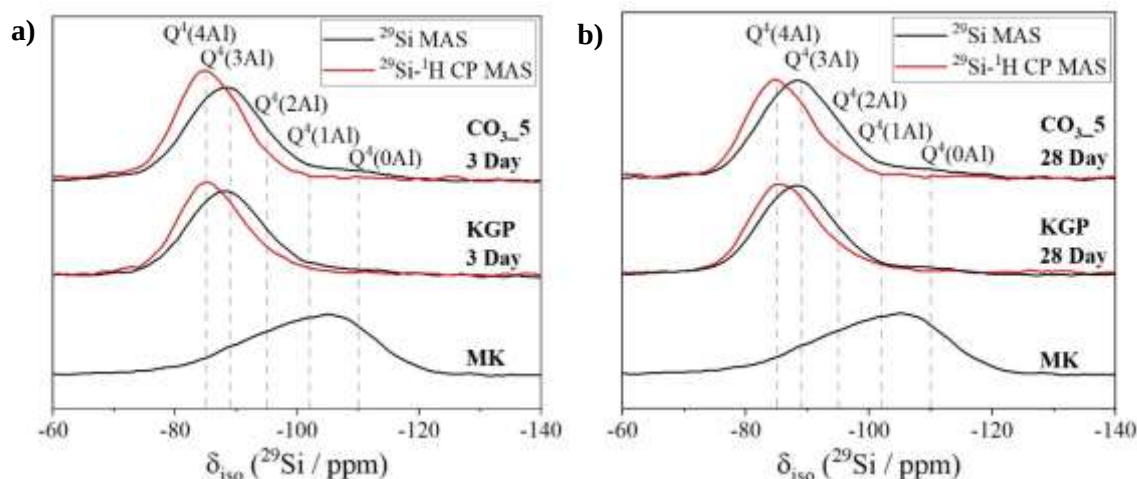


Figure 4-44: ^1H - ^{29}Si CP MAS and ^{29}Si MAS spectra for the CO_3_5 , KGP samples and the unreacted metakaolin a) 3 days and b) 28 days after reaction.

The ^1H - ^{29}Si CP MAS spectra, shown in red in Figure 4-44, display a single broad peak at δ_{iso} between $\delta_{\text{iso}} = -75$ and $\delta_{\text{iso}} = -110$ ppm. The maximum intensity is observed at a δ_{iso} of -85 ppm, confirming that the geopolymer gels are predominantly comprised of $\text{Q}^4(4\text{Al})$ and $\text{Q}^4(3\text{Al})$ silicon environments. The

differences between, and rationale for the use of both ^1H - ^{29}Si CP MAS NMR and ^{29}Si MAS NMR are discussed in Section 3.4.3.1.

The ^{29}Si MAS NMR spectra in Figure 4-44 display the entire range of Si sites present within the sample, including those that are a result of Si sites within the unreacted metakaolin, most notably $\text{Q}^4(0\text{Al})$ sites. For these spectra, the maximum peak intensity is recorded at a lower δ_{iso} of approximately $\delta_{\text{iso}} = -89$ ppm. The effect of including the silicon environments exhibited by the unreacted metakaolin is clear, with the ^{29}Si MAS spectra for both the CO_3_5 and KGP samples showing intensity in these regions, suggesting that the reaction has not sustained to completion. Further evidence for this can be seen through the deconvolution of the spectra in Figure 4-45. The spectra observed here are similar to those seen in previous work, suggesting that the K-A-S-H gel is formed by a mixture of Si environments in the form of $\text{Q}^4(\text{mAl})$ sites, where $1 \leq m \leq 4$ [67]. This is supported by Table 4-4, which shows the presence of each Si site as a percentage calculated from the ^{29}Si MAS NMR data.

Table 4-4: Relative integral areas for the Si sites present within the K-A-S-H gel of each sample both 3 and 28 days after initial reaction from the deconvoluted ^{29}Si MAS NMR spectra. The $\text{Q}^4(0\text{Al})$ site attributed to the unreacted metakaolin is disregarded for the quantification of the K-A-S-H gel.

Sample	Time point	Relative Integral Area (%)				Si/Al
		$\text{Q}^4(4\text{Al})$	$\text{Q}^4(3\text{Al})$	$\text{Q}^4(2\text{Al})$	$\text{Q}^4(1\text{Al})$	
KGP	3 Days	25	54	20	1	1.32
CO_3_5	3 Days	24	49	23	4	1.37
KGP	28 Days	28	44	26	2	1.34
CO_3_5	28 Days	24	48	27	1	1.36

For the KGP samples, Figure 4-45 shows that the gel structure is dominated by $\text{Q}^4(3\text{Al})$ sites, which is in line with data that is widely reported in the literature for potassium activated geopolymers [172]. The CO_3_5 samples also show that the gel structure is dominated by $\text{Q}^4(3\text{Al})$ sites, however, there are a greater number of $\text{Q}^4(2\text{Al})$ sites after both 3 and 28 days when compared to the KGP control sample. This difference could be attributed in part to the greater volume of unreacted metakaolin in the sample. As shown by Figure 4-44, the raw metakaolin is comprised mainly of $\text{Q}^4(2\text{Al})$, $\text{Q}^4(1\text{Al})$ and $\text{Q}^4(0\text{Al})$ sites. Therefore, the greater percentage of metakaolin in the CO_3_5 sample in comparison to the KGP control will lead to a greater percentage of $\text{Q}^4(2\text{Al})$ Si sites within the gel. Furthermore, the addition of the SrCO_3 could also lead to a reduced dissolution of the Al_2O_3 phase within the metakaolin. This would lead to an aluminium-poor gel structure in comparison to the gel seen in the control sample, with more Si-Si tetrahedral bonding and, consequently, less $\text{Q}^4(4\text{Al})$ and $\text{Q}^4(3\text{Al})$ sites. This is discussed in further detail below.

Table 4-4 also shows the molar Si/Al ratio of the K-A-S-H gel, disregarding the Si sites that are attributed to the unreacted metakaolin. This ratio is calculated using Engelhardt's formula (Equation 3-1) [276].

The Si/Al ratio of the CO₃_5 samples are greater than the corresponding values found in the KGP gels at the same timepoints. This suggests that the KGP samples have a greater binding capacity due to an increased proportion of Al atoms in tetrahedral coordination within its structure. This could be due to a potentially lower extent of reaction resulting in a larger amount of unreacted metakaolin remaining within the system. Therefore, less Al has dissolved into the solution, leading to a lower Sr/Al ratio and decreased binding capacity. However, the decreased binding capacity of the CO₃_5 sample is contrary to what has been seen in previous work, with Walkley et al. showing that the Si/Al ratio for K-activated geopolymer systems containing Sr is less than the associated control geopolymer system [67]. However, this is using much lower concentrations of Sr within the structure than in this work, which would have less of an impact on the formation of the K-A-S-H phase.

Previous analytical techniques indicated that the SrCO₃ acts as a filler within the geopolymer matrix, receiving a proportion of the heat generated during the reaction phase, as seen in the ICC (Section 4.2.2.1.1), and therefore not interacting with the K-A-S-H phase at all during the formation of the geopolymer. Figure 4-45 shows that the Q⁴(0Al) site, which is attributed to the unreacted metakaolin, is present in greater quantities in the CO₃_5 samples when compared to the KGP samples in Figure 3-6, most notably the CO₃_5 sample taken 3 days after initial reaction, which suggests that this filler effect reduces the extent of reaction as opposed to the rate. The ICC shows that the reaction occurs at the same rate, i.e. the maximum heat release occurs at the same time for all of the samples, and the NMR results seen here show that the amount of metakaolin that reacts is also reduced upon the addition of the SrCO₃. This is likely due to the wetting effect of the salt, as the activating solution will sorb to the individual crystals and be unavailable for reaction with the metakaolin. The extent of reaction of the samples, as calculated from the ²⁹Si sites, is quantified in Table 4-5.

Table 4-5: The extent of reaction of the CO₃_5 and KGP samples both 3 and 28 days after initial reaction, calculated using the ²⁹Si MAS NMR spectra.

Sample	Time point	Extent of reaction (%)
KGP	3 Days	82.17
CO ₃ _5	3 Days	80.73
KGP	28 Days	88.00
CO ₃ _5	28 Days	83.01

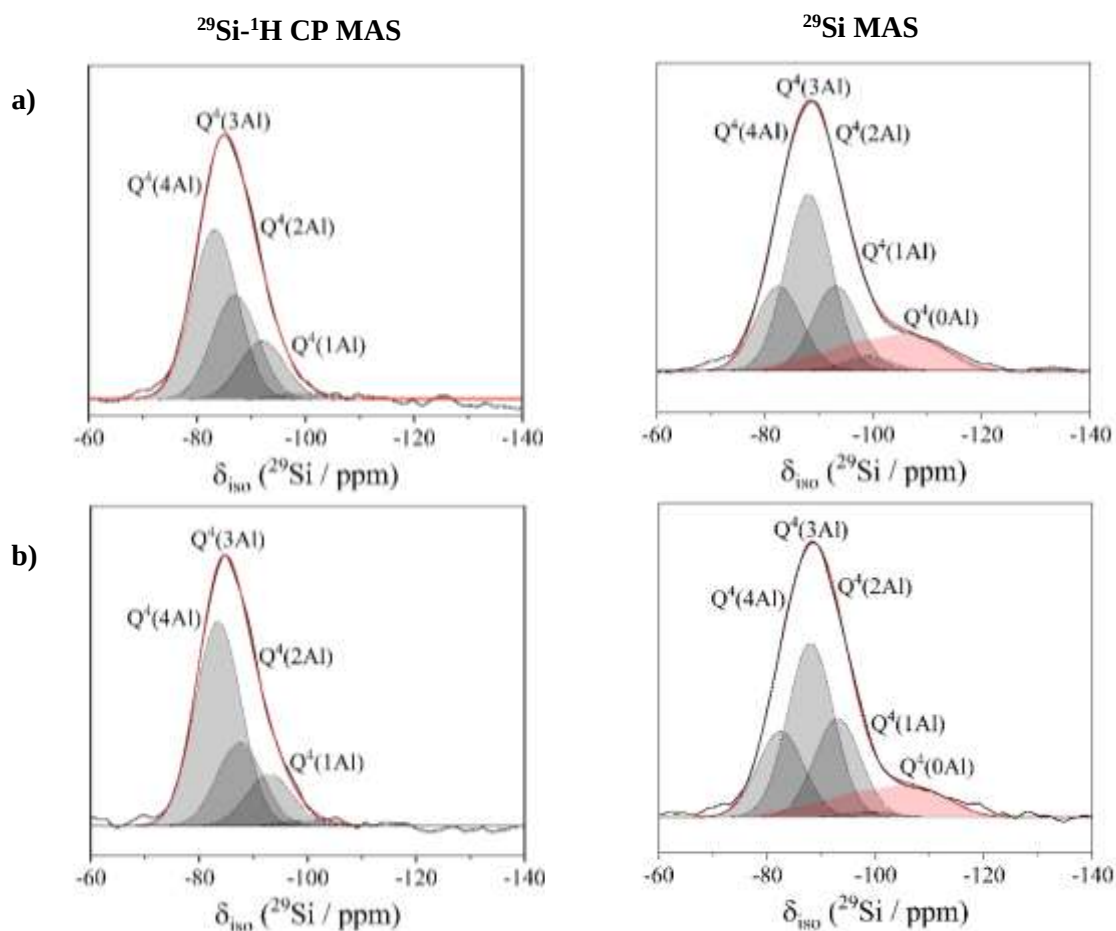


Figure 4-45: ²⁹Si-¹H CP MAS and ²⁹Si MAS NMR spectra and the associated deconvolutions for the a) CO_{3_5} sample after 3 days and b) CO_{3_5} sample after 28 days. The ²⁹Si-¹H CP MAS NMR data is shown in the left column and the ²⁹Si MAS NMR data is shown in the right column. For each spectrum, the raw data is shown as a solid black line and the model fit is shown as a solid red curve. The deconvolutions that represent each ²⁹Si site within the K-A-S-H gel are depicted as grey curves, whilst the deconvolutions that represent ²⁹Si sites within the unreacted metakaolin are shown in a faded red.

4.2.2.2.3.2 ²⁷Al MAS NMR

The ²⁷Al MAS NMR spectra for the CO_{3_5} and KGP samples both 3 and 28 days after the initial reaction are displayed in Figure 4-46.

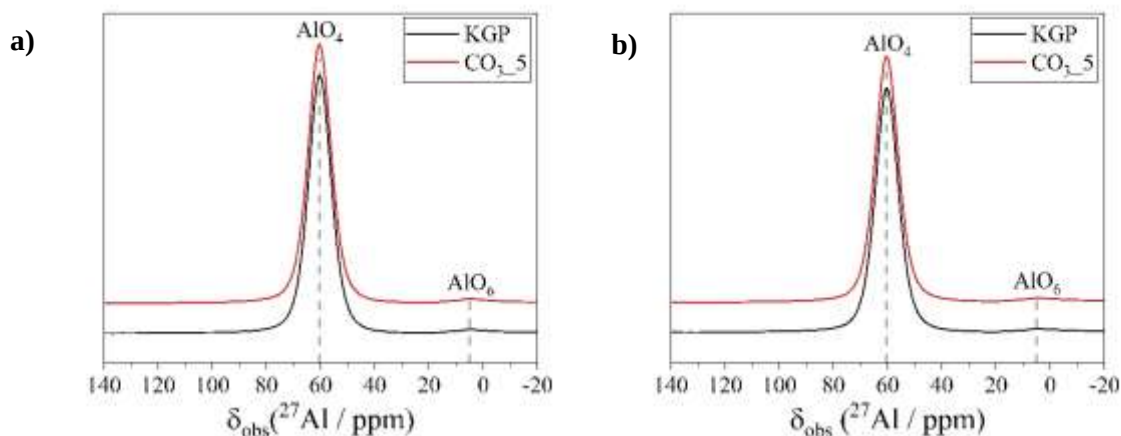


Figure 4-46: ^{27}Al MAS spectra for the CO_3_5 and KGP samples a) 3 days and b) 28 days after reaction.

Figure 4-46 shows that the ^{27}Al MAS NMR spectra for both the KGP and OH_5 samples display two distinct resonances. The most obvious resonance, centred at 60.3 ppm and spanning between $\sim \delta_{\text{obs}}=50$ and $\delta_{\text{obs}}=70$ ppm is recognisable as the tetrahedral Al site (AlO_4) found in the K-A-S-H gel phase of the geopolymer [279, 306]. This coordination is promoted by the large excess of alkali cations within the gels and gives rise to the negative charge that is intricate to the use of geopolymers in the application of the disposal of radioactive Sr, and is introduced by the substitution of Al^{3+} ions for Si^{4+} as shown by Figure 4-21 [307]. This negative charge is balanced by cations: K^+ in the KGP sample and, potentially, a combination of both K^+ and Sr^{2+} in the CO_3 sample [308]. The likelihood of Sr^{2+} cations displacing K^+ ions in this scenario is mitigated by the insolubility of the SrCO_3 limiting the number of Sr^{2+} ions available in solution [303].

The small resonance observed at $\sim \delta_{\text{obs}}=5$ ppm is attributed to the presence of octahedral Al sites (AlO_6) within the samples [274]. The intensity of this peak is negligible when compared to that of the tetrahedral Al peak, and suggests that the majority of the Al within the metakaolin has reacted as the octahedral peak corresponds exclusively to the Al found within the unreacted metakaolin [279]. This is supported by the findings of both the ^{29}Si MAS and ^1H - ^{29}Si CP MAS which display the preferential dissolution of Al during the dissolution phase of the reaction.

4.2.2.2.3.3 ^{39}K MAS NMR

The ^{39}K MAS NMR spectra of the CO_3_5 sample and the KGP control sample can be seen in Figure 4-47 at the time points of both 3 and 28 days.

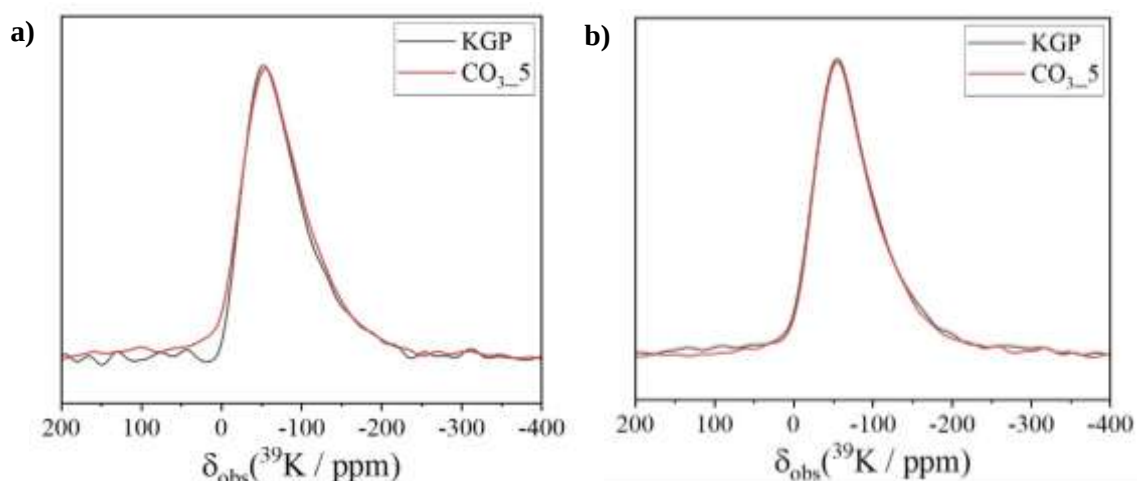


Figure 4-47: ^{39}K MAS NMR spectra for the CO_3_5 and KGP samples a) 3 days and b) 28 days after reaction.

Figure 4-47 shows that there is negligible change between the CO_3_5 samples and the KGP samples at both 3 and 28 days. Moreover, there is essentially no difference between the CO_3_5 samples at 3 and 28 days. The peaks for all samples are observed between $\delta_{\text{obs}} = -50$ and $\delta_{\text{obs}} = -55$ ppm, and the line shape across the samples is comparable, suggesting little change to the chemical environments experienced by the K atoms within the sample. The presence of only a single peak suggests that there is only one K phase within the sample. As discussed in Section 4.2.1.2.3.3, there is no shift in the peak centre, providing no evidence that the Sr is incorporated into the K-A-S-H gel in place of the K.

When these curves are compared to the literature, the comparable lineshapes add further confidence that there is no evidence of changes to the environment of K upon the addition of SrCO_3 [183].

4.2.2.2.3.4 ^{87}Sr Solid-State NMR

^{87}Sr NMR for the CO_3_5 samples could not be acquired, and further attempts to acquire this data should be made in the future.

4.2.2.2.4 EPMA

The use of electron probe microanalysis (EPMA) allows for the chemical composition of the geopolymer gel to be spatially resolved and quantified [316]. In this work, it has been used to determine the distribution of Sr throughout the geopolymer matrix.

The EPMA images observed for the CO_3_5 sample after 28 days at a magnification of x1500 are shown in Figure 4-48.

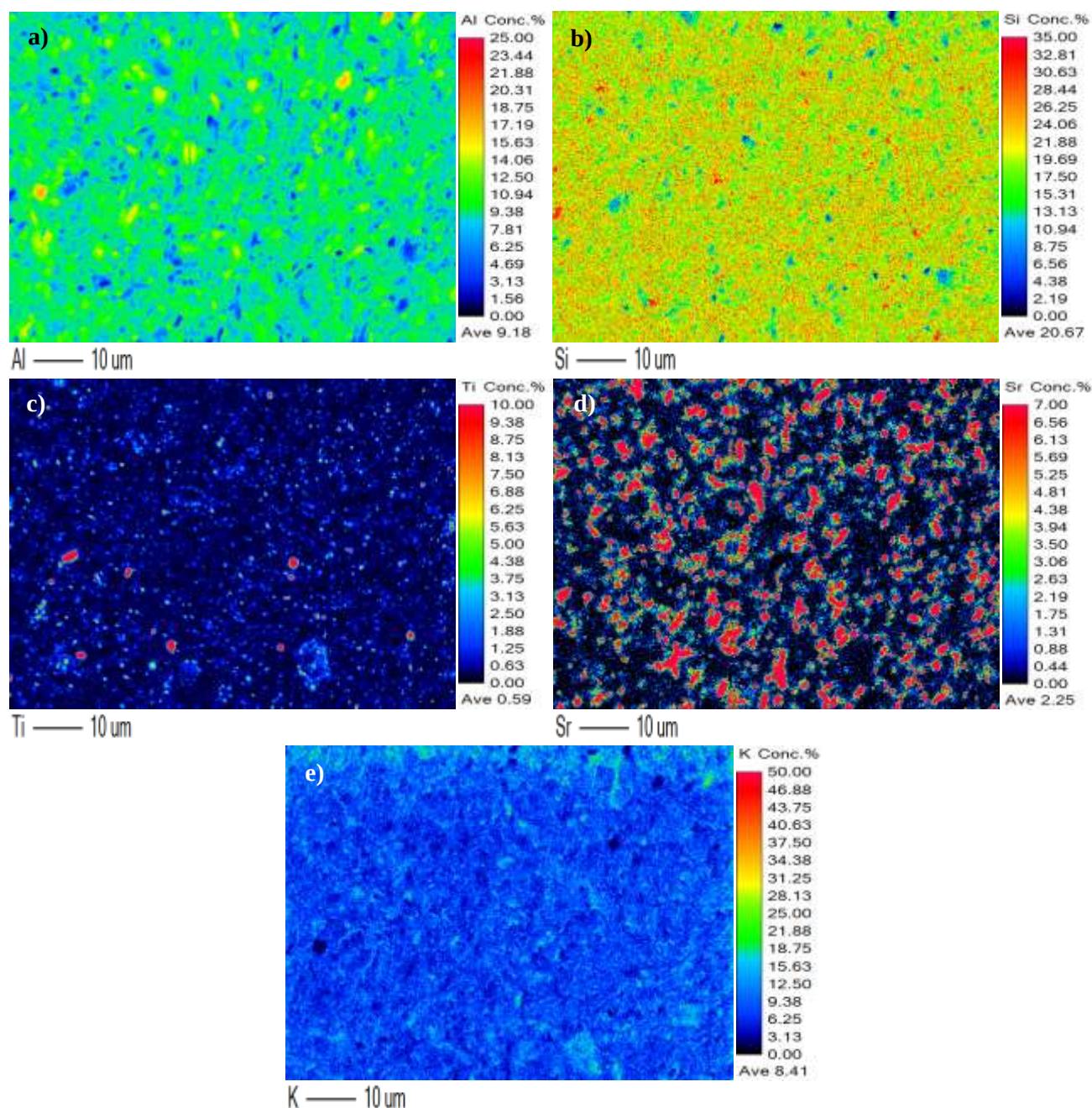


Figure 4-48: The EPMA images generated for the CO₃_5 sample after 28 days of reaction. The elements shown in each image are as follows: a) Aluminium, b) Silicon, c) Titanium, d) Strontium, and e) Potassium. The magnification factor is x1500.

Images a) and b) suggest that the K-A-S-H gel populates the majority of the sample area seen here. There are some regions of higher Al content which suggest the potential for unreacted metakaolin, and this is supported by the presence of some Ti in these regions, as shown by image c). Ti, in the form of anatase, is present as an inert impurity within the metakaolin and so will always be present within the final geopolymers sample.

There are regions of increased Si concentration (>35%), highlighted by the red areas in image b). These areas align with Al poor regions of the sample, suggesting a silica rich phase that is not part of the K-

A-S-H gel. This is likely to be a silica contaminant, potentially silica fume, that accumulated within the pores of the gel during the sample preparation of the sample.

Image d) shows that the Sr is spread relatively evenly throughout the sample. Furthermore, the prominence of areas of high concentration of Sr is consistent with the lack of dissolution of the SrCO_3 , suggesting that the Sr seen here remains in that phase as shown in much of the work in this section. Therefore, the SrCO_3 is being physically encapsulated within the gel as opposed to being incorporated into the structure. On the contrary, the relatively low spatial concentration of K, shown by image e), shows that K is most likely acting as the charge balancing cation for the K-A-S-H gel.

4.2.2.2.5 X-ray Absorption Spectroscopy

4.2.2.2.5.1 X-ray Absorption Near-Edge Structure (XANES) Spectroscopy

The normalised spectra for the Sr K-edge XAS analysis of the CO_3_5 sample after both 3 and 28 days of reaction compared to both the SrCO_3 reagent and the mineral brewsterite-Sr ($(\text{Sr,Ba})_2\text{Al}_4\text{Si}_{12}\text{O}_{32}\cdot 10\text{H}_2\text{O}$) are shown in Figure 4-49 [315].

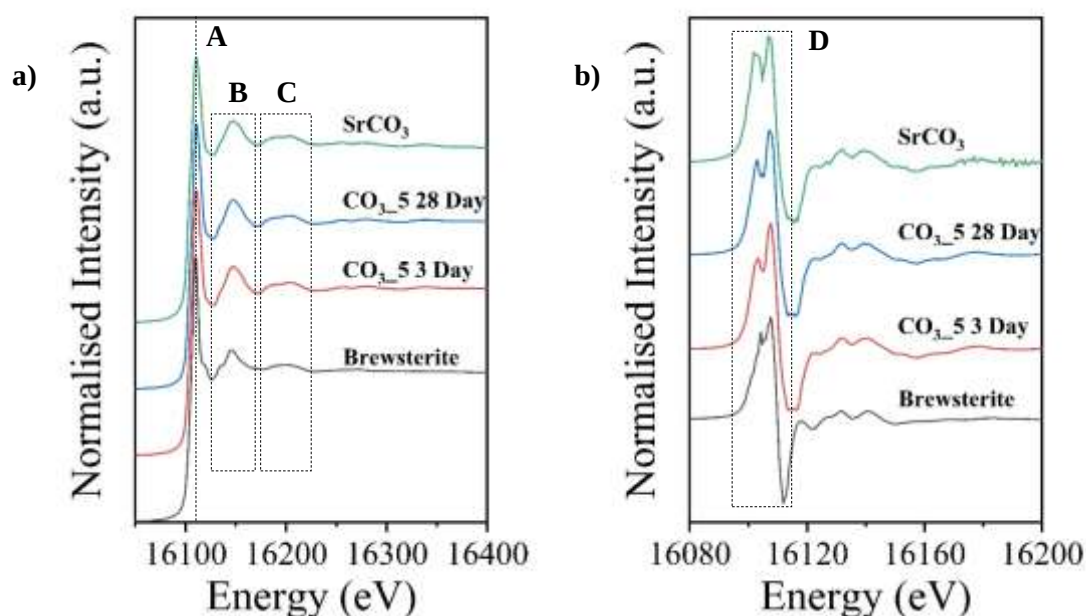


Figure 4-49: a) Normalised X-ray absorption spectra for the geopolymer samples loaded with SrCO_3 , the SrCO_3 reactant used and the mineral brewsterite-Sr. b) The 1st derivative of these spectra.

The Sr K-edge here displays an absorption edge that rises smoothly to a maximum featuring a singular peak. As previously mentioned in Section 4.2.1.2.5.1, the Sr K-edge is relatively featureless but provides enough information for a qualitative analysis to be performed. Firstly, the peak maximum, labelled A in Figure 4-49a), of the brewsterite spectra is reached at slightly lower energies to that of the SrCO_3 reagent and the CO_3_5 samples at both time points. This peak appears to be singular in this

figure, however, the utilisation of the 1st derivative figure, shown in Figure 4-49b), shows that there is a very shallow shoulder on the edge. The highlighted region of Figure 4-49b), labelled D, shows that this doublet peak in the 1st derivative data is more pronounced in the SrCO₃ when compared to the brewsterite, and that both of the CO₃_5 samples show similarities with the SrCO₃ salt spectra in this region. In addition, referring back to Figure 4-49a), the features in both highlighted region B and C appear to confirm that the majority of the Sr environments within the CO₃_5 samples at both time points correspond to those of the Sr in SrCO₃. There does not seem to be any difference between the spectra for the CO₃_5 samples at 3 and 28 days post reaction.

The qualitative analysis performed here indicates that the Sr resides within the sample in the form SrCO₃. This is supported most notably by the order-of-addition reactions, which confirm that, regardless of the order in which the salt is added to the mix, the SrCO₃ does not dissolve within the activating solution. The XRD supports this further, showing that SrCO₃ is prevalent within the samples.

4.2.2.3 Conclusions

Isothermal conduction calorimetry shows that introduction of strontium carbonate at varying Sr/Al ratios affects the kinetics of formation of the geopolymer gel. The chemical mechanisms for this have been investigated using zeta potential, EPMA and order-of-addition experiments, with the conclusion being that the Sr does not dissolve into the activating solution, and acts as a filler material within the geopolymer structure.

However, the Sr²⁺ cations do not affect the resulting structure, the primary phase of which is shown to be a K-A-S-H gel through the use of FTIR spectroscopy, ²⁹Si MAS NMR and ²⁹Si-¹H CP MAS NMR. This phase is comprised of Si and Al in tetrahedral coordination, with the Si mainly existing in Q⁴(4Al), Q⁴(3Al) and Q⁴(2Al) environments. The negative Al sites caused by Al³⁺ in tetrahedral coordination are charge balanced by K⁺, and the addition of the SrCO₃ does not change this due to its lack of solubility as shown by the zeta, order-of-addition and XANES data. XRD shows that the crystalline structure of SrCO₃ is observed within the sample, further supporting its lack of dissolution. Therefore, it is shown that the geopolymer is capable of encapsulating the salt within the matrix. It is shown that the incorporation of the SrCO₃ leads to a slight relative increase in the Si/Al ratio, most likely due to the lower extent of reaction of the system compared to the KGP control sample.

The order-of-addition experiments demonstrated that the addition of SrCO₃ into the system at any point in the mix has very little effect on the resulting kinetics and mechanisms.

This work shows that K-silicate activated geopolymers are capable of incorporating wastes containing SrCO₃ at high waste loadings of up to 5% by weight. However, in practice, the loadings are likely to be far lower due to activity limits per package on the wasteforms, owing to the radioactivity of the waste in question. Whilst this, and any impact of the radiation and resulting decay products, are not considered

in this work, it is important to note that they will likely have a notable effect on the performance of the geopolymer as a wasteform, and further work to determine how great this effect is will be crucial to determine the overall suitability of the wasteform.

Despite this, the findings of this work show that the incorporation of SrCO_3 containing waste has only a small effect on both the kinetics and mechanisms of formation of a metakaolin based, potassium silicate activated geopolymer system, suggesting that these systems show great promise as wasteforms for the long term immobilisation of radioactive waste streams containing ^{90}Sr in the form of SrCO_3 .

4.2.3 Strontium Nitrate

4.2.3.1 Fresh State

4.2.3.1.1 ICC

Figure 4-50 displays the calorimetry curves produced by the formation of the K-geopolymers loaded with $\text{Sr}(\text{NO}_3)_2$ over the first 3 days of reaction.

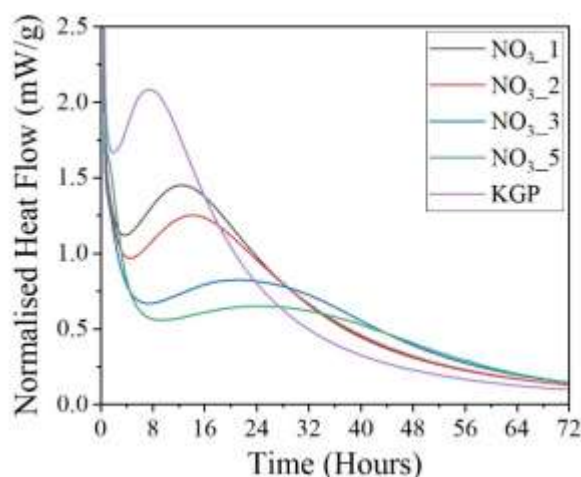


Figure 4-50: The effect on the heat evolution of reaction of loading K-activated metakaolin geopolymers with $\text{Sr}(\text{NO}_3)_2$ over the first 3 days.

The heat evolved during the formation of the K-A-S-H gel is briefly discussed in Section 4.2.1.1.1 and is also applicable for the systems here. Figure 4-50 clearly shows that the addition of $\text{Sr}(\text{NO}_3)_2$ to the geopolymer mix has an impact on the kinetics of reaction within the first 72 hours. Firstly, the maximum recorded normalised heat flow for the reaction peak decreases with the increasing addition of $\text{Sr}(\text{NO}_3)_2$; the maximum value recorded for the NO_3_5 sample, where the maximum recorded heat flow value is most impacted, is around 30% of the maximum recorded value for the KGP control sample. Furthermore, the time at which the maximum values are recorded is much later in the reaction, with this milestone being reached over 3 times later in the NO_3_5 sample (~26 hours) when compared to the KGP control sample (~7.5 hours). The period in between the initial dissolution peak and the secondary reaction peak (the time in the reaction which would be referred to as the induction period in a PC based system) is elongated as the Sr/Al ratio increases, further adding to the delay in reaction diagrammatically represented in Figure 4-50.

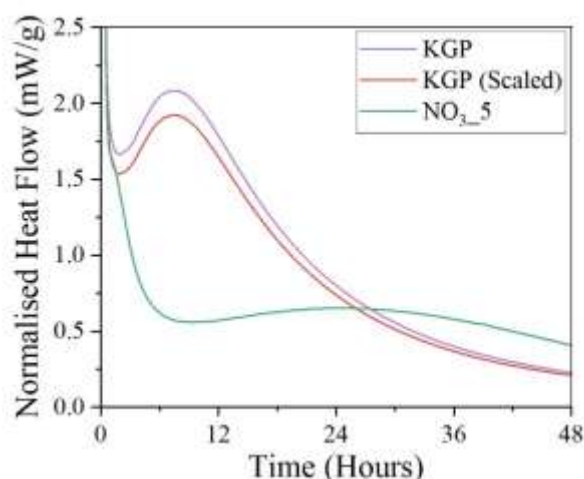


Figure 4-51: The heat evolution of the KGP and NO₃_5 samples compared to a scaled curve of the KGP sample.

Figure 4-51 shows the KGP and NO₃_5 samples seen in this work to a scaled version of the curve generated by the KGP sample, shown in red. This curve is calculated by normalising the heat evolution of the KGP sample by a mass that would be consistent with a NO₃_5 sample with the same mass of metakaolin and activating solution as the 20g KGP sample. This curve gives the normalized heat evolution of the situation that could be described as the ‘extreme case’ scenario, where none of the Sr(NO₃)₂ dissolves into the activating solution and instead, acts as a filler material. This is further support for the dissolution and subsequent reaction of the Sr(NO₃)₂ within the geopolymer mix, as the heat evolution curve for the NO₃_5 sample is considerably different to that of the scaled KGP curve.

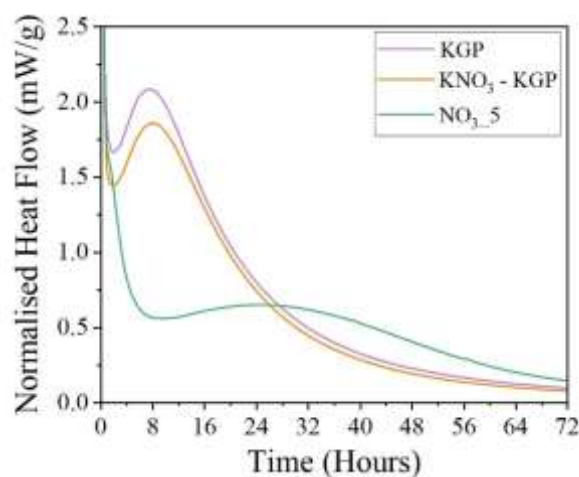


Figure 4-52: Comparing the effect on heat evolution of adding Sr(NO₃)₂ and KNO₃ to a K-silicate activated geopolymer at an (Sr or K)/Al ratio of 0.125.

Figure 4-52 displays the heat evolution curve generated by a K-silicate activated, metakaolin based geopolymer loaded with KNO₃ (KNO₃ – KGP) at a K/Al ratio of 0.125. Although this is not the true K/Al ratio, due to the presence of K atoms in the activating solution, it is the value of the additional K atoms that are added in order to keep the concentration of the anion equal to that of the corresponding Sr system. The effect of the additional K atoms will be negligible, as the mass added here is significantly

less than the mass already in the activating solution. Therefore, the entirety of the difference between this curve and the KGP control samples curve can be attributed to the addition of the anion. As can be seen here, the addition of the anion does lead to a change in the observed heat evolution of the geopolymer reaction. However, the addition of the anion does not lead to significant retardation of the reaction, and instead lowers the maximum heat of the reaction by $\sim 10.5\%$, reducing from 2.08 mW/g to 1.86 mW/g. From this, we can glean that the majority of the change seen in the NO₃_5 sample is due to the introduction of the Sr²⁺ ions into the solution, leading to the significant retardation of the reaction.

Figure 4-53 shows that the relationship between the Sr/Al ratio of the geopolymer mix and both the value and time of maximum heat evolution is linear, increasing the time of max heat evolution with increasing Sr/Al ratio and, likewise, decreasing the maximum value of heat evolved with increasing Sr/Al ratio. This also suggests that this trend would continue as the Sr/Al ratio further increases, suggesting that the addition of the salt leads to its subsequent reaction with the raw materials (most probably the activating solution) in a way which either consumes the reactants or prevents the dissolution reaction. This trend suggests that this effect will continue to increase with further addition of the salt.

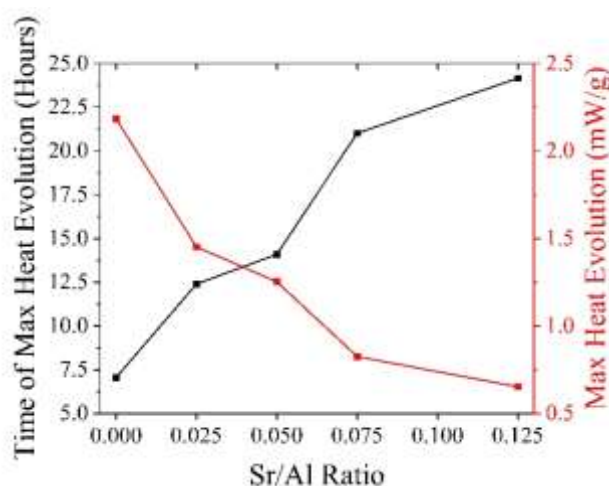


Figure 4-53: The relationship between Sr/Al ratio and the observed time of maximum heat evolution and the value of the maximum heat evolution.

The results shown here suggest that the addition of the Sr(NO₃)₂ alters the reaction pathways followed within the geopolymer mix during the early phase reaction. Sr(NO₃)₂ is very soluble, dissolving freely into the activating solution. Therefore, it is likely that either the free Sr²⁺ or NO₃⁻ ions are reacting with the ions in solution, preventing the complete dissolution of the aluminosilicate precursor or preventing the reaction of the aluminate and silicate monomers to form the fully reacted geopolymer matrix. This is explored in further detail in Sections 4.2.3.1.2 and 4.2.3.1.4.

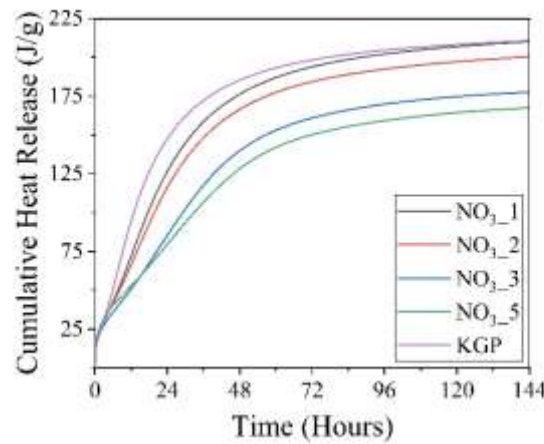


Figure 4-54: The cumulative heat release curves over the first 144 hours of reaction.

Figure 4-54 displays the cumulative heat curves generated by the samples over the first 144 hours of reaction. As can be seen, the introduction of the $\text{Sr}(\text{NO}_3)_2$ salt in all of the samples leads to a lower total cumulative heat when compared to the KGP control sample. The decrease in cumulative heat increases with the Sr/Al ratio, suggesting that the total extent of reaction is directly affected by the introduction of the salt. As discussed in Section 4.2.1.1.1, the heat release after 144 hours corresponds to roughly 2/3 of the total heat release of the system for OPC, and if it assumed to be the same for geopolymer systems, the maximum total heat release for the $\text{Sr}(\text{NO}_3)_2$ containing geopolymer samples will be around 315 J/g maximum, with the NO₃_5 sample having the lowest total heat release of ~250 J/g [297]. This is higher than the average heat release of the current nuclear standard, a Portland cement and GGBS blend, which is around 100 J/g but does not exceed the guideline value of 180 J/g over the first 24 hours set by the current UK requirements for nuclear wasteforms [298, 299]. However, Figure 4-54 shows that the total heat release of the reaction can be decreased with the addition of certain salts, in this case $\text{Sr}(\text{NO}_3)_2$. If the integrity of the final product is found to be unaffected, this can be used to engineer the wasteform in order to meet the standards set within the UK.

4.2.3.1.2 Zeta Potential

The zeta potential values obtained for the surface charge of the metakaolin in the presence of $\text{Sr}(\text{NO}_3)_2$ at different pHs is shown in Figure 4-55.

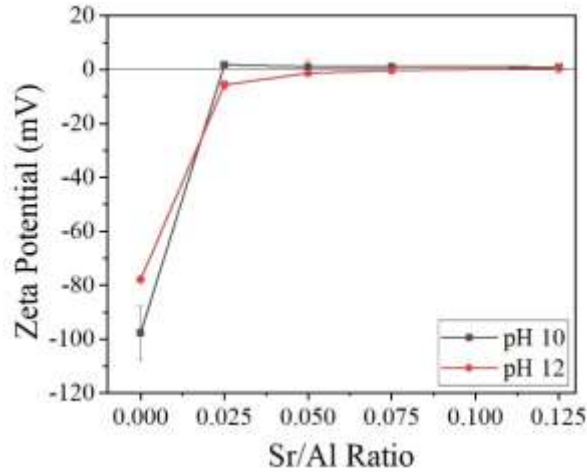


Figure 4-55: Comparing the effect of Sr/Al ratio, altered by the addition of $\text{Sr}(\text{NO}_3)_2$, on the zeta potential of metakaolin in a KOH solution at pH 10 and 12.

Figure 4-55 shows that metakaolin in the KOH solution without the presence of salts, shown by a Sr/Al ratio of 0, has a very negative surface charge, which becomes increasingly negative with increasing pH. This surface charge is caused by the deprotonation of the surface hydroxyl sites in the alkaline solution, leading to an increased negative charge on the surface of the particles [159]. Upon the addition of the $\text{Sr}(\text{NO}_3)_2$, the surface charge of the metakaolin at both of the pHs increases significantly to at or around 0, the isoelectric point. At this point, the surface charge of the metakaolin is net neutral due to the effect of the electric double layer (EDL), promoting agglomeration over time [155, 156].

Figure 4-55 displays that the pH does not have an effect on the zeta potential values recorded for the metakaolin and $\text{Sr}(\text{NO}_3)_2$ containing systems. The solubility of the $\text{Sr}(\text{NO}_3)_2$ is very high, and is unaffected by the high pH of the systems here. It also suggests that at pH 14, the pH at which many of the samples used in other areas of this work reside, the $\text{Sr}(\text{NO}_3)_2$ will dissolve and have a similar effect. Therefore, the concentration of Sr^{2+} cations within the solution is very high, leading to significant changes to the zeta potential and causing the net charge around the surface of the metakaolin to be effectively 0, at the isoelectric point. The net neutral charge results in a lack of electrostatic repulsion between the metakaolin particles, which will lead to the formation of larger metakaolin particles with a decreased surface area, substantially slowing the dissolution of the metakaolin into the solution [300, 301]. Another potential mechanism for the reduced dissolution rate is the formation of a layer of Sr^{2+} particles on the surface of the metakaolin, producing a physical barrier that lowers the concentration gradient between the metakaolin and the surrounding solution, which is supported by the high concentration of Sr^{2+} particles that are in solution due to the high solubility of the $\text{Sr}(\text{NO}_3)_2$. This mechanism is inspired by the dissolution of glass, as outlined in Frugier et al. [302]. Although the materials are different, the concept of a physical barrier to dissolution fits the work seen here, as the Sr^{2+} ions are drawn to the surface of the metakaolin. In reality, it could be either one of these

mechanisms, or a combination of both, that leads to the reduced rate of dissolution seen by the NO₃ samples in the ICC.

This mechanism is likely to be the cause for the impact on the reaction kinetics that can be seen in the ICC for these samples (Section 4.2.3.1.1). As the Sr/Al ratio increases, the high solubility of the salt results in the concentration of Sr²⁺ cations within the solution to increase which, in turn, promotes the agglomeration of the metakaolin particles through interaction with the negative surface which leads to the slower dissolution of the metakaolin and a decrease in the reaction speed overall.

4.2.3.1.3 DRIFTS

The DRIFTS spectra for the NO₃_5 sample in the first 4 hours of reaction can be seen in Figure 4-56.

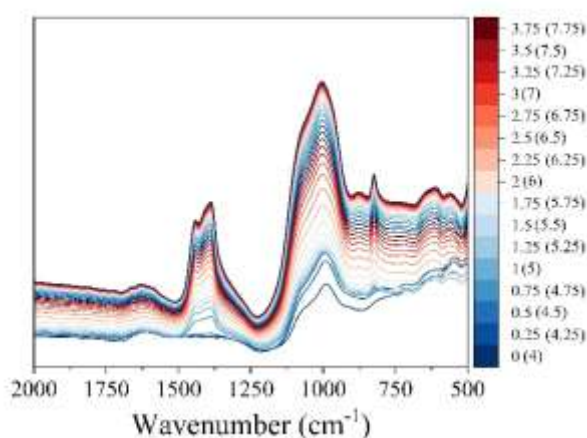


Figure 4-56: DRIFTS spectra for the NO₃_5 sample in the first 4 hours of reaction. The spectra are displayed in 15 minute intervals, beginning at $t=0$ as marked and progressing through the colour gradient. Times are shown in hours.

Within the first 1.5 hours, the Si-O-T peak centred at $\sim 1000\text{ cm}^{-1}$ grows to a maximum [253]. At this point, this peak is quite narrow, with a single clear peak present, suggesting the formation of a singular Si site, most likely the Si-O-Si peak. However, after the initial 1.5 hour time point, the formation of a second Si site is expressed by the appearance of a second peak in this region, centred at a shifted position of $\sim 1100\text{ cm}^{-1}$, most likely due to the Si-O-Al bonds beginning to form. This agrees with the assumption that the inclusion of Sr(NO₃)₂ is slowing the dissolution of the aluminium sites within the metakaolin, leading to a delayed reaction. At this point, the intensity of the initial Si-O-Si peak begins to decrease. Although this is not fully understood, it is possible that this is due to the re-formation of these sites into the Si-O-Al sites within the gel. After the first 4 hours, it is clear that there are two Si sites within the gel matrix, present at relatively similar intensities.

Furthermore, over the first 4 hours, the appearance of a secondary peak can be seen in the spectra centred at around 1400 cm^{-1} . There are two possibilities for this peak: this peak represents the NO₃⁻ anion within the structure, or any NO₃ containing compounds that may have formed such as KNO₃, or

the Sr within the system are carbonating due to contact with the air. Firstly, if the peak is to represent the NO_3 within the system, it would be expected that this peak would not grow, as the maximum amount of NO_3 is already present within the system at the beginning of the measurement. Therefore, it would be expected that the peak would be at its maximum from the beginning. This point aids the argument that the peak is representative of the carbonation of the Sr within the system. Due to the procedure for the DRIFTS measurements, it is not possible to prevent contact between the sample and the surrounding air. Furthermore, the infrared beam used for the DRIFTS measurement must pass through the surface of the sample to reach the bulk material. Therefore, artefacts from the surface of the sample, notably the point where carbonation would occur, will always be included in the spectra. Due to this, it is most likely that this peak is a reflection of the carbonation of Sr within the sample. In comparison, the DRIFTS spectra for the KGP control sample over the first 4 hours, which does not contain Sr, can be seen in Figure 4-7. There is no evidence of the growth of a peak within the same region in this spectra, suggesting that it is the Sr that is rapidly carbonating as opposed to the K. This suggests that there is a meaningful mass of Sr that is ‘free’ within the sample to migrate to the surface of the aqueous phase and react with the CO_2 in the air.

Unlike the NO_3_5 sample, the KGP control sample does not reach its maximum intensity for the first Si-O-T peak that begins to grow at a wavenumber of $\sim 1000\text{ cm}^{-1}$. However, the formation of a secondary Si environment can clearly be seen, although the growth of this appears to begin far earlier, almost immediately after measurements begin. This further supports the hypothesis that the inclusion of the $\text{Sr}(\text{NO}_3)_2$ delays the dissolution of the Al within the metakaolin.

The DRIFTS spectra for the NO_3_5 sample from 4 to 24 hours post initial mixing can be seen in Figure 4-57.

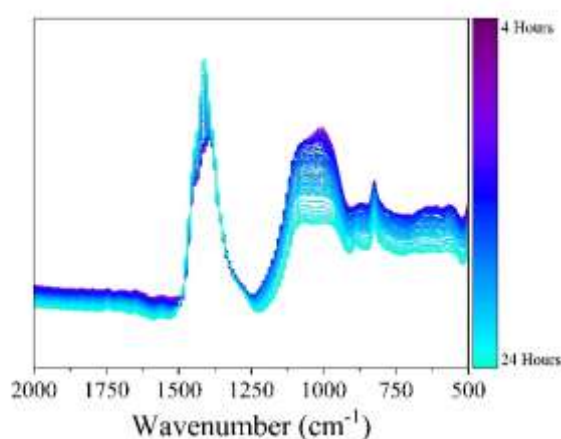


Figure 4-57: DRIFTS spectra for the NO_3_5 sample from 4 to 24 hours post initial reaction. The spectra are displayed in 15 minute intervals up until the 16-hour mark, at which the time progresses in whole hours, beginning at $t=4$ hours as marked and progressing through the colour gradient. Times are shown in hours.

After the 1.5-hour time point, the intensity of both of the Si-O-T peaks continues to drop. It is not clear why this happens, as DRIFTS is a relatively new analysis technique for cement. Therefore, further research is required to fully understand the phenomena that is seen. It is possible that the shrinkage of the cement is responsible for this drop; as the cement begins to harden, it shrinks, changing the distance between the surface of the sample and the detector [269, 270]. This could alter the amount of signal that reaches the detector, reducing the intensity. However, the relative intensities of the two peaks at any one timepoint suggests that there are increasingly similar quantities of both as the time approaches 24 hours. This is consistent with the formation of a highly cross-linked aluminosilicate material, the geopolymer, and suggests that there is capacity to bind the Sr as the charge balancing cation for the negatively charged AlO_4^- tetrahedra. Figure 4-9 displays the DRIFTS spectra for the KGP control sample from 4 to 24 hours post initial mixing. A similar drop in intensity can be seen in the Si-O-T peaks, although the overall intensity appears to be higher, most likely due to the distance between the sample and the detector being shorter than for the NO_3_5 sample. The intensity of the second Si site, thought to represent the Si-O-Al bond, does not appear to be as great as seen in the NO_3_5 sample, suggesting that the inclusion of the $\text{Sr}(\text{NO}_3)_2$, despite slowing the initial dissolution of the Al, actually promotes its inclusion into the aluminosilicate structure. This is consistent with samples where the Sr is incorporated into the K-A-S-H gel in the place of K, as the Si/Al ratio decreases [67]. This is consistent with the NMR results for the NO_3_5 sample (Section 4.2.3.2.3.1), albeit at a far increased pace. The ^{29}Si MAS NMR suggests that after 3 days, the Si/Al ratio is greater than the equivalent KGP control sample, but after 28 days, the Si/Al ratio has decreased in the NO_3_5 sample. It is possible that the Si-O-Si sites continue to form up until the 3 day time point, and then after this, the Al, the dissolution of which is slowed by the inclusion of the $\text{Sr}(\text{NO}_3)_2$, becomes available in greater quantities to form more Si-O-Al sites.

Figure 4-57 also shows that the carbonation peak at $\sim 1400\text{ cm}^{-1}$ continues to grow up to the 24 hour time point. This is unsurprising, as the carbonation will continue due to the contact with the air. However, this peak begins to form in the KGP control sample from around 13 hours post mixing. The peak seen in this sample is most probably due to the carbonation of the K within the sample to form K_2CO_3 . This finding provides an argument that the original carbonation seen in the NO_3_5 sample could have been due to there being a greater concentration of ‘free’ K available to carbonate due to its displacement from its place as the charge balancing cation within the structure by the Sr. Therefore, it is possible that this is further evidence for the incorporation of Sr into the K-A-S-H gel phase.

4.2.3.1.4 Order-of-addition Experiments

In order to determine whether the point at which the Sr salt is added to the mix impacts the performance of the geopolymer, order-of-addition experiments were performed as outlined in Section 2.1.1.2.

4.2.3.1.4.1 Order-of-addition #1

1. The $\text{Sr}(\text{NO}_3)_2$ dissolves completely within the water.
2. The addition of the solid KOH led to the formation of a white solid. This could be potassium nitrate, or the addition of the KOH could have increased the pH to a point at which the strontium nitrate could have re-precipitated out of solution. Or, this solid could be a mixture of both of these salts; This is discussed below. The FTIR spectra of this solid can be seen in Figure 4-58.

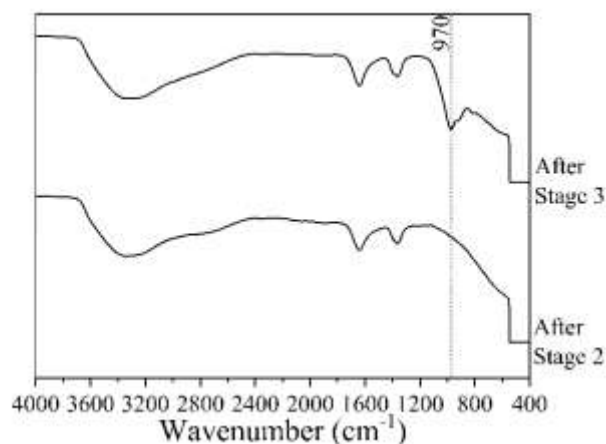


Figure 4-58: FTIR spectra of the white solid observed after stages 2 and 3 of the OoA #1 experiment containing $\text{Sr}(\text{NO}_3)_2$.

3. The addition of the potassium silicate stock solution further drives the precipitation of the white solid. This suggests that the precipitation of this solid is pH driven, with a greater pH reducing the solubility limit of the solution further. The FTIR spectra of this solid can be seen in Figure 4-58.
4. The metakaolin was unable to be added to the solution as it had completely solidified. An attempt was made to mix the two but nothing came of it.

Figure 4-58 shows that the solid after both stages contains a nitrate component, which is shown by the peak centred at 1360 cm^{-1} . This nitrate component is more likely to be caused by the presence of KNO_3 as opposed to $\text{Sr}(\text{NO}_3)_2$ as shown by Figure 4-59. There is no evidence of the secondary peak seen in the $\text{Sr}(\text{NO}_3)_2$ centred at around 1435 cm^{-1} , which provides further evidence that the formation of KNO_3 occurs.

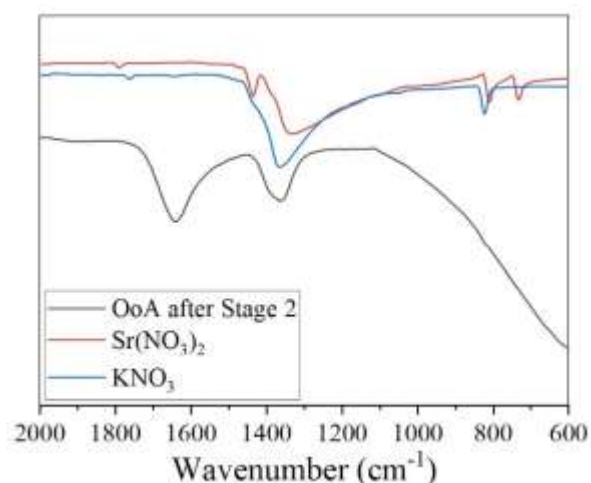


Figure 4-59: FTIR spectra of the white solid observed after stage 2 of the OoA #1 experiment containing $\text{Sr}(\text{NO}_3)_2$ compared to pure $\text{Sr}(\text{NO}_3)_2$ and KNO_3 .

Furthermore, the ‘gloopy’ nature of the solid is explained by the presence of water, displayed by the broad peak at $3200\text{--}3600\text{ cm}^{-1}$ and the peak representing bound water at 1600 cm^{-1} . There is also a broad shoulder present around 2800 cm^{-1} ; This is most probably another bound water environment introduced due to the reaction with the nitrate.

The addition of silicate in stage 3 also leads to the appearance of a band at 970 cm^{-1} that is attributed to the Si-O bond. There is also another peak present at $\sim 925\text{ cm}^{-1}$. This peak could indicate the presence of a further silicate compound within the solid, or potentially a secondary silicate site within the compound. This is further evidence for the formation of a strontium silicate compound in some form, whether it be pure strontium silicate or a potassium strontium silicate as discussed in Section 4.2.1.1.4.1.

4.2.3.1.4.2 Order-of-addition #2

1. The addition of solid KOH to water leads to an exothermic dissolution reaction.
2. The addition of solid $\text{Sr}(\text{NO}_3)_2$ led to the formation of a viscous, white solid suspension. The liquid component was barely visible, although the solid was gloopy. The FTIR spectra of this solid can be seen in Figure 4-60.

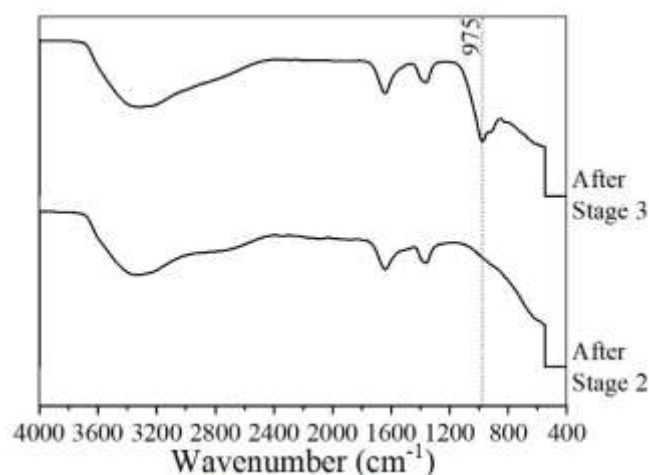


Figure 4-60: FTIR spectra of the white solid observed after stages 2 and 3 of the OoA #2 experiment containing $\text{Sr}(\text{NO}_3)_2$.

3. The addition of the K-silicate stock solution disperses the solid for a short period of time, allowing the magnetic stirrer to turn again. However, after a period of 5-10 minutes, the solid becomes too viscous for the stirrer to turn. The FTIR spectra of this solid can be seen in Figure 4-60.
4. The metakaolin was unable to be added to the solution as it had completely solidified. An attempt was made to mix the two but nothing came of it.

Much like for the OoA #1 experiments, the FTIR of the resulting solid after stage 2 shows the presence of a nitrate compound and both bound and free water. The FTIR spectra at both stages is compared to that of the $\text{Sr}(\text{NO}_3)_2$ and the KNO_3 in Figure 4-61. Similarly to OoA experiment #1, the solid appears to contain KNO_3 preferentially as opposed to $\text{Sr}(\text{NO}_3)_2$.

After the addition of the K-silicate, the bridging oxygen bond appears at 975 cm^{-1} . The shoulders at around 925 cm^{-1} could potentially be due to another silicate site within the structure causing a shift to the lower wave numbers.

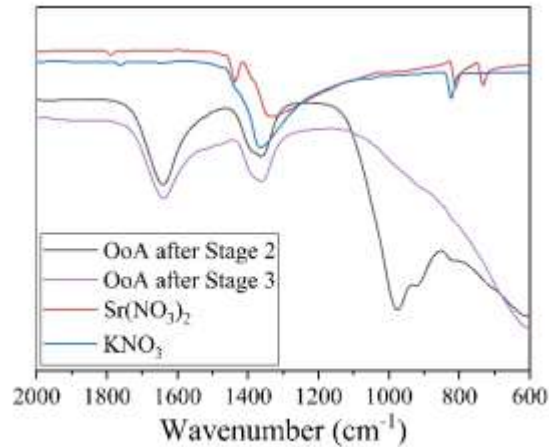


Figure 4-61: FTIR spectra of the white solid observed after stage 2 and 3 of the OoA #2 experiment containing $\text{Sr}(\text{NO}_3)_2$ compared to pure $\text{Sr}(\text{NO}_3)_2$ and KNO_3 .

4.2.3.1.4.3 Order-of-addition #3

1. The addition of solid KOH to water leads to an exothermic dissolution reaction.
2. The addition of the K-silicate stock solution to the KOH solution resulted in a clear liquid mix.
3. The addition of solid $\text{Sr}(\text{NO}_3)_2$ led to the formation of the same solid as observed in OoA #2 stage 2, but in this case, the solid is more translucent and appears more dispersed.
4. The addition of the metakaolin was difficult due to the high viscosity of the activating solution. The solution reacted with the metakaolin but its high viscosity led to clumping which prevented all of the metakaolin from reacting.

4.2.3.1.4.4 Order-of-addition ICC

Figure 4-62 shows the calorimetry curves generated by the OoA samples compared to the control KGP sample over the first 3 days of reaction. The samples for OoA #1 and #2 were completely solid and so were unable to facilitate dissolution of the metakaolin.

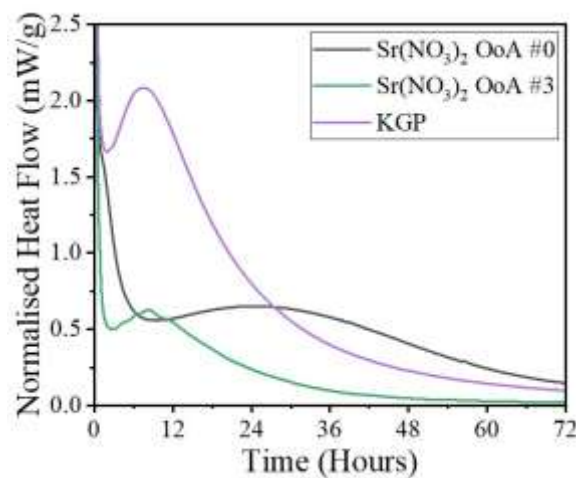


Figure 4-62: The effect on the heat evolution of reaction of adding $\text{Sr}(\text{NO}_3)_2$ at different stages to K-activated metakaolin geopolymers over the first 3 days.

The OoA #1 and #2 activating solutions containing $\text{Sr}(\text{NO}_3)_2$ had completely solidified before ICC could be performed. This made them impossible to use as they were incapable of dissolving the metakaolin. The sole activating solution containing the $\text{Sr}(\text{NO}_3)_2$ that was usable, OoA #3, had a high viscosity, mainly due to the presence of the ‘gloopy’ white solid. This higher viscosity made it difficult to transfer to the ampoule and, once in, it did not migrate sufficiently to cause thorough dissolution of the metakaolin particles. For this sample, the relatively short reaction time observed in the ICC, accompanied by the low heat flow is indicative of the lack of reaction occurring within the sample. This is expected due to the difficulty of mixing the high viscosity activating solution with the metakaolin in this particular experiment. Therefore, it is not possible to reliably compare the kinetics of reaction between this sample, the KGP control sample and even the OoA #0 sample here beyond stating that the maximum recorded heat for the OoA #0 and #3 are very similar.

However, this similarity may be purely coincidental, occurring due to the OoA #3 reaction stopping at this value after all of the metakaolin that managed to dissolve reacts. Likewise, it is possible that any reaction that does happen completes much faster than the reaction in OoA #0, which is supported by the sharpness of the peak. Finally, it could be a combination of both of these factors.

4.2.3.1.4.5 *Order-of-addition Conclusions*

The introduction of $\text{Sr}(\text{NO}_3)_2$ into the aqueous phase at any point in the activating solution production process causes the precipitation of a white solid, potentially a mix of Sr and K nitrate, a strontium silicate phase, or even a strontium potassium silicate phase, although this is unlikely. The presence of this solid in the mix is detrimental, potentially causing the significant level of retardation seen in the ICC of the reaction process; as shown by OoA #1 and #2, the entirety of the activating solution precipitates, preventing the migration of the high pH solution which, in turn, leads to a lack of dissolution of the metakaolin. Instead of suggesting a slower reaction, the decrease in the maximum heat flow observed in Section 4.2.3.1.4.4 for the $\text{Sr}(\text{NO}_3)_2$ sample compared to the control sample could be due to a lesser extent of reaction, as some of the activating solution required to release the aluminate and silicate oligomers from the metakaolin has reacted with the nitrate to form a solid.

These results suggest that the inclusion of Sr as a nitrate salt should be done as late in the process as possible, potentially after the initial mixing of the activating solution and the metakaolin.

4.2.3.2 *Hardened State*

4.2.3.2.1 FTIR

Figure 4-63 shows the FTIR spectra of the K-geopolymers loaded with $\text{Sr}(\text{NO}_3)_2$ after the first 3 days of reaction.

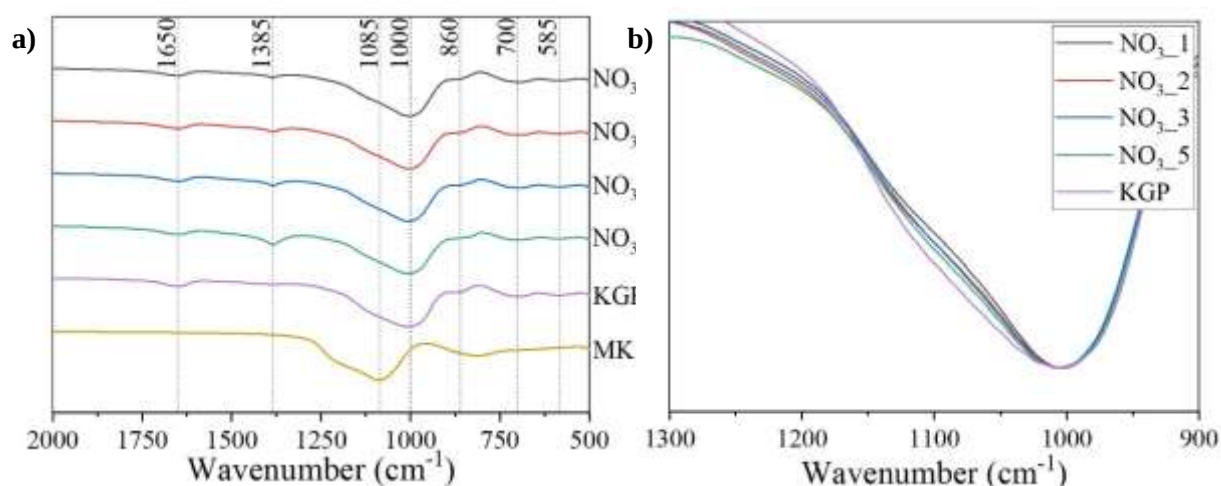


Figure 4-63: The FTIR spectra generated by loading K-activated metakaolin geopolymers with $\text{Sr}(\text{NO}_3)_2$, the KGP control sample and the unreacted metakaolin after the first 3 days of reaction. Plot b) is focused on the 900-1300 cm^{-1} range of plot (excluding the metakaolin) a), and the lines are overlaid.

For Figure 4-63 a), the bond vibrations that are responsible for the resonances seen are discussed in Section 3.4.2 and summarised in Table 3-4. The apparent shoulder on the upper wavenumber end of this peak (1050-1100 cm^{-1}) shows the presence of metakaolin within these samples. This is due to the spectra for metakaolin exhibiting the main Si-O-T peak at a slightly higher wavenumber of approximately 1085 cm^{-1} [254].

The main observable difference between the KGP control and the nitrate containing samples seen in Figure 4-63 a) is the intensity centred at 1385 cm^{-1} . This is due to the presence of undissolved KNO_3 within samples, as discussed below. This peak becomes more prominent as the concentration of $\text{Sr}(\text{NO}_3)_2$ (Sr/Al ratio) within the sample increases. Excluding this difference, the spectra are almost identical, showing the distinctive characteristics seen in the FTIR spectra of metakaolin-based geopolymers. Figure 4-63 b) shows the superimposed curves of the KGP sample and the NO_3 samples: the shoulder that represents the presence of unreacted metakaolin at $\sim 1100 \text{ cm}^{-1}$ is more intense in the KGP sample than any of the nitrate bearing samples. This could suggest that there is a greater concentration of unreacted metakaolin within the KGP sample and that the level of dissolution is greater in the samples containing the Sr salt. This potential increase in dissolution does not increase the kinetics of the reaction, as shown by the ICC curves. This could suggest that the increased concentration of free Sr^{2+} ions leads to a delay in the reaction onset.

Walkley et al. (2020) showed that the incorporation of alkaline earth cations such as Sr results in a shift of the band attributed to the asymmetric stretching of the Si-O-T towards higher wavenumbers [67]. The lack of shift of this band suggests that the Sr is not significantly incorporated into the structure, which would further explain the lack of change in the spectra between samples.

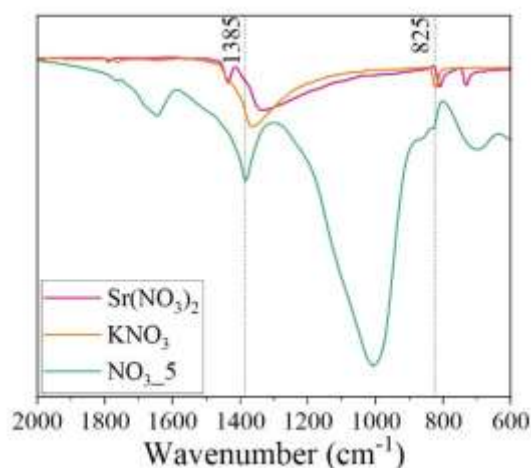


Figure 4-64: The FTIR spectra of the NO₃_5 sample after 3 days of reaction compared to pure Sr(NO₃)₂ and KNO₃.

As shown in Figure 4-64, the peak attributed to the nitrate phase in the NO₃_5 does not line up perfectly with the respective peaks in the Sr(NO₃)₂ and the KNO₃ materials. However, the peaks seen in the KNO₃ material centred at 825 cm⁻¹, 1370 cm⁻¹ and 1765 cm⁻¹ align closely with those seen in the NO₃_5 sample. Therefore, it is possible that the Sr is displacing the K, causing the K to precipitate into the KNO₃ phase whilst the Sr acts as a charge balancing cation within the matrix.

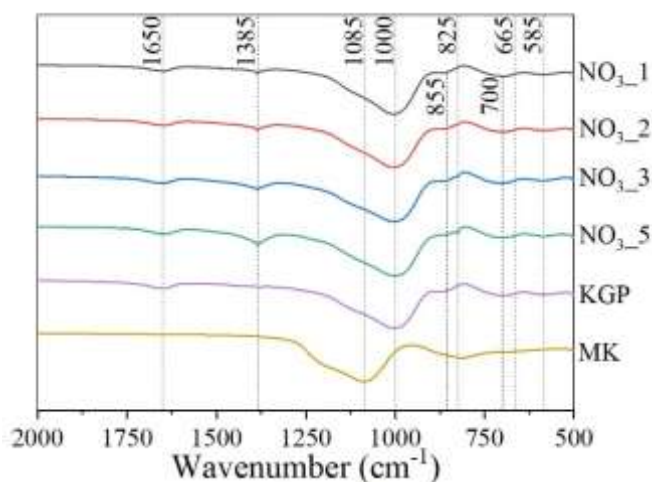


Figure 4-65: The FTIR spectra generated by loading K-activated metakaolin geopolymers with Sr(NO₃)₂, the KGP control sample and the unreacted metakaolin after the first 28 days of reaction.

Figure 4-65 shows the FTIR spectra of the samples after 28 days of reaction. Very little change is visible from this, suggesting that the majority of the reaction has occurred by the 3-day time point. The shoulder peak seen at 855 cm⁻¹ has moved slightly from its position after 3 days from 860 cm⁻¹ however, this is still within the region for the asymmetric stretching of the bridging oxygen bonds [258]. The sharp peaks at 665 cm⁻¹ and 825 cm⁻¹ are potentially evidence of crystalline phases within the structure. The peak at 825 cm⁻¹ is consistent with the presence of crystalline KNO₃, as shown in Figure 4-59 in Section 4.2.1.1.4.1. The presence of this salt is also verified in the XRD (Section 4.2.1.2.2).

4.2.3.2.2 XRD

Figure 4-66 displays the X-ray diffraction spectra for the geopolymer samples containing $\text{Sr}(\text{NO}_3)_2$ 3 days after initial reaction.

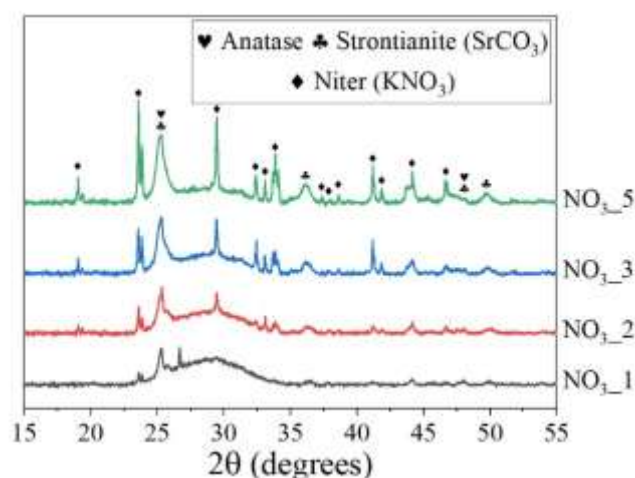


Figure 4-66: The X-ray diffraction spectra generated by loading K-activated metakaolin geopolymers with $\text{Sr}(\text{NO}_3)_2$ after the first 3 days of reaction.

The XRD patterns for each sample are comparable, exhibiting a broad diffraction peak between 24° 2θ and 33° 2θ . This peak indicates the presence of an amorphous phase within the sample, notably the presence of the K-A-S-H gel [164].

The XRD patterns for the samples do indicate the presence of some crystalline phases within the hardened gel. The presence of anatase (TiO_2 , PDF # 01-084-1286) is indicative of the unreacted metakaolin that remains within the structure, as supported by both the FTIR and NMR data.

The presence of niter (KNO_3 , PDF # 01-071-1558) suggests that the NO_3^- ions in solution due to the dissolution of the $\text{Sr}(\text{NO}_3)_2$ are reacting with the aqueous K^+ ions to precipitate out a solid crystalline K phase. This phase becomes more prominent with increasing Sr/Al ratio, with the greatest concentration in the NO₃_3 and NO₃_5 samples and very little evidence of it in the NO₃_1 sample. This aligns with a greater concentration of NO_3^- ions in solution. The increase in the concentration of this phase also contributes to the delay seen in the ICC (Section 4.2.3.1.1), as the increase in Sr/Al ratio leads to a greater interaction with the K in the activating solution, and a greater volume of the solid seen in the OoA experiments (Section 4.2.3.1.4) precipitating out. This will slow the reaction to form the geopolymer and explains the difference in the ICC curves between the samples of differing Sr/Al ratios.

The presence of strontianite (SrCO_3 , PDF #00-005-0418) is most likely due to the carbonation of the sample due to contact with the air, and the amount of this phase appears to increase with increasing Sr/Al.

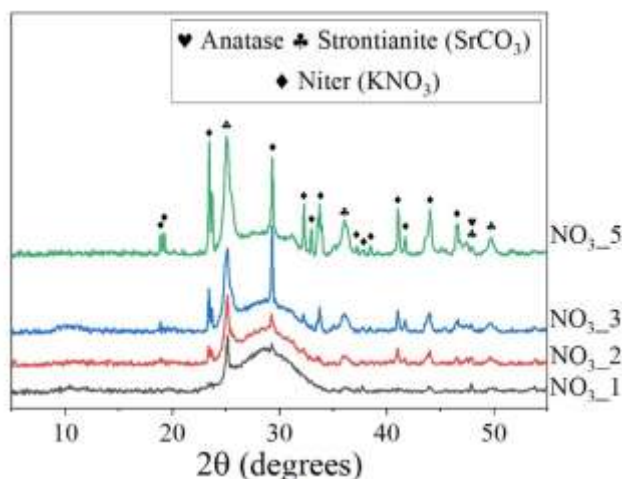


Figure 4-67: The X-ray diffraction spectra generated by loading K-activated metakaolin geopolymers with $\text{Sr}(\text{NO}_3)_2$ after the first 28 days of reaction.

The XRD patterns for the NO_3 samples are presented in Figure 4-67. As can be seen, there is very little difference between the crystalline phases present within the samples between 3 and 28 days post reaction suggesting that no further crystalline phases are formed during this time.

4.2.3.2.3 NMR

4.2.3.2.3.1 ^1H - ^{29}Si CP MAS and ^{29}Si MAS NMR

The ^1H - ^{29}Si CP MAS and ^{29}Si MAS spectra for the NO_3_5 and KGP samples both 3 and 28 days after the initial reaction are displayed in Figure 4-68.

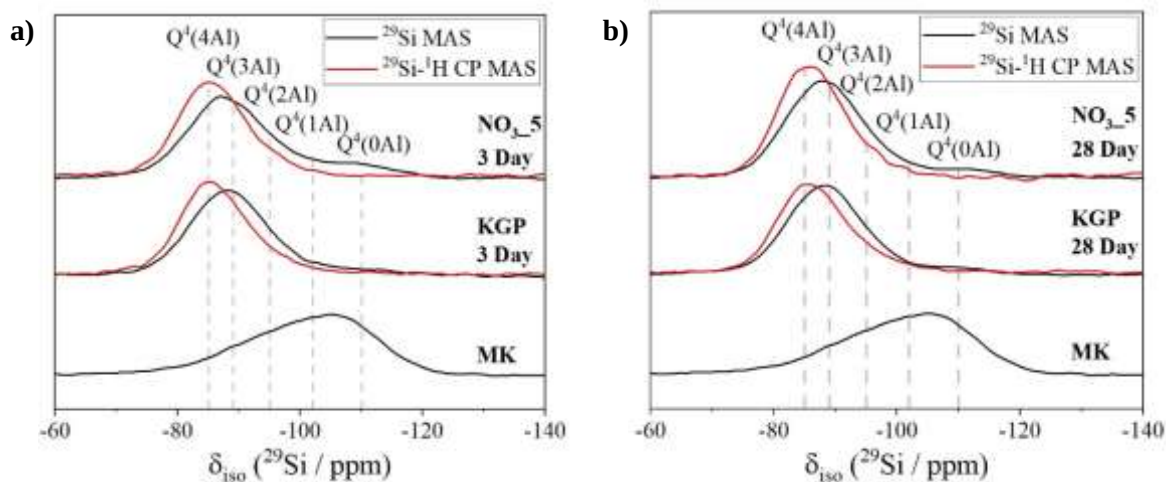


Figure 4-68: ^{29}Si - ^1H CP MAS and ^{29}Si MAS spectra for the NO_3_5 , KGP samples and the unreacted metakaolin a) 3 days and b) 28 days after reaction.

The ^1H - ^{29}Si CP MAS NMR spectra, shown in red in Figure 4-68, display a single broad peak at δ_{iso} between ~ -75 and -110 ppm. The maximum intensity is reached at ~ -85 ppm, suggesting that the hydrated geopolymer gels are principally composed of $\text{Q}^4(4\text{Al})$ sites in all cases. The differences between, and rationale for the use of both ^1H - ^{29}Si CP MAS NMR and ^{29}Si MAS NMR are discussed in Section 3.4.3.1.

The shift to lower δ_{iso} values is a result of the anhydrate Si sites from the unreacted metakaolin being introduced into the spectra, as shown in Figure 4-68 where the peaks for the $Q_4(1\text{Al})$ and $Q_4(0\text{Al})$ are clearly related to the peaks exhibited by metakaolin. Furthermore, the absence of any peaks other than the main broad resonance show that all of the samples are cured without any free soluble silicon components present within the pore solution of the material. The spectra observed here are similar to those seen in previous work, suggesting that the K-A-S-H gel is formed by a mixture of Si environments in the form of $Q^4(m\text{Al})$ sites, where $1 \leq m \leq 4$ [67]. This is supported by Table 4-6, which shows the presence of each Si site as a percentage calculated from the ^{29}Si MAS NMR data.

Table 4-6: Relative integral areas for the Si sites present within the K-A-S-H gel of each sample both 3 and 28 days after initial reaction from the deconvoluted ^{29}Si MAS NMR spectra. The $Q^4(0\text{Al})$ site attributed to the unreacted metakaolin is disregarded for the quantification of the K-A-S-H gel.

Sample	Time point	Relative Integral Area (%)				Si/Al
		$Q^4(4\text{Al})$	$Q^4(3\text{Al})$	$Q^4(2\text{Al})$	$Q^4(1\text{Al})$	
KGP	3 Days	25	54	20	1	1.32
NO ₃ _5	3 Days	30	38	30	2	1.35
KGP	28 Days	28	44	26	2	1.34
NO ₃ _5	28 Days	39	40	20	1	1.26

The deconvolution of the NMR spectra allows the percentage of each individual ^{29}Si chemical site to be quantified [172]. For the KGP samples, the ^{29}Si MAS NMR spectra in Figure 4-69 for the NO₃_5 samples and Figure 3-6 for the KGP samples, show that the gel structure is dominated by $Q^4(3\text{Al})$ sites after both 3 and 28 days of reaction, which is in line with data that is widely reported in the literature for potassium activated geopolymers [172]. The NO₃_5 samples appear to have a gel structure dominated by $Q^4(4\text{Al})$, $Q^4(3\text{Al})$ and $Q^4(2\text{Al})$ silicon sites after 3 days but after 28 days, the percentage of $Q^4(2\text{Al})$ sites drops significantly to a structure dominated by $Q^4(4\text{Al})$ and $Q^4(3\text{Al})$ sites. This shows that the Al content of the K-A-S-H gel is increasing over time, agreeing with the Si/Al ratios shown in Table 4-6. This is explainable by the zeta potential results which suggest that the dissolution of the metakaolin is slowed due to the adsorption of Sr^{2+} cations to its surface. The results here show that this leads to a Si-rich phase in the early stages of the reaction which becomes more Al-rich as the sample ages.

Table 4-6 also shows the molar Si/Al ratio of the K-A-S-H gel, disregarding the Si sites that are attributed to the unreacted metakaolin. This ratio is calculated using Engelhardt's formula (Equation 3-1) [276]. For the NO₃_5 sample, the reduction in the Si/Al ratio from the 3 day timepoint to the 28 day timepoint corresponds to an increase in the percentage of $Q^4(4\text{Al})$ sites, which is unsurprising due

to the greater proportion of Al tetrahedra within the gel. The Si/Al ratio for the NO₃_5 sample after 28 days, 1.26, is also lower than the Si/Al ratio of the KGP sample at the same time point, 1.35. Therefore, the NO₃_5 sample contains a greater number of Al tetrahedra in relation to the number of Si tetrahedra, suggesting that the addition of the Sr(NO₃)₂ leads to a greater initial dissolution of Al₂O₃, or a reduced initial dissolution of SiO₂. Due to the slower rate of dissolution of the SiO₂ when compared to the Al₂O₃ in the metakaolin, and the effect seen in the order-of-addition reactions involving Sr(NO₃)₂ (Section 4.2.3.1.4), it is more likely the latter of these possibilities is occurring. The reaction between the silicate activating solution and the Sr(NO₃)₂ occurs upon the addition of the activator to the solid metakaolin and Sr(NO₃)₂ mixture, with the formation of the potassium silicate solid seen in section 4.2.3.1.4. This solid renders the activating solution unable to dissolve any further metakaolin particles. Therefore, the Al₂O₃ that has already been preferentially dissolved into solution is present in greater quantities than the SiO₂, which does not have sufficient time to react with the activating solution, leading to an Al rich reaction mixture. This is supported by the reduction in the extent of reaction when compared to the KGP samples shown in Table 4-7.

Table 4-7: The extent of reaction of the NO₃_5 and KGP samples both 3 and 28 days after initial reaction, calculated using the ²⁹Si MAS NMR spectra.

Sample	Time point	Extent of reaction (%)
KGP	3 Days	82.17
NO ₃ _5	3 Days	73.32
KGP	28 Days	88.00
NO ₃ _5	28 Days	77.73

In their PhD thesis, Kuenzel postulates that the inclusion of Sr(NO₃)₂ into the geopolymer mix results in the formation of Sr(OH)₂, lowering the pH and reducing the extent of reaction [322]. This would result in the shift of the main Si-O-T vibration within the FTIR data towards higher wavenumbers with an increasing Sr/Al as the volume of unreacted metakaolin increases. This phenomenon is not seen in this work, with the main Si-O-T peak remaining at similar wavenumbers to the KGP control. Furthermore, the XRD diffraction pattern does not support the presence of Sr(OH)₂ within the system, suggesting that, if this situation is to occur, the amount of Sr(OH)₂ that is formed is minimal. However, the extent of reaction of the NO₃ samples is considerably lower than that of the KGP samples at the corresponding time points. The mechanisms for this can be attributed to the reactions of the Sr(NO₃)₂ with both the metakaolin and the activating solution. However, there is a possibility that this could also be due to the reduction in the pH that comes about due to the consumption of the OH⁻ anions via reaction with the Sr(NO₃)₂ salt as suggested by Kuenzel [322].

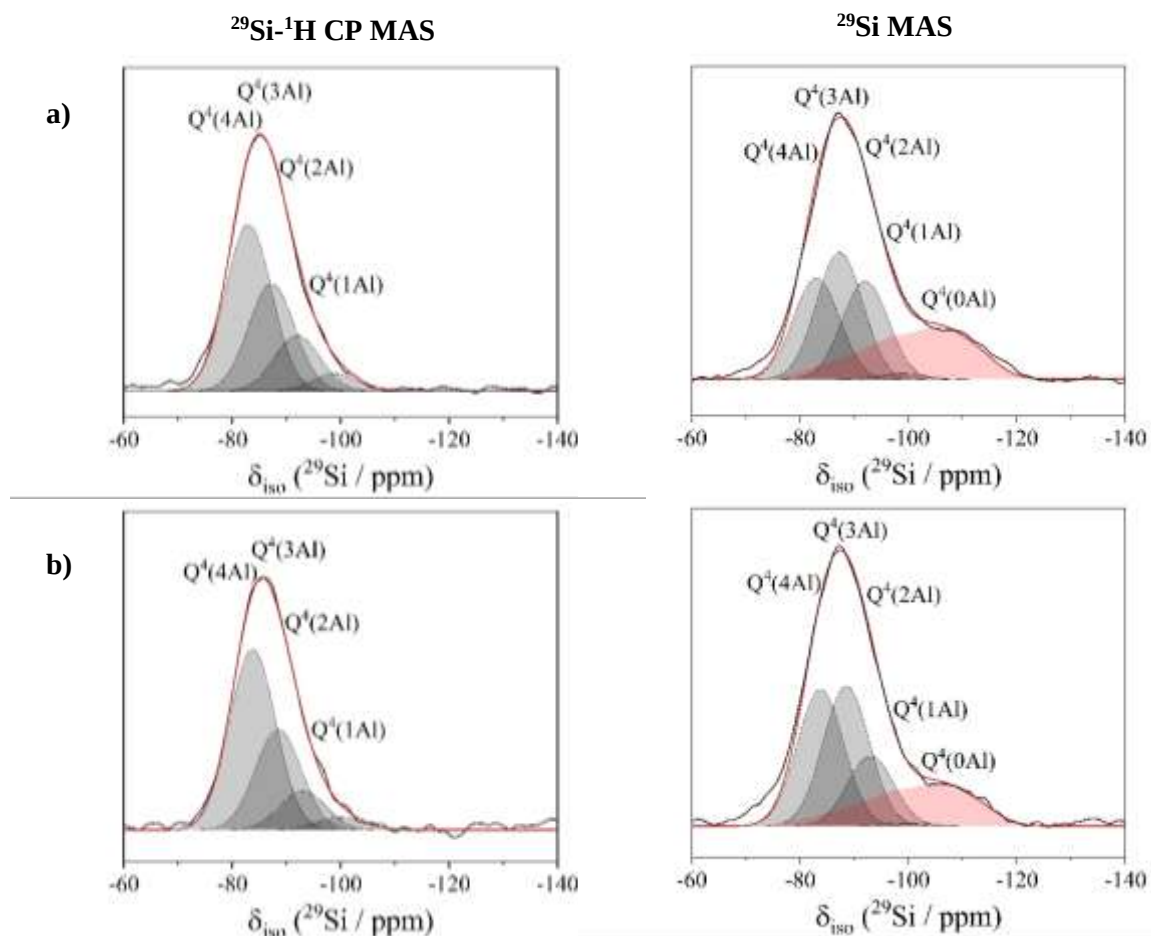


Figure 4-69: $^{29}\text{Si}\text{-}^1\text{H}$ CP MAS and ^{29}Si MAS NMR spectra and the associated deconvolutions for the a) NO_3_5 sample after 3 days and b) NO_3_5 sample after 28 days. The $^{29}\text{Si}\text{-}^1\text{H}$ CP MAS NMR data is shown in the left column and the ^{29}Si MAS NMR data is shown in the right column. For each spectrum, the raw data is shown as a solid black line and the model fit is shown as a solid red curve. The deconvolutions that represent each ^{29}Si site within the K-A-S-H gel are depicted as grey curves, whilst the deconvolutions that represent ^{29}Si sites within the unreacted metakaolin are shown in a faded red.

4.2.3.2.3.2 ^{27}Al MAS NMR

The ^{27}Al MAS NMR spectra for the NO_3_5 and KGP samples both 3 and 28 days after the initial reaction are displayed in Figure 4-70.

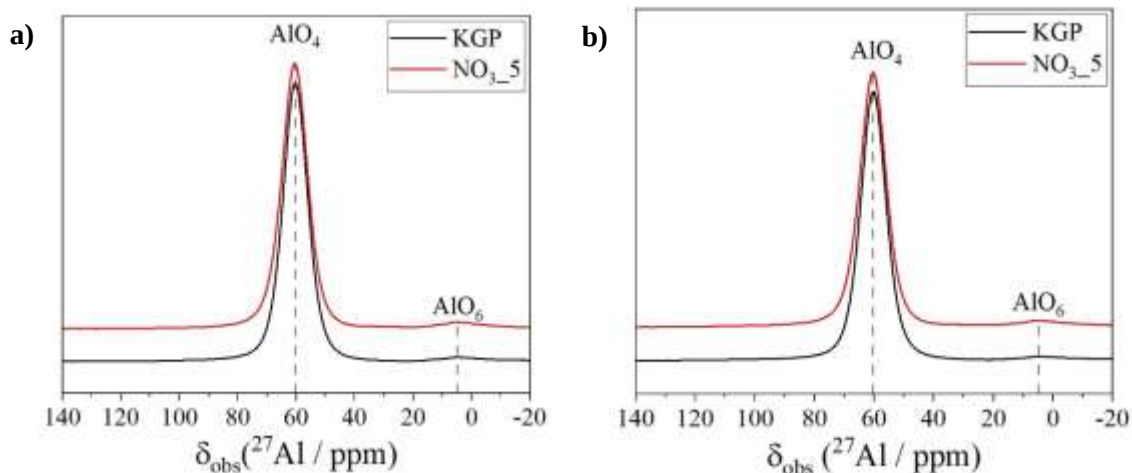


Figure 4-70: ^{27}Al MAS spectra for the NO_3_5 and KGP samples a) 3 days and b) 28 days after reaction.

Figure 4-70 shows that the ^{27}Al MAS NMR spectra for both the KGP and NO_3_5 samples display two distinct resonances. The most obvious resonance, centred at a δ_{obs} of 60.3 ppm and spanning between ~ 50 and 70 ppm is recognisable as the tetrahedral Al site (AlO_4) found in the K-A-S-H gel phase of the geopolymer [279, 306]. This coordination is promoted by the large excess of alkali cations within the gels and gives rise to the negative charge that is intricate to the use of geopolymers in the application of the disposal of radioactive Sr, and is introduced by the substitution of Al^{3+} ions for Si^{4+} as shown by Figure 4-70 [307]. This negative charge is balanced by cations: K^+ in the KGP sample and a combination of both K^+ and Sr^{2+} in the NO_3_5 sample [308].

The small resonance observed at a $\delta_{\text{obs}} \sim 5$ ppm is attributed to the presence of octahedral Al sites (AlO_6) within the samples [274]. The intensity of this peak is negligible when compared to that of the tetrahedral Al peak, and suggests that the majority of the Al within the metakaolin has reacted as the octahedral peak corresponds exclusively to the Al found within the unreacted metakaolin [279]. This is supported by the findings of both the ^{29}Si MAS and ^1H - ^{29}Si CP MAS which display the preferential dissolution of Al during the dissolution phase of the reaction.

4.2.3.2.3.3 ^{39}K MAS NMR

The ^{39}K MAS NMR spectra for the NO_3_5 and KGP samples both 3 and 28 days after the initial reaction are displayed in Figure 4-71.

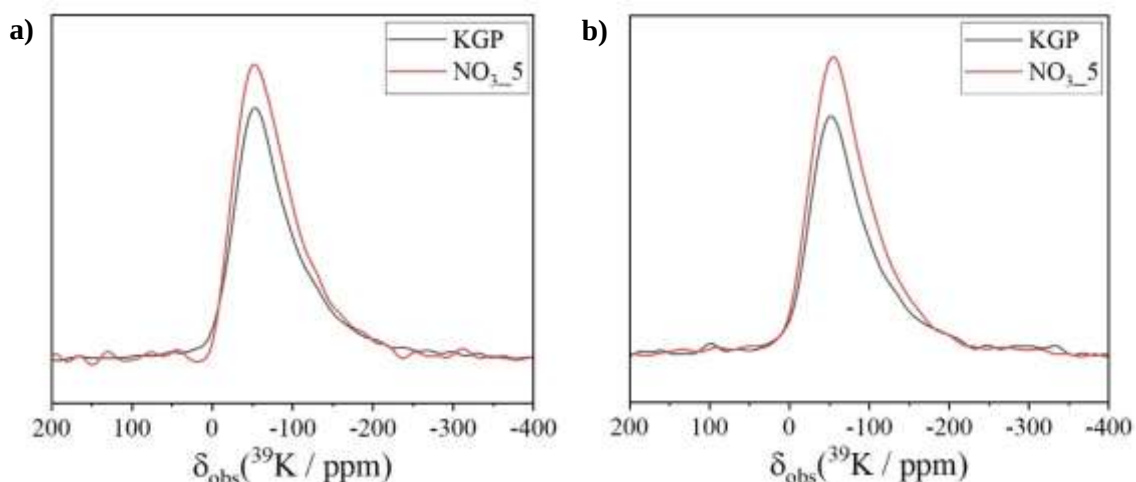


Figure 4-71: ^{39}K MAS NMR spectra for the NO_3_5 and KGP samples a) 3 days and b) 28 days after reaction.

From Figure 4-71, it is clear that there is very little change to the K chemical environments within the KGP control geopolymer sample and the NO_3_5 samples after both 3 and 28 days. For the 3-day sample, the peaks for both samples are seen at a δ_{obs} of $\sim -52/-53$ ppm, exhibiting the broad peak expected due to the strong quadrupolar interactions of the K atoms. The line shape of both of the peaks are comparable, suggesting that there is one consistent K chemical environment in the samples, that of K^+ ions charge balancing the negative AlO_4^- tetrahedral within the K-A-S-H gel. This is much like the spectra seen for the 28-day samples, exhibiting a consistent line shape between the two samples with a singular, broad peak visible. The lack of change in the range of δ_{obs} seen between the KGP control spectra and the NO_3_5 samples, which contain the Sr^{2+} ions, suggests that the Sr is readily accommodated by the K-A-S-H gel at the Sr/Al ratio of 0.125 used here, accredited to the highly disordered local structure of the systems enabling the distortion of bond lengths and angles locally in the gel [323]. This suggests that the K-A-S-H gel in ‘clean’ geopolymers is likely to exhibit similar physicochemical properties to the modified K-A-S-H gel seen in loaded geopolymers, further promoting their use as a wasteform for the encapsulation of radioactive waste streams.

In the 28-day sample, shown in Figure 4-71 b), there is a slight shift in the peak centre between the two samples, with the KGP centring at -55 ppm and the NO_3_5 sample centring at -52 ppm. This shift is consistent with increased shielding of the K^+ ions, suggesting that after the addition of the Sr^{2+} ions, some of the K^+ ions are displaced from their charge balancing sites. This is due to the change in the local magnetic field caused by the difference in electronegativity between Sr and K. In recent work by Geddes et al., it is shown that this phenomenon is seen in the ^{23}Na MAS NMR of geopolymer gels activated by sodium silicate [183]. However, in the same work, this is not seen for geopolymer systems activated by potassium silicate in the corresponding ^{39}K MAS NMR results. In this work, Sr was added to the geopolymer at a maximum of 3 wt.% and in the form of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ which has a much lower solubility than the $\text{Sr}(\text{NO}_3)_2$ used in this section [303]. Therefore, it is likely that, due to the much higher

concentration of Sr^{2+} ions in solution, a larger majority of the K^+ ions are displaced from their charge balancing sites, which is consequently shown in Figure 4-71 b). This could also be aided by the formation of KNO_3 , as shown by the XRD (Section 4.2.3.2.2), which uses up some of the K^+ anions, increasing the likelihood that the Sr^{2+} will have space to become a charge balancing cation with the K-A-S-H gel. This argues with the statement made in Geddes et al.'s work, where it is suggested that the lack of inclusion of Sr into the K-A-S-H gel has significant implications for the use of potassium silicate activated geopolymers for the encapsulation of nuclear waste, showing that these materials are capable of immobilising waste streams containing $\text{Sr}(\text{NO}_3)_2$ [183].

4.2.3.2.3.4 ^{87}Sr Solid-State NMR

The ^{87}Sr solid-state NMR spectra for the NO_3_5 samples after both 3 and 28 days of reaction are displayed in Figure 4-72.

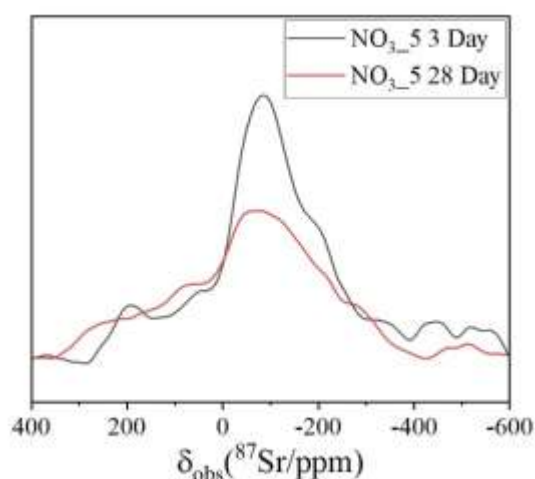


Figure 4-72: ^{87}Sr solid-state NMR spectra for the NO_3_5 sample after 3 and 28 days of reaction.

The spectra seen here show that there is Sr present within the sample at both timepoints, although the peak visible in the spectrum for the sample after 28 days is not as intense, owing to the difficulty of acquiring data using this technique. The spectrum for the sample after 3 days of reaction shows a main peak that centres at $\delta_{\text{obs}} = \sim -85\text{ppm}$. However, there appears to be a shoulder on this peak at approximately $\delta_{\text{obs}} = -200\text{ppm}$, suggesting that there is at least a second Sr chemical environment within the sample. This pattern can also be seen in the spectrum for the sample after 28 days, however, the broadness of the peak means that it is open to interpretation as to whether this is evidence of two Sr environments.

One of the peaks present in the spectrum for the sample after 3 days is likely to be caused by the presence of SrCO_3 within the sample, which appears due to the carbonation of the Sr within the sample due to contact with CO_2 in the air. The presence of this compound within the sample is shown by the XRD data, and suggests that the Sr^{2+} that exists in solution due to the dissolution of the $\text{Sr}(\text{NO}_3)_2$ is, for the most part, just existing within the pore solution and not being chemically incorporated into the aluminosilicate gel framework structure. However, the presence of a secondary peak suggests that some

of the Sr^{2+} does displace the K^{+} cations to within the charge balancing sites of the K-A-S-H gel. This is also supported by the presence of KNO_3 within the sample as shown by XRD, which shows that some of the K that would be occupying the charge balancing sites is within a solid crystalline structure.

4.2.3.2.4 EPMA

The use of electron probe microanalysis (EPMA) allows for the chemical composition of the geopolymer gel to be spatially resolved and quantified [316]. In this work, it has been used to determine the distribution of Sr throughout the geopolymer matrix.

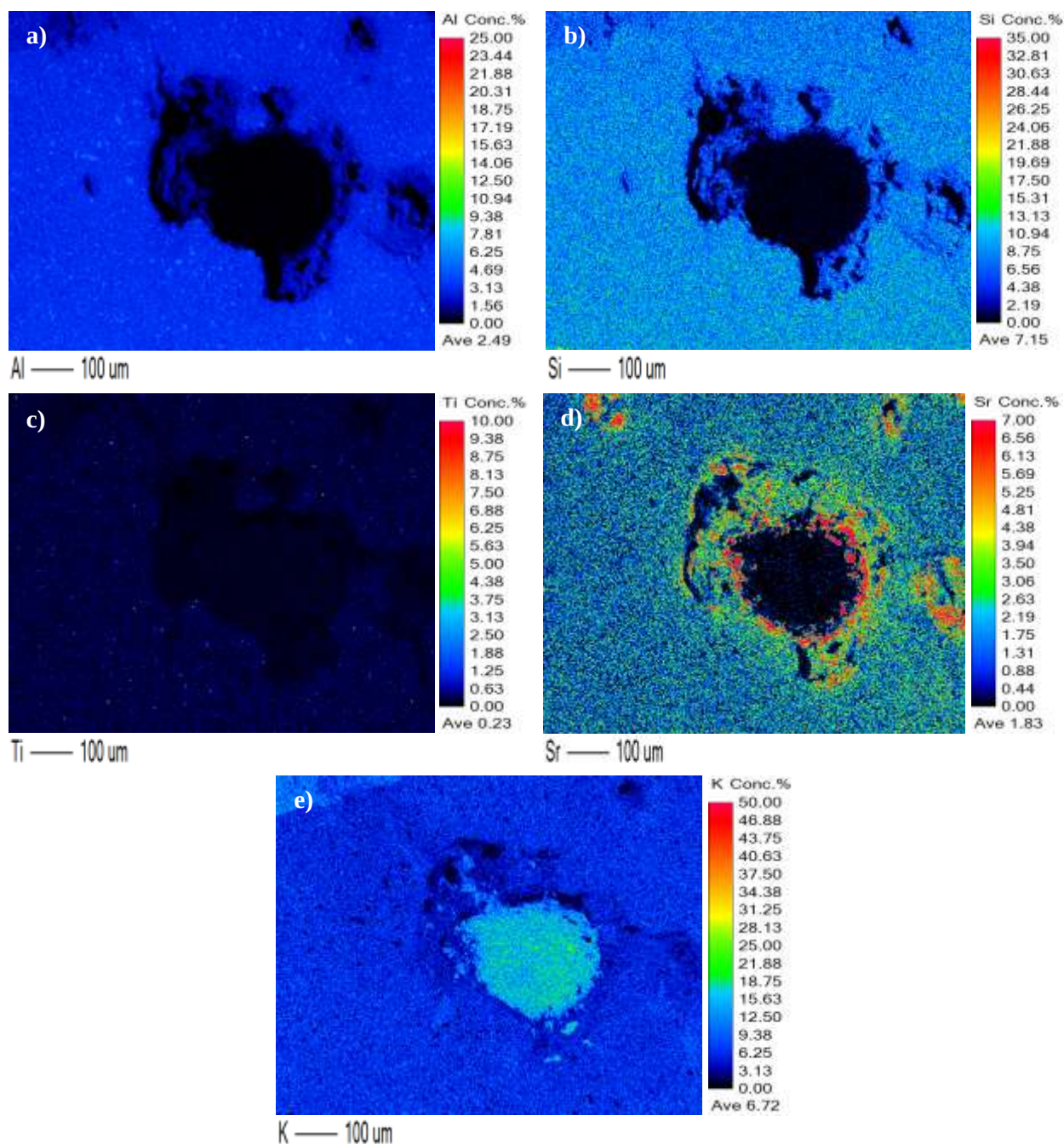


Figure 4-73: The EPMA images generated for the NO₃_5 sample after 28 days of reaction. The elements shown in each image are as follows: a) Aluminium, b) Silicon, c) Titanium, d) Strontium, and e) Potassium. The magnification factor is x120.

Figure 4-73 displays the EPMA images for the NO₃_5 sample after 28 days of reaction. Within this region, image a) and image b) show that the concentration of Al and Si respectively are very low, much less than would be expected for the K-A-S-H gel phase seen in this work. The lower concentration of Al means that this region of the sample has a lower capacity for cation binding, resulting in less capability to immobilise the Sr²⁺ ions in solution. However, image d) shows that the Sr within this area is present throughout the sample, aligning with the areas where Al is present. This suggests that, due to the Sr²⁺ ions being in solution, as shown by the order of addition experiments in Section 4.2.3.1.4, the

Sr could be incorporated into the K-A-S-H gel in place of some of the K^+ ions, which is also implied by the XANES (Section 4.2.3.2.5.1). This is partially supported by image e), which shows a K-rich phase in the centre of the image. This suggests that the K is reacting to form a secondary phase, and is not available to charge balance the negative Al sites within the gel. The composition of this phase is unknown, however, it is likely that the phase contains the nitrate ion that is in present due to the dissolution of the $Sr(NO_3)_2$, potentially a KNO_3 phase. This cannot be confirmed via this method as the detection of nitrogen is difficult due to the low fluorescence yield of the element [324, 325]. However, the FTIR of this sample, seen in Section 4.2.3.2.1, shows evidence of the presence of a KNO_3 phase. This is also shown in the XRD results (Section 4.2.3.2.2), suggesting that this KNO_3 is a crystalline solid that has precipitated out of solution. Image d) also shows that the K-rich phase is surrounded by regions of high Sr concentration. This Sr phase could be: $SrCO_3$, supported by the presence of crystalline $SrCO_3$ is shown in the XRD (Section 4.2.3.2.2), undissolved $Sr(NO_3)_2$, although unlikely due to its high solubility, or even $Sr(OH)_2$ within the sample. However, it is likely that this phase is in fact $SrCO_3$; after the $Sr(NO_3)_2$ salt dissolves within the activating solution, the NO_3^- ions react with the K^+ ions to form the KNO_3 phase seen. The Sr^{2+} cations are trapped surrounding this phase as it precipitates out of solution. At this point, the Sr^{2+} cations are able to readily react with the CO_2 within the air to form $SrCO_3$, and this is supported by the XRD and the XANES analysis performed on these samples.

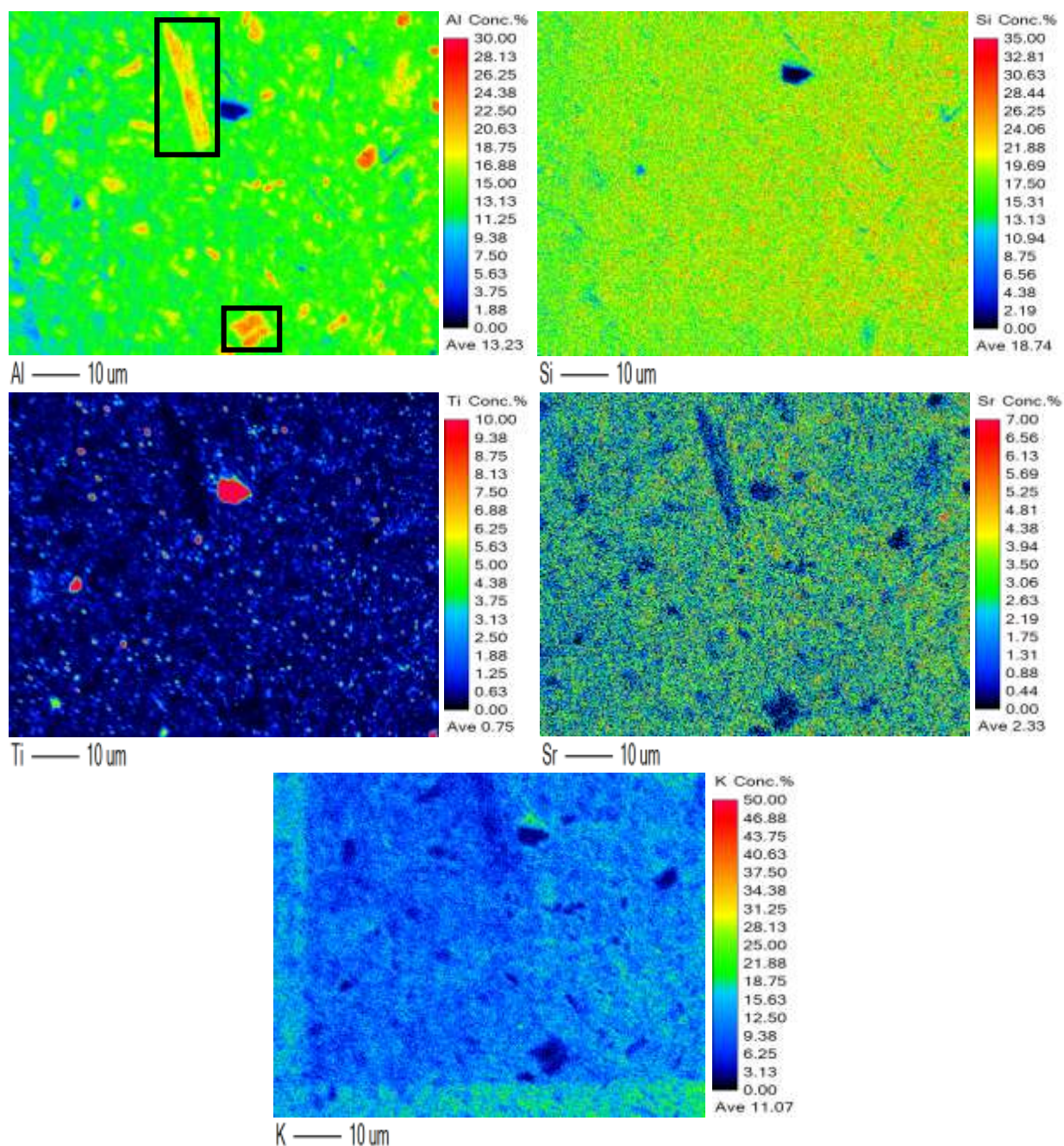


Figure 4-74: The EPMA images generated for the NO_3_5 sample after 28 days of reaction. The elements shown in each image are as follows: a) Aluminium, b) Silicon, c) Titanium, d) Strontium, and e) Potassium. The magnification factor is x1500.

At the magnification of x1500, Figure 4-74 image a) shows that the concentration of Al is higher than that seen at x120 magnification in Figure 4-73. This could suggest that the region shown in this figure is an anomaly within the matrix, and is purely a result of the introduction of $\text{Sr}(\text{NO}_3)_2$. Image a) also shows the presence of unreacted metakaolin, shown by the regions of high Al concentration exemplified by the regions in the black boxes. These regions do not show an increased concentration of Si, as shown by image b), which would potentially be expected in a metakaolin particle. The Si is distributed evenly throughout the sample, supporting the presence of the K-A-S-H gel.

Image c) shows that there are multiple regions of high concentration of Ti which are particles of anatase, an inert impurity within the metakaolin. These particles are encased within the surrounding K-A-S-H gel. There is no evidence of anatase within the unreacted metakaolin particles highlighted in image a), but this is explainable by the anatase being a relatively low level impurity which will not be present in every particle of metakaolin.

Image d) shows that the Sr is distributed evenly across the area shown here. This again supports the possibility that Sr is displacing the K as the charge balancing cation within the K-A-S-H gel. The lower concentration levels of Sr align with the particles of unreacted metakaolin; This does not agree with the zeta potential results shown in Section 4.2.3.1.2, which suggests that the Sr^{2+} ions are attracted to the negative surface charge of the metakaolin particles in solution. Therefore, it would be expected that a high concentration of Sr would be found surrounding the unreacted metakaolin particles seen here, but that is not the case. Despite this, we do see that there is the presence of Sr in these regions, albeit scarcely. This could be because the Sr does not populate the surface of the metakaolin in high concentrations.

Image e) shows that the K is, like the Sr, distributed evenly throughout the matrix. This suggests that, despite the K-rich phase witnessed in Figure 4-73, the K is still present as the charge balancing cation in the majority of the negative Al binding sites.

4.2.3.2.5 X-ray Absorption Spectroscopy

4.2.3.2.5.1 X-ray Absorption Near-Edge Structure (XANES) Spectroscopy

The normalised spectra for the Sr K-edge XAS analysis of the NO_3_5 sample after both 3 and 28 days of reaction compared to both the $\text{Sr}(\text{NO}_3)_2$ reagent and the mineral brewsterite-Sr ($(\text{Sr},\text{Ba})_2\text{Al}_4\text{Si}_{12}\text{O}_{32}\cdot 10\text{H}_2\text{O}$) are shown in Figure 4-75 [315].

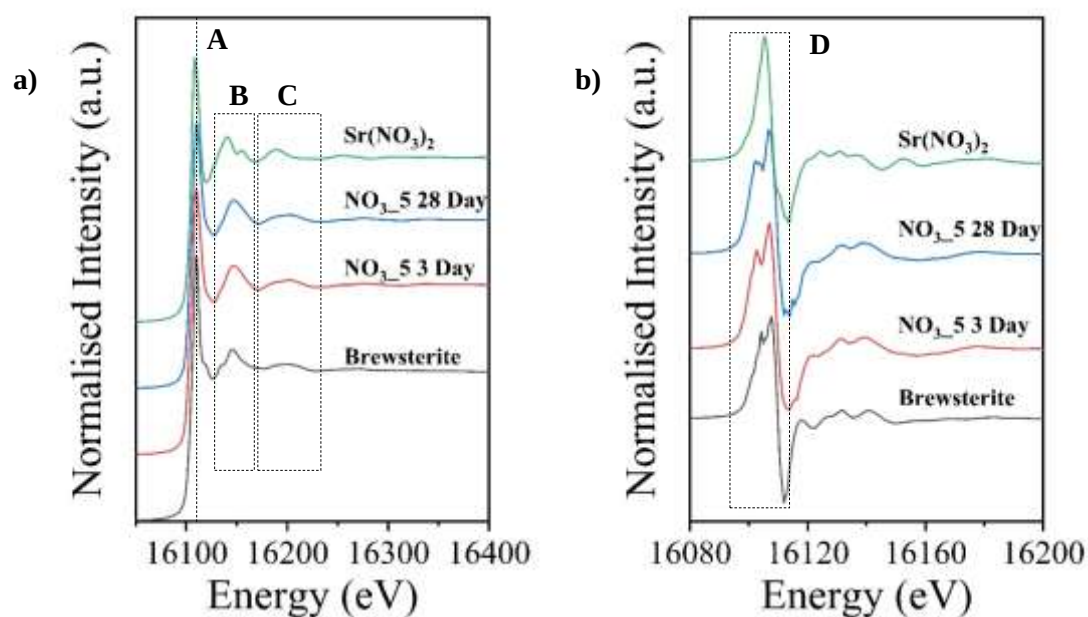


Figure 4-75: a) Normalised X-ray absorption spectra for the geopolymer samples loaded with $\text{Sr}(\text{NO}_3)_2$, the $\text{Sr}(\text{NO}_3)_2$ reactant used and the mineral brewsterite-Sr. b) The 1st derivative of these spectra.

The Sr K-edge here displays an absorption edge that rises smoothly to a maximum featuring a singular peak. As previously mentioned in Section 4.2.1.2.5.1, the Sr K-edge is relatively featureless but provides enough information for a qualitative analysis to be performed. Upon initial inspection of the highlighted regions in both Figure 4-75a) and b), the NO_3_5 samples align better with the spectra for the brewsterite-Sr mineral than the original $\text{Sr}(\text{NO}_3)_2$ reagent. When inspecting the maximum of the peak, indicated by the dashed line labelled A in Figure 4-75a), more closely, it can be seen that the peak for the $\text{Sr}(\text{NO}_3)_2$ is at a slightly lower energy value than that of the brewsterite and the NO_3_5 samples. From Figure 4-75a), the absorption edge appears to culminate in a single peak, and there is barely evidence for a slight shoulder on the leading edge. However, using the 1st derivative plot, displayed in Figure 4-75b), shows that, for all but the $\text{Sr}(\text{NO}_3)_2$ spectra, this shoulder is present. However, there is very little similarity between the spectra of the NO_3_5 sample and those of the brewsterite and $\text{Sr}(\text{NO}_3)_2$, suggesting that there is unlikely to be Sr residing in either of these states in great volumes within the samples.

Referring back to Figure 4-75a), and focusing on the features of the spectra above the absorption edge, it can be seen that in the hatched box labelled B, the $\text{Sr}(\text{NO}_3)_2$ reagent spectra exhibits a further double peak which is not mirrored in any of the samples or the other standard, brewsterite. This is evidence that there is no $\text{Sr}(\text{NO}_3)_2$ remaining within the sample, and that all of the salt dissolves within the activating solution, as supported by the order-of-addition experiments and the XRD.

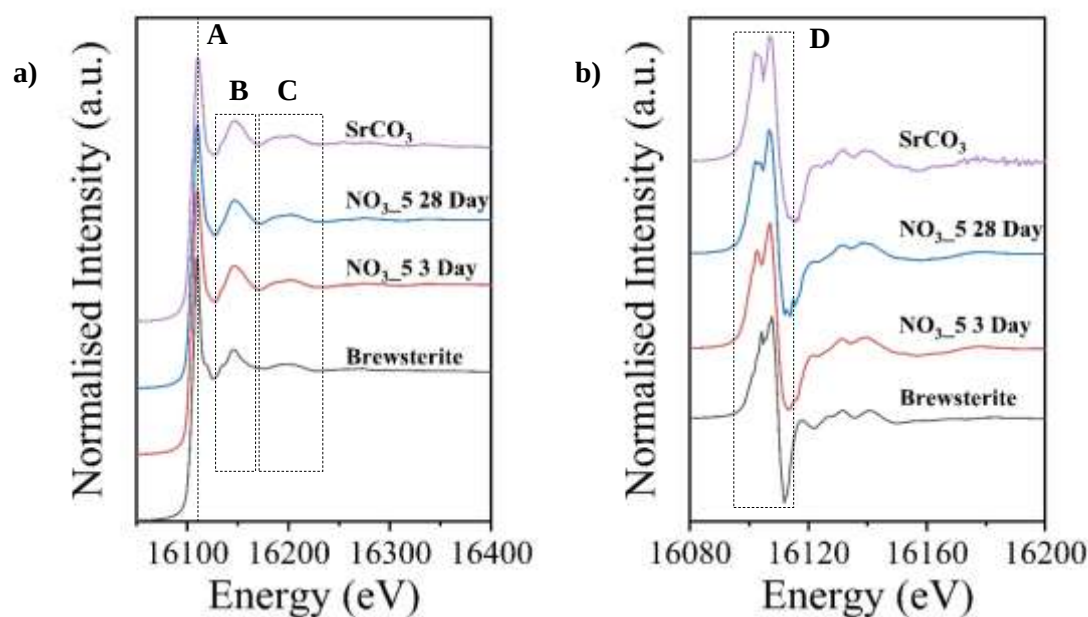


Figure 4-76: a) Normalised X-ray absorption spectra for the geopolymer samples loaded with $\text{Sr}(\text{NO}_3)_2$, an SrCO_3 standard and the mineral brewsterite-Sr. b) The 1st derivative of these spectra.

The XRD data in Section 4.2.3.2.2 shows that there is quantity of SrCO_3 within the NO_3_5 sample, and so it may be more prevalent to compare the XANES spectra to a SrCO_3 standard, as is shown in Figure 4-76. Firstly, by inspecting the region labelled as B in Figure 4-76a), the line shape of the spectra for both NO_3_5 samples aligns more closely with the line shape of the SrCO_3 standard as opposed to the brewsterite. The shoulder on the peak that is easily seen in the brewsterite spectra cannot be seen so clearly in the spectra for the NO_3_5 samples. Moreover, the feature in region C aligns closely between the SrCO_3 and the NO_3_5 samples. The evidence here suggest that the Sr is likely to be mainly found in the form of SrCO_3 , and there is little to show that the Sr is present in a form similar to brewsterite.

Overall, the spectra here suggest that all of the $\text{Sr}(\text{NO}_3)_2$ dissolves within the activating solution upon its initial addition, which is supported by the order-of-addition experiments. The Sr^{2+} cations that are subsequently released into solution are likely to react with the CO_2 in the air to form crystalline SrCO_3 , which is supported by the XRD and the XANES spectra here.

4.2.3.3 Conclusions

Isothermal conduction calorimetry shows that introduction of strontium nitrate at varying Sr/Al ratios affects the kinetics of formation of the geopolymer gel. The chemical mechanisms for this have been investigated using zeta potential, EPMA and order-of-addition experiments, with the conclusion being that the Sr dissolves into the activating solution, and absorbs onto the surface of the metakaolin, slowing its dissolution and retarding the reaction to form the geopolymer.

However, the Sr^{2+} cations do not affect the resulting structure, the primary phase of which is shown to be a K-A-S-H gel through the use of FTIR spectroscopy, ^{29}Si MAS NMR and ^{29}Si - ^1H CP MAS NMR. This phase is comprised of Si and Al in tetrahedral coordination, with the Si mainly existing in $\text{Q}^4(4\text{Al})$, $\text{Q}^4(3\text{Al})$ and $\text{Q}^4(2\text{Al})$ environments. The negative Al sites caused by Al^{3+} in tetrahedral coordination are charge balanced by K^+ , and the XANES spectra suggest that this is not impacted by the introduction of Sr^{2+} cations due to the dissolution of the $\text{Sr}(\text{NO}_3)_2$ salt. XRD shows that the crystalline structure of $\text{Sr}(\text{NO}_3)_2$ is not observed within the sample, further supporting its complete dissolution. It is shown that the incorporation of the $\text{Sr}(\text{NO}_3)_2$ leads to a relative increase in the Si/Al ratio, most likely due to the lower extent of reaction of the system compared to the KGP control sample resulting in less Al becoming available for reaction.

The order of addition experiments demonstrated that the addition of $\text{Sr}(\text{NO}_3)_2$ into the system at any point in the mix has a huge effect on the resulting kinetics of reaction, and should be added as late as possible to avoid this.

This work shows that K-silicate activated geopolymers are capable of incorporating wastes containing $\text{Sr}(\text{NO}_3)_2$ at high waste loadings of up to 5% by weight without causing significant damage to the structure of the geopolymer. However, in practice, the loadings are likely to be far lower due to activity limits per package on the wasteforms, owing to the radioactivity of the waste in question. Whilst this, and any impact of the radiation and resulting decay products, are not considered in this work, it is important to note that they will likely have a notable effect on the performance of the geopolymer as a wasteform, and further work to determine how great this effect is will be crucial to determine the overall suitability of the wasteform.

Despite this, the findings of this work show that the incorporation of $\text{Sr}(\text{NO}_3)_2$ containing waste has only a small effect on both the kinetics and mechanisms of formation of a metakaolin based, potassium silicate activated geopolymer system suggests that these systems show great promise as wasteforms for the long term immobilisation of radioactive waste streams containing ^{90}Sr in the form of $\text{Sr}(\text{NO}_3)_2$.

4.2.4 Strontium Sulphate

4.2.4.1 Fresh State

4.2.4.1.1 ICC

Figure 4-77 displays the calorimetry curves produced by the reaction of the K-geopolymers loaded with SrSO_4 over the first 3 days of reaction.

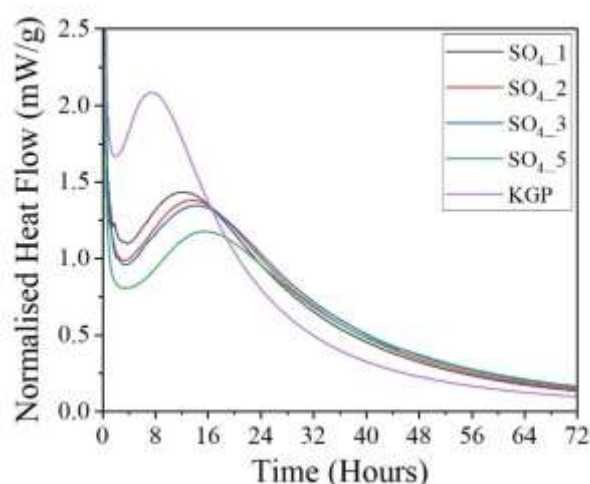


Figure 4-77: The effect on the heat evolution of reaction of loading K-activated metakaolin geopolymers with SrSO_4 over the first 3 days.

The heat evolved during the formation of the K-A-S-H gel is briefly discussed in Section 4.2.1.1.1 and is also applicable for the systems here. The addition of the SrSO_4 in all of the samples has a noticeable impact on the kinetics of the reaction, in some cases even doubling the time taken for the maximum heat evolution to occur when compared to the control geopolymer sample. For the SO_4_5 sample, the value of this maximum heat decreases by $\sim 45\%$ when compared to the KGP control. The difference in maximum heat flow between the SO_4_1 , SO_4_2 and SO_4_3 samples is minimal, with the main difference being the time at which this maximum heat occurs increasing with increasing Sr/Al ratio. The dormant period between the initial dissolution (the peak that is not visible in Figure 4-77) and the observed reaction peak increases in time as the Sr/Al ratio of the samples increases.

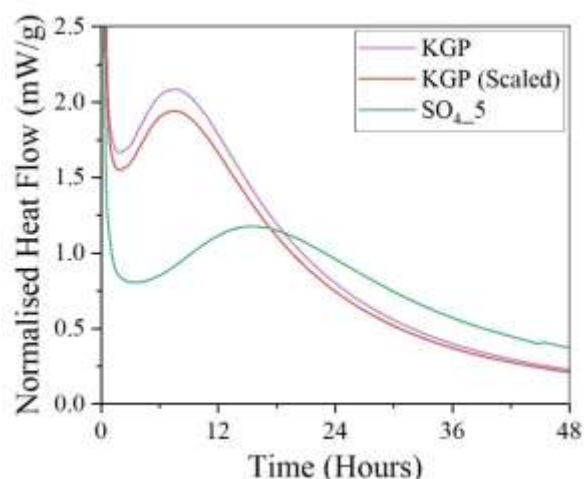


Figure 4-78: The heat evolution of the KGP and SO₄_5 samples compared to a scaled curve of the KGP sample.

Figure 4-78 shows the KGP and SO₄_5 samples seen in this work to a scaled version of the curve generated by the KGP sample, shown in red. This curve is calculated by normalising the heat evolution of the KGP sample by a mass that would be consistent with a corresponding SO₄_5 sample with the same mass of metakaolin and activating solution as the 20g KGP sample. This curve gives the normalized heat evolution of the situation that could be described as the ‘extreme case’ scenario, where none of the SrSO₄ dissolves into the activating solution and all of it acts as a filler material. This is further support for the dissolution and subsequent reaction of the SrSO₄ within the geopolymer mix, as the curve for the SO₄_5 sample is vastly different from the scaled curve.

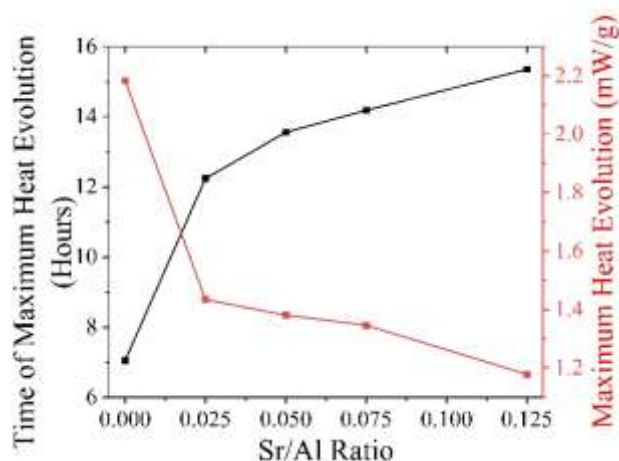


Figure 4-79: The relationship between Sr/Al ratio and the observed time of maximum heat evolution and the value of the maximum heat evolution.

Figure 4-79 visualises the effect of increasing the Sr/Al ratio on both the maximum observed heat evolution and the corresponding time of this maximum. As was seen in Figure 4-77, increasing the Sr/Al ratio leads to a decrease in the value of the maximum heat flow observed, as well as an increase in the time it takes for this to occur after the initial reaction.

The SrSO_4 salt dissolves readily in the activating solution, releasing the Sr^{2+} cation and the SO_4^{2-} anion into solution. This means it is unlikely that the SrSO_4 is acting as a filler material and reducing the heat evolution in this manner. It is possible that the ions released during the dissolution of the salt reacts with either the metakaolin or the activating solution, which disrupts the dissolution of the metakaolin into the aluminate and silicate tetrahedra that are required for the formation of the geopolymer gel.

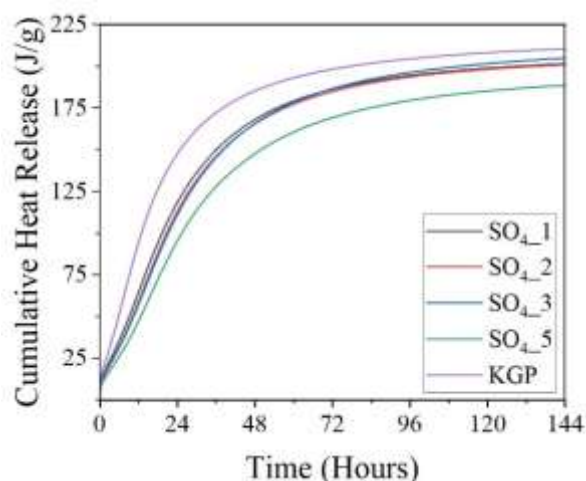


Figure 4-80: The cumulative heat release curves over the first 144 hours of reaction.

Figure 4-80 shows the cumulative heat release of the systems over the first 6 days of reaction. The cumulative heat release is a measure of the thermal release due to the polymerisation reaction of the geopolymer, along with any further metakaolin dissolution that occurs after the introduction of the sample to the chamber. As discussed in Section 4.2.1.1.1, the heat release after 144 hours is equivalent to approximately 2/3 of the total heat release of the system for PC, and if it assumed to be the same for geopolymer systems, the total heat release of the geopolymers containing strontium sulphate will be no more than 308 J/g even in the case of the $\text{SO}_4\text{-1}$ sample, which shows the greatest cumulative heat release [297]. This is higher than the average heat release of the current nuclear standard, a Portland cement and GGBS blend, which is around 100 J/g but is within the guideline value of 180 J/g over the first 24 hours of reaction set by the current UK requirements for nuclear wastefoms [298, 299].

4.2.4.1.2 Zeta Potential

The zeta potential values obtained for the surface charge of the metakaolin in the presence of SrSO_4 at different pHs is shown in Figure 4-81.

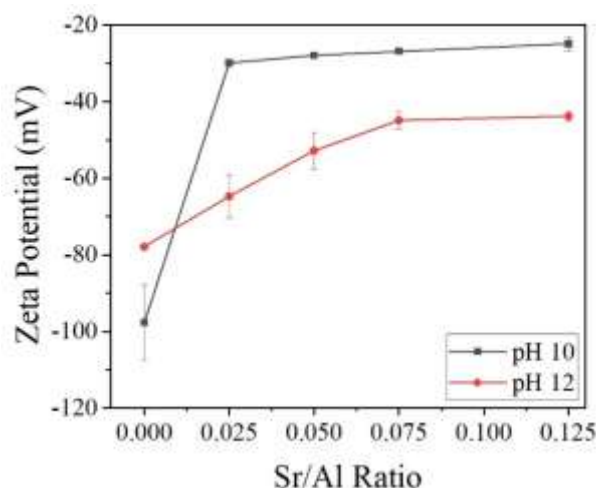


Figure 4-81: Comparing the effect of Sr/Al ratio, altered by the addition of SrSO_4 , on the zeta potential of metakaolin in a KOH solution at pH 10 and 12.

At pH 10, the introduction of SrSO_4 leads to a significant increase in the recorded zeta potential at all of the Sr/Al ratios. However, there does not appear to be a noticeable difference between the change seen at an Sr/Al ratio of 0.025 when compared with an Sr/Al ratio of 0.125. This suggests that, at pH 10, the SrSO_4 is saturated within the solution at an Sr/Al ratio of 0.025.

At pH 12, the effect on the zeta potential caused by the SrSO_4 is far less significant. Moreover, unlike at pH 10, the increase in the Sr/Al ratio leads to an increase in the zeta potential. These results show that the solubility of the SrSO_4 decreases with increasing pH. This can be said due to the lesser increase seen in the zeta potential at the higher pH point, suggesting that there are less Sr^{2+} cations within the system.

These results suggest that it is unlikely that the adsorption of the Sr^{2+} cations to the surface of the metakaolin is the main mechanism for the retardation of the reaction seen in the ICC (Section 4.2.4.1.1). As the pH increases to higher pH's, the solubility of the SrSO_4 is likely to decrease further, resulting in a lower concentration of Sr^{2+} cations within the solution which will lead to a lesser change in the surface charge of the metakaolin. Therefore, this mechanism will not lead to the significant changes seen in the ICC and there is the potential that the SrSO_4 could be reacting with the activating solution to retard the reaction to form the geopolymer.

4.2.4.1.3 DRIFTS

The DRIFTS spectra for the SO4_5 sample for the first 4 hours of reaction is shown in Figure 4-82.

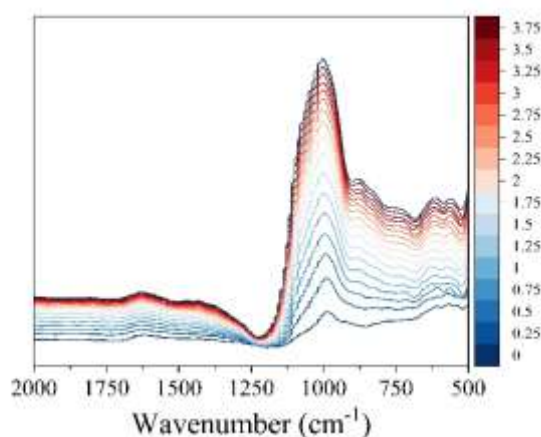


Figure 4-82: DRIFTS spectra for the SO_4_5 sample in the first 4 hours of reaction. The spectra are displayed in 15 minute intervals, beginning at $t=0$ as marked and progressing through the colour gradient. Times are shown in hours.

Over the first 4 hours, the peak representing the Si-O-T peak, centred around 1000 cm^{-1} , continues to grow [253]. This is representative of the formation of cross-linked silica chains, most commonly that of SiO_4 tetrahedra bonded to adjacent SiO_4 tetrahedra. There is potentially some evidence that the formation of a further Si-O-T peak centred at $\sim 1100\text{ cm}^{-1}$, representative of the Si-O-Al bond between SiO_4 and AlO_4 tetrahedra. However, this peak is not as prominent as the peak at 1000 cm^{-1} suggesting that there is a low amount of Al free within the system to react. This could be due to a slower than expected dissolution of the metakaolin, reducing the available Al within the system. The mechanism for this is likely the reaction between the SrSO_4 and the activating solution, as seen in the order-of-addition experiments (Section 4.2.4.1.4).

The difference between spectra for the SO_4_5 sample and the KGP sample, shown in Figure 4-7, is minimal. The growth progression of the main peak is equivalent in both, suggesting that, despite the consumption of some of the activating solution via the reaction with the SrSO_4 salt upon addition in the SO_4_5 sample, the formation of the K-A-S-H gel continues in a similar manner to the control sample. Therefore, it would be expected that the overall nanostructure would be similar in both samples. Although, the overall extent of reaction will be lower.

Following the first 4 hours of reaction, the SO_4_5 sample continues to follow a similar pattern, as shown in Figure 4-83. The inflection, the point at which the intensity of the peaks begins to decrease, occurs after 14.5 hours of reaction. This is slower than for the KGP control sample, wherein the intensity of the peaks begins to decrease after 8 hours of reaction, as can be seen in Figure 4-9. The beginning of the decrease corresponds to the point at which the samples begin to reach the maximum heat evolution, and therefore maximum point of reaction, seen in the ICC data (Section 4.2.4.1.1). At this point, the temperature within the samples is at its greatest, and therefore, it is likely that the sample is undergoing

shrinkage, changing the distance between the sample surface and the detector and altering the intensity of the signal [269, 270].

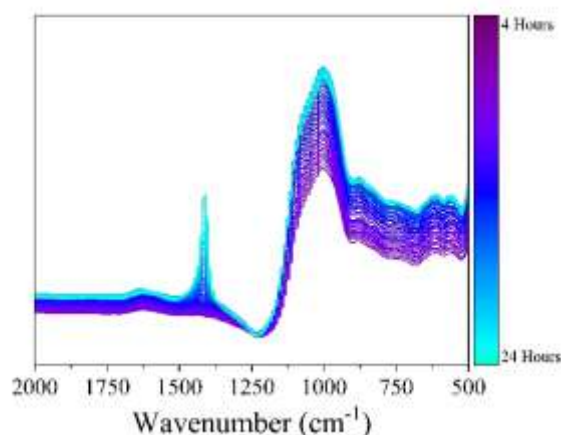


Figure 4-83: DRIFTS spectra for the SO_4_5 sample from 4 to 24 hours post initial reaction. The spectra are displayed in 15 minute intervals up until the 16-hour mark, at which the time progresses in whole hours, beginning at $t=4$ hours as marked and progressing through the colour gradient. Times are shown in hours.

The major change that occurs following the first 4 hours of reaction is the appearance of a peak at $\sim 1400 \text{ cm}^{-1}$. In the SO_4_5 sample, this peak is narrow, whereas in the KGP sample, the peak is broader, and also begins to form later in the reaction. The peak forms in the region that signifies the formation of carbonates within the sample, suggesting that the sample is reacting with the CO_2 in the air [271]. As this peak occurs at an earlier time-point than in the SO_4_5 sample, it is likely that the inclusion of Sr within the system promotes the carbonation of the sample, suggesting that the peak seen is primarily caused by SrCO_3 within the system. As there is not any Sr within the KGP sample, it can also be deduced that the K within the sample begins to carbonate and is solely responsible for the carbonation of the KGP sample, and contributes to the carbonation of the SO_4_5 sample.

4.2.4.1.4 Order-of-addition Experiments

In order to determine whether the point at which the Sr is added to the mix impacts the performance of the geopolymer, order-of-addition experiments were performed as outlined in Section 2.1.1.2.

4.2.4.1.4.1 Order-of-addition #1

1. The addition of SrSO_4 turns the water from a clear liquid into a foamy white liquid. This does not solidify the entirety of the mix, and is not very viscous. It is likely that the majority of the SrSO_4 has dissolved into the water.
2. The addition of the KOH, which appears to dissolve into solution, causes a solid to form. The solid is thick, but does not prevent the stirrer from spinning. The FTIR spectra of this solid can be seen in Figure 4-84. The visible peak at $\sim 1100 \text{ cm}^{-1}$, along with the peak at $\sim 600 \text{ cm}^{-1}$ are characteristic of the solid phase. Figure 4-85 shows that these peaks are caused primarily by

K_2SO_4 which is formed by the reaction of the aqueous K^+ cations and the introduced SO_4^{2-} ions form the $SrSO_4$. The peaks for water at 1600 and 3200-3600 cm^{-1} are also visible.

3. The addition of the silicate solution causes a gloopy white solid to form, which later solidifies into a translucent white solid which stops the stirrer from spinning. The FTIR spectra of this solid can be seen in Figure 4-84. The characteristic peak for the S-O bond can be seen at ~ 1000 cm^{-1} whereas the presence of water is signified by the peaks at 1600 cm^{-1} and 3200-3600 cm^{-1} . The peaks representing K_2SO_4 that are present after stage 2 appear to have mostly gone, suggesting that the silicate peak from the introduced K-silicate are masking the main peak. The small peak at around 600 cm^{-1} is still slightly visible.

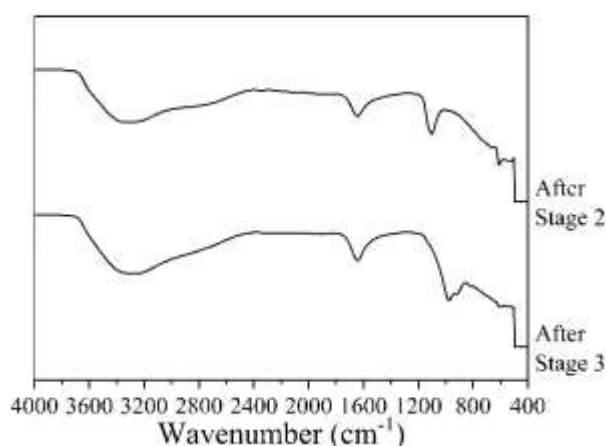


Figure 4-84: FTIR spectra of the white solids observed after stage 2 and 3 of the OoA #1 experiment containing $SrSO_4$.

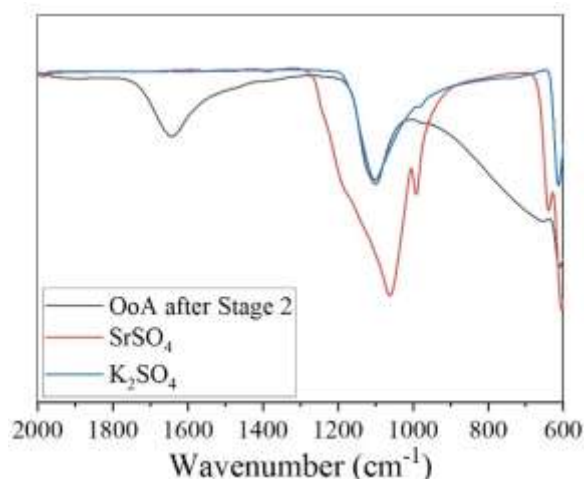


Figure 4-85: The FTIR spectra of the OoA #1 sample after stage 2 compared to pure $SrSO_4$ and K_2SO_4 .

4. The metakaolin was unable to be added to the solution as it had completely solidified. An attempt was made to mix the two but nothing came of it.

4.2.4.1.4.2 Order-of-addition #2

1. The addition of solid KOH to water leads to an exothermic dissolution reaction.

2. The addition of SrSO_4 leads to the formation of a solid which prevents the stirrer from turning. The FTIR spectra for this solid can be seen in Figure 4-86. From the spectra seen in Figure 4-87, it is most likely that this solid is K_2SO_4 dispersed throughout the solution. There is also, the possibility that there is some undissolved SrSO_4 present, but the peaks for the OoA experiment are not very strong and so it is hard to distinguish the identity of the solid.

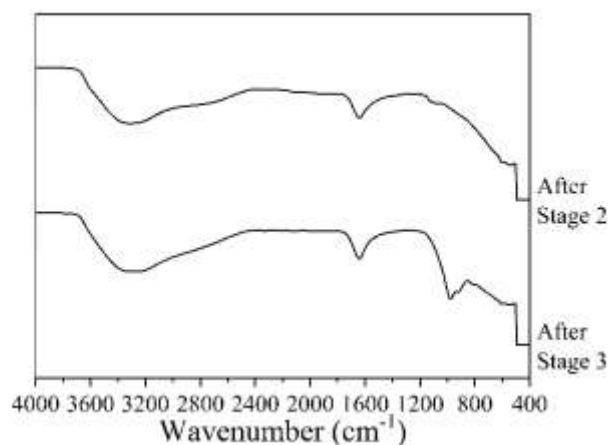


Figure 4-86: FTIR spectra of the white solids observed after stage 2 and 3 of the OoA #2 experiment containing SrSO_4 .

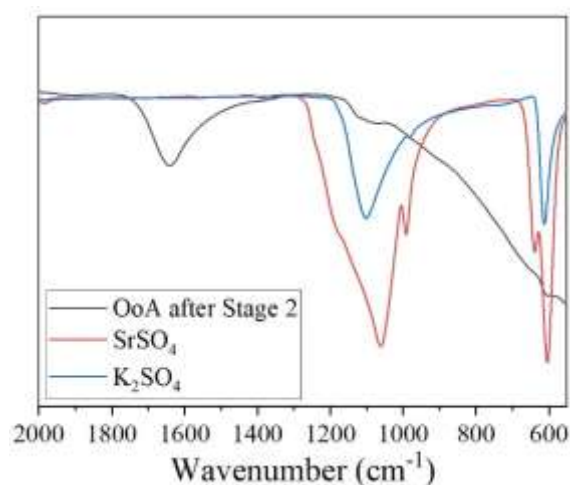


Figure 4-87: The FTIR spectra of the OoA #2 sample after stage 2 compared to pure SrSO_4 and K_2SO_4 .

3. The addition of the silicate stock solution causes the solid to slightly dissolve as the stirrer is able to begin spinning again. However, this is short-lived as the solid re-precipitates shortly after. The FTIR spectra for this solid can be seen in Figure 4-86. The characteristic peak for the Si-O-T bond can be seen at $\sim 1000\text{ cm}^{-1}$ whereas the presence of water is signified by the peaks at 1600 and $3200\text{--}3600\text{ cm}^{-1}$. The solid here could contain the K_2SO_4 and SrSO_4 discussed in stage 2, but any peaks to verify this are masked by the Si-O-T peak. There is also the possibility that the solid is comprised of a silicate phase.

4. The metakaolin was unable to be added to the solution as it had completely solidified. An attempt was made to mix the two but nothing came of it.

4.2.4.1.4.3 Order-of-addition #3

1. The addition of solid KOH to water leads to an exothermic dissolution reaction.
2. The addition of the K-silicate stock solution to the KOH solution resulted in a clear liquid mix.
3. The addition of the SrSO_4 in this case did not lead to the formation of a solid, similar to that of the OoA #1 and #2 experiments.
4. The activating solution containing the SrSO_4 was fluid enough to pour but still had a level of viscosity. When pouring, large solid particles were visible within the fluid (it appeared as if most were floating but it was hard to see as the particles were almost the exact same colour as the solution). When added to the MK, mixing was mostly achieved, but some small sections of the MK remained undissolved.

4.2.4.1.4.4 Order-of-addition ICC

Figure 4-88 shows the calorimetry curves generated by the OoA samples compared to the control KGP sample over the first 3 days of reaction. The samples for OoA #1 and #2 were completely solid and so were unable to facilitate dissolution of the metakaolin.

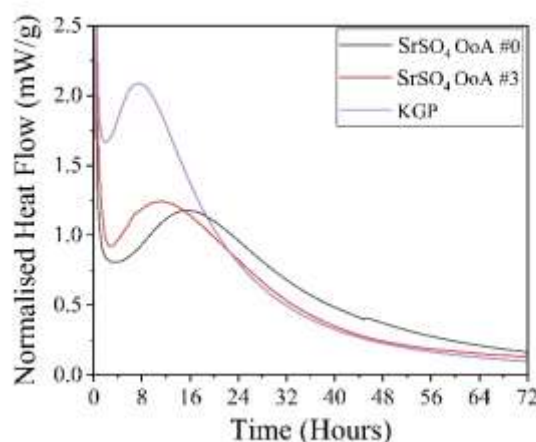


Figure 4-88: The effect on the heat evolution of the reaction of adding SrSO_4 at different stages to K-activated metakaolin geopolymers over the first 3 days.

The addition of SrSO_4 into the geopolymer has a similar effect in both cases seen in Figure 4-88. For OoA #3, the addition of the salt mainly effects the maximum value of the normalised heat flow, reducing it from ~ 2.1 mW/g in the KGP sample to ~ 1.25 mW/g, a 40% reduction. There is a slight retardation of the reaction, with the peaks maximum value occurring at 11 hours as opposed to the 7.5-hour mark seen in the KGP. The reaction for the OoA #3 sample did not carry through to completion; The metakaolin did not completely dissolve within the activating solution due to the increase in viscosity seen. Therefore, it is possible that, if all of the metakaolin had of dissolved, the maximum normalised heat

flow seen here would be of a greater value, explaining the significant change from the KGP control sample.

The addition of the SrSO_4 in the OoA #0 sample retards the reaction to a greater extent than is seen in the OoA #3 sample. This could be due to the formation of the K_2SO_4 or SrSO_4 seen in the OoA #2 and #3 experiments. The lower viscosity of the activating solution in OoA #0 allows the activating solution to easily migrate through the solid metakaolin and SrSO_4 mix. However, when the SrSO_4 dissolves into this activating solution, the formation of the solid phases seen creates a pseudo-barrier, preventing the activating solution from migrating at the same rate. This results in a slower reaction and could be the reason for the retardation of the reaction seen in OoA #0. In addition to this, the zeta potential results in Section 4.2.4.1.2 show that the Sr in solution adsorbs to the surface of the metakaolin and slows the dissolution. It is likely that these two phenomena are both contributing to the change in the heat evolved from the reaction in OoA #0.

4.2.4.1.4.5 *Order-of-addition Conclusion*

The introduction of SrSO_4 at any point in the reaction causes a change in the resultant geopolymer. In OoA #1 and #2, this appears as the formation of a white solid which completely solidifies the activating solution and prevents the formation of a geopolymer at all. This solid is likely to be a mix of undissolved SrSO_4 and K_2SO_4 . For OoA #3, the addition of the salt does allow for the reaction to take place. However, the high viscosity of the activating solution means that the entirety of the metakaolin does not dissolve. This results in an incomplete reaction which does not generate the heat expected, as shown by the ICC.

The results seen here suggest that, if SrSO_4 is to be incorporated into the geopolymer, it should be added as late as possible to avoid change to the geopolymer's heat evolution.

4.2.4.2 *Hardened State*

4.2.4.2.1 FTIR

Figure 4-89 shows the FTIR spectra of the K-geopolymers loaded with SrSO_4 after the first 3 days of reaction.

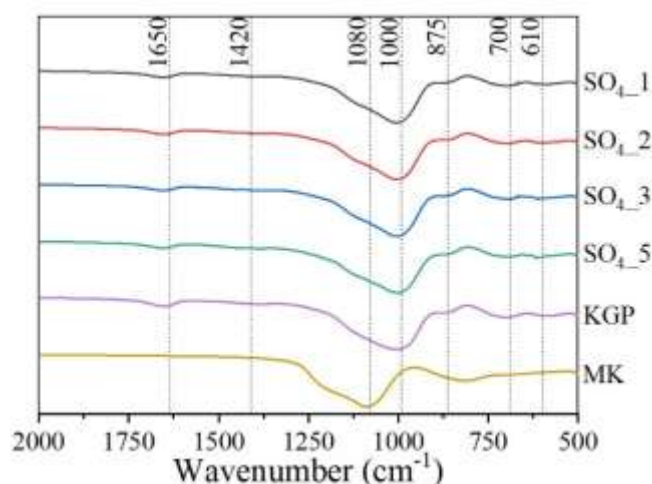


Figure 4-89: The FTIR spectra generated by loading K-activated metakaolin geopolymers with SrSO_4 , the KGP control sample and the unreacted metakaolin after the first 3 days of reaction.

For all samples, the bond vibrations that are responsible for the resonances seen are discussed in Section 3.4.2 and summarised in Table 3-4. The very low intensity band that can be seen centred at 1420 cm^{-1} is indicative of the carbonation of the samples due to exposure to air [271]. This carbonate compound could be potassium carbonate or strontium carbonate, or potentially a mixture of the two.

The spectra seen in Figure 4-89 show very similar traits regardless of the Sr/Al ratio of the samples. Therefore, it is likely that the K-A-S-H structure is not altered by the addition of the SrSO_4 and, despite the clear effects on the kinetics, the eventual structure is still forming in the same way. This is further supported by

Figure 4-90, which displays that the structure after 28 days shows little differences between the samples. There are a few noticeable differences between the spectra at 3 days and the spectra at 28 days, most prominently the sharp peaks that are seen at 667 cm^{-1} in the SO_4_1 and SO_4_5 samples. It is possible that these peaks are due to the presence of kalistrontite within the sample, as shown by the XRD in Section 4.2.4.2.2. Moreover, the peak that is attributed to the carbonation of the samples is not overtly present in the spectra. This lack of intensity is likely due to the samples undergoing less carbonation than the 3 day samples, however, there are still signs of carbonation, as shown in Figure 4-91. This is probably due to the way in which the samples are ground and stored, with some samples potentially experiencing more contact with the air than others.

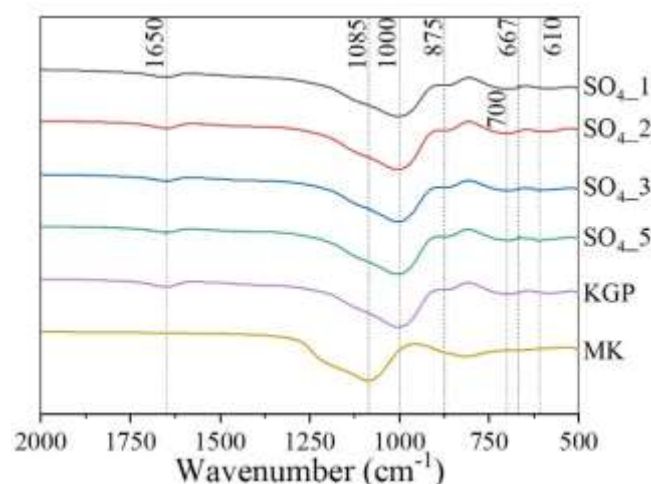


Figure 4-90: The FTIR spectra generated by loading K-activated metakaolin geopolymers with SrSO_4 , the KGP control sample and the raw metakaolin after the first 28 days of reaction.

Figure 4-91 shows the SO_4_5 sample compared to the SrSO_4 salt that was used to load the geopolymers in this work. Due to the main peak for the SrSO_4 completely overlapping with the main silicate peak of the SO_4_5 geopolymer sample, it is difficult to confirm whether there is any solid SrSO_4 residing within the hardened sample. Some comparison can be made between the peaks seen around the 600 cm^{-1} region, but these are not a perfect match and so it is not possible to conclusively say that solid SrSO_4 remains within the sample, despite the zeta potential results suggesting that the dissolution of the salt decreases with increasing pH. This is similar for the presence of K_2SO_4 , which exhibits similar peaks to the SrSO_4 . However, the peak for this salt at $\sim 1105\text{ cm}^{-1}$ aligns nicely with the shoulder on the main silicate peak seen at approximately the same position in the SO_4_5 sample. Equally, the peak at 615 cm^{-1} aligns with the peak seen in this region in the SO_4_5 sample. Therefore, it is likely that the SO_4_5 sample contains some undissolved SrSO_4 as well as some K_2SO_4 that has formed due to the introduction and consequent dissolution of the added SrSO_4 .

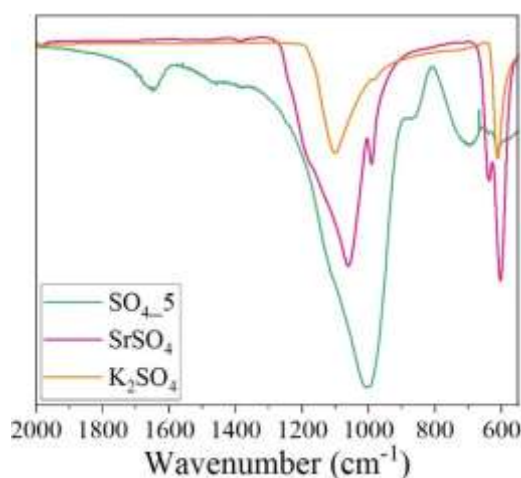


Figure 4-91: The FTIR spectra of the SO_4_5 sample after 28 days of reaction compared to pure SrSO_4 and K_2SO_4 .

4.2.4.2.2 XRD

The X-ray diffraction patterns for the geopolymer samples containing SrSO_4 3 days after initial reaction are shown in Figure 4-92.

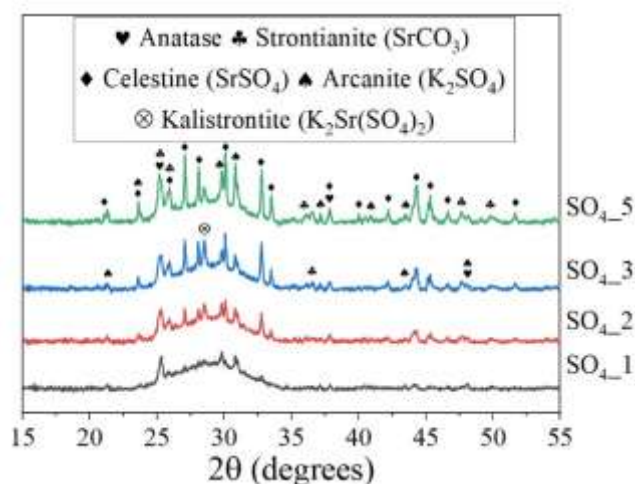


Figure 4-92: The X-ray diffraction spectra generated by loading K-activated metakaolin geopolymers with SrSO_4 after the first 3 days of reaction.

The XRD patterns for each sample are comparable, exhibiting a broad diffraction peak between 24° 2θ and 33° 2θ . This peak indicates the presence of an amorphous phase within the sample, notably the presence of the K-A-S-H gel [164].

The XRD patterns for the samples do indicate the presence of some crystalline phases within the hardened gel. The presence of anatase (TiO_2 , PDF # 01-086-1157) is indicative of the unreacted metakaolin that remains within the structure, as supported by both the FTIR and NMR data.

The presence of celestine (SrSO_4 , PDF # 04-009-9879) confirms that not all of the SrSO_4 dissolves into the activating solution. The presence of this becomes greater with increasing Sr/Al ratio, suggesting that the solubility limit is reached between the SO_4_1 and SO_4_2 samples. This would explain the zeta potential results seen in Section 4.2.4.1.2, where the increase in zeta potential decreases as the Sr/Al ratio increases. The presence of arcanite (K_2SO_4 , PDF #00-024-0703) suggests that the dissolved SO_4^{2-} anions react with the K^+ ions in solution to precipitate a solid, crystalline K_2SO_4 phase. The presence of this also increases with increasing Sr/Al ratio, suggesting that, as more SrSO_4 dissolves, there are more SO_4^{2-} anions available to react with the K^+ cations as would be expected. This is similar for the kalistrontite ($\text{K}_2\text{Sr}(\text{SO}_4)_2$, PDF # 04-025-4251), which increases in prominence as mass of SrSO_4 in the sample increases. The formation of kalistrontite is not unexpected, as it is seen in the literature that deposits of kalistrontite have been found in the presence of SrSO_4 and K-bearing phases [326, 327]. The presence of this crystalline solid could explain the changes seen to the reaction kinetics in the ICC (Section 4.2.4.1.1), as the SrSO_4 clearly reacts with the activating solution upon its addition. The crystallisation, and probable resultant precipitation, of this solid will prevent the migration of the

activating solution fully around the solid metakaolin. Moreover, the consumption of both K^+ and Sr^{2+} , the two cations within solution that are responsible for the charge balancing of the AlO_4^- sites in the gel phase, could result in less of the K-A-S-H gel being able to form in a stable state. For a combination of these reasons, the heat of reaction is less than that of the control KGP geopolymers when $SrSO_4$ is added to the mix.

The presence of strontianite ($SrCO_3$, PDF # 00-005-0418) is most likely due to the carbonation of the sample via contact with air. However, there is very little of this compound present within the sample and this is further evidence that there is a minimal amount of ‘free’ Sr within the sample, as the majority of it has either not dissolved (remains as $SrSO_4$), reacted with the activating solution to form kalistrontite, or has been incorporated into the K-A-S-H gel in place of K.

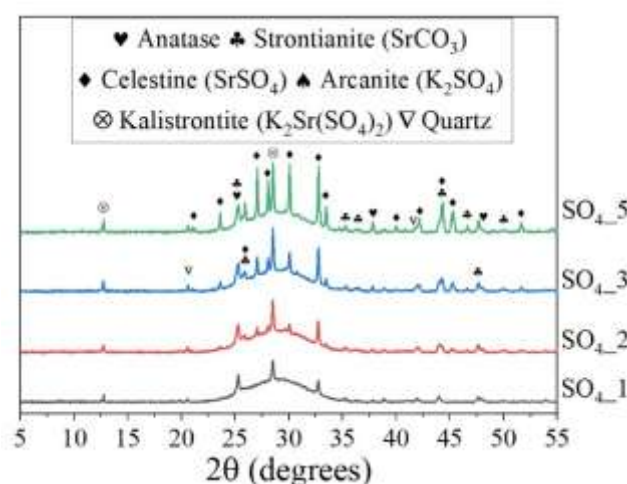


Figure 4-93: The X-ray diffraction spectra generated by loading K-activated metakaolin geopolymers with $SrSO_4$ after the first 28 days of reaction.

After 28 days, the diffraction patterns show the presence of all of the crystalline phases seen after 3 days. The presence of quartz (SiO_2 , PDF # 01-078-2315) is also seen, an inert compound found in the raw metakaolin precursor.

4.2.4.2.3 NMR

4.2.4.2.3.1 ^1H - ^{29}Si CP MAS and ^{29}Si MAS NMR

The ^1H - ^{29}Si CP MAS and ^{29}Si MAS NMR spectra for the SO_4_5 and KGP samples both 3 and 28 days after the initial reaction are displayed in Figure 4-94.

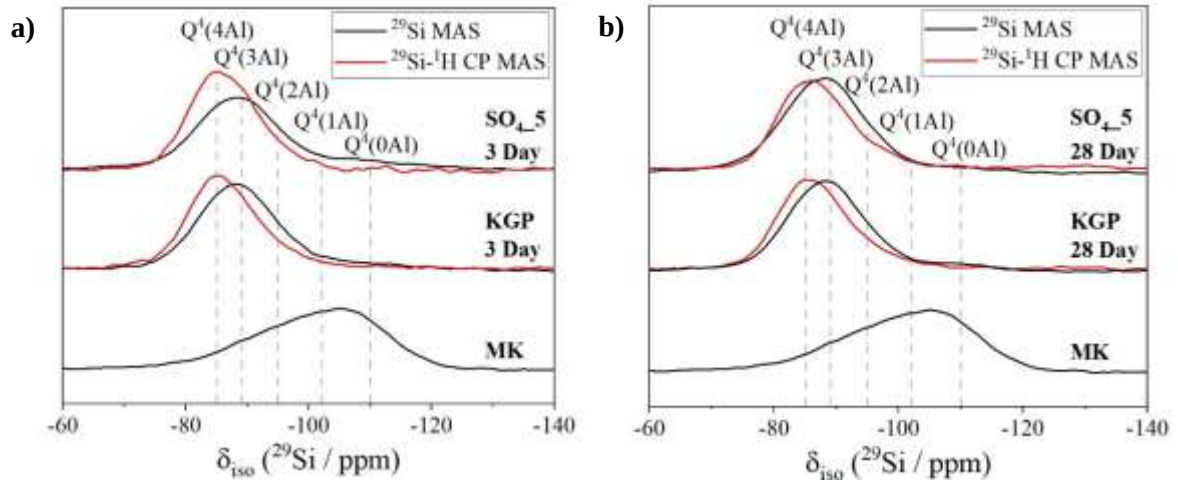


Figure 4-94: ^1H - ^{29}Si CP MAS and ^{29}Si MAS spectra for the SO_4_5 , KGP samples and the unreacted metakaolin a) 3 days and b) 28 days after reaction.

The ^1H - ^{29}Si CP MAS NMR spectra for the geopolymers, shown in red in Figure 4-94, display a single broad peak at δ_{iso} between -75 and -105 ppm. The maximum intensity is observed at a δ_{iso} of -85 ppm, confirming that the geopolymer gels are predominantly comprised of $\text{Q}^4(4\text{Al})$ and $\text{Q}^4(3\text{Al})$ silicon environments. There has been a clear shift of the main peak to higher ppm from the spectra exhibited by the metakaolin on its own which further supports the formation of a geopolymer. The differences between, and rationale for the use of both ^1H - ^{29}Si CP MAS NMR and ^{29}Si MAS NMR are discussed in Section 3.4.3.1.

The ^{29}Si MAS NMR spectra shows that the maximum peak intensity is at a lower δ_{iso} when related to the ^1H - ^{29}Si CP MAS NMR spectra. This is due to the introduction of the silicon sites that are anhydrous as a result of the unreacted metakaolin within the sample. As is shown in Figure 4-94, the maximum intensity for the metakaolin peak in the ^{29}Si MAS NMR is shown to be at a far lower wavenumber than the geopolymer samples. Therefore, it is trivial that the maximum intensity peaks observed in the ^{29}Si MAS NMR spectra for the geopolymer samples will be at a lower wavenumber than the peaks in the ^1H - ^{29}Si CP MAS NMR for the same sample. The spectra observed here are similar to those seen in previous work, suggesting that the K-A-S-H gel is formed by a mixture of Si environments in the form of $\text{Q}^4(m\text{Al})$ sites, where $1 \leq m \leq 4$ [67]. This is supported by Table 4-8 which shows the presence of each Si site as a percentage calculated from the ^{29}Si MAS NMR data.

Table 4-8: Relative integral areas for the Si sites present within the K-A-S-H gel of each sample both 3 and 28 days after initial reaction from the deconvoluted ^{29}Si MAS NMR spectra. The $\text{Q}^4(0\text{Al})$ site attributed to the unreacted metakaolin is disregarded for the quantification of the K-A-S-H gel.

Sample	Time point	Relative Integral Area (%)				Si/Al
		$\text{Q}^4(4\text{Al})$	$\text{Q}^4(3\text{Al})$	$\text{Q}^4(2\text{Al})$	$\text{Q}^4(1\text{Al})$	
KGP	3 Days	25	54	20	1	1.32

SO ₄ _5	3 Days	25	33	37	5	1.44
KGP	28 Days	28	44	26	2	1.34
SO ₄ _5	28 Days	31	34	28	7	1.39

The deconvolution of the NMR spectra allows the amount of each individual ²⁹Si site to be quantified [172]. For the KGP samples, Figure 4-95 for the SO₄_5 samples and Figure 3-6 for the KGP samples shows that the gel structure is dominated by Q⁴(3Al) sites, which is in line with data that is widely reported in the literature for potassium activated geopolymers [172]. The SO₄_5 samples have a gel structure that appears to be dominated by Q⁴(2Al) sites after 3 days of reaction. However, after 28 days of reaction, the gel structure displays an increased number of Q⁴(4Al) and Q⁴(3Al). This is likely due an increase in availability of Al within the reaction mixture as the reaction progresses, coupled with the reordering of the K-A-S-H gel into a more stable state. Table 4-8 also shows the molar Si/Al ratio of the K-A-S-H gel, disregarding the Si sites that are attributed to the unreacted MK. This ratio is calculated using Engelhardt's formula (Equation 3-1) [276].

The Si/Al ratio of the SO₄_5 samples after both 3 and 28 days are greater than that of the KGP sample suggesting that the incorporation of SrSO₄ at such a high Sr/Al ratio slightly decreases the cation binding capability of the gel. This is contrary to what has been seen in previous work, with Walkley et al. showing that the Si/Al ratio for K-activated geopolymer systems containing Sr is less than the associated control geopolymer system [67]. However, this is using much lower concentrations of Sr within the structure, which would have less of an impact on the formation of the K-A-S-H phase.

Table 4-9: The extent of reaction of the SO₄_5 and KGP samples both 3 and 28 days after initial reaction, calculated using the ²⁹Si MAS NMR spectra.

Sample	Time point	Extent of reaction (%)
KGP	3 Days	82.17
SO ₄ _5	3 Days	84.40
KGP	28 Days	88.00

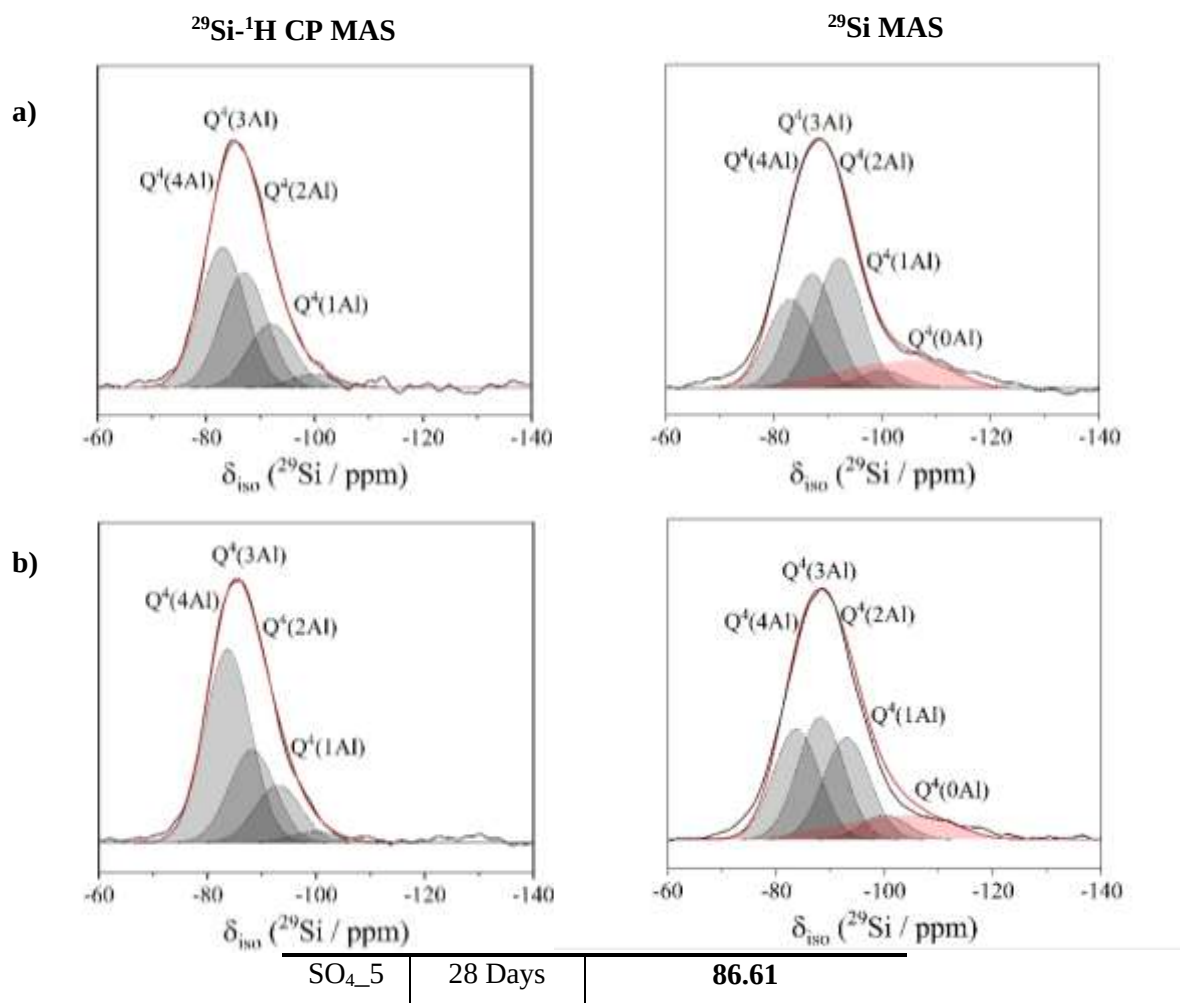


Figure 4-95: ²⁹Si-¹H CP MAS and ²⁹Si MAS NMR spectra and the associated deconvolutions for the a) SO₄_5 sample after 3 days and b) SO₄_5 sample after 28 days. The ²⁹Si-¹H CP MAS NMR data is shown in the left column and the ²⁹Si MAS NMR data is shown in the right column. For each spectrum, the raw data is shown as a solid black line and the model fit is shown as a solid red curve. The deconvolutions that represent each ²⁹Si site within the K-A-S-H gel are depicted as grey curves, whilst the deconvolutions that represent ²⁹Si sites within the unreacted metakaolin are shown in a faded red.

4.2.4.2.3.2 ²⁷Al MAS NMR

The ²⁷Al MAS NMR spectra for the SO₄_5 and KGP samples both 3 and 28 days after the initial reaction are displayed in Figure 4-96.

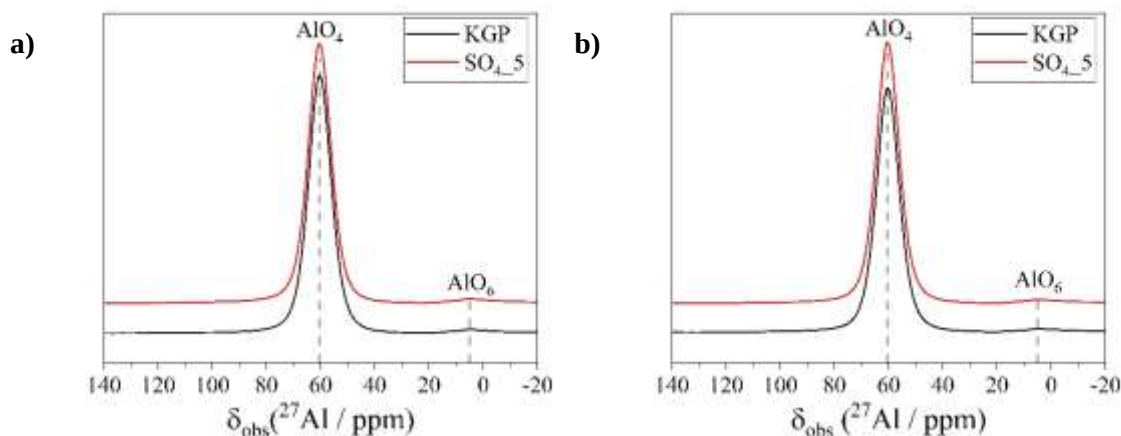


Figure 4-96: ^{27}Al MAS spectra for the SO_4_5 and KGP samples a) 3 days and b) 28 days after reaction.

Figure 4-96 shows that the ^{27}Al MAS NMR spectra for both the KGP and SO_4_5 samples display two distinct resonances. The most obvious resonance, centred at 59.5 ppm and spanning between ~ 50 and 70 ppm is recognisable as the tetrahedral Al site (AlO_4^-) found in the K-A-S-H gel phase of the geopolymer [279, 306]. This coordination is promoted by the large excess of alkali cations within the gels and gives rise to the negative charge that is intricate to the use of geopolymers in the application of the disposal of radioactive Sr, and is introduced by the substitution of Al^{3+} ions for Si^{4+} as shown by Figure 4-21 [307]. This negative charge is balanced by cations: K^+ in the KGP sample and a combination of both K^+ and Sr^{2+} in the SO_4_5 sample [308].

The small resonance observed at ~ 5 ppm is attributed to the presence of octahedral Al sites (AlO_6) within the samples [274]. The intensity of this peak is negligible when compared to that of the tetrahedral Al peak, and suggests that the majority of the Al within the MK has reacted as the octahedral peak corresponds exclusively to the Al found within the unreacted MK [279]. This corresponds to the results seen in the ^{29}Si MAS NMR, which show that the reaction is over 85% completed.

As can be seen in Figure 4-96, there is very little change between the KGP and the SO_4_5 samples at both time points. Likewise, there is minimal change between the corresponding samples at 3 and 28 days, suggesting that the Al environments are not altered by the addition of the SrSO_4 .

4.2.4.2.3.3 ^{39}K MAS NMR

The ^{39}K MAS NMR spectra for the SO_4_5 and KGP samples both 3 and 28 days after the initial reaction are displayed in Figure 4-97.

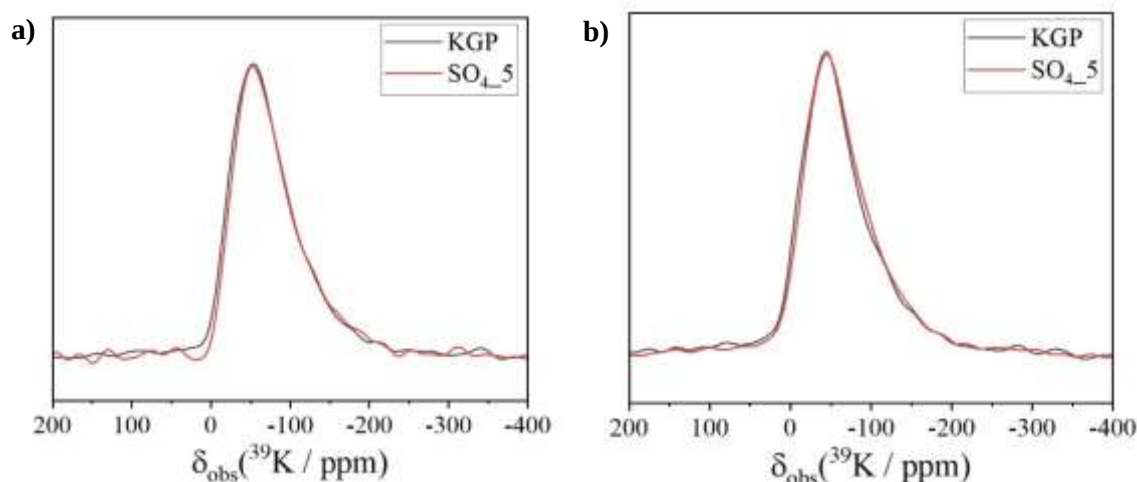


Figure 4-97: ^{39}K MAS spectra for the SO_4_5 and KGP samples a) 3 days and b) 28 days after reaction.

From Figure 4-97, it is clear that there is very little change to the K chemical environments within the KGP control geopolymer sample and the SO_4_5 samples after both 3 and 28 days. For the 3-day sample, the peaks for both samples are seen at a δ_{obs} of $\sim -52/-53$ ppm, exhibiting the broad peak expected due to the strong quadrupolar interactions of the K atoms. The line shape of both of the peaks are comparable, suggesting that there is one consistent K chemical environment in the samples, that of K^+ ions charge balancing the negative AlO_4^- tetrahedral within the K-A-S-H gel. This is much like the spectra seen for the 28-day samples, exhibiting a consistent line shape between the two samples with a singular, broad peak visible. The lack of change in the range of δ_{obs} seen between the KGP control spectra and the SO_4_5 samples, which contain the Sr^{2+} ions, suggests that the Sr is readily accommodated by the K-A-S-H gel at the Sr/Al ratio of 0.125 used here, accredited to the highly disordered local structure of the systems enabling the distortion of bond lengths and angles locally in the gel [323]. This suggests that the K-A-S-H gel in ‘clean’ geopolymers is likely to exhibit similar physicochemical properties to the modified K-A-S-H gel seen in loaded geopolymers, further promoting their use as a wasteform for the encapsulation of radioactive waste streams.

As the lineshape of the samples are comparable with literature, further confidence that there is no evidence of changes to the environment of K upon the addition of SrSO_4 can be taken.

4.2.4.2.3.4 ^{87}Sr Solid-State NMR

The ^{87}Sr solid-state NMR spectra for the SO_4_5 samples after both 3 and 28 days of reaction are displayed in Figure 4-98.

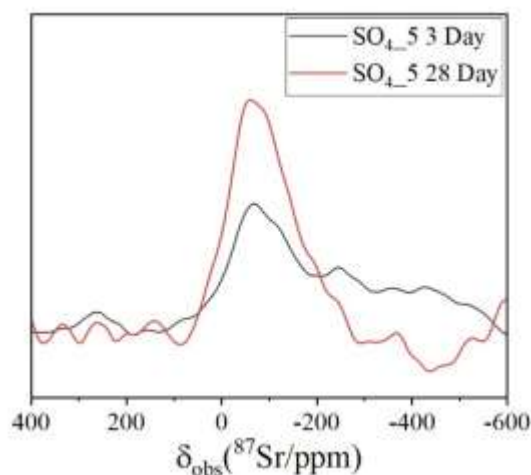


Figure 4-98: ^{87}Sr solid-state NMR spectra for the SO_4_5 sample after 3 and 28 days of reaction.

The spectra for the SO_4_5 samples after 3 and 28 days of reaction show differing intensities, but both show a main central peak centred at $\delta_{\text{obs}} = \sim -65\text{ppm}$. The difference in intensity is likely due to the difficulty in obtaining data using this analytical technique. It could be argued that, due to the broadness of the peaks and what appears to be a shoulder close to the tip of the peak, there are two distinct Sr chemical environments present within both of the samples. The close proximity of these peaks suggest that the compounds have a similar chemical and structural layout; therefore, it is likely that these two peaks are caused by the presence of undissolved SrSO_4 and SrCO_3 , which is present due to the reaction of the dissolved Sr with CO_2 in the air. Both of these compounds are shown to be present in significant quantities by the XRD data. The XRD data also suggest that the sample contains a $\text{K}_2\text{Sr}(\text{SO}_4)_2$ phase, and the broadness of the peaks mean that it is possible that the peak representing this phase is encompassed within the main peak. In a similar manner, there is no clear evidence that the Sr has displaced the K from its role as the charge balancing cation in the aluminosilicate gel framework structure, but it is feasible that this peak is encompassed within the broad peak seen in the spectra.

4.2.4.2.4 EPMA

The use of electron probe microanalysis (EPMA) allows for the chemical composition of the geopolymer gel to be spatially resolved and quantified [316]. In this work, it has been used to determine the distribution of Sr throughout the geopolymer matrix.

The EPMA images for the SO_4_5 sample, 28 days after reaction and at a magnification of x1000, are shown in Figure 4-99.

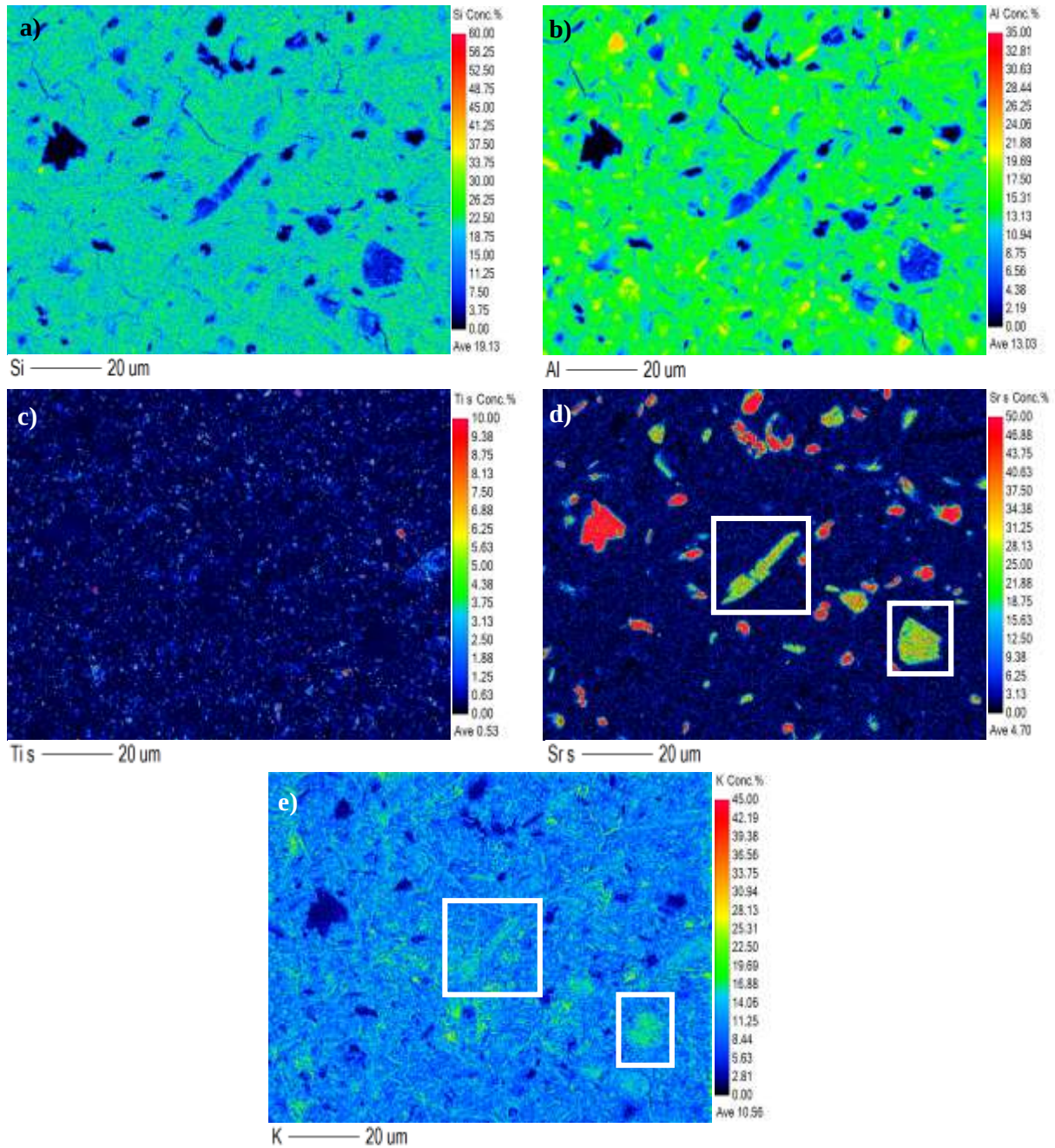


Figure 4-99: The EPMA images generated for the SO_4_5 sample after 28 days of reaction. The elements shown in each image are as follows: a) Aluminium, b) Silicon, c) Titanium, d) Strontium, and e) Potassium. The magnification factor is $\times 1000$ and the notation of *s* for some of the elements relates to the use of a sharpening filter to improve the differentiation in composition.

From images a) and b), it can be seen that the majority of the structure is formed of the K-A-S-H gel as expected from a geopolymer gel matrix. This is due to the relatively high concentrations of Si and Al that populate the majority of the sample.

Image c) shows the presence of Ti in very high concentration in small particles across the sample. This is indicative of anatase within the sample, as shown by the XRD. This is a result of the small impurities within the metakaolin used as a raw material for the formation of the geopolymer.

From image d), it can be seen that Sr is present within the sample in multiple phases. Firstly, the regions of very high Sr content, depicted by the red regions in the image, suggest the presence of unreacted and undissolved SrSO_4 salt which was added as the reagent. It is likely that this phase is SrSO_4 due to the low concentration of the other elements in these areas. This phase is seen throughout the sample, and suggests that the SrSO_4 mixed within the geopolymer gel, but has become encapsulated within the gel as opposed to becoming incorporated chemically into the structure in place of the K^+ cations as the charge balancing ion. To add to this, the widespread concentration of K shown in image e) suggests that it is acting as the charge balancing cation in the K-A-S-H gel in the majority of cases.

Secondly, image d) suggests that there is a phase that contains relatively high concentrations of both Sr and K. By comparing image d) with image e), it is possible to determine areas of this phase, as shown by the white boxes in both images. This phase is potentially that of the kalistrontite that is seen in the XRD analysis (Section 4.2.4.2.2), and this is supported by the small concentration of Si that can be seen in these regions in image a). This finding provides further evidence for the reaction between the SrSO_4 salt and the activating solution, the only reagent containing K, which is likely to be causing the kinetic changes seen within the ICC (Section 4.2.4.1.1).

4.2.4.2.5 X-ray Absorption Spectroscopy

4.2.4.2.5.1 X-ray Absorption Near-Edge Structure (XANES) Spectroscopy

The normalised spectra for the Sr K-edge XAS analysis of the SO_4_5 sample after both 3 and 28 days of reaction compared to both the SrSO_4 reagent and the mineral brewsterite-Sr ($(\text{Sr},\text{Ba})_2\text{Al}_4\text{Si}_{12}\text{O}_{32}\cdot 10\text{H}_2\text{O}$) are shown in Figure 4-100 [315].

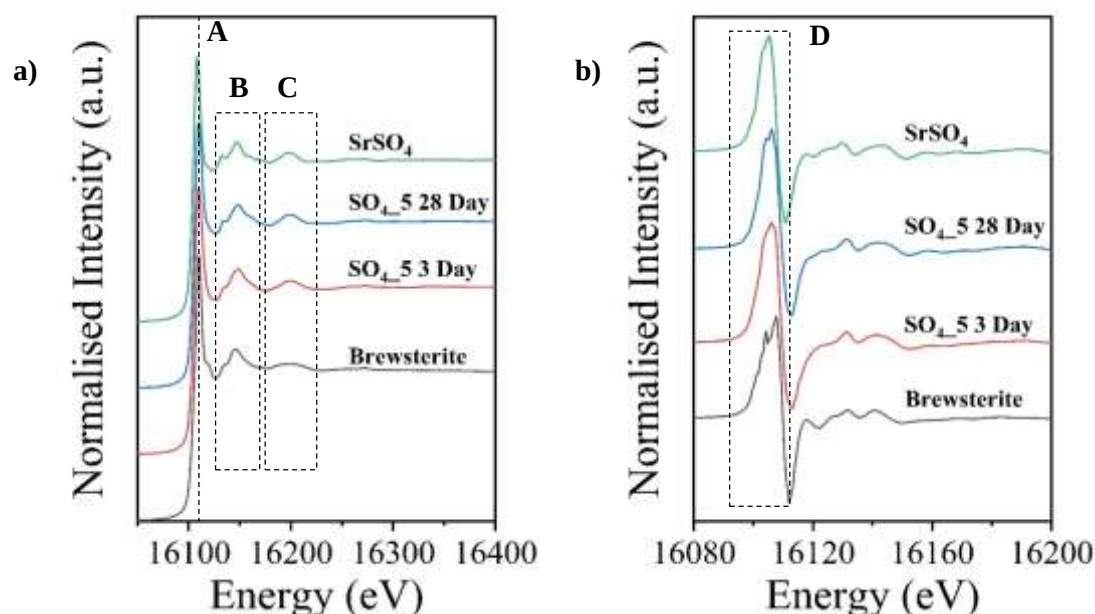


Figure 4-100: a) Normalised X-ray absorption spectra for the geopolymer samples loaded with SrSO_4 , the SrSO_4 reactant used and the mineral brewsterite-Sr. b) The 1st derivative of these spectra.

The Sr K-edge here displays an absorption edge that rises smoothly to a maximum featuring a singular peak. As previously mentioned in Section 4.2.1.2.5.1, the Sr K-edge is relatively featureless but provides enough information for a qualitative analysis to be performed. When initially focusing on the peak maximum in Figure 4-100a), labelled as A, the value of the peak appears to move to slightly higher energies when the SrSO₄ is included in the geopolymer mix when compared to the SrSO₄ reagent. The energy at which the brewsterite-Sr mineral reaches its maximum peak is comparable to the SO₄_5 samples. This peak can be explored in more detail in Figure 4-100b), which displays the 1st derivative of this peak. This allows us to further distinguish the features of the leading edge, and shows that there is a potential feature here, most notably in the brewsterite standard. However, the line shape of the spectra for the SO₄_5 samples both follow that of the SrSO₄ more closely, with the doublet being far closer to the tip of the peak in both samples.

When exploring the regions above the absorption edge, inspection of the region labelled B in Figure 4-100a) does not provide a great deal of insight due to the similarities presented here between the SrSO₄ standard and the brewsterite standard. However, region C shows that the SO₄_5 samples at both time points relate more closely to the SrSO₄ standard than the brewsterite.

The spectra here suggest that the Sr within the SO₄_5 samples are unlikely to be incorporated into the K-A-S-H gel as charge balancing cations, and are not existing in a pseudo-zeolitic structure within the samples. It is more likely that the Sr remains as the solid SrSO₄ physically trapped within the structure, and this is further evidenced by the XRD and the order-of-addition reactions. However, there is also strong evidence for the existence of Sr in a further phase of K₂Sr(SO₄)₂, but a standard for this is not readily available.

4.2.4.3 Conclusions

Isothermal conduction calorimetry shows that introduction of SrSO₄ at varying Sr/Al ratios affects the kinetics of formation of the geopolymer gel. The chemical mechanisms for this have been investigated using zeta potential, EPMA and order-of-addition experiments, with the conclusion being that some of the SrSO₄ dissolves into the activating solution and absorbs onto the surface of the metakaolin, slowing its dissolution and retarding the reaction to form the geopolymer. However, the SO₄²⁻ ions within solution are reacting with the K⁺ ions in solution to form K₂SO₄ which inhibits the ability of the activating solution to fully migrate around the metakaolin. The remaining SrSO₄ suspended in solution does one of two things; reacts with K⁺ ions within the activating solution to form a solid K₂Sr(SO₄)₂ phase, or remains as a solid and acts as a filler material within the pores.

However, the Sr²⁺ cations do not affect the resulting structure, the primary phase of which is shown to be a K-A-S-H gel through the use of FTIR spectroscopy, ²⁹Si MAS NMR and ²⁹Si-¹H CP MAS NMR. This phase is comprised of Si and Al in tetrahedral coordination, with the Si mainly existing in Q⁴(4Al), Q⁴(3Al) and Q⁴(2Al) environments. The negative Al sites caused by Al³⁺ in tetrahedral coordination are

charge balanced by K^+ , and the XANES does not provide evidence that the introduction of the Sr^{2+} cations changes this. XRD shows that the crystalline structure of $SrSO_4$ and K_2SO_4 are both observed within the solid sample. It is shown that the incorporation of the $SrSO_4$ leads to a relative increase in the Si/Al ratio, most likely due to the inhibition of the dissolution of the metakaolin.

The order-of-addition experiments demonstrated that the addition of $SrSO_4$ into the system at any point in the mix has a huge effect on the resulting kinetics of reaction, and should be added as late as possible to avoid this.

This work shows that K-silicate activated geopolymers are capable of incorporating wastes containing $SrSO_4$ at high waste loadings of up to 5% by weight without causing significant damage to the structure of the geopolymer. However, in practice, the loadings are likely to be far lower due to activity limits per package on the wasteforms, owing to the radioactivity of the waste in question. Whilst this, and any impact of the radiation and resulting decay products, are not considered in this work, it is important to note that they will likely have a notable effect on the performance of the geopolymer as a wasteform, and further work to determine how great this effect is will be crucial to determine the overall suitability of the wasteform.

Despite this, the findings of this work show that the incorporation of $SrSO_4$ containing waste has only a small effect on both the kinetics and mechanisms of formation of a metakaolin based, potassium silicate activated geopolymer system, suggesting that these systems show great promise as wasteforms for the long term immobilisation of radioactive waste streams containing ^{90}Sr in the form of $SrSO_4$.

4.2.5 Comparison of Salts

4.2.5.1 Overview

The four salts of strontium used in this work: $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, SrCO_3 , $\text{Sr}(\text{NO}_3)_2$ and SrSO_4 offer very different properties which effect the ability of the geopolymer to accommodate them into the K-A-S-H structure. Firstly, the solubility of the salts causes vast discrepancies between the phases in which Sr is present within the geopolymer; the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and SrCO_3 are very insoluble, and so, for the most part, remain as such when added to the activating solution whereas the $\text{Sr}(\text{NO}_3)_2$ and SrSO_4 are relatively soluble and so dissolve into the activating solution, separating into the constituent ions. In this section, where appropriate, the effect of adding the salts to the geopolymer mix at an Sr/Al ratio of 0.125 will be compared and discussed.

4.2.5.2 Fresh State

The isothermal calorimetry curves generated by the heat released during the reaction to form the K-A-S-H gel is seen in Figure 4-101.

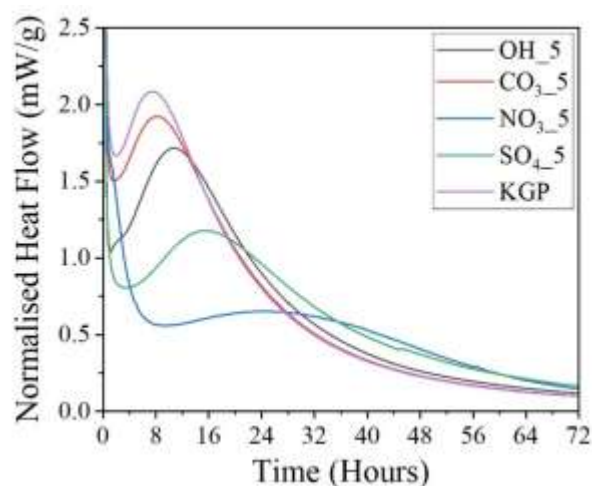


Figure 4-101: The effect on the heat evolution of reaction of loading K-activated metakaolin geopolymers with $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, SrCO_3 , $\text{Sr}(\text{NO}_3)_2$ and SrSO_4 at an Sr/Al ratio of 0.125 over the first 3 days of reaction.

The CO_3_5 and OH_5 samples show the least deviation from the KGP control sample in Figure 4-101. This is expected, as the low solubility of these salts means that the ions present within the paste are almost identical to those seen in the KGP sample. For the CO_3_5 sample, it is posed that this is due to the salt acting as a filler material, absorbing some of the heat that is released during the reaction as well as withholding some of the activating solution from the metakaolin due to the wetting effect. This is similar to the effect seen in the OH_5 sample, with a large proportion of the salt remaining within the paste as a crystal. However, it is clear that some of the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ does dissolve, as the reaction is retarded by 3.3 hours. This delay in reaction separates the OH_5 and CO_3_5 samples, providing clear evidence that the introduction of Sr^{2+} cations into the paste alters the speed at which the reaction occurs.

This is further compounded by the curves generated by the reaction of the NO₃_5 and SO₄_5 samples. The delay witnessed in these reactions is more pronounced; in the case of the NO₃_5 sample it takes over 3 times as long to reach maximum reaction. The relationship between these two samples and the OH_5 sample dictates that as more Sr²⁺ cations are released into the paste, the reaction is delayed further, resulting in the maximum heat decreasing as the reaction is spread out over a greater time period. From this, we can rule out the filler effect as the mechanism for the change for the NO₃_5 and SO₄_5 samples, compounded by the high solubility of the two salts in question [303].

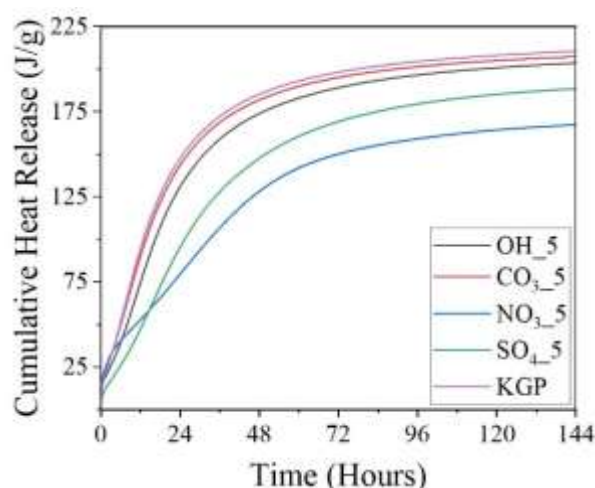


Figure 4-102: The cumulative heat release curves over the first 144 hours of reaction of the geopolymers containing Sr(OH)₂·8H₂O, SrCO₃, Sr(NO₃)₂ and SrSO₄ compared to the control KGP sample.

The collective cumulative heat curves in Figure 4-102 mostly agree with the results seen in the ICC curves over a 3 day period. However, the spike in the heat release of the NO₃_5 sample in the first 8 hours is unexpected. It is possible that this is seen due to more of the dissolution peak being recorded within the apparatus. This is possible as it is posed that the addition of Sr(NO₃)₂ reduces the rate of dissolution of the metakaolin into the activating solution, a suggestion that is ratified throughout Section 4.2.3 of this work. It is well documented that the dissolution of the metakaolin within the activating solution is highly exothermic and so if this is happening in greater quantities in the NO₃_5 sample when compared to the others it is no surprise that the cumulative heat at this point is higher [128, 292]. Despite this, the cumulative heat curves show that the introduction of the salts reduces the cumulative heat release of the geopolymers reaction in all cases after 6 days of reaction.

The interactions of the Sr²⁺ cations within the paste can be partially explained by the zeta potential values shown in Figure 4-103.

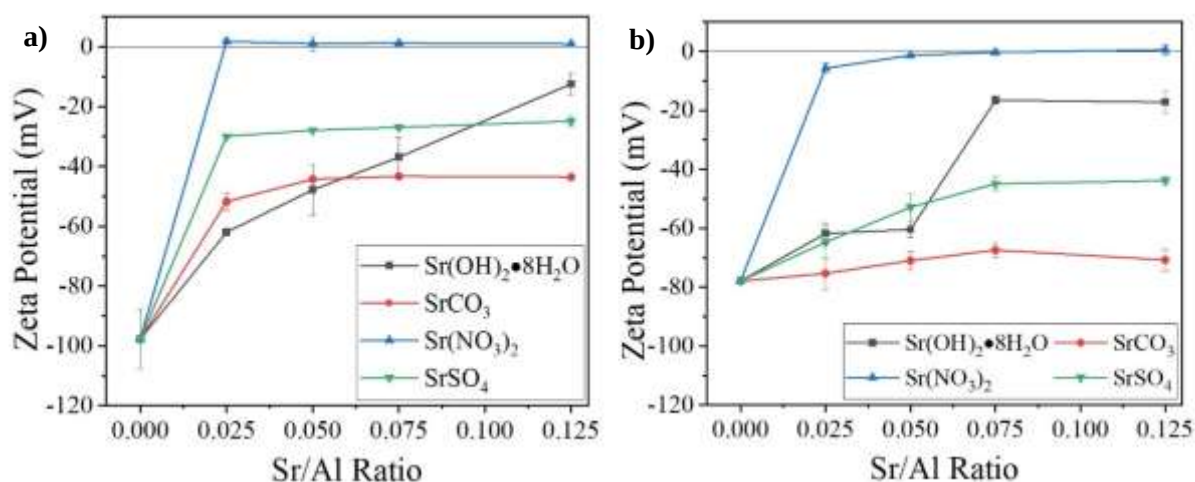


Figure 4-103: Comparing the effect of Sr/Al ratio, altered by the addition of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, SrCO_3 , $\text{Sr}(\text{NO}_3)_2$ and SrSO_4 , on the zeta potential of metakaolin in a KOH solution at differing pH's: a) pH 10 and b) pH 12.

The zeta potential results clearly indicate the impact of combining the Sr^{2+} ions with the metakaolin, most notably in the $\text{Sr}(\text{NO}_3)_2$ samples. A rise in the zeta potential recorded from the baseline at an Sr/Al ratio of 0 correlates with an interaction between the Sr^{2+} and the metakaolin particles suspended in the solution; the greater this rise is, the greater the level of interaction. If the zeta potential rises to a point in which it becomes/ gets close to becoming positive, it will reach the isoelectric point at a zeta potential of 0mV, where the electrostatic repulsion between the metakaolin particles in solution is at its lowest which is not beneficial for the dissolution of the metakaolin and consequent reaction to form a geopolymer. Therefore, the significant impact on the heat flow observed in the ICC for the NO_3_5 sample can be attributed to the interactions between the dissolved Sr^{2+} ions with the metakaolin particles.

Likewise, the zeta potential results provide further assurance that the mechanism for the CO_3_5 sample is the filler effect, as the introduction of the salt in any of the Sr/Al ratios here does not cause the zeta potential to rise significantly, and this effect diminishes with increasing pH. When compared to the $\text{Sr}(\text{NO}_3)_2$ samples, the effect is barely noticeable.

The $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ sample results here are interesting; increasing the Sr/Al ratio leads to an increase in the zeta potential in an almost linear manner, especially in the pH 10 results. This increase is not as prominent as can be seen in the NO_3_5 sample, and it is clearly a larger increase than is seen in the SrCO_3 samples. This suggests that, despite the similarity between the ICC results of the CO_3_5 and OH_5 samples, the mechanisms for this change are not the same. For samples containing $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, the mechanism for the change in the reaction kinetics is a combination of the filler effect of the undissolved salt, and the effect of the adsorption of the dissolved Sr^{2+} ions to the surface of the metakaolin, which is responsible for the slight retardation of the reaction as the dissolution of the metakaolin is slowed.

The SrSO_4 containing samples lead to an increase in the recorded zeta potential at pH 10, and the curve shape is similar to that of the $\text{Sr}(\text{NO}_3)_2$ samples, suggesting that the maximum effect is almost reached after the addition of the salt in the sample with an Sr/Al ratio of 0.025. However, the values of zeta potential for the SrSO_4 samples are more negative than the corresponding SrNO_3 containing samples, and so the effect on the dissolution of metakaolin is lesser. As the pH increases into a more alkaline environment, the effect on the zeta potential decreases in the SrSO_4 containing samples, whereas this is not the case in the $\text{Sr}(\text{NO}_3)_2$ samples. This variance could partially explain the difference seen in the ICC between the SO_4_5 and NO_3_5 samples, as the SO_4_5 sample experiences a slowed dissolution of the metakaolin, but not to the same extent that the NO_3_5 sample is slowed. However, it is clear that this is not the only mechanism acting within the SO_4_5 sample, as the recorded zeta potential for the OH_5 sample is closer to 0 at both pH 10 and 12 than the SO_4_5 sample, but displays less of a variation from the KGP control sample in the ICC.

The XRD patterns for the samples with an Sr/Al ratio of 0.125 after 28 days are displayed in Figure 4-104.

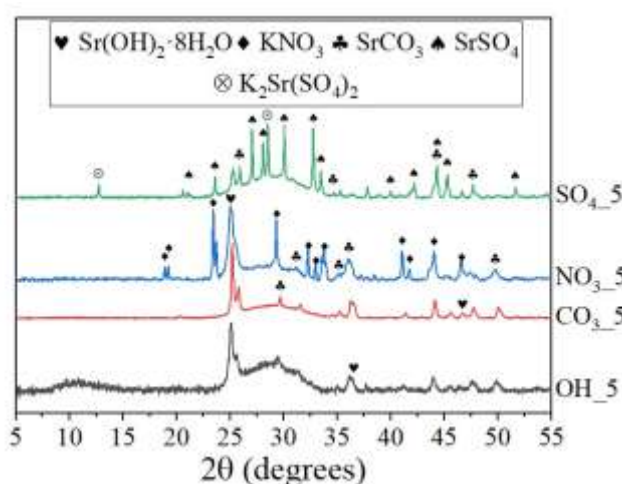


Figure 4-104: The X-ray diffraction patterns after 28 days of reaction of the geopolymers containing $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, SrCO_3 , $\text{Sr}(\text{NO}_3)_2$ and SrSO_4 . Only relevant crystalline phases (initial salts plus reaction products between the salts and the activating solution) have been annotated here.

As can be seen, in both the NO_3_5 and SO_4_5 samples, the Sr salt has reacted with a component of the activating solution; in the NO_3_5 sample, the dissolved NO_3^- anions reacts with the K^+ cations to form KNO_3 , and in the SO_4_5 sample, the SrSO_4 salt reacts with the K^+ cations to form $\text{K}_2\text{Sr}(\text{SO}_4)_2$. Both of these phases are crystalline and precipitate out of solution. The precipitation of these solids provides a physical barrier between the activating solution and the metakaolin, preventing the solution from migrating around the metakaolin to cause dissolution. This phenomenon, accompanied by the subsequent adsorption of the remaining Sr^{2+} cations in solution to the surface of the metakaolin particles, leads to the large retardation of the geopolymer formation reaction seen in these two samples, that is not seen in the CO_3_5 and OH_5 samples.

From these findings, the impact of each of these mechanisms on the heat of reaction seen in the ICC can be described separately: a) The filler effect does not affect the time of maximum heat evolution, only reducing the value of the maximum heat flow, b) The Sr^{2+} adsorbing to the surface of the metakaolin both reduces the value of the maximum heat flow and retards the reaction in a relationship where these extents are greater as the solubility of the Sr salt increases, c) The reaction of the Sr salt with the activating solution leads to mainly to a reduction in the maximum recorded heat flow, however, this may also be responsible for some retardation of the reaction. The mechanisms for the alteration of the reaction kinetics discussed here caused by the different Sr salts are shown in Table 4-10.

Table 4-10: A summary of the effects of the Sr salts on the reaction kinetics of the geopolymer and the mechanisms responsible.

Salt	Retards the reaction?	Reduces maximum heat flow?	Mechanism
$\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	✓	✓	Filler effect + adsorbs to the surface of the metakaolin
SrCO_3	X	✓	Filler effect
$\text{Sr}(\text{NO}_3)_2$	✓	✓	Adsorbs to the surface of the metakaolin + reaction with the activating solution
SrSO_4	✓	✓	Filler effect + reaction with the activating solution + adsorbs to the surface of the metakaolin

4.2.5.3 Hardened State

The FTIR spectra of the samples after 28 days can be seen in Figure 4-105.

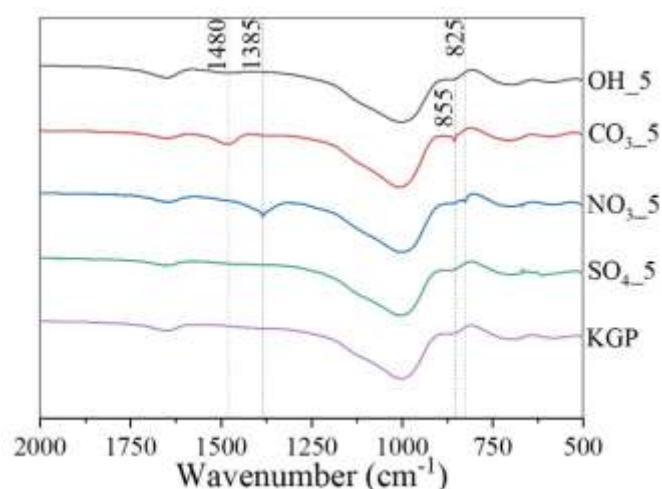


Figure 4-105: The FTIR spectra generated by the OH_5, CO₃_5, NO₃_5, SO₄_5 and KGP samples after the first 28 days of reaction.

The gel structure, for the most part, remains constant across the samples. All of the samples exhibit the Si-O-T peak at 1000 cm⁻¹ that is associated with the K-A-S-H gel, and the only significant difference is attributed to the Sr salts remaining as solids within the samples, or any solid phases that may be formed via a reaction of the salt with the activating solution. All of the samples contain chemically bound water, as shown by the peak at ~1600 cm⁻¹ [253, 328]. The FTIR as a whole confirms that all samples are of a similar composition, suggesting that the addition of the salts does not have a significant effect on the K-A-S-H gel.

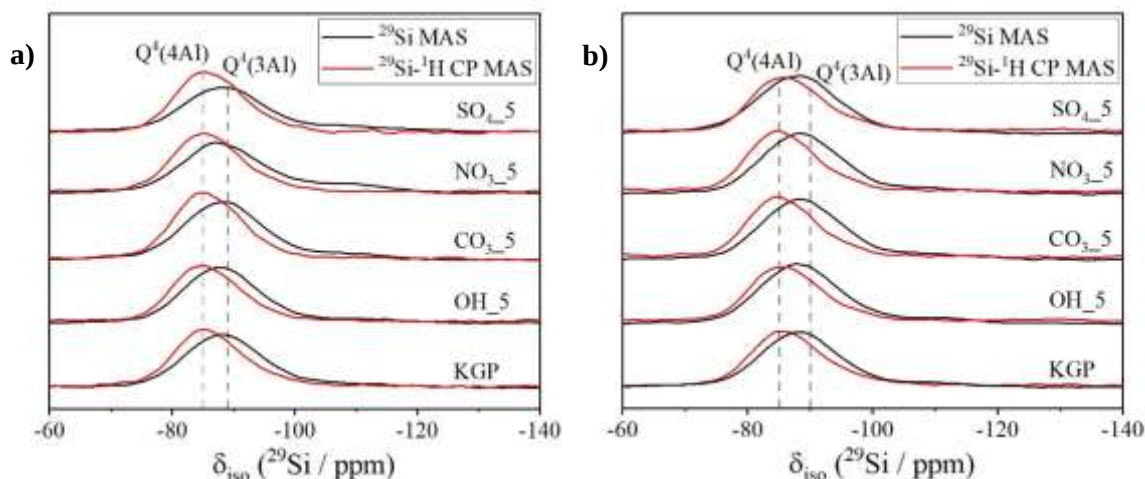


Figure 4-106: ²⁹Si-¹H CP MAS and ²⁹Si MAS NMR spectra for the OH_5, CO₃_5, NO₃_5, SO₄_5 and KGP samples after the first a) 3 and b) 28 days of reaction.

Comparing the ²⁹Si-¹H CP MAS and ²⁹Si MAS NMR spectra for all of the samples after 3 and 28-days seen in Figure 4-106, it can be seen that there is very little difference in the local Si chemical environments between the samples. All of the samples demonstrate that a geopolymer has been formed, with Q⁴(4Al) and Q⁴(3Al) Si sites dominating. From Figure 4-106, the NO₃_5 sample contains the most

unreacted metakaolin, denoted by the area between the red and black curves between δ_{iso} of 100 and 120 ppm. This directly relates to the extents of reaction of the samples shown in Table 4-11.

Table 4-11: The extent of reaction of each sample both a) 3 and b) 28 days after initial reaction, calculated using the corresponding ^{29}Si MAS NMR spectra.

	Sample	Time point	Extent of reaction (%)
a)	KGP	3 Days	82.17
	OH_5	3 Days	87.28
	CO ₃ _5	3 Days	80.73
	NO ₃ _5	3 Days	73.32
	SO ₄ _5	3 Days	84.40
b)	KGP	28 Days	88.00
	OH_5	28 Days	87.44
	CO ₃ _5	28 Days	83.01
	NO ₃ _5	28 Days	77.73
	SO ₄ _5	28 Days	86.61

The extents of reaction, as calculated by the ^{29}Si MAS NMR deconvolutions, show that all of the samples continue to react between the 3 and 28-day mark. After 28 days of reaction, the KGP control sample has the least remaining unreacted metakaolin, but all of the samples have undergone a significant amount of reaction. The NO₃_5 sample has undergone the least amount of reaction after both 3 and 28-days, most likely due to the significant change seen in the ICC caused by the adsorption of the Sr^{2+} to the surface of the metakaolin.

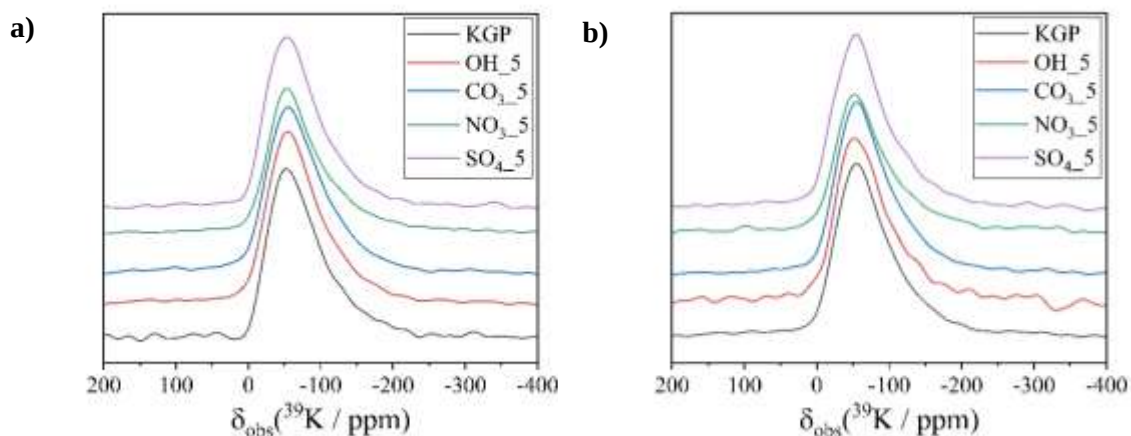


Figure 4-107: ^{39}K MAS NMR spectra for the OH_5, CO₃_5, NO₃_5, SO₄_5 and KGP samples after the first a) 3 and b) 28 days of reaction.

The ^{39}K MAS NMR spectra seen in Figure 4-107 shows that the chemical environment surrounding the K within the system does not vary across the majority of the samples at both time points seen here and the line shape and full width at half maximum (FWHM) of all of the peaks are generally consistent across all samples. This suggests that the addition of the salts does not alter the local structure surrounding K, or the role of K as the charge balancing cation within the K-A-S-H gel. However, for the SO₄_5 and NO₃_5 samples, this does not agree with the result of the XRD and EPMA, which suggest that there are other K-rich phases present, such as K₂SO₄ and KNO₃. It would be expected that these would alter the spectra seen for these samples in comparison to the KGP control. A slight change is seen in the OH_5 and NO₃_5 sample after 28 days of reaction, with the peak centre shifting to a more positive δ_{obs} compared to the KGP control, a change of around 5% related to the FWHM. With the change also occurring in the OH_5 sample, it suggests that there is the potential for the K to have been displaced from some of the charge balancing sites that it occupies in favour of Sr²⁺ cations, as suggested by the Sr solid-state NMR in Section 4.2.1.2.3.4. Into which phase the K transitions during this process is not clear.

4.3 Implications of This Work

Despite the relatively high concentration of Sr (which is used as an analogue for ^{90}Sr) in all salts used in this work when compared to industrial standards, the changes in the local environments surrounding the Al and Si in the K-A-S-H gel are minimal, if present at all. This suggests that the chemical and physical properties of the geopolymer, most notably the durability and ion sorption properties, are unlikely to be adversely affected by the incorporation of these salts, enforcing the case that they are excellent candidates for use as wasteforms for the safe disposal of ^{90}Sr containing wastes. This work also suggests that higher waste loadings can be achieved in the wasteform through the use of geopolymers, without negatively impacting the structural integrity of the monolith.

Furthermore, the fresh state work shown here suggests that the Sr salts that are being termed as waste can actually prolong the reaction to form the geopolymer in the early stages of reaction. This is potentially industrially advantageous; as not only does this allow the ‘waste’ to act as a key player in the reaction process, it reduces the need for further additives such as superplasticisers to perform this job, reducing the working costs of the process. The inclusion of some of the Sr salts also significantly lowers the heat of reaction seen within the geopolymers, allowing the geopolymer systems to contain further elements that may be ideal for inclusion in this waste form, but are more sensitive to higher temperatures.

4.4 Future Work

To add to this work, the impact on the addition of the salts on the dissolution peaks in the isothermal conduction calorimetry would be very beneficial. Considering that it is postulated that the addition of the salts dramatically changes the dissolution of the metakaolin, seeing the change between samples of this peak would allow this to be confirmed directly.

An investigation into the effect of adding the salts at much lower weight percentages would also be beneficial to mimic what would be seen if these formulations were realistically used in industry. Likewise, investigating the effect of using much higher waste loadings would give the maximum use case that these systems could reach. This would be useful if, for example, waste sludges of unknown composition were to be incorporated into a geopolymer sample.

Exploring the effects of the inclusion of Sr salts on the physicomaterial properties of the geopolymer would provide further information on the bulk structural changes seen upon the incorporation of the salts. For example, utilising compression strength testing to check whether the strength of the geopolymer is affected by the addition of the salts. Do the crystalline phases seen, such as the KNO_3 in the NO_3 samples, disrupt the amorphous K-A-S-H gel and create a mechanically weaker wasteform? Although the strength of the wasteform is not the primary concern for nuclear wasteforms, they must still meet a minimum requirement and so showing that this is possible with the formulations used in this work would add to the geopolymers use case [298].

The Si/Al ratio of the systems use in this work lead to a relatively low pH, and are on the upper end of the formation envelope that the UK National Nuclear Laboratory (NNL) and Sellafield Ltd are working within. Therefore, an investigation into the performance of these systems with a lower Si/Al ratio may result in a significant change to the results, as the higher pH may lead to a faster and more complete initial dissolution of the metakaolin. This could make the effects of adding the Sr salts less prominent and improve the use case for these materials.

This work focuses entirely on the early stage kinetics and mechanisms of the geopolymers loaded with Sr salts but, to justify the use of these materials as encapsulants for radioactive waste, the long term

ability of the geopolymers to contain the waste and resist leaching must be considered. Therefore, leaching tests on aged geopolymers should be performed.

The effect of temperature on the geopolymers will be paramount when considering the change in temperature that any wasteform containing radioactive Sr waste will undergo throughout its lifetime in a geological disposal facility [329]. It is projected that temperatures could rise to 80°C, and so the stability of these materials at this temperature will be important.

Finally, the effect of adding multiple salts of strontium into a sample simultaneously will further support the use case for geopolymers encapsulating waste sludges.

5 Chapter 5: The Effect of Caesium Salts on the Kinetics and Mechanisms of Geopolymer Cement Formation

5.1 Introduction

As the global push for a greener and more environmentally friendly energy portfolio continues to gain traction, nuclear fission becomes an ever-present feature in many countries plans [330]. With the expected increase in fission using the current generation of reactors comes the consequent increase in the volume of produced radioactive waste [331]. Caesium-137 (^{137}Cs) is a product of the fission of uranium-235 (^{235}U) which is present in radioactive waste at relatively high percentages of ~6% by mass [332]. The electropositivity of ^{137}Cs leads to it readily reacting with water, which results in a waste stream that can be difficult to contain and process [43]. This property means it is commonly found in cooling pond water, and also within the complex legacy waste deposits found at Sellafield and Fukushima Daiichi as examples. It is important to find a safe and effective solution for the disposal of waste streams containing ^{137}Cs for its eventual final storage in a geological disposal facility (GDF) which will meet the long term disposal and storage strategy implemented by the UK [45].

The half-life of ^{137}Cs is 30.17 years, meaning that it will continue to pose a threat to the environment for over 300 years after its formation as a fission product [36]. This timeframe, plus the advantages of a low cost, low temperature but high maturity disposal route, means that cementitious materials are ideal for use as a wasteform for the disposal of ^{137}Cs [62, 113, 333]. The traditional route for cementation is through the use of Portland cement (PC), but this material is reported to simply entomb the waste within the pore structure as opposed to chemically binding the waste to the binding calcium silicate hydrate (C-S-H) phase [334]. However, some studies show that small amounts of Cs are capable of being substituted into the structure of the C-S-H phase [102]. This uncertainty only further necessitates the need for further research into more novel cementitious materials. On top of this, the high CO_2 emissions associated with the production of PC - 8% of anthropological CO_2 emissions globally - is a further issue which is becoming more prominent in the current climate, and is viewed as increasingly important in the nuclear sector [116, 335]. Due to these issues, research into alternative cementitious materials is vital to develop a sustainable, high-performance material for the safe and effective containment of ^{137}Cs -bearing wastes.

Geopolymer cements are a highly cross-linked, structurally disordered aluminosilicate material containing a network of bridging Al-O-Si bonds between tetrahedral Si and Al groups. These materials have the capability to chemically bind the waste into its structure through the presence of cation binding sites introduced by the net negative charge of the AlO_4^- tetrahedra. It is these sites that allow for the uptake of positively charged cations such as Cs^+ via ion exchange reactions [96, 97, 199]. This potential to chemically bind the radionuclides, coupled with the impressive chemical and thermal stability of the

geopolymers, has led to a progressive effort to learn more about their ability to act as a wasteform for radioactive waste disposal [77, 287, 336].

Commonly, sodium and potassium have been utilized as the alkali metals to balance the net negative charge of the geopolymer gels. The inclusion of these metals results in the formation of the primary binding phase of a sodium, or potassium, aluminosilicate hydrate phase, commonly abbreviated to (Na,K)-A-S-H. Geopolymers behave similarly to zeolites over short distances, hence they are termed as pseudo-zeolitic, but differ to zeolites over long distances, comprising of a structure that is entirely X-ray amorphous [123, 133]. Geopolymers comprise of Si and Al in tetrahedral co-ordination, with the chemical environment of Si being described using $Q^n(mAl)$ nomenclature (where n is the number of other bonded tetrahedral units via oxygen bridges, of which m is the number of these units that are Al tetrahedra), most commonly $Q^4(mAl)$ and Al existing most commonly in the $q^4(4Si)$ coordination. The negative charge that is introduced by each Al tetrahedra (arising from Al^{3+} in four-fold coordination) is charge-balanced by the presence of alkali metal cations.

Previous work has focused on the interaction between sodium silicate-activated geopolymers and strontium containing wasteforms yet, potassium silicate-activated geopolymers have been shown to possess more preferential flow characteristics and rheological properties than an equivalent sodium activated geopolymer formulation [287-289].

The setting period of the geopolymer is of paramount importance for its use as a wasteform for the disposal of radioactive waste. The maintained fluidity of the material dictates its ability to navigate tortuous pathways within complex waste types, and this property is a direct result of the kinetics of the initial reaction period [290, 291]. This reaction can be impacted by a number of factors, be it the inclusion of further chemicals or even the order at which the components of the reaction mixture are mixed in: the literature displays varying observations about the speed of the reaction between the solid precursor (most commonly metakaolin or fly ash) and the aqueous activating solution constituents to form the aluminosilicate gel, and an understanding of the role of each constituent and its point of addition carries both scientific and industrial importance [337, 338].

The binding capacity of the geopolymer gel comes as direct result of the reaction pathways that form the main binding phase of the material, the K-A-S-H gel in a potassium activated geopolymer. To evaluate the suitability of these materials for the safe disposal of radioactive waste streams, an in depth understanding of the fundamental chemical reactions must be achieved, ranging from the dissolution of the solid precursor, through the initial reaction to form the aluminosilicate gel and as far as the reordering and transformation of the gel into a more thermodynamically stable coordination [128, 129, 339]. Furthermore, the dissolution, and consequent reaction, of the geopolymer can be altered by the order and time at which the reactants and any waste streams are added to the geopolymer mix. An understanding of when to add each constituent to maximize the chemical immobilisation of the

radionuclide is essential to develop a robust wasteform that will perform over the required period of time.

The results shown here will focus on the impact of adding salts of non-radioactive isotopes of caesium (Cs) into the geopolymer reaction mixture on the kinetics and mechanisms of the initial reaction alongside the formation of the K-A-S-H gel. The chemical environments created by the introduction of CsOH, Cs₂CO₃, CsNO₃ and Cs₂SO₄ to the geopolymer reaction mixture simulate the potential interactions observed when complex waste streams resulting from e.g. cooling water, radioactive sludge/slurries, spent-ion exchange materials, etc., containing Cs are encapsulated/immobilised within a geopolymer wasteform. Isothermal conduction calorimetry (ICC) is used to monitor the heat evolution of the system, and zeta potential measurements are taken to determine the electrokinetic potential on the surface of the solid reactant particles, which can help to reveal the reaction mechanisms of any changes to the heat evolution. Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction are coupled with solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy probing the local environments of ²⁷Al, ²⁹Si, ³⁹K and ¹³³Cs are used to observe the any nanostructural changes caused by the presence of the Cs salts. The findings of this work provide an important overview of the early stage reactions within the geopolymer wasteforms, and suggest that these materials are suitable for the long-term immobilisation of radioactive waste streams containing ¹³⁷Cs.

5.2 Results and Discussion

5.2.1 Caesium Hydroxide

5.2.1.1 Fresh State

5.2.1.1.1 ICC

Figure 5-1 displays the calorimetry curves produced by the formation of the K-geopolymers loaded with CsOH over the first 3 days of reaction.

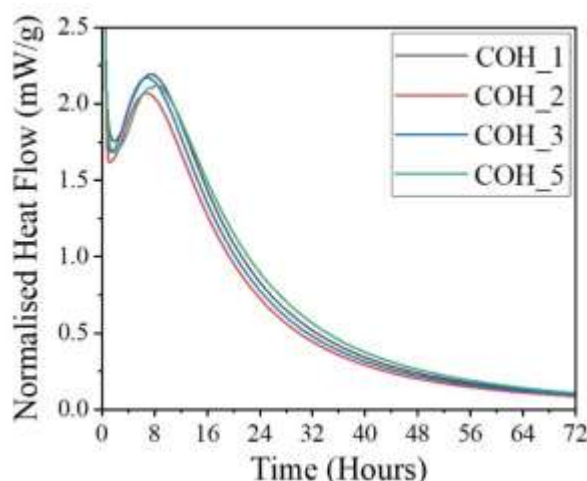


Figure 5-1: The effect on the heat evolution of reaction of loading K-activated metakaolin geopolymers with CsOH over first 24 hours of reaction.

Due to the data collection of the KGP control sample, shown in Figure 3-1, and the CsOH containing samples being carried out at differing times, the normalised heat flow per gram of sample cannot be directly numerically compared due to slight differences in the reaction conditions. As can be seen when comparing the figures, it is possible to compare the lineshapes of the KGP sample and the COH samples, with each having a ‘dormant’ period between the initial dissolution and the reaction peak, and each sample having a comparable width of reaction peak and decrease in the heat flow towards 0mW/g. A possible reason for this is the treatment of the reagents prior to mixing; the reagents were not stored at 20°C, meaning that seasonal changes will impact the results achieved. As the KGP Control sample was recorded during the summer months compared to the winter months in which the Cs samples were recorded, it is most likely that the differences observed in the maximum recorded heat flow value are due to the temperature of both the reagents and the ampoule at the time that they were submitted into the machine.

Figure 5-1 suggests that the addition of the CsOH to the samples with Cs/Al ratios of between 0.02 and 0.10 has a minimal effect on the heat released during the reaction. There is a small deviation between the maximum observed heat flows for each of the samples, although it could be argued that this difference is within an acceptable range. This is supported by the lack of pattern displayed by the results,

with COH_2 exhibiting the greatest deviation from COH_1, shown more clearly in Figure 5-2 which would not be expected if the addition of CsOH had an increasing effect with increasing Cs/Al ratio.

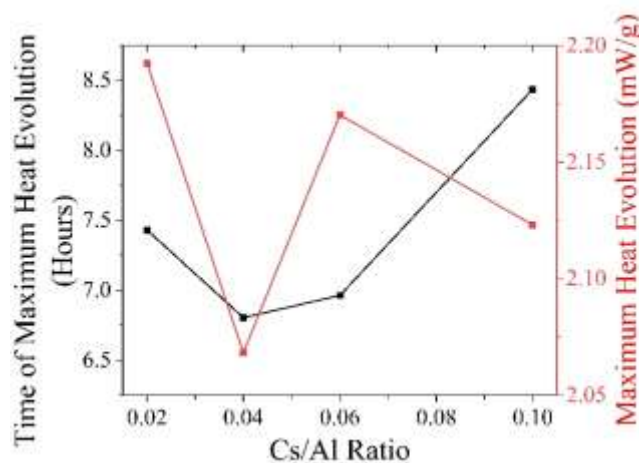


Figure 5-2: The relationship between Cs/Al ratio and the observed time of maximum heat evolution and the value of the maximum heat evolution.

Figure 5-2 shows that there is no discernible pattern between Cs/Al ratio and the time and value of the maximum heat evolution for any of the samples. There are two possible reasons for this; firstly, the Cs is readily incorporated into the geopolymer matrix, and does not have any chemical penalty associated with its incorporation as a charge balancing action, displacing the K^+ cations. On the other hand, the Cs could have no impact at all on the reaction and exist within the solution, simply being encapsulated within the pores of the matrix.

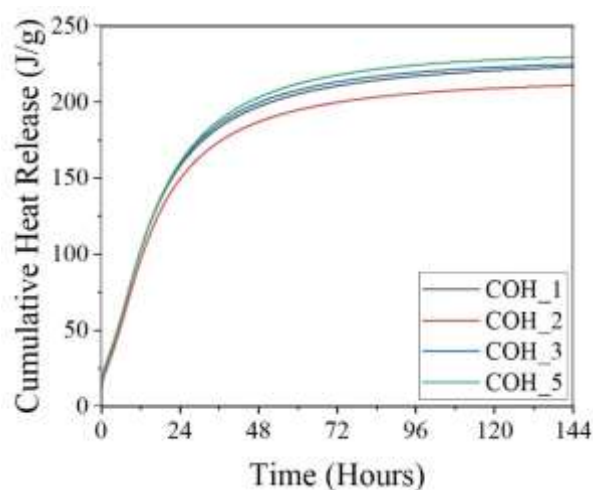


Figure 5-3: The cumulative heat release curves over the first 144 hours of reaction.

Figure 5-3 shows the cumulative heat release of the COH systems over the first 6 days of reaction. The cumulative heat release is representative of the heat released during the entirety of the reaction. This includes the dissolution of the metakaolin throughout the reaction, disregarding the heat released during the mixing of the geopolymer outside of the calorimeter, plus the thermal release due to the polymerisation reaction of the geopolymer systems. The heat release after 144 hours is equivalent to approximately 2/3 of the total heat release of the system for PC, and this can be assumed to be the same

for geopolymer systems [297]. Both geopolymer and PC systems undergo the majority of their reaction in the first few days after the initial mixing of the reactants. Heat release after the first week in both systems is mainly down to the reorganisation of the phases into more ordered and thermodynamically favourable configurations. Therefore, due to the similarity of the reaction profiles of the two cements, it is valid to assume that the heat release profiles will also be comparable. Using this assumption, the total heat release of the geopolymers mixed with CsOH will be no more than 345 J/g even in the case of the COH_5 sample, which shows the greatest cumulative heat release [297]. This is higher than the average heat release of the current nuclear standard, a Portland cement and GGBS blend, which is around 100 J/g but is within the guideline value of 180 J/g over the first 24 hours of reaction set by the current UK requirements for nuclear wastefoms [298, 299].

5.2.1.1.2 Zeta Potential

The zeta potential values obtained for the surface charge of metakaolin in the presence of CsOH at different pHs is shown in Figure 5-4.

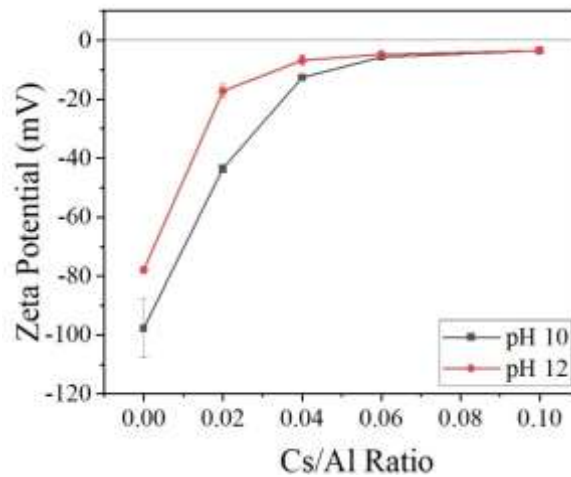


Figure 5-4: Comparing the effect of Cs/Al ratio, altered by the addition of CsOH, on the zeta potential of metakaolin in a KOH solution at pH 10 and 12.

The zeta potential measurements for the metakaolin without the presence of the CsOH, denoted by a Cs/Al ratio of 0 in Figure 5-4, are very negative, $\sim -100\text{mV}$ at pH 10 and $\sim -80\text{mV}$ at pH 12. The tendency for the zeta potential to become more positive as the pH increases disagrees with findings from Derkani et al. which show that the zeta potential becomes more negative between pH 10 and pH 12 [159]. However, the apparatus for the zeta potential measurements in this work are different, and a better comparison can be made with N'Cho et al. who also measured the zeta potential of various metakaolin powders with the Stabino II equipment [340]. The work by N'Cho et al. shows that the zeta potential value at a pH of 10 can actually be more negative than at pH 12 depending on the chemical composition of the metakaolin [340]. There are slight differences between the work of N'Cho et al. and this work, such as their use of NaOH as opposed to KOH, but it gives confidence in the zeta potential results seen here.

The addition of CsOH in any capacity at both pHs leads to an increase in the recorded zeta potential values, as shown by Figure 5-4. The increase in the pH towards 0 reaches a maximum value of -3.5mV at a Cs/Al ratio of 0.1 but begins to plateau at a much lower Cs/Al ratio than this at around 0.04. The plateau is reached at a lower Cs/Al ratio at the higher pH, suggesting that there is greater dissolution of the salt at higher pH.

The effect of K^+ ions introduced into the solution by the KOH could potentially effect the recorded zeta potential of the metakaolin particles. Both K^+ and Cs^+ are monovalent cations and are likely to have similar effects on the surface charge of the metakaolin. However, the concentration of K^+ ions is not altered between the experiments at on pH and, on that note, is only altered by the change in pH. Therefore, any change in zeta potential seen here is attributed solely to the introduction of the CsOH and no the presence of K^+ ions.

The mechanism for the increase in zeta potential is unknown, however, it is posed that the shift in surface charge towards neutral promotes the agglomeration of the metakaolin particles in solution [300, 301]. This agglomeration results in a reduction to the total surface area of metakaolin available and, therefore, a reduction in the dissolution rate via the alkali solution attack. Another potential mechanism for the reduced dissolution rate is the formation of a layer of Cs^+ particles on the surface of the metakaolin, producing a physical barrier that lowers the concentration gradient between the metakaolin and the surrounding solution. This mechanism is inspired by the dissolution of glass, as outlined in Frugier et al. [302]. Although the materials are different, the concept of a physical barrier to dissolution fits the work seen here, as the Cs^+ ions are drawn to the negatively charged surface of the metakaolin. In reality, it could be either one of these mechanisms, or a combination of both, that leads to the change in the zeta potential seen here. Interestingly, this change in the zeta potential does not appear to have a significant effect on the ICC seen in Section 5.2.1.1.1, although the zeta potential for the CsOH containing samples at high pH shows very little variance and, with no direct numerical comparison to the KGP control sample, it is not possible to see if there is a difference between a Cs/Al ratio of 0 and 0.02-0.1.

5.2.1.1.3 Order-of-addition Experiments

In order to determine whether the point at which the Cs salt is added to the mix impacts the performance of the geopolymer, order-of-addition experiments were performed as outlined in Section 2.1.1.2.

5.2.1.1.3.1 Order-of-Addition #1

1. The CsOH dissolves in the water leaving a clear solution.
2. The addition of the KOH leads to a release of heat due to the exothermic nature of the KOH dissolution. The KOH dissolves and the solution remains clear.
3. The silicate mixes with the solution and the solution remains clear.
4. The addition of the metakaolin lead to the formation of a geopolymer.

5.2.1.1.3.2 Order-of-Addition #2

5. The addition of solid KOH to water leads to an exothermic dissolution reaction.
6. The CsOH dissolves in the KOH solution, which remains clear.
7. The silicate mixes with the solution and the solution remains clear.
8. The addition of the metakaolin lead to the formation of a geopolymer.

5.2.1.1.3.3 Order-of-Addition #3

1. The addition of solid KOH to water leads to an exothermic dissolution reaction.
2. The addition of the K-silicate stock solution to the KOH solution resulted in a clear liquid mix.
3. The CsOH dissolves in the silicate solution, which remains clear.
4. The addition of the metakaolin lead to the formation of a geopolymer.

5.2.1.1.3.4 Order-of-Addition ICC

Figure 5-5 shows the calorimetry curves generated by the order-of-addition samples over the first 3 days of reaction.

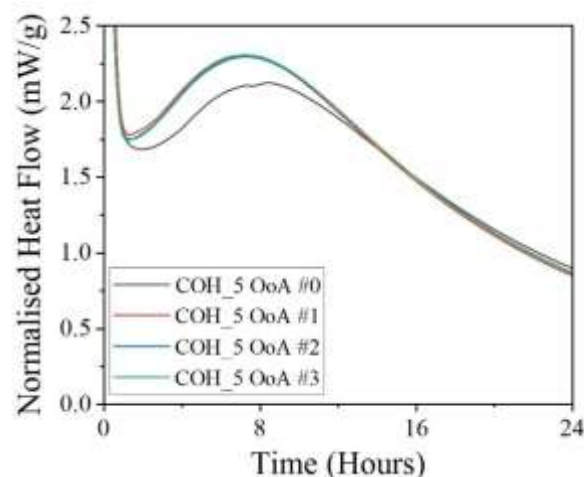


Figure 5-5: The effect on the heat evolution of the reaction of adding CsOH at different stages to K-activated metakaolin geopolymers over the first 3 days.

There is no observable difference between the heat evolution of order-of-addition samples #1-3. This shows that adding the salt to the aqueous phase of the mix at any point does not make a considerable difference, as the salt dissolves into its constituent ions almost immediately. Therefore, the systems are chemically identical and react with the metakaolin in the exact same manner. However, if the CsOH is added to the solid phase prior to mixing, as is shown in order-of-addition #0, the mixing profile changes, leading to a reduced release of heat and slight retardation of the reaction. This could be due to the fact that it is no longer just the metakaolin dissolving within the activating solution but the CsOH as well. This could reduce the rate of dissolution of both the solids due to the ‘wetting’ of the solution on the surface of the solids, potentially reducing the volume of liquid available for metakaolin dissolution and retarding the reaction.

However, it is also possible that the time of mixing has an effect on the heat evolution curves seen in Figure 5-5, as order-of-addition #0 was mixed at a different time and date to the other order-of-addition experiments. This may explain why the curve for this sample is different to the others when it could be argued that it would be expected that all the samples would be the same due to the high solubility of the CsOH salt.

5.2.1.1.3.5 Order-of-Addition Conclusions

The high solubility of the CsOH salt means that introducing it into the aqueous activating solution at any stage results in almost immediate dissolution. As the Cs^+ and OH^- ions do not react with any of the other constituents of the activating solution, this results in a chemically identical mixture for order-of-addition experiments #1-3. When adding the salt to the solid metakaolin prior to mixing, the reaction is retarded and the ICC suggests that the extent of reaction may also be affected. Therefore, it is advised that any CsOH containing wasteforms are added to the aqueous phase prior to the mixing of the geopolymer. This is advantageous as, in industrial context, the radioactive waste is usually added to the aqueous phases of the cementitious mix before mixing with the solids. This prevents the need for further radiation protection, as a hopper full of irradiated solids poses a significant safety hazard.

Despite this experiment suggesting that the method used in this work, order-of-addition #0, has the greatest effect on the kinetics of reaction, the information gleaned is important when considering the effect of solids within the bulk wasteform. This method is the most suitable for identifying the effects of dissolved Cs content on the reaction mechanisms and kinetics of the geopolymer samples. Therefore, for all following analysis and discussion, order-of-addition #0 has been used in this work.

5.2.1.1.4 DRIFTS

The DRIFTS spectra for the OH_5 sample in the first 8 hours of reaction can be seen in Figure 5-6.

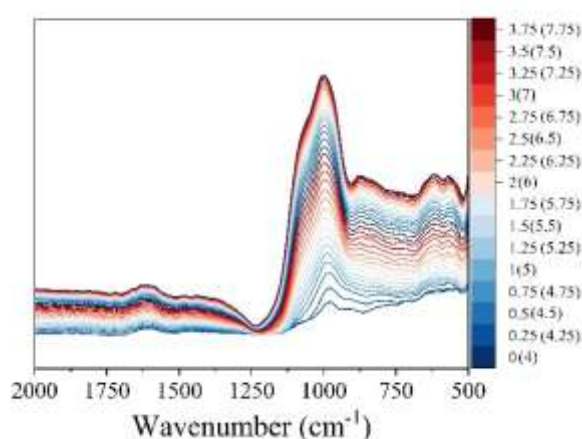


Figure 5-6: DRIFTS spectra for the COH_5 sample in the first 8 hours of reaction. The spectra are displayed in 15 minute intervals, beginning at $t=0$ as marked and progressing through the colour gradient which repeats itself after 4 hours. Times are shown in hours.

Over the first 8 hours of reaction, the peak that is associated most closely with the formation of a geopolymer, the Si-O-T peak centred at $\sim 1000\text{ cm}^{-1}$, grows continuously [253]. This growth commences immediately, suggesting that the reaction to form the geopolymer occurs immediately post dissolution, agreeing with the findings of Duxson et al. in the state-of-the-art review of 2007 [129]. The peak continues to grow at a steady rate over this time suggesting that the reaction has not reached its maximum by the 8-hour mark. This agrees with the trend that is seen in the ICC data (Section 5.2.1.1.1), where the peak of reaction is seen at approximately 8.5 hours. This trend is similar to that seen in the KGP control sample, the spectra of which can be seen in Figure 3-3.

The growth of the Si-O-T peak in the KGP sample is very similar to that seen in the COH_5 sample, which agrees with the postulations made that the introduction of Cs has no impact on the reaction, meaning it is readily incorporated as a charge balancing cation in the K-A-S-H gel or it does not interact with the formation of the gel at all. The main difference between this peak for the two samples is that the KGP sample reaches its peak of reaction slightly sooner than that of the COH_5 sample. In both cases, there does not appear to be significant growth of any other peaks.

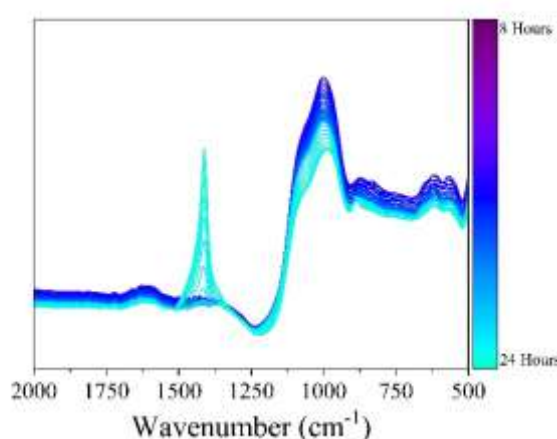


Figure 5-7: DRIFTS spectra for the COH_5 sample from 8 to 24 hours post initial reaction. The spectra are displayed in 15 minute intervals up until the 16-hour mark, at which the time progresses in whole hours, beginning at $t=8$ hours as marked and progressing through the colour gradient. Times are shown in hours.

The spectra for the COH_5 sample for the remainder of the first day of reaction (8 hours to 24 hours) is displayed in Figure 5-7. After the 8-hour mark, the intensity of the Si-O-T peak that is so prominent in the spectra begins to diminish. It is not clear why this happens, as, as previously mentioned, DRIFTS is a relatively new analysis technique for cement. Therefore, further research is required to fully understand the phenomena that is seen. It is most likely that the shrinkage of the cement is responsible for this drop; as the cement begins to harden, it shrinks, changing the distance between the surface of the sample and the detector [269, 270]. This occurs in this situation as the same sample is used throughout the measurement and, during this time, no changes are made to the apparatus and so the

measurement distance does not change. It is unlikely that the peak is shrinking due to a reduction in the mass of the K-A-S-H gel, which is responsible for the peak, as this phase is likely to continue to materialise throughout the first day of reaction. Also, as the cement hardens, the surface of the sample may become quite flat as the reaction to form the geopolymer continues. The geometry of this surface may prevent effective diffuse scattering of the infrared radiation, meaning that there is a distinct drop in the intensity of the received signal [341].

As the reaction reaches its 16th hour, a second peak begins to form at $\sim 1400\text{ cm}^{-1}$ in the spectra, and grows rapidly up until the 24-hour mark. The cause of this peak is likely to be the carbonation of the sample due to reaction with the CO_2 in the air [271]. The infrared beam used for the DRIFTS measurement must pass through the surface of the sample to reach the bulk material. Therefore, artefacts from the surface of the sample, notably the point where carbonation would occur, will always be included in the spectra. Due to this, it is most likely that this peak is a reflection of the carbonation of Sr within the sample. This peak is also visible in the spectra for the KGP sample for the 4 to 24 hour period after initial reaction, as seen in Figure 3-4.

The main difference in this spectra when compared to the COH_5 spectra is that the carbonation peak begins to form slightly earlier in the reaction, at approximately 14 hours post initial mixing. Despite this, the intensity of the peak in the COH_5 sample grows much faster and reaches a greater value by the end of the first 24 hours. Therefore, it could be suggested that the introduction of Cs is an accelerant for the carbonation, because, even though it begins later, the time it takes to carbonate to a similar level as the KGP sample is far lower.

5.2.1.2 Hardened State

5.2.1.2.1 FTIR

Figure 5-8 shows the FTIR spectra of the K-geopolymers loaded with CsOH after the first 3 days of reaction.

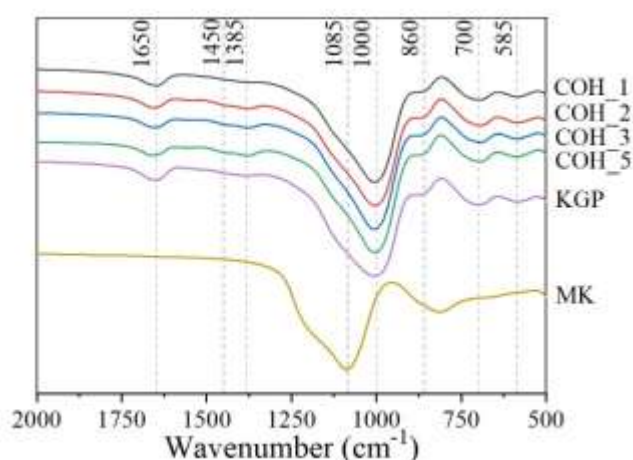


Figure 5-8: The FTIR spectra generated by loading K-activated metakaolin (MK) geopolymers with CsOH, the KGP control sample and the unreacted metakaolin after the first 3 days of reaction.

Figure 5-8 shows that both the KGP and the COH samples have structurally formed geopolymers, fingerprinted by the presence of the peak at 975 cm^{-1} , which is indicative of the asymmetric stretching of Si-O-T bonds within the aluminosilicate framework, where T can be either silicon (Si) or aluminium (Al) atoms in tetrahedral coordination [253]. When compared to the spectra for the metakaolin, the wavenumber for this peak has shifted to lower wavenumbers from the value of 1070 cm^{-1} . This is due to the increased concentration of AlO_4 tetrahedra within the disordered geopolymeric structure [254]. The presence of unreacted metakaolin within the COH samples is presented by the shoulder between $\sim 1050\text{ cm}^{-1}$ and 1150 cm^{-1} , and this becomes more apparent with increasing Cs/Al ratio, suggesting that there is more unreacted metakaolin in COH_5 than COH_3 and so on. The peak seen at 1250 cm^{-1} is also attributed to the asymmetric stretching of Si-O-T bonds. The peak at 860 cm^{-1} is attributed to the asymmetric stretching of the bridging oxygen bonds linking the tetrahedral AlO_4 and SiO_4 groups within the structure [258]. The peak at 690 cm^{-1} has been seen in synthetic geopolymer gels curated by Walkley et al. and is thought to signify the pseudo-lattice vibrations of small aluminosilicate rings [67]. The peak at 1650 cm^{-1} is indicative of both chemically bound and free water within the sample [328]. The peak at 1450 cm^{-1} more noticeably present in the COH samples is attributed to the C-O bond that is present due to the natural carbonation of the samples due to contact with air. The peak at 1385 cm^{-1} is indicative of some remaining CsOH within the matrix. This peak grows as the Cs/Al ratio increases, suggesting that the maximum dissolution of the salt is reached in the samples within the COH_1 sample, disagreeing with the results seen in the order-of-addition experiments where the CsOH dissolved easily in the activating solution.

Table 5-1: The characteristic infrared stretching vibrational bands of metakaolin-based geopolymers, recreated from Onutai, Osugi and Sone (2023) [264].

Wavenumber (cm^{-1})	Bonding
690-700	Asymmetric stretching (Si-O-Si and Al-O-Si)
800-820	Al-O bending vibrations
850-880	Si-O stretching and OH bending (Si-OH)
950-980	Si-O stretching (Si-O-K or Cs)
950-1060	Asymmetric stretching (Si-O-Si and Al-O-Si)
1105-1160	Asymmetric stretching (Si-O-Si)
1200-1250	Asymmetric stretching (Si-O-Si and Al-O-Si)

As previously stated, the increase in the Cs/Al ratio leads to an apparent increase in the amount of unreacted metakaolin. This cannot be properly quantified by this technique, and the ^{29}Si MAS NMR will be useful to verify this. Moreover, this is not clearly supported by the ICC for these samples (Section 5.2.1.1.1) as there is no clear correlation between the extent of reaction, signified by the

normalised heat flow, and the Cs/Al ratio. Other than this small disparity, the spectra appear to be almost identical, suggesting that there is no significant difference in the chemical structure of the geopolymer gels containing CsOH.

When comparing the CsOH containing samples to the control KGP sample, the main observable differences are the lack of carbonation of the KGP sample, and the presence of the peak at 1250 cm^{-1} which indicates the asymmetric stretching of Si-O-T bonds. The lack of carbonation is likely due to the handling of the samples, with the Cs containing samples likely residing in air for a longer time than the KGP control. This is unlikely to be an artefact of the chemical structure itself, as there are no carbon containing raw materials within the geopolymer mix. The introduction of Cs^+ ions into the mix may alter the bonding environments surrounding the Al-O-Si bonds. This is due to the close proximity of the Cs^+ ions which are larger than the K^+ ions. The presence of this peak in the COH samples and not the KGP samples suggests that some of the charge balancing K^+ ions have been displaced by the Cs^+ ions within the gel structure.

The peak at 815 cm^{-1} appears more prominent in the samples with a lower Cs/Al ratio; in COH_1 and COH_2, it is clearly visible but by COH_5, this peak has almost disappeared. Therefore, the inclusion of the CsOH within the samples at lower wt.%'s could lead to a decrease in the Si/Al ratio, suggesting that there are more Al sites available for the Cs^+ ions to displace the K^+ ions as the charge balancing cations within the structure [342].

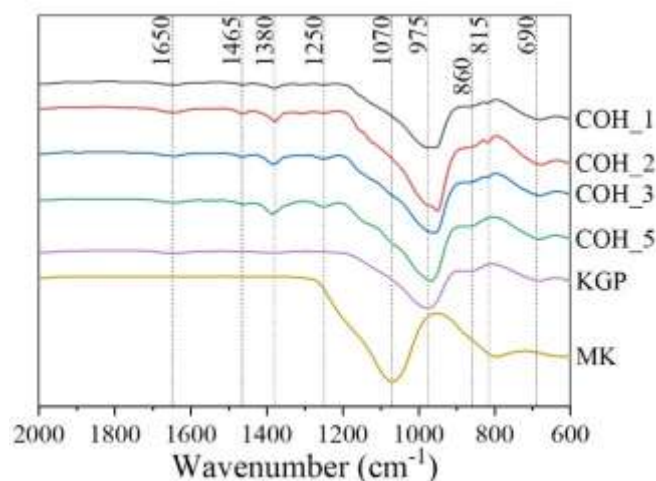


Figure 5-9: The FTIR spectra generated by loading K-activated metakaolin (MK) geopolymers with CsOH, the KGP control sample and the unreacted metakaolin after the first 28 days of reaction.

Figure 5-9 shows that the spectra after 28 days are very similar to those seen after 3 days. This suggests that there is not a huge alteration to the structure of the samples during this time frame, and that the majority of the structure is ordered by the 3-day time point.

5.2.1.2.2 XRD

The x-ray diffraction spectra for the geopolymer samples containing CsOH 3 days after initial reaction are shown in Figure 5-10.

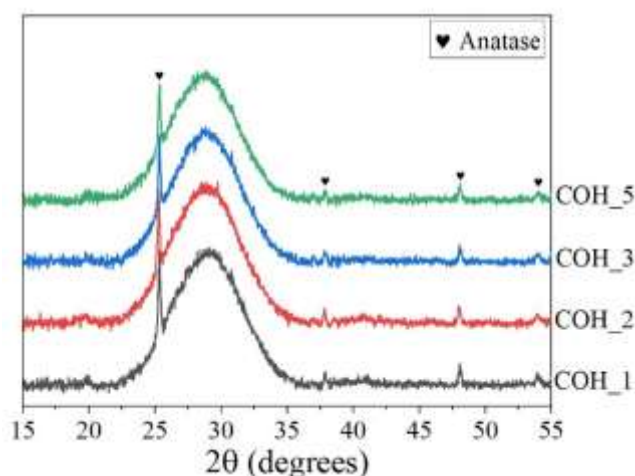


Figure 5-10: The x-ray diffraction spectra generated by loading K-activated metakaolin geopolymers with CsOH after the first 3 days of reaction.

The XRD spectra for all samples after 3 days are almost identical, with a clear absence of crystalline phases within the samples. The only noticeable crystalline phase is that of anatase (TiO₂, Powder Diffraction file (PDF) # 01-086-1157) which is present as an inert phase in the raw, unreacted metakaolin. The anatase does not participate in the reaction to form a geopolymer, and does not dissolve in the activating solution and so, in turn, is present within the samples in its original form after 3 days of reaction.

The broad diffraction peak between $\sim 23^\circ 2\theta$ and $34^\circ 2\theta$ is evidence that a geopolymer has formed, as this peak is attributed to the amorphous K-A-S-H gel [164]. The lack of crystalline phases in the spectra supports the notion that all of the CsOH dissolves within the activating solution. Moreover, there is no evidence that the Cs⁺ that is within solution due to this dissolution reacts with any other ions to form a solid, which agrees with the observations seen in the order-of-addition experiments (Section 5.2.1.1.3). Therefore, it is increasingly possible that the Cs is being incorporated into the K-A-S-H gel in place of the K⁺ ions in the charge balancing sites of the geopolymer.

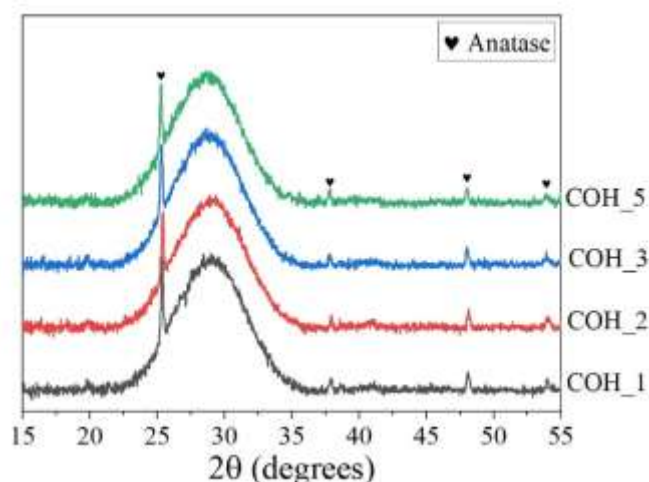


Figure 5-11: The x-ray diffraction spectra generated by loading K-activated metakaolin geopolymers with CsOH after the first 28 days of reaction.

The XRD patterns for the same samples after the first 28 days of reaction are shown in Figure 5-11. Similarly to the samples after 3 days, the only crystalline phase present is that of anatase, and the broad peak for the K-A-S-H gel is still visible as would be expected.

5.2.1.2.3 Nuclear Magnetic Resonance (NMR) Spectroscopy

5.2.1.2.3.1 ^1H - ^{29}Si CP MAS and ^{29}Si MAS NMR

The ^1H - ^{29}Si CP MAS NMR and ^{29}Si MAS NMR spectra for the COH_5 and KGP samples both 3 and 28 days after the initial reaction are displayed in Figure 5-12.

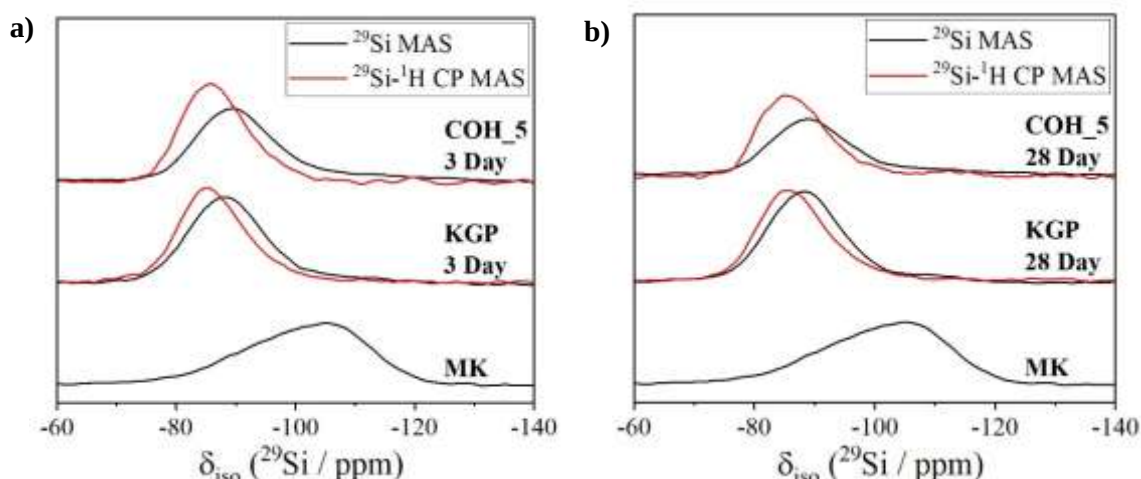


Figure 5-12: ^1H - ^{29}Si CP MAS and ^{29}Si MAS spectra for the COH_5, KGP samples and the unreacted metakaolin a) 3 days and b) 28 days after reaction.

The spectra observed here are similar to those seen in previous work, suggesting that the K-A-S-H gel is formed by a mixture of Si environments in the form of $\text{Q}^4(\text{mAl})$ sites, where $1 \leq m \leq 4$ [67]. The close proximity of hydrogen (H) nuclei to Si atoms within the geopolymer sample is a clear indication that these Si sites are present within the K-A-S-H gel, and are in the hydrated state [273]. This allows the use of ^1H - ^{29}Si CP MAS NMR to distinguish between the Si sites in the sample that are present due

to unreacted metakaolin within the sample through the preferential enhancement of the resonances of Si atoms in the hydrated state [273]. The ^1H - ^{29}Si CP MAS NMR spectra, shown in red in Figure 5-12, exhibit a single broad peak between $\sim \delta_{\text{iso}} = -75$ and $\delta_{\text{iso}} = -110$ ppm. The peak centre is at higher wavenumbers when compared to the ^{29}Si MAS NMR spectra, and this is due to the ^1H - ^{29}Si CP MAS NMR disregarding the Si sites due to metakaolin, which occur at lower wavenumbers.

The ^{29}Si MAS NMR spectra is impacted by all of the Si sites present within the sample, which means that any sites due to metakaolin are also shown here; The most prominent Si site that is present within the metakaolin but not the K-A-S-H gel is the $\text{Q}^4(0\text{Al})$ site. This results in the maximum peak intensity being recorded at the lower δ_{iso} of approximately $\delta_{\text{iso}} = -88/89$ ppm. It would be expected that the greater the mass of unreacted metakaolin, the further the peak would move to a lower δ_{iso} value. This is most notable when comparing the 3 day COH_5 and 28 day COH_5 samples, with the former containing more metakaolin and peaking at $\delta_{\text{iso}} = -89$ ppm as opposed to -89.5 ppm. The extents of reaction, in terms of percentage, can be seen in Table 5-2.

Table 5-2: The extent of reaction of the COH_5 and KGP samples both 3 and 28 days after initial reaction, calculated using the ^{29}Si MAS NMR spectra.

Sample	Time point	Extent of reaction (%)
KGP	3 Days	82.17
COH_5	3 Days	83.68
KGP	28 Days	88.00
COH_5	28 Days	88.64

The extent of reaction is calculated by subtracting the total percentage of silicon sites present due to the unreacted metakaolin, shown in light pink in Figure 5-13, from 100%. Figure 5-13 shows the deconvolution of the NMR spectra for the COH_5 samples. For the KGP samples, the ^{29}Si MAS NMR spectra in Figure 3-6 show that the gel structure is dominated by $\text{Q}^4(3\text{Al})$ sites, which agrees with data reported in the literature for potassium activated geopolymers [172]. Table 5-3 shows the relative integral areas of the Si sites within the samples, essentially displaying the percentage of each Si site within the K-A-S-H gel according to the deconvolution model.

Table 5-3: Relative integral areas for the Si sites present within the K-A-S-H gel of each sample both 3 and 28 days after initial reaction from the deconvoluted ^{29}Si MAS NMR spectra. The $\text{Q}^4(0\text{Al})$ site attributed to the unreacted metakaolin is disregarded for the quantification of the K-A-S-H gel.

Sample	Time point	Relative Integral Area (%)				Si/Al
		$\text{Q}^4(4\text{Al})$	$\text{Q}^4(3\text{Al})$	$\text{Q}^4(2\text{Al})$	$\text{Q}^4(1\text{Al})$	
KGP	3 Days	25	54	20	1	1.32
COH_5	3 Days	20	52	25	3	1.38
KGP	28 Days	28	44	26	2	1.34
COH_5	28 Days	25	50	22	3	1.38

The COH_5 sample is also mainly comprised of $\text{Q}^4(3\text{Al})$ sites, but there is a distinct change in the quantity of $\text{Q}^4(2\text{Al})$ sites from 3 to 28 days, as they decrease in favour of the formation of $\text{Q}^4(4\text{Al})$ sites. This agrees with the reaction pathway though to lead to the formation of the geopolymer gel, where the geopolymer continues to reorganise and restructure over time to form a more cross-linked and thermodynamically stable structure [129, 137, 343]. Table 5-3 also shows the molar Si/Al ratio of the K-A-S-H gel, disregarding the Si sites that are attributed to the unreacted metakaolin. This ratio is calculated using Engelhardt's formula (Equation 3-1) [276].

The Si/Al ratio of the COH_5 sample after 3 days is greater than that of the KGP sample, at 1.38. This suggests that the introduction of CsOH into the mix leads to a slight decrease in the concentration of Al sites within the gel matrix compared to the KGP sample; This subsequently reduces the cation binding capacity of the gel, as this property is directly proportional to the number of Al sites within the system [279]. This is also true for the COH_5 sample after 28 days.

However, the differences seen here in both the extent of reaction change over time, and the composition of silicon sites, as illuminated by the deconvolution of the ^{29}Si MAS NMR spectra, suggest that the formation of the geopolymer gel in the COH_5 sample is very similar to that in the KGP control sample, which is seen in the ICC data. The initial extents of reaction after 3 days are very close, and the increase in this extent over the first 28 days is also comparable, suggesting that a similar level of reaction is occurring regardless of the inclusion of the CsOH. The main difference between these samples is seen in the calculated Si/Al ratio of the gel, which, it should be noted, is lower than the nominal 1.5 value designed for these samples. This suggests that the incorporation of Al into the structure is favoured during the reaction and formation of the K-A-S-H gel. Regardless, the Si/Al ratio of the COH_5 sample is slightly higher than that of the KGP control sample after both 3 and 28 days, suggesting that the introduction of CsOH leads to a slower rate of dissolution and incorporation of the Al from the metakaolin. This is contrary to what is seen in the usual reaction pathway of geopolymer formation, as

Al_2O_3 within the metakaolin dissolves preferentially when compared to the SiO_2 due to Al-O-Al bonds being weaker than Al-O-Si and Si-O-Si bonds [279]. Therefore, through potential reaction of the CsOH with the raw metakaolin, as discussed in Section 5.2.1.1.2, the dissolution of Al may be slowed, resulting in a smaller concentration of free AlO_4^- within the initial aqueous mixture that is available to react with the SiO_4 to form the K-A-S-H gel.

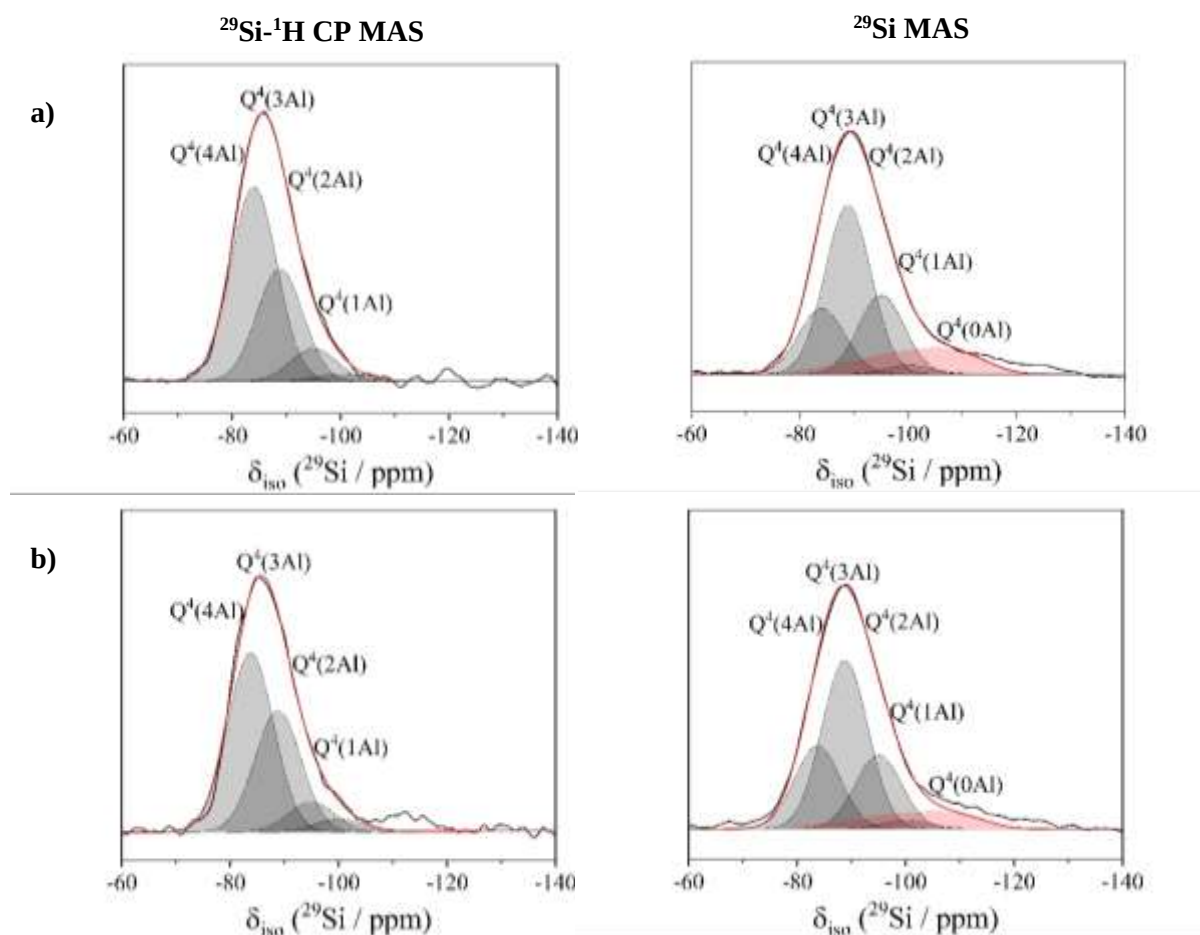


Figure 5-13: $^{29}\text{Si}\text{-}^1\text{H}$ CP MAS and ^{29}Si MAS NMR spectra and the associated deconvolutions for the a) COH_5 sample after 3 days and b) COH_5 sample after 28 days. The $^{29}\text{Si}\text{-}^1\text{H}$ CP MAS NMR data is shown in the left column and the ^{29}Si MAS NMR data is shown in the right column. For each spectrum, the raw data is shown as a solid black line and the model fit is shown as a solid red curve. The deconvolutions that represent each ^{29}Si site within the K-A-S-H gel are depicted as grey curves, whilst the deconvolutions that represent ^{29}Si sites within the unreacted metakaolin are shown in a faded red.

5.2.1.2.3.2 ^{27}Al MAS NMR

The ^{27}Al MAS NMR spectra for the COH_5 and KGP samples both 3 and 28 days after the initial reaction are displayed in Figure 5-14.

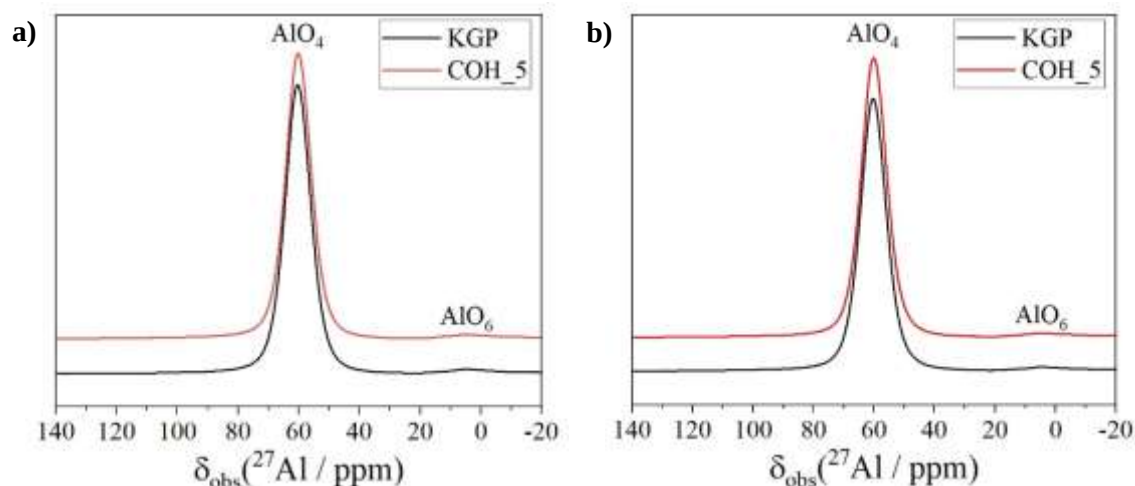


Figure 5-14: ^{27}Al MAS spectra for the COH_5 and KGP samples a) 3 days and b) 28 days after reaction.

Figure 5-14 shows that the ^{27}Al MAS NMR spectra for the KGP and COH_5 samples display two distinct resonances. The intense resonance, centred at $\delta_{\text{obs}}=60.3$ ppm and spanning between $\sim \delta_{\text{obs}}=50$ ppm and $\delta_{\text{obs}}=70$ ppm is recognisable as the tetrahedral Al site (AlO_4^-) found in the K-A-S-H gel phase of the geopolymer [279, 306]. This coordination is promoted by large excess of alkali cations within the aqueous reaction mixture and gives rise to the negative charge that is paramount to the use of geopolymers in the application of the disposal of radioactive Cs, and is introduced by the substitution of Al^{3+} ions for Si^{4+} as shown by Figure 4-21. This negative charge is balanced by cations: K^+ in the KGP sample and, theoretically, a combination of both K^+ and Cs^+ in the COH_5 sample [308]. The preference of Al to exist within the $\text{q}^4(4\text{Si})$ coordination is due to the energetic penalty associated with Al-O-Al bonding [284, 285].

The small resonance observed at ~ 5 ppm is attributed to the presence of octahedral Al sites (AlO_6) within the samples [274]. The intensity of this peak is negligible when compared to that of the tetrahedral Al peak, and suggests that the majority of the Al within the metakaolin has reacted as the octahedral peaks correspond exclusively to the Al found within the unreacted metakaolin [279]. The ^1H - ^{29}Si CP MAS NMR and ^{29}Si MAS NMR spectra in Section 5.2.1.2.3.1 show that the majority, but not all, of the metakaolin has reacted, which explains the presence of this peak at such low intensities.

5.2.1.2.3.3 ^{39}K MAS NMR

The ^{39}K MAS NMR spectra of the COH_5 and KGP samples after 3 and 28 days are displayed in Figure 5-15.

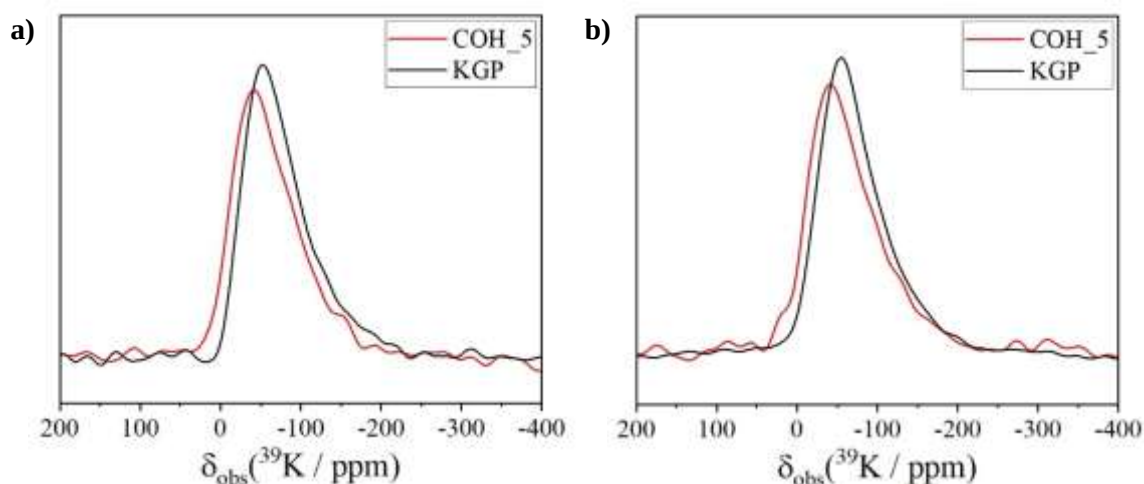


Figure 5-15: ^{39}K MAS NMR spectra for the COH_5 and KGP samples a) 3 days and b) 28 days after reaction.

It is clear from Figure 5-15 that there is a slight difference between the peak centre for the COH_5 and KGP samples. The peaks for the KGP samples are observed between $\delta_{\text{obs}} = -50$ and $\delta_{\text{obs}} = -55$ ppm, whereas the peaks for the COH_5 samples are observed at the higher ppm of $\sim \delta_{\text{obs}} = -45$ ppm. This shift suggests that the introduction of the CsOH leads to a change in the environments in which the K resides within the geopolymer. Despite the fact that there is only one visible peak in the spectra, the peak is very broad and, in the event of multiple K environments within the sample, is likely to contain more than one environment within it.

The shift seen here is evidence for the inclusion of the Cs^+ ions within the K-A-S-H gel as a charge balancing cation, displacing some of the K^+ ions that would occupy this position otherwise. This introduces at least a second K environment, which would contribute to the shift of the peak to higher wavenumbers. In work by Geddes et al., undertaken on Na-based geopolymers, it was shown that the observed peak in ^{23}Na NMR data shifts upon the incorporation of strontium, another cation, as a charge balancing cation into the geopolymer gel matrix [183]. This shift is comparable to that seen in Figure 5-15, suggesting that the shift here indicates that the Cs is chemically immobilised within the structure.

As discussed in Section 3.4.3.3, the comparison to literature should focus on the lineshape of the peaks. Therefore, it is possible to conclude that it is likely that some of the K^+ cations have substituted by Cs^+ cations as charge balancing cations within the geopolymer gel structure.

5.2.1.2.3.4 ^{133}Cs Solid-State NMR

^{133}Cs NMR of CsOH containing geopolymers was carried out in collaboration with Charlotte Nevin and her PhD work. The samples used in both investigations are chemically identical and were produced and analysed in collaboration, the only difference being the water binder ratio changing to 13:1 as opposed to the 11:1 used in this work. This change is not expected to alter the lineshape for the ^{133}Cs NMR shown here. The maximum Cs content used in Charlotte's work is 3wt.%, comparable to the COH_3

samples in this work, and these samples are to be discussed in this section. Although the percentage used is slightly lower than what is seen for the other NMR techniques, it is still indicative of the Cs environments within the geopolymers used. Figure 5-16 shows the ^{133}Cs NMR spectra for the geopolymers mixed with a 3 wt.% of CsOH both pre- and post-leaching in deionised water as outlined in the ASTM C1308 experimental outline [344]. Prior to the leaching, the samples were cured for 28 days at 20°C, meaning that the pre-leaching data is comparable in curing time to the 28 day samples seen elsewhere in this work.

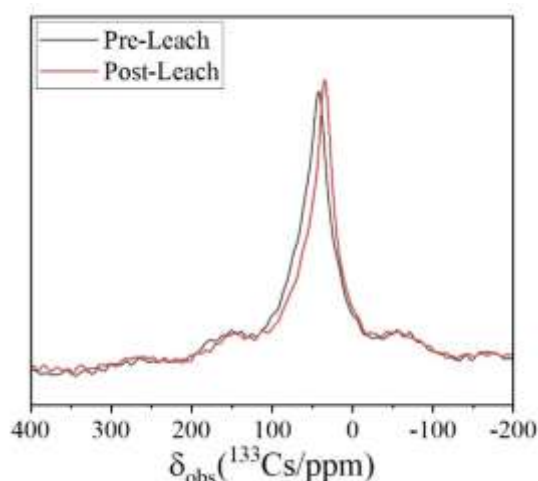


Figure 5-16: ^{133}Cs solid-state NMR spectra for the pre-leach and post-leach COH₃ analogue samples.

There is a clear shift between the peaks for the pre-leach and the post-leach samples. Therefore, it can be deduced that there is more than one Cs environment present within the sample. These two environments are likely to represent the Cs chemically bound as a charge balancing cation in the (Cs,K)-A-S-H gel and the Cs that is ‘free’ within the sample, residing as CsCO_3 or another compound of Cs. However, there is no evidence of a crystalline Cs compound seen within the XRD data (Section 5.2.1.2.2), suggesting that the Cs could be present as Cs^+ cations existing within the pore solution of the geopolymer.

The shift seen towards lower δ_{obs} values after the leaching of the samples is evidence for the Cs residing as a charge balancing cation, displacing the K within the K-A-S-H gel. Further evidence of this has been seen in the literature at Cs concentrations of similar and greater values [174]. Although the findings in said literature used a Na-based geopolymer system, it is likely that the interactions seen would be comparable to K-based systems [174].

The data here shows the quadrupolar nature of the Cs nucleus, represented on the right hand side of the peak. The broad shoulder on the left hand side of the spectra suggests that there are 2 overlapping peaks here, more notably in the post-leach samples, which, when superimposed, lead to the lineshape of the peaks seen here. The pre-leach data displays a more symmetrical Gaussian peak, which is indicative of a weak quadrupolar interaction of the Cs in the sample and a high degree of symmetry around the nucleus. In work by Arbel-Haddad et al., leaching experiments on geopolymer samples containing

similar wt.% of Cs elucidated the appearance of two distinct peaks in the Cs NMR data after 46 hours of leaching [174]. They posited that the Cs had exchanged into zeolite phases within the geopolymer, notably zeolites A and X. The shift seen between the pre-leach and post-leach samples seen in Figure 5-16 agrees with the results seen by Arbel-Haddad et al., whereby, after leach testing, the Cs in the system mainly occupied spots within the zeolites, and this was shown by the intensity of the peaks seen in the Cs NMR data [174]. The peak for the Cs residing within zeolite A is found at a lower δ_{obs} value, and this explains the shift to these values seen in Figure 5-16. Therefore, it can be suggested that the Cs that remains within the sample after leaching is mainly found within crystalline zeolitic phases within the geopolymer, but the amount of these sites is too low to be seen in the XRD data. This is a positive when considering the use of geopolymers to contain radioactive Cs containing waste streams.

5.2.1.3 Conclusions

The isothermal conduction calorimetry data displayed in this work shows that the inclusion of CsOH into the geopolymer mix has minimal impact on the kinetics of formation of the geopolymer gel. The data shows that the alteration of the Cs/Al ratio does not display a distinct pattern in the data, and that the high solubility of the CsOH salt results in the release of the Cs^+ ions into solution. The mechanisms for this have been investigated using zeta potential, diffuse reflectance infrared Fourier transform spectroscopy, order-of-addition experiments, and x-ray diffraction with the conclusion being that the Cs dissolves into solution and interacts with the negatively charged surface of the metakaolin particles. The Cs/Al ratio has a slight correlation with the level of interaction, which increases minimally with increasing Cs/Al ratio. The DRIFTS show that this interaction has very little impact on the kinetics of dissolution of the metakaolin and the geopolymer gel forms comparably to the KGP control sample.

However, the dissolved Cs^+ cations do not significantly affect the resulting structure, the primary phase of which is shown to be a K-A-S-H gel through the use of FTIR spectroscopy, ^{29}Si MAS NMR and ^1H - ^{29}Si CP MAS NMR. This phase is comprised of Si and Al in tetrahedral coordination, with the Si mainly existing in $\text{Q}^4(4\text{Al})$ and $\text{Q}^4(3\text{Al})$ environments. The negative Al sites caused by Al^{3+} in tetrahedral coordination are charge balanced by K^+ , although, upon the introduction of Cs^+ cations, some of the K^+ is displaced in favour of the Cs^+ . XRD shows that no crystalline phases related to the Cs are precipitated out during the reaction process. This is further evidence for the Cs^+ ions displacing the K^+ ions in the charge balancing sites within the K-A-S-H gel. It is shown that the introduction of CsOH to the reaction mix leads to an increase in the Si/Al ratio of the K-A-S-H gel, showing that the introduction of the CsOH leads to a gel with a slightly lower charge balancing capacity.

The order-of-addition experiments show that the addition of the CsOH at any point in the reaction process does not lead to the formation of any by-products, and does not affect the reaction mechanism for the geopolymer formation.

^{39}K MAS NMR and ^{133}Cs NMR show that the inclusion of the CsOH leads to a change in both the K and Cs chemical environments respectively. This is direct evidence that Cs is incorporated into the charge balancing sites of the K-A-S-H gel in place of K.

This work shows that K-silicate activated geopolymers are capable of incorporating wastes containing CsOH at high waste loadings of up to 5% by weight. However, in practice, the loadings are likely to be far lower due to activity limits per package on the wasteforms, owing to the radioactivity of the waste in question. Whilst this, and any impact of the radiation and resulting decay products, are not considered in this work, it is important to note that they will likely have a notable effect on the performance of the geopolymer as a wasteform, and further work to determine how great this effect is will be crucial to determine the overall suitability of the wasteform.

However, the findings outlined in this work show that the inclusion of CsOH within the geopolymer reaction mixture have a minimal effect on the kinetics and mechanisms of formation of a metakaolin based, potassium silicate activated geopolymer system, suggesting that these systems show great promise as wasteforms for the long term immobilisation of radioactive waste streams containing ^{137}Cs in the form of CsOH.

5.2.2 Caesium Carbonate

5.2.2.1 Fresh State

5.2.2.1.1 ICC

Figure 5-17 displays the calorimetry curves produced by the formation of the K-geopolymers loaded with Cs_2CO_3 over the first 3 days of reaction.

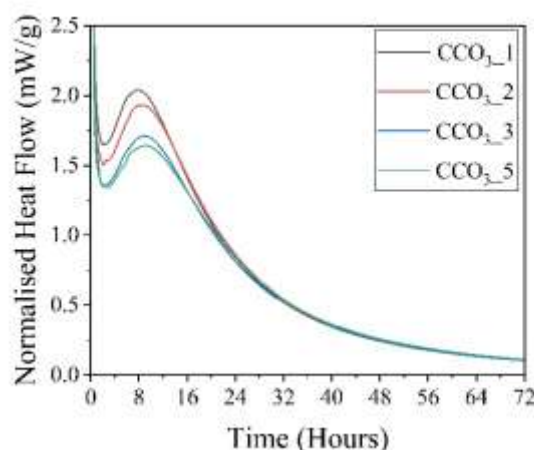


Figure 5-17: The effect on the heat evolution of reaction of loading K-activated metakaolin geopolymers with Cs_2CO_3 over first 24 hours of reaction.

As discussed in Section 4.2.1.1.1, the initial dissolution peak is disregarded in this analysis, and only the visible reaction peak is analysed. In addition, the KGP control sample's heat of evolution, shown in Figure 3-1, is only used to verify the lineshape of the curves for the CCO_3 samples.

As can be seen from Figure 5-17, the inclusion of Cs_2CO_3 into the geopolymer mix leads to a change to the heat evolved during the reaction as the Cs/Al ratio changes. With increasing Cs_2CO_3 content, the maximum observed heat flow decreases, and the time at which this is observed also shifts to a later timepoint. Furthermore, the period between the end of the dissolution peak and the beginning of the reaction peak, which is similar to the induction period seen in PC systems, appears to elongate with increasing Cs/Al ratio [128, 345]. This elongation suggests that the presence of the Cs^+ ions within solution is preventing the reaction from occurring, potentially by forming a physical barrier surrounding the negatively charged, Al-based reaction products of the metakaolin dissolution, preventing their reaction to form the geopolymer gel. The greater the number of Cs^+ ions, which increase with increasing Cs/Al ratio, the greater surface coverage of the dissolution products and the slower the initial reaction. This is further discussed in the analysis of the zeta potential results seen in Section 5.2.2.1.2.

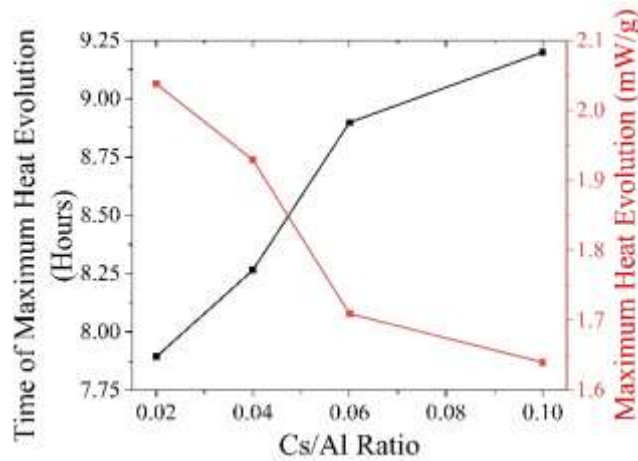


Figure 5-18: The relationship between Cs/Al ratio and the observed time of maximum heat evolution and the value of the maximum heat evolution.

Figure 5-18 shows that there is a linear pattern between the Cs/Al ratio and both the time and value of maximum heat evolution observed for the samples respectively. Between the samples with a Cs/Al ratio of 0.02 and 0.10, there is a decrease in the maximum observed heat value of ~25%. This decrease does not appear to reach its conclusion at a Cs/Al ratio of 0.10, and so it is probable that with increasing Cs/Al ratio, the maximum heat evolution will continue to decrease.

The increase in the time taken to reach the maximum observed heat flow is likely to be altered by the increase in the ‘induction’ period seen for the CCO_3 samples in Figure 5-17. There is minimal change to the lineshape of the peak for the samples, with slight broadening of the peaks with increasing Cs/Al ratio. Therefore, it would be expected that less reaction occurs throughout the 3 days of reaction observed here, and this is supported by the cumulative heat curves shown in Figure 5-19.

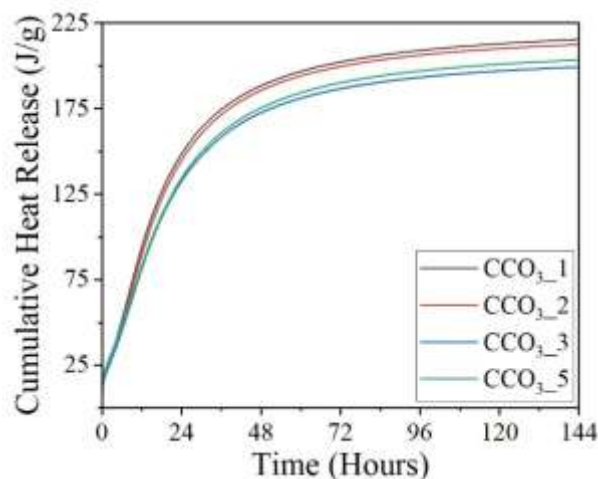


Figure 5-19: The cumulative heat release curves over the first 144 hours of reaction.

Figure 5-19 shows the cumulative heat release of the CCO_3 systems over the first 6 days of reaction. The heat release after 144 hours is equivalent to approximately 2/3 of the total heat release of the system for PC, and this can be assumed to be the same for geopolymer systems [297]. Using this assumption,

the total heat release of the geopolymers mixed with Cs_2CO_3 will be no more than 320 J/g even in the case of the CCO_3_1 sample, which shows the greatest cumulative heat release. This is higher than the average heat release of the current nuclear standard, a Portland cement and GGBS blend, which is around 100 J/g and but is below the guideline value of 180 J/g over the first 24 hours of reaction set by the current UK requirements for nuclear wasteforms [298, 299].

5.2.2.1.2 Zeta Potential

The zeta potential values obtained for the surface charge of metakaolin in the presence of Cs_2CO_3 at different pHs is shown in Figure 5-20.

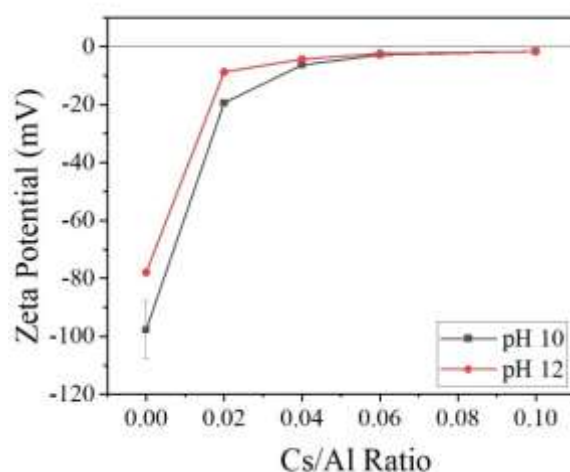


Figure 5-20: Comparing the effect of Cs/Al ratio, altered by the addition of Cs_2CO_3 , on the zeta potential of metakaolin in a KOH solution at pH 10 and 12.

Irrespective of the pH of the solution, Figure 5-20 shows that the introduction of Cs_2CO_3 leads to an increase in the recorded zeta potential significantly towards the isoelectric point, reaching a maximum of -1.6mV for the CCO_3_5 sample at pH 10. However, the maximum at pH 12 is -1.65mV, suggesting that the pH seems to have very little effect on the maximum recorded zeta potential at higher Cs/Al ratios.

At pH 10, the addition of Cs_2CO_3 at a Cs/Al ratio of 0.02 leads to a significant increase in the zeta potential, from $\sim -100\text{mV}$ to -20mV , an increase of 80%. This is then followed by a further increase to -6.3mV at a Cs/Al ratio of 0.04 before plateauing for the final two data points. At a pH of 12, the introduction of Cs_2CO_3 at a Cs/Al ratio of 0.02 results in an increase in the recorded zeta potential from -78mV at a Cs/Al of 0 to 9mV , increasing by $\sim 90\%$, followed by an increase to -4.3mV at a Cs/Al ratio of 0.04. These results could suggest that the Cs^+ ions within solution have reached their maximum effect by this point, adhering to all of the available negatively charged sites on the surface of the metakaolin. It is unlikely that this is due to the fact that there is no increase in the number of Cs^+ ions within solution as it is not probable that the solubility limit of Cs_2CO_3 within the solution is reached due to the high solubility of the salt, 261g/100g of water at 15°C [303]. This is also supported by the findings of the order-of-addition experiments seen in Section 5.2.2.1.3.

The increase in the Cs/Al ratio has very little impact after a Cs/Al ratio of ~ 0.04 at both pH points, where the zeta potential remains almost constant with increasing Cs content. This is mirrored in the ICC seen in Section 5.2.2.1.1, where the retardation of the reaction is readily visible for samples CCO₃_1 and CCO₃_2, but the difference between the time that the maximum heat flow is reached for samples CCO₃_3 and CCO₃_5 are separated by only a small margin. This supports the hypothesis that the interaction of the Cs⁺ ions with the metakaolin is the main mechanism for the retardation of the reaction for the KGP samples containing Cs₂CO₃.

5.2.2.1.3 Order-of-addition Experiments

In order to determine whether the point at which the Cs salt is added to the mix impacts the performance of the geopolymer, order-of-addition experiments were performed as outlined in Section 2.1.1.2.

5.2.2.1.3.1 Order-of-Addition #1

1. The Cs₂CO₃ dissolves in the water leaving a clear solution.
2. The addition of the KOH leads to a release of heat due to the exothermic nature of the KOH dissolution. The KOH dissolves and the solution remains clear.
3. The silicate mixes with the solution and the solution remains clear.
4. The addition of the metakaolin lead to the formation of a geopolymer.

5.2.2.1.3.2 Order-of-Addition #2

1. The addition of solid KOH to water leads to an exothermic dissolution reaction.
2. The Cs₂CO₃ dissolves in the KOH solution, which remains clear.
3. The silicate mixes with the solution and the solution remains clear.
4. The addition of the metakaolin lead to the formation of a geopolymer.

5.2.2.1.3.3 Order-of-Addition #3

1. The addition of solid KOH to water leads to an exothermic dissolution reaction.
2. The addition of the K-silicate stock solution to the KOH solution resulted in a clear liquid mix.
3. The Cs₂CO₃ dissolves in the silicate solution, which remains clear.
4. The addition of the metakaolin lead to the formation of a geopolymer.

5.2.2.1.3.4 Order-of-Addition ICC

Figure 5-21 shows the calorimetry curves generated by the order-of-addition samples over the first 3 days of reaction.

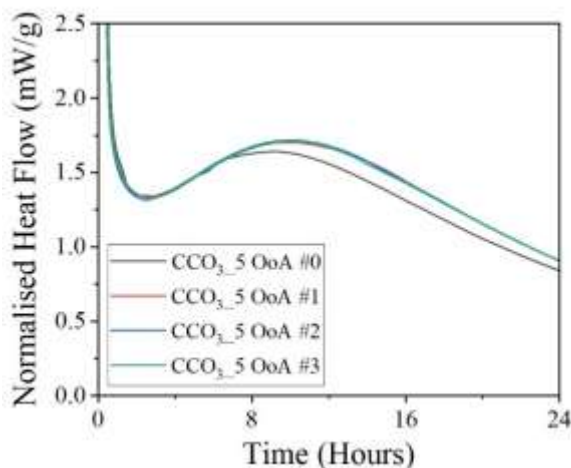


Figure 5-21: The effect on the heat evolution of the reaction of adding Cs_2CO_3 at different stages to K-activated metakaolin geopolymers over the first 3 days.

The addition of Cs_2CO_3 to the activating solution at different points appears to have no impact on the reaction kinetics of the reaction to form the geopolymer matrix. This is to be expected considering the ease in which the salt dissolves into the solutions in each of the order-of-addition experiments. In all of these cases, the final activating solution will contain the same constituents; the original potassium silicate activating solution and the dissociated Cs^+ and CO_3^{2-} ions. Therefore, the final geopolymer will be forming in identical conditions, which is supported by the reaction kinetics seen here.

From Figure 5-21, there is a slight difference in the heat evolution of the reaction between adding the Cs_2CO_3 to the aqueous phase, as is done in order-of-addition experiments #1-3, and the solid phase, as is done in order-of-addition experiment #0. The main difference is that the maximum heat evolution is reached sooner in the reaction, and has a lower value when the salt is added to the solid phase. There is no obvious difference between experiments #1-3, which is unsurprising due to the observations made for these experiments. It is important to note that the measurements for experiments #1-3 were taken at a different time to experiment #0. This could have had the very small effect that can be seen in the first 24 hours of the reaction shown in Figure 5-21. However, it is also possible that the inclusion of the Cs_2CO_3 within the aqueous phase leads to a greater rate and extent of dissolution of the metakaolin compared to including the salt in the solid phase. This is due to the activating solution being required to dissolve both the metakaolin and the salt simultaneously, meaning that there is a greater mass of solid components which, in turn, takes longer to dissolve for the fixed mass of aqueous component. The lesser dissolution in experiment #0 leads to a lower extent of reaction, meaning the reaction completes at an earlier time and has a lower maximum value of heat evolution than experiments #1-3. Despite this, the impact is very small and is unlikely to make a significant difference to the overall heat output of the systems.

5.2.2.1.3.5 Order-of-Addition Conclusions

The Cs_2CO_3 dissolves readily into the activating solution, meaning that its addition to the aqueous phase prior to mixing with the solid phase will not result in any physical changes to the solution. When added to the solid phase prior to mixing, there appears to be a slight impact on the kinetics of the reaction, as shown in the order-of-addition ICC. However, this is unlikely to make a significant difference, although it is thought that there is a slight reduction in the extent of reaction which is suboptimal for the application of a nuclear wasteform. Regardless, it is suggested that for waste streams containing Cs_2CO_3 , the waste should be added to the aqueous phase prior to the formation of a geopolymer.

Despite this experiment suggesting that the method used in this work, order-of-addition #0, has the greatest effect on the kinetics of reaction, the information gleaned is important when considering the effect of solids within the bulk wasteform. This method is the most suitable for identifying the effects of dissolved Cs content on the reaction mechanisms and kinetics of the geopolymer samples. Therefore, for all following analysis and discussion, order-of-addition #0 has been used in this work.

5.2.2.1.4 DRIFTS

The DRIFTS spectra for the CCO_3_5 sample in the first 8 hours of reaction can be seen in Figure 5-22.

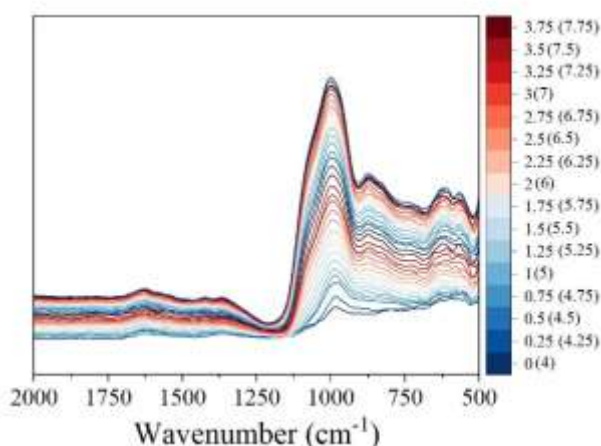


Figure 5-22: DRIFTS spectra for the CCO_3_5 sample in the first 8 hours of reaction. The spectra are displayed in 15 minute intervals, beginning at $t=0$ as marked and progressing through the colour gradient which repeats itself after 4 hours. Times are shown in hours.

Immediately following the initial mixing, the main binding phase, the K-A-S-H gel, begins to form, as shown by the growth of the peak representing the Si-O-T peak at $\sim 1000\text{ cm}^{-1}$ [253]. This growth continues as the 8-hour mark is reached as the peak of reaction is not reached until just over 9 hours post-mixing, as shown by the ICC (Section 5.2.2.1.1). When compared to the spectra exhibited by the KGP sample, shown in Figure 3-3, it is clear that the Si-O-T peak in the KGP sample spectra has a secondary peak centred at $\sim 1100\text{ cm}^{-1}$. This is possibly due to further silicate sites beginning to form within the matrix. The introduction of Cs_2CO_3 appears to promote the formation of a single silicate site over the multiple sites seen in the KGP sample. This suggests that the introduction of the Cs^+ cations

from the very soluble Cs_2CO_3 does encourages the formation of more Si-O-Si bonds in the K-A-S-H gel.

The spectra for the CCO_3_5 sample for the remainder of the first day of reaction (8 hours to 24 hours) is displayed in Figure 5-23.

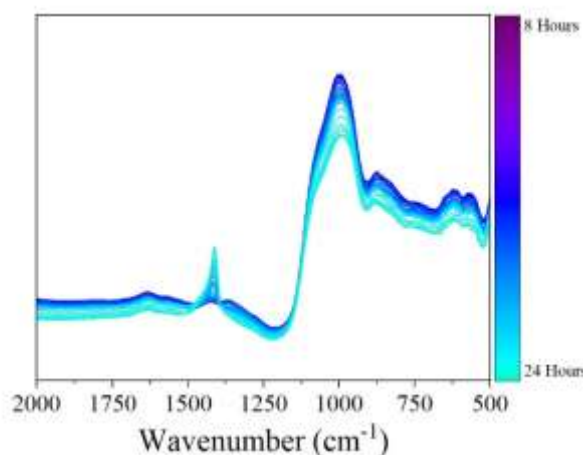


Figure 5-23: DRIFTS spectra for the CCO_3_5 sample from 8 to 24 hours post initial reaction. The spectra are displayed in 15 minute intervals up until the 16-hour mark, at which the time progresses in whole hours, beginning at $t=8$ hours as marked and progressing through the colour gradient. Times are shown in hours.

The maximum intensity for the Si-O-T peak is reached at around 8.5 hours after the initial mixing, which is slightly earlier than the 9.5 hours post reaction at which the maximum reaction is reached, as shown by the ICC. This shows that the intensity of the peak in the DRIFTS spectra is not necessarily directly comparable with extent of reaction, as the intensity here is affected by more than just the concentration of bonds within the sample. It is likely that the shrinkage of the cement begins at around this point and is responsible for the witnessed drop in intensity; as the cement begins to harden, it shrinks, changing the distance between the surface of the sample and the detector [269, 270]. This could alter the amount of signal that reaches the detector, reducing the intensity. Another mechanism for this reduction in intensity is the use of diffuse reflectance as a measurement technique. As the cement hardens, the surface of the sample becomes flat, which may reduce the efficiency of the technique [341].

During the period between 8 hours and 24 hours post initial mixing, a secondary peak begins to develop, beginning at approximately the 12-hour mark. This peak appears at around 1400 cm^{-1} and represents the carbonation of the samples due to air. It could be argued that, due to there already being a carbonate compound in the system, this peak should be present in the spectra from the outset. However, as this technique obtains the majority of its dataset from the surface of the sample, it is possible that the CO_3^{2-} ions from the dissolved Cs_2CO_3 within the sample do not migrate to the surface and so are not detected. Upon the carbonation of the sample surface, the carbonate compounds formed are readily detected by the infrared waves and so appear on the spectra. The intensity of the carbonation peaks is different, with

the intensity being far greater in the spectra for the KGP sample, shown in Figure 3-4. This could suggest that a proportion of the Cs within the system is incorporated into the K-A-S-H gel in place of the K^+ cations and is unavailable to migrate to the surface and readily carbonate.

5.2.2.2 Hardened State

5.2.2.2.1 FTIR

Figure 5-24 shows the FTIR spectra of the K-geopolymers loaded with Cs_2CO_3 after the first 3 days of reaction.

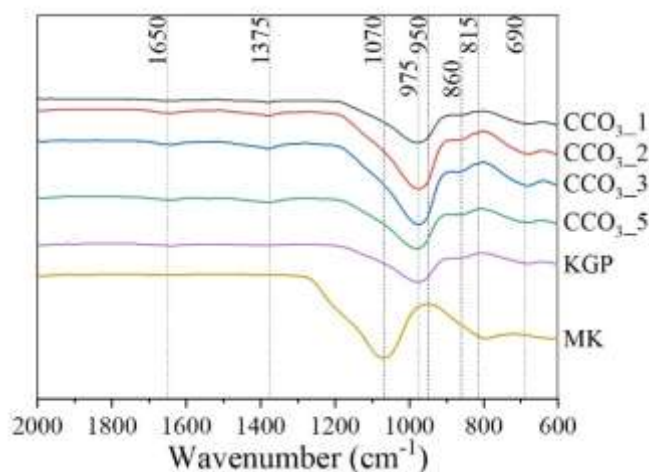


Figure 5-24: The FTIR spectra generated by loading K-activated metakaolin geopolymers with Cs_2CO_3 , the KGP control sample and the unreacted metakaolin after the first 3 days of reaction.

The main peak centred at $\sim 975\text{ cm}^{-1}$ in Figure 5-24 is characteristic of geopolymer systems and is clearly present in all of the samples here. It indicates the asymmetric stretching of Si-O-T bonds within the aluminosilicate framework, where T can be either Si or Al atoms in tetrahedral coordination [253]. On the higher wavelength end of this peak, most notably between 1050 cm^{-1} and 1150 cm^{-1} , a shoulder indicates the presence of some unreacted metakaolin within the sample. This appears to become more apparent as the Cs/Al ratio increases which agrees with the trend seen in the ICC (Section 5.2.1.1.1), which suggests the extent of reaction reduces as the Cs/Al ratio increases which results in a higher concentration of metakaolin residing within the samples. On the lower wavelength of the main peak, there is a shoulder at 860 cm^{-1} which is indicative of the presence of tetrahedral AlO_4 and SiO_4 groups within the structure, through the asymmetric stretching of the bridging oxygen bonds linking the two [258]. The peak at 1650 cm^{-1} is indicative of both chemically bound and free water within the sample [328]. The peak at 690 cm^{-1} is thought to be caused by the pseudo-lattice vibrations of small aluminosilicate rings, which were previously observed in synthetic geopolymer gels by Walkley et al. [67]. The peak at $\sim 1465\text{ cm}^{-1}$ indicates the presence of carbonate groups within the sample. This could be residual Cs_2CO_3 that has not dissolved within the structure, or it could potentially be due to the carbonation of the samples due to exposure to air [271]. Therefore, the carbonate compound could be a potassium carbonate, a caesium carbonate, or even a mixture of the two. The carbonation of each of the

samples appears to be similar, suggesting that the presence of this compound is mainly due to the carbonation due to air as opposed to undissolved Cs_2CO_3 .

The similarity of the spectra seen in Figure 5-24 is evident, suggesting that the structure of the different samples are largely identical. However, closer inspection reveals that there are some subtle differences. As previously mentioned, the shoulder indicating the presence of unreacted metakaolin becomes more pronounced as the Cs/Al ratio increases, supporting the evidence seen in the zeta potential results that an increase in Cs^+ content reduces the rate of dissolution of the metakaolin. The centre of the main Si-O-T peak at 975 cm^{-1} appears to move to higher wavenumbers as the Cs/Al increases. This suggests that the CCO₃_1 sample has a higher degree of geopolymerisation, with the structure containing more AlO_4 tetrahedra than the CCO₃_5 sample, resulting in a greater shift from the value of this peak in the metakaolin [346].

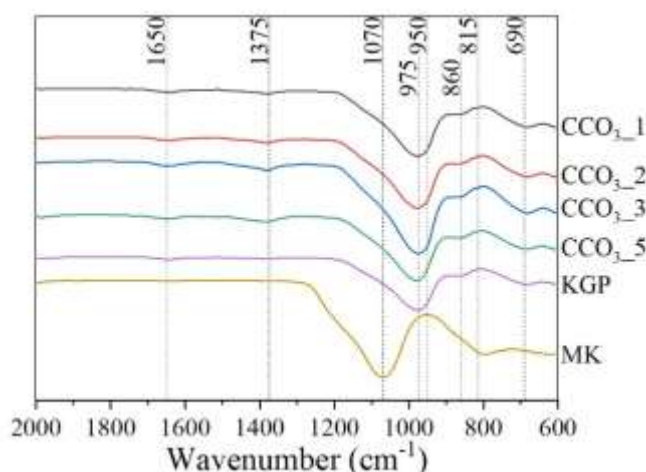


Figure 5-25: The FTIR spectra generated by loading K-activated metakaolin geopolymers with Cs_2CO_3 , the KGP control sample and the unreacted metakaolin after the first 28 days of reaction.

Figure 5-25 shows that the spectra after 28 days are very similar to those seen after 3 days. This suggests that there is not a huge alteration to the structure of the samples during this time frame, and that the majority of the structure is ordered by the 3-day time point. This is supported by both the XRD and the ^{29}Si MAS NMR data collected for these samples, as both show very little, if any, structural alteration between these time points.

5.2.2.2.2 XRD

The XRD spectra for the geopolymer samples containing Cs_2CO_3 3 days after initial reaction are shown in Figure 5-26.

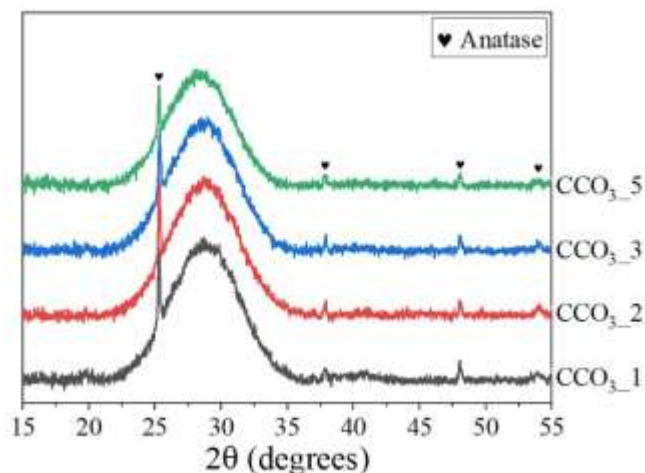


Figure 5-26: The x-ray diffraction spectra generated by loading K-activated metakaolin geopolymers with Cs_2CO_3 after the first 3 days of reaction.

The XRD spectra for the CCO_3 samples show that there is only one clear crystalline phase seen within the samples at all Cs/Al ratios, that of anatase (TiO_2 , PDF # 01-086-1157). This compound is found in the metakaolin reactant prior to mixing, and does not dissolve within the activating solution. Besides this crystalline phase, there is an intense, broad diffraction peak between $\sim 23^\circ$ 2θ and 34° 2θ which represents the amorphous K-A-S-H gel that is indicative of the formation of a geopolymer gel [164]. There is no evidence that any solid Cs_2CO_3 exists within the sample, suggesting that the entirety of the salt has dissolved within the activating solution. This is supported by the high solubility of the salt, alongside the observations seen in the order-of-addition experiments (Section 5.2.2.1.3) [303].

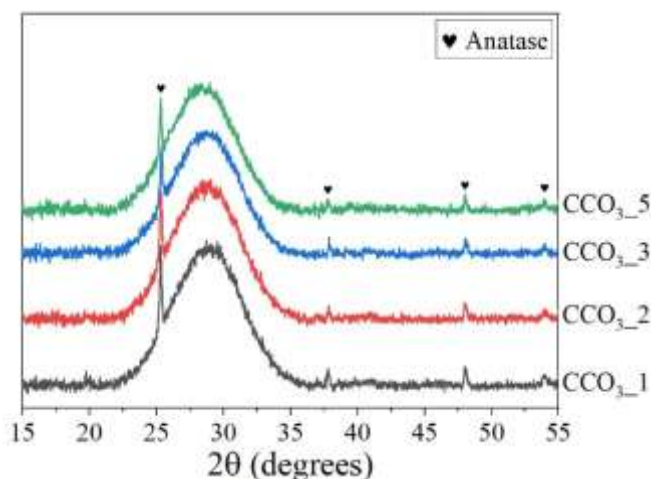


Figure 5-27: The x-ray diffraction spectra generated by loading K-activated metakaolin geopolymers with Cs_2CO_3 after the first 28 days of reaction.

Again, after 28 days of reaction, the spectra of which is shown in Figure 5-27, the only crystalline phase present is anatase. The spectra are comparable between 3 and 28 days, with the broad peak for the K-A-S-H gel still prominent. The implied dissolution of the Cs_2CO_3 results in the Cs^+ ions being present within the sample in some capacity. After dissolution, the Cs is in a favourable configuration to be

incorporated into the K-A-S-H gel as a charge balancing cation, and therefore, this is compelling supporting evidence that the Cs is chemically bound within the geopolymer.

5.2.2.2.3 NMR

5.2.2.2.3.1 ^1H - ^{29}Si CP MAS and ^{29}Si MAS NMR

The ^1H - ^{29}Si CP MAS NMR and ^{29}Si MAS NMR spectra for the CCO_3_5 and KGP samples both 3 and 28 days after the initial reaction are displayed in Figure 5-28.

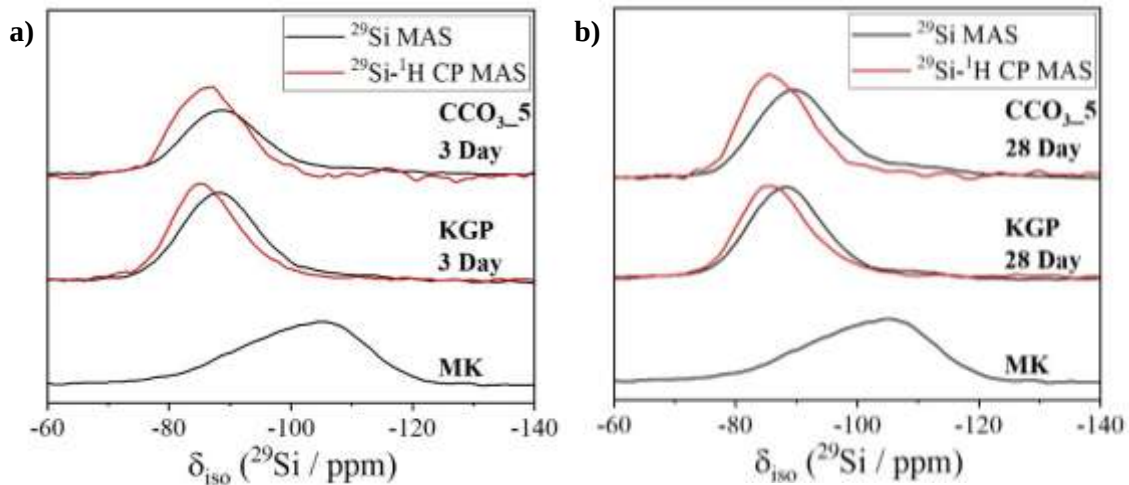


Figure 5-28: ^1H - ^{29}Si CP MAS and ^{29}Si MAS spectra for the CCO_3_5 , KGP samples and the unreacted metakaolin a) 3 days and b) 28 days after reaction.

The ^1H - ^{29}Si CP MAS NMR spectra, shown in red in Figure 5-28, display a single broad peak between $\delta_{\text{iso}} = -75$ and $\delta_{\text{iso}} = -100$ ppm. The maximum intensity is observed at a δ_{iso} of -85 ppm, confirming that the geopolymer gels are predominantly comprised of $\text{Q}^4(4\text{Al})$ and $\text{Q}^4(3\text{Al})$ silicon environments as would be expected from the literature [67, 347]. The rationale for the use of, and differences between the ^1H - ^{29}Si CP MAS NMR and ^{29}Si MAS NMR techniques are discussed in Section 5.2.1.2.3.1.

The ^{29}Si MAS NMR spectra in Figure 5-28 display the entire range of Si sites present within the sample, including those that are a result of Si sites within the unreacted metakaolin, most notably $\text{Q}^4(0\text{Al})$ sites. For these spectra, the maximum peak intensity is recorded at a lower δ_{iso} of $\delta_{\text{iso}} = -88$ ppm for the KGP sample and $\delta_{\text{iso}} = -90$ ppm for the CCO_3_5 sample. The effect of including the silicon environments exhibited by the unreacted metakaolin is clear, with the ^{29}Si MAS spectra for both samples showing intensity in these regions, suggesting that the reaction has not sustained to completion. This is more prominent in the CCO_3_5 sample after 3 days than it is after 28 days, suggesting that there should be an increase in the extent of reaction for this sample over this time. The extents of reaction for these samples, in terms of percentage, can be seen in Table 5-4.

Table 5-4: The extent of reaction of the CCO_3_5 and KGP samples both 3 and 28 days after initial reaction, calculated using the ^{29}Si MAS NMR spectra.

Sample	Time point	Extent of reaction (%)
KGP	3 Days	82.17
CCO ₃ _5	3 Days	83.60
KGP	28 Days	88.00
CCO ₃ _5	28 Days	84.01

As suggested by Figure 5-28, the extent of reaction does increase between 3 and 28 days after the initial mixing, albeit, not by a significant amount. The extent of reaction is calculated by subtracting the total percentage of silicon sites present due to the unreacted metakaolin from 100%, which comprises of Si sites from the hydrated gel and the metakaolin, which are calculated using the deconvolutions of the ²⁹Si MAS NMR and the ¹H-²⁹Si CP MAS spectra respectively. Figure 5-29 shows the deconvolution of the two NMR spectra for the CCO₃_5 samples; The deconvolution of the NMR spectra allows the amount of each of the individual ²⁹Si sites to be quantified [172]. For the KGP samples, the ²⁹Si MAS NMR spectra in Figure 3-6 show that the gel structure is dominated by Q⁴(3Al) sites, which agrees with data reported in the literature for potassium activated geopolymers [172]. The spectra observed here are similar to those seen in previous work, suggesting that the K-A-S-H gel is formed by a mixture of Si environments in the form of Q⁴(mAl) sites, where 1 ≤ m ≤ 4 [67]. This is supported by Table 5-5, which shows the presence of each Si site as a percentage calculated from the ²⁹Si MAS NMR data.

Table 5-5: Relative integral areas for the Si sites present within the K-A-S-H gel of each sample both 3 and 28 days after initial reaction from the deconvoluted ²⁹Si MAS NMR spectra. The Q⁴(0Al) site attributed to the unreacted metakaolin is disregarded for the quantification of the K-A-S-H gel.

Sample	Time point	Relative Integral Area (%)				Si/Al
		Q ⁴ (4Al)	Q ⁴ (3Al)	Q ⁴ (2Al)	Q ⁴ (1Al)	
KGP	3 Days	25	54	20	1	1.32
CCO ₃ _5	3 Days	28	53	18	1	1.38
KGP	28 Days	28	44	26	2	1.34
CCO ₃ _5	28 Days	28	49	20	3	1.35

Table 5-5 shows the molar Si/Al ratio of the K-A-S-H gel, disregarding the Si sites that are attributed to the unreacted metakaolin. This ratio is calculated using Engelhardt's formula (Equation 3-1) [276]. In this equation, $I_{AQ}^{4(mAl)}$ represents the relative integral areas beneath the deconvoluted resonances in the ²⁹Si MAS NMR spectra. This equation can only be used under the assumption that Loewenstein's

rule is followed, where Al-O-Al bonds are negligible [277]. Previous work has shown that this assumption is valid for geopolymer systems where $\text{Si/Al} > 1$ through the use of ^{17}O 3QMAS NMR spectroscopy [278]. Table 5-5 shows that the KGP sample, which has the lower Si/Al ratio of the two sets of samples, has a Si/Al ratio of 1.32 after 3 days, increasing to 1.34 after 28 days, validating the assumption.

After 3 days of reaction, the Si/Al ratio of the CCO_3_5 sample is greater than that of the KGP sample at the same time point. This results in the early stage CCO_3_5 sample having a lower charge balancing capability than the corresponding KGP sample, as the number of Al sites is lesser. However, after 28 days, the charge balancing capability of the CCO_3_5 sample is increased, as shown by the reduction of the Si/Al ratio of the sample. Therefore, between 3 and 28 days' post initial mixing, more Al sites are incorporated into the K-A-S-H gel suggesting that more Al tetrahedra have been released and are available to react. This suggests that the introduction of the Cs_2CO_3 impacts the dissolution of the Al from the metakaolin, which is supported by the interaction of the salt with the metakaolin as shown by the zeta potential in Section 5.2.2.1.2. Moreover, the ICC (Section 5.2.2.1.1) shows that the extent of reaction, signified by the lower maximum value of heat evolution, decreases with increasing Cs/Al ratio. Thus, the introduction of Cs clearly has an impact on the dissolution of the metakaolin and, coupled with the change in Si/Al ratio seen here, this is likely to be preferentially slowing the dissolution of the Al within the metakaolin. This is a significant change compared to the reaction pathway in the KGP sample as the Al_2O_3 within the metakaolin dissolves preferentially when compared to the SiO_2 due to Al-O-Al bonds being weaker than Al-O-Si and Si-O-Si bonds [279].

However, it is also possible that the interaction of the Cs_2CO_3 into the reaction mixture simply slows the dissolution of the metakaolin as a whole. The Si tetrahedra that are introduced into the reaction mixture come primarily from the activating solution due to its high concentration within this reactant compared to the metakaolin. Therefore, if the dissolution of the metakaolin as a whole is slowed, the concentration of Al tetrahedra within the aqueous phase of the mix will still be lower than that of the corresponding KGP sample. However, this is not supported by the extents of reaction after 3 days calculated from the deconvolution of the ^{29}Si MAS NMR spectra, which suggest that more of the metakaolin has reacted in the CCO_3_5 sample after 3 days than the KGP sample. Despite this, it is likely that this is the mechanism that explains the difference in the Si/Al ratio between the CCO_3_5 and KGP samples after 3 days of reaction, as the slight change in the extent of reaction percentage falls within the inherent error in the deconvolution of the ^{29}Si MAS NMR spectra.

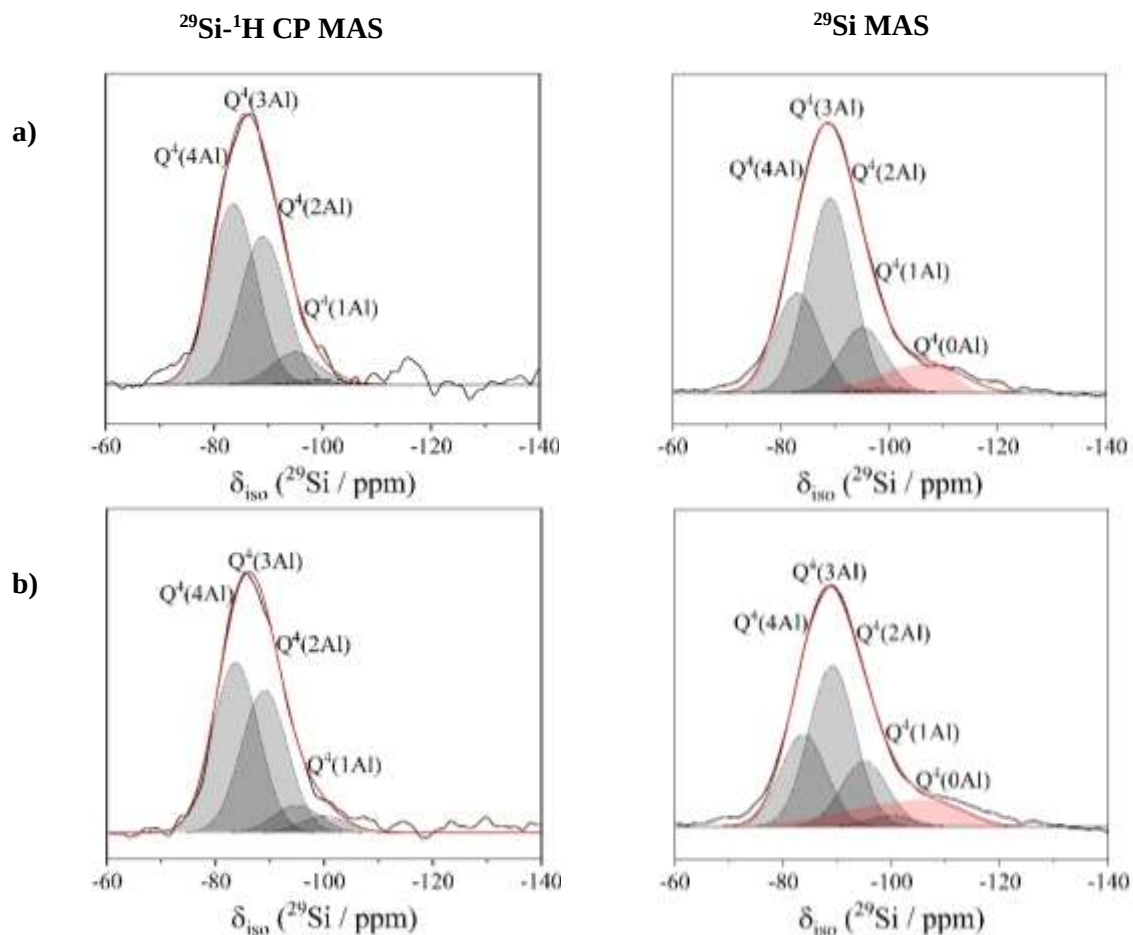


Figure 5-29: $^{29}\text{Si}-^1\text{H}$ CP MAS and ^{29}Si MAS NMR spectra and the associated deconvolutions for the a) CCO_3_5 sample after 3 days and b) CCO_3_5 sample after 28 days. The $^{29}\text{Si}-^1\text{H}$ CP MAS NMR data is shown in the left column and the ^{29}Si MAS NMR data is shown in the right column. For each spectrum, the raw data is shown as a solid black line and the model fit is shown as a solid red curve. The deconvolutions that represent each ^{29}Si site within the K-A-S-H gel are depicted as grey curves, whilst the deconvolutions that represent ^{29}Si sites within the unreacted metakaolin are shown in a faded red.

5.2.2.2.3.2 ^{27}Al MAS NMR

The ^{27}Al MAS NMR spectra for the CCO_3_5 and KGP samples at the 3 and 28 day time points post initial mixing are displayed in Figure 5-30.

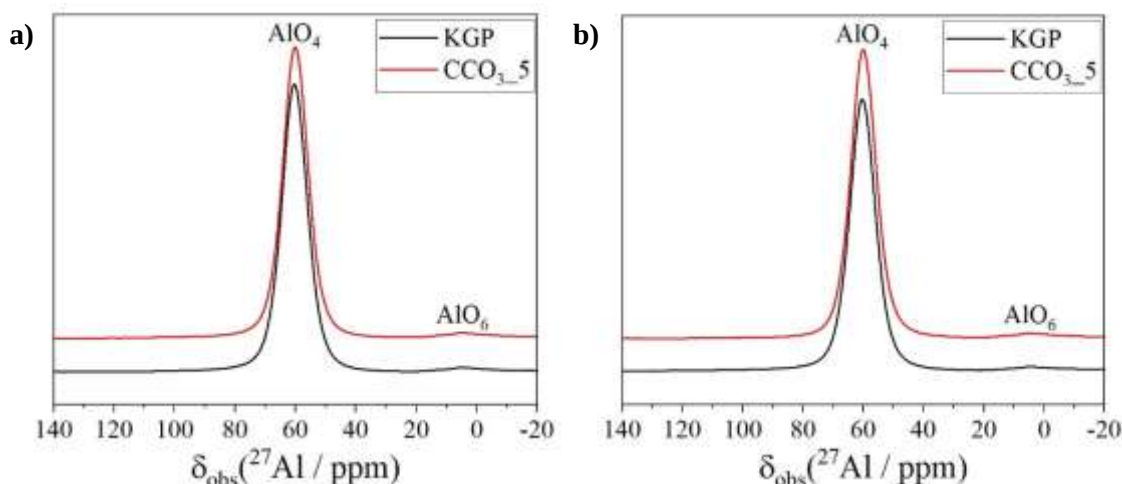


Figure 5-30: ^{27}Al MAS spectra for the CCO_3_5 and KGP samples a) 3 days and b) 28 days after reaction.

Figure 5-30 shows that the ^{27}Al MAS NMR spectra for the KGP and CCO_3_5 samples display two distinct resonances. The clearest resonance, centred at $\delta_{\text{obs}}=60.3$ ppm and spanning between $\sim \delta_{\text{obs}}=50$ ppm and $\delta_{\text{obs}}=70$ ppm, is recognisable as the tetrahedral Al site (AlO_4^-) found in the K-A-S-H gel phase of the geopolymer [279, 306]. This coordination is promoted by the large excess of alkali cations within the aqueous reaction mixture and gives rise to the negative charge that is paramount to the use of geopolymers in the application of the disposal of radioactive Cs, and is introduced by the substitution of Al^{3+} ions for Si^{4+} within the K-A-S-H gel [307]. This negative charge is balanced by cations: K^+ in the KGP sample and, theoretically, a combination of both K^+ and Cs^+ in the CCO_3_5 sample [308]. There is no clear difference between the CCO_3_5 and the KGP sample as the Al environments are unchanged by the addition of the Cs_2CO_3 .

The small resonance observed at ~ 5 ppm is attributed to the presence of octahedral Al sites (AlO_6) within the samples [274]. The intensity of this peak is negligible when compared to that of the tetrahedral Al peak, and suggests that the majority of the Al within the metakaolin has reacted as the octahedral peaks correspond exclusively to the Al found within the unreacted metakaolin [279]. The ^1H - ^{29}Si CP MAS NMR and ^{29}Si MAS NMR spectra for these samples show that the majority, but not all, of the metakaolin has reacted, which explains the presence of this peak at such low intensities.

5.2.2.2.3.3 ^{39}K MAS NMR

The ^{39}K MAS NMR spectra for the CCO_3_5 and KGP samples at the 3 and 28 day time points post initial mixing are displayed in Figure 5-31.

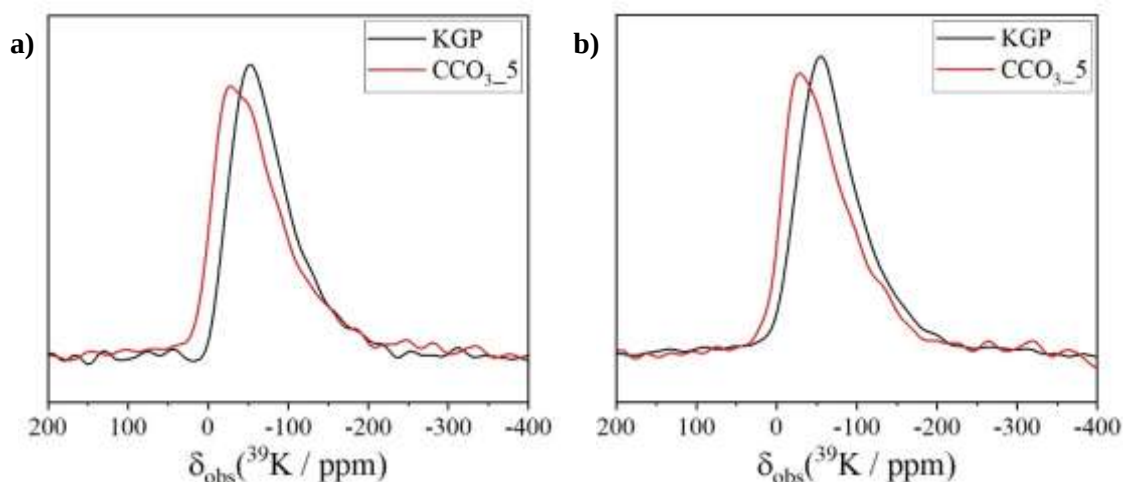


Figure 5-31: ^{39}K MAS NMR spectra for the CCO_3_5 and KGP samples a) 3 days and b) 28 days after reaction.

Figure 5-31 illustrates that there is an alteration in the peak centres between the spectra for the CCO_3_5 and KGP samples. The peaks in both a) and b) for the KGP samples are observed between $\delta_{\text{obs}} = -50$ and $\delta_{\text{obs}} = -55$ ppm, whereas the peaks for the CCO_3_5 samples are observed at the higher ppm of $\sim \delta_{\text{obs}} = -45$ ppm. This shift suggests that the inclusion of the highly soluble Cs_2CO_3 within the reaction mixture leads to a change in the environments in which the K resides within the geopolymer. Despite the fact that there is only one visible peak in the spectra, the peak is very broad and, in the event of multiple K environments within the sample, is likely to contain more than one environment within it.

The shift seen here is evidence for the inclusion of the Cs^+ ions within the K-A-S-H gel as a charge balancing cation, displacing some of the K^+ ions that would occupy this position otherwise. This introduces at least a second K environment, which would contribute to the shift of the peak to higher wavenumbers. In currently unpublished work by Geddes et al., undertaken on Na-based geopolymers, it was shown that the observed peak in ^{23}Na NMR data shifts upon the incorporation of strontium, another cation, as a charge balancing cation into the geopolymer gel matrix [183]. This shift is comparable to that seen in Figure 5-15, suggesting that the shift here indicates that the Cs is chemically immobilised within the structure.

As discussed in Section 3.4.3.3, the comparison to literature should focus on the lineshape of the peaks. Therefore, it is possible to conclude that it is likely that some of the K^+ cations have substituted by Cs^+ cations as charge balancing cations within the geopolymer gel structure.

5.2.2.2.3.4 ^{133}Cs Solid-State NMR

Figure 5-32 shows the ^{133}Cs NMR spectra for the CCO_3_5 sample after 28 days of reaction.

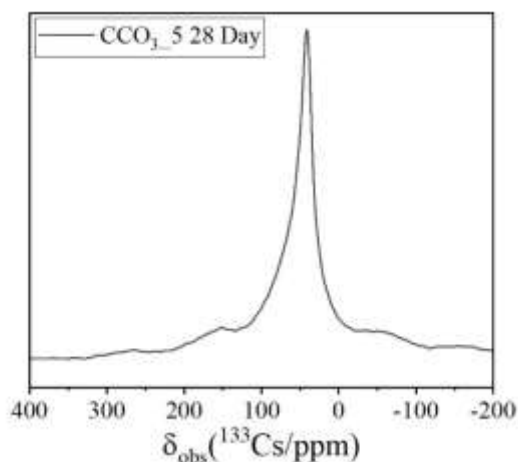


Figure 5-32: ^{133}Cs solid-state NMR spectrum for the CCO_3_5 sample after 28 days of reaction.

The spectrum here appears to show that there is a single clear peak in the spectra that centres around $\delta_{\text{obs}} = 40$ ppm. However, as discussed in Section 4.2.1.2.3.4, the quadrupolar nature of the Cs nucleus should lead to an asymmetrical peak, with a lesser gradient seen as the δ_{obs} decreases to negative values. This is not seen here, instead appearing to have a lesser gradient of descent as the δ_{obs} increases to higher values. This suggests that the peak seen here is the result of two overlapping peaks within the region, but that the instrument power is not strong enough to resolve these peaks. Work by Arbel-Haddad et al. investigated the effect of different wt.% of Cs in metakaolin based geopolymer samples activated by a (Na/Cs)OH activating solution [174]. They showed that the Cs is capable of becoming loaded into zeolitic phases within the geopolymer at similar wt.% as is seen in this work, notably zeolites A and X. Moreover, the peak centres seen in their work align with the peak range that is seen in Figure 5-32. However, the XRD does not show the presence of any crystalline zeolitic phases in the CCO_3_5 sample, but this does not necessarily mean that they are not present, but are instead within the samples at very low concentrations. Also, the use of Na in the activator also promotes that formation of zeolitic phases as opposed to the use of K, which means that it is less likely that these phases are forming in significant quantities in the samples in this work [193]. Therefore, it is possible that the Cs is present in the zeolitic phases, but it is also likely that the Cs^+ is displacing the K^+ ions within the amorphous K-A-S-H gel, which is shown to be in the sample through the use of XRD, FTIR and other NMR techniques used in this work.

5.2.2.3 Conclusions

The delay in the reaction to form geopolymer for samples loaded with Cs_2CO_3 is shown to positively correlate with the increasing Cs/Al ratios of the samples by the isothermal conduction calorimetry. This increase in reaction retardation is accompanied by a slight reduction in reaction. The mechanisms for these changes have been investigated using zeta potential, diffuse reflectance infrared Fourier transform

spectroscopy, order-of-addition experiments, and x-ray diffraction, which show that the high solubility of the Cs_2CO_3 within the activating solution leads to the release of Cs^+ ions into the solution which interact with the negatively charged surface of the metakaolin particles, slowing the dissolution reaction. The DRIFTS shows that the slowing of the dissolution has a minimal effect on the reaction pathway to form the main K-A-S-H binding phase of the geopolymer, highlighting the comparability between this for the CCO_3_5 and KGP control samples.

The primary phase of the formed geopolymer in all cases is shown to be the K-A-S-H gel by the use of FTIR spectroscopy, ^{29}Si MAS NMR and ^1H - ^{29}Si CP MAS NMR. The negative Al sites caused by Al^{3+} in tetrahedral coordination are charge balanced by K^+ , although, upon the introduction of Cs^+ cations, some of the K^+ is displaced in favour of the Cs^+ . The XRD data shows that the only crystalline phase present within the sample is that of the inert impurity, anatase. Therefore, any chemical incorporation of the Cs must be within amorphous phases, which supports the Cs acting as charge balancing cations within the K-A-S-H gel, further supported by the findings of the ^{133}Cs SS NMR. It is shown that the introduction of Cs_2CO_3 to the reaction mix leads to an increase in the Si/Al ratio of the K-A-S-H gel, showing that these gels have a slightly lower charge balancing capacity.

The order-of-addition experiments show that the addition of the Cs_2CO_3 at any point in the reaction process does not lead to the formation of any by-products, and does not affect the reaction mechanism for the geopolymer formation.

^{39}K MAS NMR shows that there is a clear shift in the K chemical environments after the inclusion of the Cs_2CO_3 as the Cs displaces some of the K in charge balancing sites in the K-A-S-H gel.

This work shows that K-silicate activated geopolymers are capable of incorporating wastes containing Cs_2CO_3 at high waste loadings of up to 10.3% by weight. However, in practice, the loadings are likely to be far lower due to activity limits per package on the wasteforms, owing to the radioactivity of the waste in question. Whilst this, and any impact of the radiation and resulting decay products, are not considered in this work, it is important to note that they will likely have a notable effect on the performance of the geopolymer as a wasteform, and further work to determine how great this effect is will be crucial to determine the overall suitability of the wasteform.

The findings discussed in this work suggest that the addition of Cs_2CO_3 to the reaction mixture has an impact on the kinetics of reaction but only a minimal effect on the mechanisms that control the formation of the K-A-S-H gel. Consequently, this suggests that these systems show great promise as wasteforms for the long term immobilisation of radioactive waste streams containing ^{137}Cs in the form of Cs_2CO_3 .

5.2.3 Caesium Nitrate

5.2.3.1 Fresh State

5.2.3.1.1 ICC

Figure 5-33 displays the calorimetry curves produced by the formation of the K-geopolymers loaded with CsNO_3 over the first 3 days of reaction.

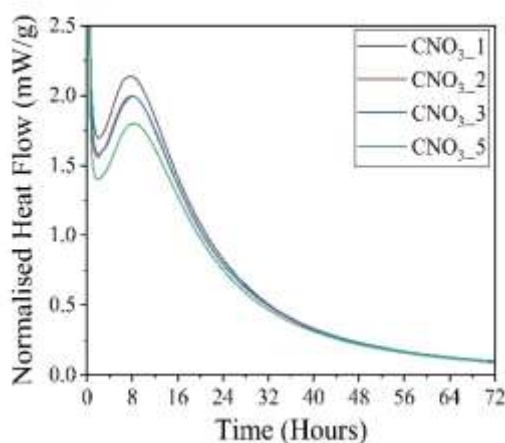


Figure 5-33: The effect on the heat evolution of reaction of loading K-activated metakaolin geopolymers with CsNO_3 over first 24 hours of reaction.

As discussed in Section 4.2.1.1.1, the initial dissolution peak is disregarded in this analysis, and only the visible reaction peak is analysed. In addition, the KGP control sample's heat of evolution, seen in Figure 3-1 is only used to verify the lineshape of the curves for the CNO_3 samples.

This impact could be due to the addition of the CsNO_3 resulting in a lesser mass of both activating solution and metakaolin available to react. The wt.% of the CsNO_3 salt in the CNO_3_5 sample is 6.16%, and the maximum drop in heat flow is observed for this sample drops by $\sim 17\%$ compared to the KGP control, suggesting that the decline in available reactive material could be the reason for the reduction in heat flow. Furthermore, it is likely that 'wetting' of the CsNO_3 molecules is occurring, with the activating solution becoming adhered to the surface of the salt, preventing it from commencing the dissolution reaction in the first instance. A combination of these two explanations is the likely cause of the decrease in heat flow, suggesting that no changes should be found in the structure of the resulting geopolymer matrices.

A useful analogy to this is the use of quartz in the R^3 test method for the chemical reactivity of SCMs. In order to monitor the reactivity of varying supplementary cementitious materials (SCMs) such as ground granulated blast furnace slag (GGBFS) and pulverized fly ash (PFA), the R^3 test introduces the SCM into a pseudo-cementitious system composing of $\text{Ca}(\text{OH})_2$, calcite, alkali and sulphate to replicate 'real' PC without the PC clinker itself [294, 295]. Within this test, quartz is utilised as an inert material, meaning it does not react with the system and acts as a filler material within the structure [294, 296].

Upon the addition of quartz, a reduction in the heat evolved during the reaction is observed, much like that seen in Figure 5-33 upon the addition of CsNO_3 [295]. Therefore, it could be suggested that the addition of CsNO_3 to the geopolymer mix leads to the CsNO_3 acting as a filler material and not partaking in the reaction.

Figure 5-33 shows that the addition of CsNO_3 to the geopolymer mix results in a reduction to the maximum observed heat with increasing Cs/Al ratio. This reduction is the main observable difference, with a reduction of ~18% between the samples with a Cs/Al ratio of 0.02 and 0.10. There is a slight retardation of the reaction, with the time at which the maximum heat flow is observed occurring around 30 minutes later at a maximum. This is a relatively minor difference and is potentially due to the elongation of the induction period that can be seen as opposed to an elongation of the actual reaction peak itself. The time and value of the maximum heat flow is compared to the Cs/Al ratio of the samples in Figure 5-34.

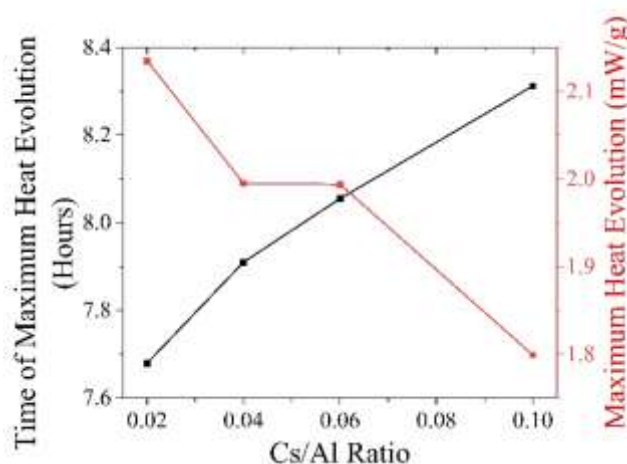


Figure 5-34: The relationship between Cs/Al ratio and the observed time of maximum heat evolution and the value of the maximum heat evolution.

Figure 5-34 shows that the relationship between the Cs/Al ratio and the time and value of the maximum heat evolution respectively are linear. The only anomaly to this relationship is the value of the maximum heat evolution for the CNO_3_3 (Cs/Al ratio of 0.06) sample, but even then it is not far out of trend and could be considered an artefact of the data collection. The linearity of the relationship suggests that, if the Cs/Al ratio was increased further still, the effects seen here would continue in a similar fashion. The reduction in the maximum observed heat evolution suggests that less reaction is occurring as the Cs/Al ratio increases, which would lead to a lower heat release overall. This is supported by the results shown in Figure 5-35.

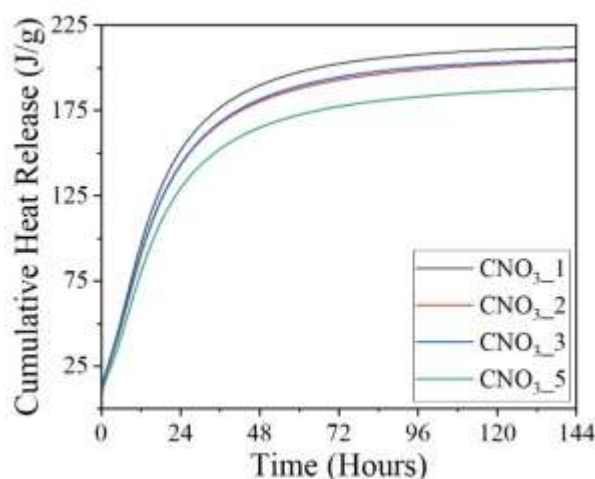


Figure 5-35: The cumulative heat release curves over the first 144 hours of reaction.

Figure 5-35 shows the cumulative heat release of the CNO₃ systems over the first 6 days of reaction. The heat release after 144 hours is equivalent to approximately 2/3 of the total heat release of the system for PC, and this can be assumed to be the same for geopolymer systems [297]. Using this assumption, the total heat release of the geopolymers mixed with CsNO₃ will be no more than 320 J/g even in the case of the CNO₃_1 sample, which shows the greatest cumulative heat release. This is higher than the average heat release of the current nuclear standard, a Portland cement and GGBS blend, which is around 100 J/g, however, it meets the guideline value of 180 J/g over the first 24 hours set by the current UK requirements for nuclear wastefoms [298, 299].

5.2.3.1.2 Zeta Potential

The zeta potential values obtained for the surface charge of metakaolin in the presence of CsNO₃ at different pHs is shown in Figure 5-36.

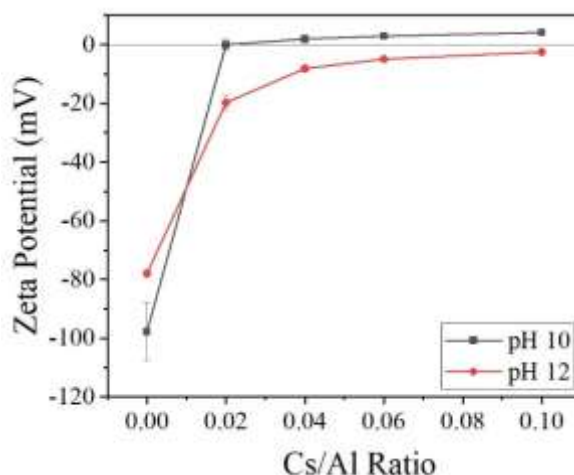


Figure 5-36: Comparing the effect of Cs/Al ratio, altered by the addition of CsNO₃, on the zeta potential of metakaolin in a KOH solution at pH 10 and 12.

Figure 5-36 shows that metakaolin in the KOH solution without the presence of salts, shown by a Cs/Al ratio of 0, has a very negative surface charge, which becomes increasingly negative with increasing pH.

This surface charge is caused by the deprotonation of the surface hydroxyl sites in the alkaline solution, leading to an increased negative charge on the surface of the particles [159]. The addition of the CsNO_3 leads to an increase in the recorded zeta potential at both pH 10 and 12, having a greater effect on the former. However, in both cases, the introduction of the CsNO_3 leads to the surface charge of the metakaolin becoming more positive, displaying a recorded zeta potential of around 0mV, the isoelectric point. At this point, the surface charge of the metakaolin is net neutral due to the effect of the electric double layer (EDL), promoting agglomeration over time [155, 156].

At pH 10, the addition of CsNO_3 at all of the Cs/Al ratios leads to an increase in the zeta potential to the isoelectric point, in the case of a Cs/Al ratio of 0.02, and beyond it in the case of the greater Cs/Al ratios. At the isoelectric point, the electrostatic repulsion between the particles is at its minimum. This neutrality prevents the particles from repelling one another within the suspension, promoting agglomeration of the particles and, theoretically, reducing the surface area and slowing the dissolution.

As the pH increases, the zeta potential at each respective Cs/Al ratio decreases. This suggests that the interactions between the Cs^+ ions and the negatively charged surface of the metakaolin decrease as the pH increases; therefore, at the higher pH of the samples in this work, it is likely that this effect is lesser still. This could potentially be linked to the lower solubility of the CsNO_3 at the high pH; the solubility of the salt in water is 27.9g/100g of water at 25°C but the order-of-addition experiments seen in Section 5.2.3.1.3 suggest that this solubility decreases significantly at the higher pH seen in the geopolymer samples in this work [303]. This could explain the minimal retardation of the reaction with increasing Cs/Al ratio seen in the ICC in Section 5.2.3.1.1. However, this interaction is still likely to be the main mechanism for the minimal retardation of the reaction that is seen.

5.2.3.1.3 Order-of-addition Experiments

In order to determine whether the point at which the Cs salt is added to the mix impacts the performance of the geopolymer, order-of-addition experiments were performed as outlined in Section 2.1.1.2.

5.2.3.1.3.1 Order-of-Addition #1

1. The CsNO_3 does not fully dissolve within the water. It resides at the bottom of the container and leaves a clear solution.
2. The addition of the KOH leads to a release of heat due to the exothermic nature of the KOH dissolution. This leads to the dissolution of the CsNO_3 within the solution. However, after 5 minutes, the salt had precipitated out of solution, and the crystals are clearly visible. The solution is now not clear.
3. The addition of the potassium silicate leads to a cloudy solution, and the salt crystals are no longer visible.
4. The addition of the metakaolin did lead to the formation of what appeared to be a geopolymer. Upon pouring the activating solution (which was very fluid) containing the CsNO_3 into the

metakaolin, it became clear that the mixture was a suspension of CsNO_3 within the activating solution. The suspension easily mixed with the metakaolin to form a GP.

5.2.3.1.3.2 *Order-of-Addition #2*

1. The addition of solid KOH to water leads to an exothermic dissolution reaction.
2. The CsNO_3 does not dissolve within the KOH solution. The solution is clear and the salt crystals are clearly visible on the bottom of the container. This supports the hypothesis that it is heat that drove the dissolution of the CsNO_3 in OoA#1.
3. The addition of the potassium silicate does not cause the CsNO_3 to dissolve. The solution is clear but the salt crystals are still visible on the bottom of the container.
4. The addition of the metakaolin did lead to the formation of what appeared to be a geopolymer. Upon pouring the activating solution containing the CsNO_3 into the metakaolin, the CsNO_3 remained at the bottom of the container and did not fully enter the mixing ampoule. Therefore, a geopolymer was formed but without the full amount of CsNO_3 contained within it.

5.2.3.1.3.3 *Order-of-Addition #3*

1. The addition of solid KOH to water leads to an exothermic dissolution reaction.
2. The addition of the K-silicate stock solution to the KOH solution resulted in a clear liquid mix.
3. The CsNO_3 does not dissolve in the silicate solution, and instead rests at the bottom of the container.
4. The addition of the metakaolin did lead to the formation of what appeared to be a geopolymer. Upon pouring the activating solution containing the CsNO_3 into the metakaolin, the CsNO_3 remained at the bottom of the container and did not fully enter the mixing ampoule. Therefore, a geopolymer was formed but without the full amount of CsNO_3 contained within it.

5.2.3.1.3.4 *Order-of-Addition ICC*

Figure 5-37 shows the calorimetry curves generated by the order-of-addition samples containing CsNO_3 over the first 3 days of reaction.

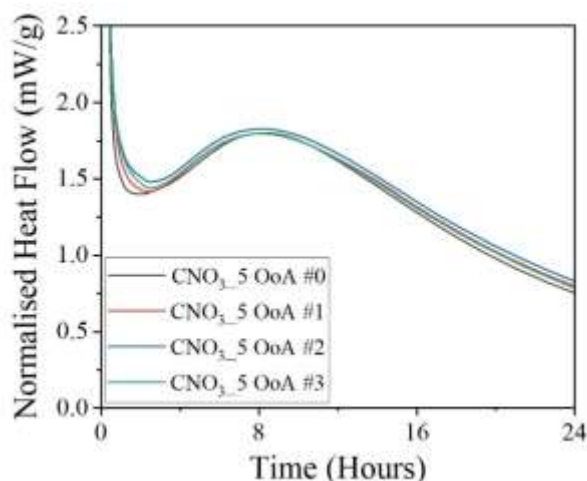


Figure 5-37: The effect on the heat evolution of the reaction of adding CsNO_3 at different stages to K -activated metakaolin geopolymers over the first 3 days.

The addition of CsNO_3 to the systems at any point appears to have a negligible impact on the kinetics of reaction for the dissolution of the metakaolin and the initial formation of the geopolymer gel. This is most likely due to the lack of solubility of the CsNO_3 salt, meaning that it simply acts as a filler material within the system as discussed in Section 5.2.3.1.1. Therefore, it is irrelevant as to at which point the salt is added, as it essentially acts as an inert additive to the mixture, which is further supported by the order-of-addition experiments seen here. Moreover, the fact that not all of the CsNO_3 entered the calorimeter for experiments #1-3 suggest that the reactions proceeded without the presence of the majority of the CsNO_3 and still produced heat evolution curves that are comparable to experiment #0. This provides further evidence that the inclusion of CsNO_3 has no effect on the reaction progression.

5.2.3.1.3.5 Order-of-Addition Conclusions

The insolubility of the CsNO_3 within the activating solution means that it does not matter whether the salt is added to the solid phase or aqueous phase prior to the mixing of the geopolymer, the impact is going to be negligible in either case. Therefore, it is reasonable to use OoA #0 in this work to investigate the properties of the geopolymer during the formation phase of the material.

5.2.3.1.4 DRIFTS

The DRIFTS spectra for the CNO_3_5 sample in the first 8 hours of reaction can be seen in Figure 5-38.

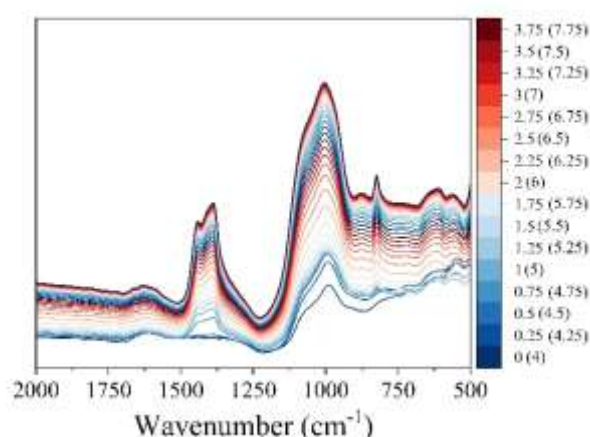


Figure 5-38: DRIFTS spectra for the CNO₃_5 sample in the first 8 hours of reaction. The spectra are displayed in 15 minute intervals, beginning at $t=0$ as marked and progressing through the colour gradient which repeats itself after 4 hours. Times are shown in hours.

There are numerous peaks present in this spectra, but only one of these begins to materialise immediately after mixing; the peak at $\sim 1000\text{ cm}^{-1}$ represents the Si-O-T bond, where T represents either Si or Al, which is characteristic of a geopolymer cement [253]. This peak continues to grow, and is comparable in lineshape to that of the same peak in the KGP sample, shown in Figure 3-3. This suggests the development of the K-A-S-H gel is not impacted by the CsNO₃, which would be expected due to its limited solubility [303].

After 45 minutes, 3 other peaks begin to appear in the spectra at $\sim 820\text{ cm}^{-1}$, 1390 cm^{-1} and 1450 cm^{-1} . The peaks at 820 cm^{-1} and 1390 cm^{-1} can be attributed to the presence of CsNO₃ within the sample, as shown in Figure 5-39. This further supports the fact that the CsNO₃ does not dissolve within the activating solution. However, the reason it takes 45 minutes post-reaction for this to appear on the spectra could be due to its migration towards the surface of the sample as the mix begins to settle within the crucible. This would also explain why the carbonation peak, centred at around 1450 cm^{-1} appears so early into the reaction for the CNO₃_5 sample when compared to the KGP sample. The reaction of the CsNO₃ with the carbon dioxide within the air leads to the formation of the carbonation peak. This does not happen in the KGP sample as the carbonation does not occur until a sufficient mass of the K-A-S-H gel has formed, providing an outlet for the K in the gel to react with the air.

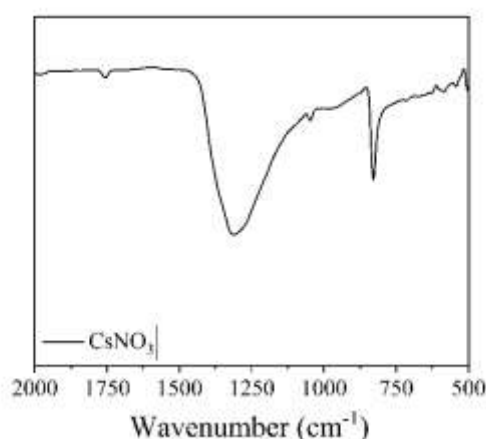


Figure 5-39: The FTIR spectra of pure CsNO_3 .

The spectra for the CNO_3_5 sample for the remainder of the first day of reaction (8 hours to 24 hours) is displayed in Figure 5-40.

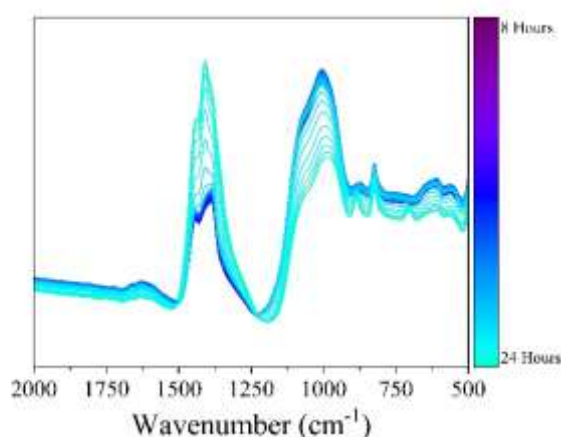


Figure 5-40: DRIFTS spectra for the CNO_3_5 sample from 8 to 24 hours post initial reaction. The spectra are displayed in 15 minute intervals up until the 16-hour mark, at which the time progresses in whole hours, beginning at $t=8$ hours as marked and progressing through the colour gradient. Times are shown in hours.

The peak attributed to the Si-O-T peak reaches its maximum intensity at around 11.5 hours after the initial mixing. This is much later than the point at which the maximum heat evolution is reached, which is 8.5 hours post mixing as shown by the ICC (Section 5.2.3.1.1). This suggests that the point of maximum intensity in the DRIFTS spectra does not directly correlate with the extent of reaction. After reaching its maximum intensity, the peak intensity begins to decrease. It is unknown as to why this occurs, but it is most likely that the shrinkage of the cement is responsible for this drop; as the cement begins to harden, it shrinks, changing the distance between the surface of the sample and the detector [269, 270]. This occurs in this situation as the same sample is used throughout the measurement and, during this time, no changes are made to the apparatus and so the measurement distance does not

change. Also, as the cement hardens, the surface of the sample may become quite flat as the reaction to form the geopolymer continues. The geometry of this surface may prevent effective diffuse scattering of the infrared radiation, meaning that there is a distinct drop in the intensity of the received signal [341].

The anomaly to the shrinking intensity is that of the peak at around 1380-1450 cm^{-1} . In the early stage of reaction, these two separate peaks are attributed to the CsNO_3 and the carbonation of the sample respectively. However, as the reaction progresses, these peaks begin to merge towards a more central value. This could be due to the carbonation of the CsNO_3 at the surface consuming the salt whilst still producing the carbonation product. This is a reasonable assumption, as the peak continues to grow whilst there is also a significant reduction of intensity seen in the peak at 850 cm^{-1} which is also attributed to the CsNO_3 in the sample. Moreover, this aligns with what is seen in the KGP sample, shown in Figure 3-4, where the carbonation grows continuously to the 24 hour mark.

5.2.3.2 Hardened State

5.2.3.2.1 FTIR

Figure 5-41 shows the FTIR spectra of the K-geopolymers loaded with CsNO_3 after the first 3 days of reaction.

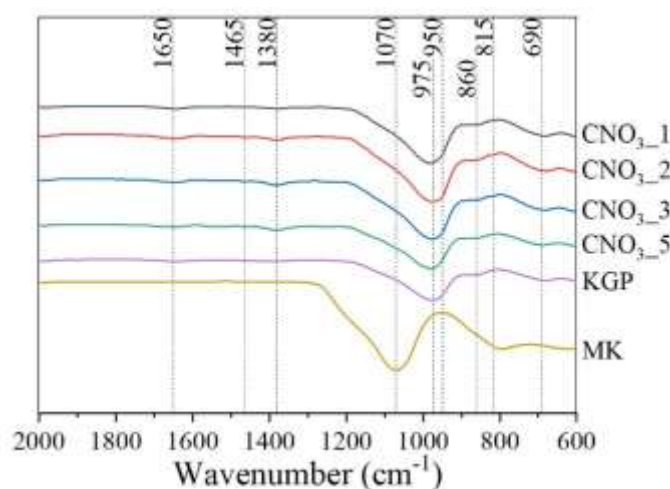


Figure 5-41: The FTIR spectra generated by loading K-activated metakaolin geopolymers with CsNO_3 , the KGP control sample and the unreacted metakaolin after the first 3 days of reaction.

The bond vibrations that are responsible for the resonances seen are discussed in more detail in Section 3.4.2 and summarised in Table 3-4. The main peak centred at $\sim 975 \text{ cm}^{-1}$ in Figure 5-41 is characteristic of geopolymer systems and is clearly present in all of the samples here. On the higher wavelength end of this peak, around 1070 cm^{-1} , a shoulder indicates that there is unreacted metakaolin within the sample. This appears to become more apparent as the Cs/Al ratio increases which agrees with the trend seen in the ICC (Section 5.2.3.1.1), suggesting that the extent of reaction reduces as the Cs/Al ratio increases which results in a higher concentration of metakaolin residing within the samples. The peak at ~ 1465

cm^{-1} indicates the presence of carbonate groups within the sample. This is due to the carbonation of the samples due to exposure to air [271]. Therefore, the carbonate compound could be a potassium carbonate, a caesium carbonate, or even a mixture of the two. The peak at 1380 cm^{-1} signifies the asymmetric stretching of the NO_3 that is caused by the large proportion of CsNO_3 that does into dissolve into the activating solution [348].

The addition of CsNO_3 does not cause a significant change to the structure of the geopolymer, most likely due to the fact that the solubility of the CsNO_3 is so low, meaning that the chemical environment in which the geopolymer forms is largely unchanged. The main difference in the spectra is a direct result of this; the peak at 1380 cm^{-1} which stems from the unreacted CsNO_3 .

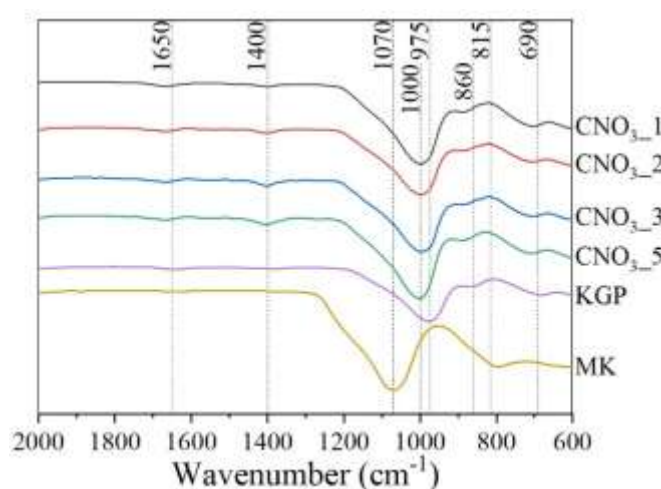


Figure 5-42: The FTIR spectra generated by loading K-activated metakaolin geopolymers with CsNO_3 , the KGP control sample and the unreacted metakaolin after the first 28 days of reaction.

Figure 5-42 shows that there is very little difference between the spectra 3 days post-reaction and the spectra 28 days post-reaction suggesting that there is not a lot of structural change within the samples between these time points. The main observable difference is the shifting of the centre of the main Si-O-T peak to higher wavenumbers with increasing Cs content. This is due to 1 of 2 possibilities; Firstly, the extent of reaction decreases as the Cs/Al ratio increases, resulting in an increased concentration of metakaolin within the structure. Therefore, the peak position moves to higher wavenumbers due to this environment. The second possibility is that the Si/Al ratio is impacted by the addition of the CsNO_3 , resulting in more Si sites being incorporated into the structure.

5.2.3.2.2 XRD

The XRD spectra for the CNO_3 samples after the first 3 days of reaction are displayed in Figure 5-43.

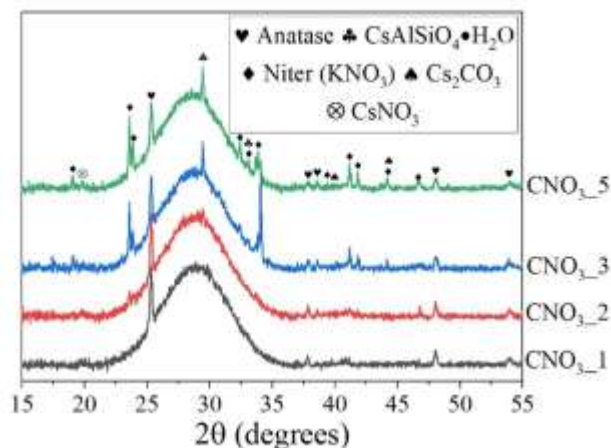


Figure 5-43: The x-ray diffraction spectra generated by loading K-activated metakaolin geopolymers with CsNO_3 after the first 3 days of reaction.

The XRD spectra indicate that there are a number of crystalline phases present within the sample after the first 3 days of reaction. Firstly, the presence of anatase (TiO_2 , PDF # 01-086-1157) is expected, as this inert phase is shown in the XRF data for the metakaolin (Table 2-1) and will therefore be present in the sample in small quantities. The presence of CsNO_3 (PDF # 00-009-0403) agrees with the observations made in the order-of-addition experiments (Section 5.2.3.1.3), which suggest that the solubility of the CsNO_3 used in this work in the activating solution is very low. The solubility of CsNO_3 in water is high, and so this observation suggests that the solubility alters dramatically as the pH increases into the alkaline region [303]. However, the solubility limit in these conditions is not so small as for none of the salt to dissolve. This is proven by the presence of niter (KNO_3 , PDF # 00-005-0377) which is a result of the reaction between the K^+ ions in solution with the NO_3^- ions introduced by the Cs salt. The intensity of the peaks associated with this phase increase with increasing Cs/Al ratio, suggesting that there are more available NO_3^- anions as the percentage of Cs salt added to the mix rises. Therefore, it can be deduced that more of the salt dissolves as the concentration of the salt increases, although this was not readily observed within the order-of-addition experiments. The Cs^+ cations that are ‘free’ within solution are shown to react with the forming geopolymer K-A-S-H gel by the presence of a crystalline caesium aluminium silicate hydrate ($\text{CsAlSiO}_4 \cdot \text{H}_2\text{O}$, PDF # 00-039-0131) phase. This presence of this phase is crucial, proving that the K-A-S-H gel, or a similar crystalline phase, is capable of forming and, subsequently, chemically immobilising the Cs within the structure. This phase could form as a microcrystalline phase that is intimately mixed with the K-A-S-H gel within the sample, but the long range ordering of the $\text{CsAlSiO}_4 \cdot \text{H}_2\text{O}$ is more consistent across the bulk of the sample than that of K-A-S-H gel hence its appearance in the XRD spectra. The intensity of the peaks associated with this phase only begin to appear for the CNO_3_2 sample and increase with intensity with increasing Cs/Al ratio. This suggests that the phase does not crystallise initially, potentially remaining as an amorphous phase with Cs as a direct substitute for the K in the K-A-S-H gel. However, this does not

agree with previous work, suggesting that the formation of a crystalline Cs-A-S-H phase is more favourable at lower Cs wt.%, with the amorphous phase appearing after all of the available crystalline sites have been inhabited [174]. The final crystalline phase is that of caesium carbonate (Cs_2CO_3 , PDF # 00-035-0962). This is most likely due to the carbonation of the geopolymer due to air, forming Cs_2CO_3 crystals.

Aside from the crystalline phases, the single broad peak between $\sim 23^\circ 2\theta$ and $34^\circ 2\theta$ which represents the amorphous K-A-S-H gel that is indicative of the formation of a geopolymer gel [164]. Moreover, there could be non-crystalline Cs-A-S-H phases captured within this amorphous peak as well [174].

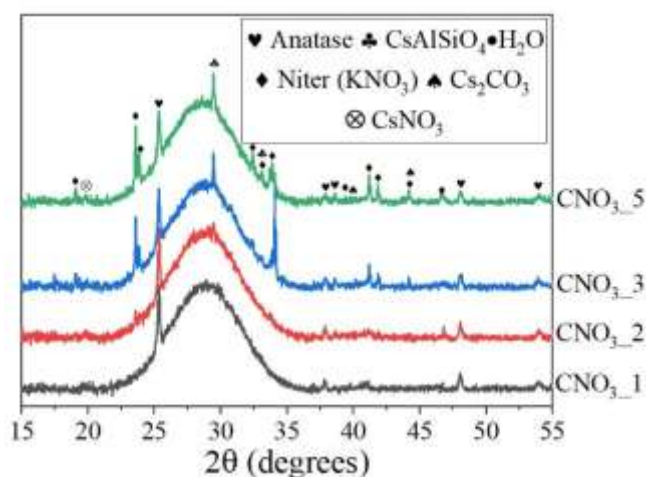


Figure 5-44: The x-ray diffraction spectra generated by loading K-activated metakaolin geopolymers with CsNO_3 after the first 28 days of reaction.

The spectra for the CNO_3 samples after 28 days, displayed in Figure 5-44, are similar to those seen after 3 days. The same phases are present, and the peaks show very similar intensities. The main difference is seen in the CNO_3_3 sample, at $\sim 34.5^\circ 2\theta$. This peak relates to niter within the sample, although it does not follow the pattern between the samples and is likely to be an anomaly.

5.2.3.2.3 NMR

5.2.3.2.3.1 ^1H - ^{29}Si CP MAS and ^{29}Si MAS NMR

The ^1H - ^{29}Si CP MAS NMR and ^{29}Si MAS NMR spectra for the CNO_3_5 and KGP samples both 3 and 28 days after the initial reaction are displayed in Figure 5-45.

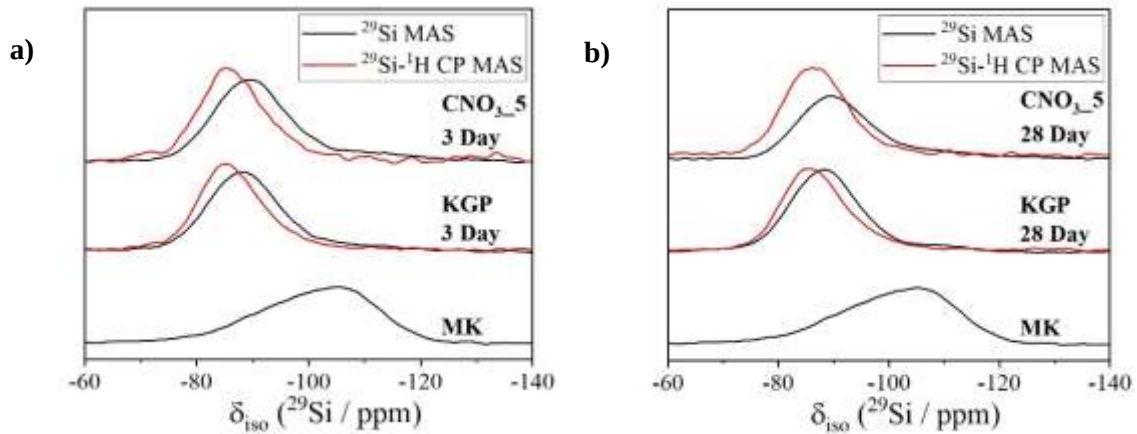


Figure 5-45: ^1H - ^{29}Si CP MAS and ^{29}Si MAS spectra for the CNO_3_5 , KGP samples and the unreacted metakaolin a) 3 days and b) 28 days after reaction.

The ^1H - ^{29}Si CP MAS NMR spectra in Figure 5-45 constitute a single broad peak between $\delta_{\text{iso}} = -75$ and $\delta_{\text{iso}} = -100$ ppm. The maximum intensity is observed at a δ_{iso} of -85 ppm, confirming that the geopolymer gels are predominantly comprised of $\text{Q}^4(4\text{Al})$ and $\text{Q}^4(3\text{Al})$ silicon environments as would be expected from the literature [67, 347]. The rationale for the use of, and differences between the ^1H - ^{29}Si CP MAS NMR and ^{29}Si MAS NMR techniques are discussed in Section 5.2.1.2.3.1.

The black curves in Figure 5-45 represent the ^{29}Si MAS NMR spectra for the samples. These spectra are comprised of all of the Si chemical environments present within the samples, including those for the unreacted metakaolin that remains post reaction. For these spectra, the maximum peak intensity is recorded at a lower δ_{iso} of $\delta_{\text{iso}} = -88$ ppm for the KGP sample and $\delta_{\text{iso}} = -89$ ppm for the CNO_3_5 sample. The intensity of the ^{29}Si MAS NMR spectra for the CNO_3_5 sample after both 3 and 28 days is relatively low in comparison to the KGP samples.

For both samples, the peak centres shift to lower δ_{iso} values when compared with the ^1H - ^{29}Si CP MAS NMR spectra, showing that there is a non-zero component for the number of Si sites in $\text{Q}^4(1\text{Al})$ and $\text{Q}^4(0\text{Al})$ configurations coming from the unreacted metakaolin. This is evidence that the reaction has not fully occurred, however, for the CNO_3_5 sample, the intensity for the spectra in the metakaolin region is lesser after 28 days than after 3. This suggests that the reaction continues between these time points, with more of the metakaolin dissolving in the high pH environment. The extents of reaction for these samples, in terms of percentage, can be seen in Table 5-6 and appear to agree with the visual hypothesis from Figure 5-45.

Table 5-6: The extent of reaction of the CNO₃_5 and KGP samples both 3 and 28 days after initial reaction, calculated using the ²⁹Si MAS NMR spectra.

Sample	Time point	Extent of reaction (%)
KGP	3 Days	82.17
CNO ₃ _5	3 Days	80.06
KGP	28 Days	88.00
CNO ₃ _5	28 Days	83.06

With respect to the deconvolutions seen in Figure 5-46, the ²⁹Si MAS NMR spectra show that the gel structure is dominated by Q⁴(3Al) sites, which agrees with data reported in the literature for potassium activated geopolymers [172]. The spectra observed here are similar to those seen in previous work, suggesting that the K-A-S-H gel is formed by a mixture of Si environments in the form of Q⁴(mAl) sites, where $1 \leq m \leq 4$ [67]. This is supported by Table 5-7, which shows the presence of each Si site as a percentage calculated from the ²⁹Si MAS NMR data.

Table 5-7: Relative integral areas for the Si sites present within the K-A-S-H gel of each sample both 3 and 28 days after initial reaction from the deconvoluted ²⁹Si MAS NMR spectra. The Q⁴(0Al) site attributed to the unreacted metakaolin is disregarded for the quantification of the K-A-S-H gel.

Sample	Time point	Relative Integral Area (%)				Si/Al
		Q ⁴ (4Al)	Q ⁴ (3Al)	Q ⁴ (2Al)	Q ⁴ (1Al)	
KGP	3 Days	25	54	20	1	1.32
CNO ₃ _5	3 Days	23	50	26	1	1.36
KGP	28 Days	28	44	26	2	1.34
CNO ₃ _5	28 Days	21	51	28	0	1.45

Table 5-7 shows the molar Si/Al ratio of the K-A-S-H gel, disregarding the Si sites that are attributed to the unreacted metakaolin. This ratio is calculated using Engelhardt's formula (Equation 3-1) [276]. Table 5-6 shows that the extent of reaction for the CNO₃_5 samples is lower than the corresponding KGP sample after both 3 and 28 days. Therefore, the amount of unreacted metakaolin within the sample is greater in the CNO₃_5 sample. The reasoning for this lies within the introduction of the CsNO₃ into the reaction mixture. The XRD, discussed in Section 5.2.3.2.2, shows that there is a significant quantity of KNO₃ present within the samples after 3 days of reaction. This solid, crystalline phase, which precipitates straight out of the aqueous solution, is likely to create a physical barrier within the system,

preventing the efficient migration of the activating solution around the metakaolin to facilitate dissolution. On top of this, the zeta potential data, discussed in Section 5.2.3.1.2, shows that there is a clear reaction between the dissolved Cs^+ ions and the metakaolin particles in solution. This coulombic interaction can lead to the formation of a physical barrier of Cs^+ ions surrounding the metakaolin. The combination of these two barriers may slow the dissolution of the metakaolin dramatically, and, in agreement with the ICC in Section 5.2.3.1.1, this phenomena will naturally increase with increasing Cs/Al ratio.

The Si/Al ratios in Table 5-7 show that the reaction of the metakaolin with the activating solution continues between 3 and 28 days post initial mixing. The Si/Al ratio increases between this point, which suggests that more Si tetrahedra are incorporated into the K-A-S-H gel. This is likely due to the continuing dissolution of the metakaolin. This shows that, despite the rate of dissolution being heavily affected by the introduction of the CsNO_3 , the dissolution reaction itself is not deeply impacted. That is to say, the relative rates of dissolution of the individual components of the metakaolin is not impacted by the CsNO_3 . The Al_2O_3 within the metakaolin dissolves preferentially when compared to the SiO_2 due to Al-O-Al bonds being weaker than Al-O-Si and Si-O-Si bonds, and so it is expected that the Al components will dissolve faster, with the Si components taking longer to be incorporated into the geopolymer gel as is shown by the Si/Al ratios here [279].

The higher Si/Al ratio of the CNO_3_5 sample compared to the KGP samples at each time point suggests that including the CsNO_3 into the reaction mixture lowers the charge balancing capability of the resultant K-A-S-H gel due to a relative reduction in the number of Al tetrahedral within the gel. Despite this, the deconvolution of the ^{29}Si MAS NMR spectra in Figure 5-46 for the CNO_3_5 samples and Figure 3-6 for the KGP samples, shows that the samples are mainly comprised of $\text{Q}^4(3\text{Al})$ sites which promote the inclusion of either K^+ or Cs^+ as a charge balancing cation. The suggestion that the Cs^+ , which is shown to be in solution through both the zeta potential and XRD data, could be incorporated into the K-A-S-H gel through these charge balancing sites is heavily supported by the XRD. Not only is the precipitation of a crystalline Cs-A-S-H phase discovered, but the high concentration of KNO_3 suggests that a large proportion of the K^+ ions that would otherwise occupy these sites are unavailable to do so. These findings provide strong evidence to insinuate that the Cs is chemically immobilised within the

main binding phase of the geopolymer which has positive implications for the potential use of geopolymers as a nuclear waste form.

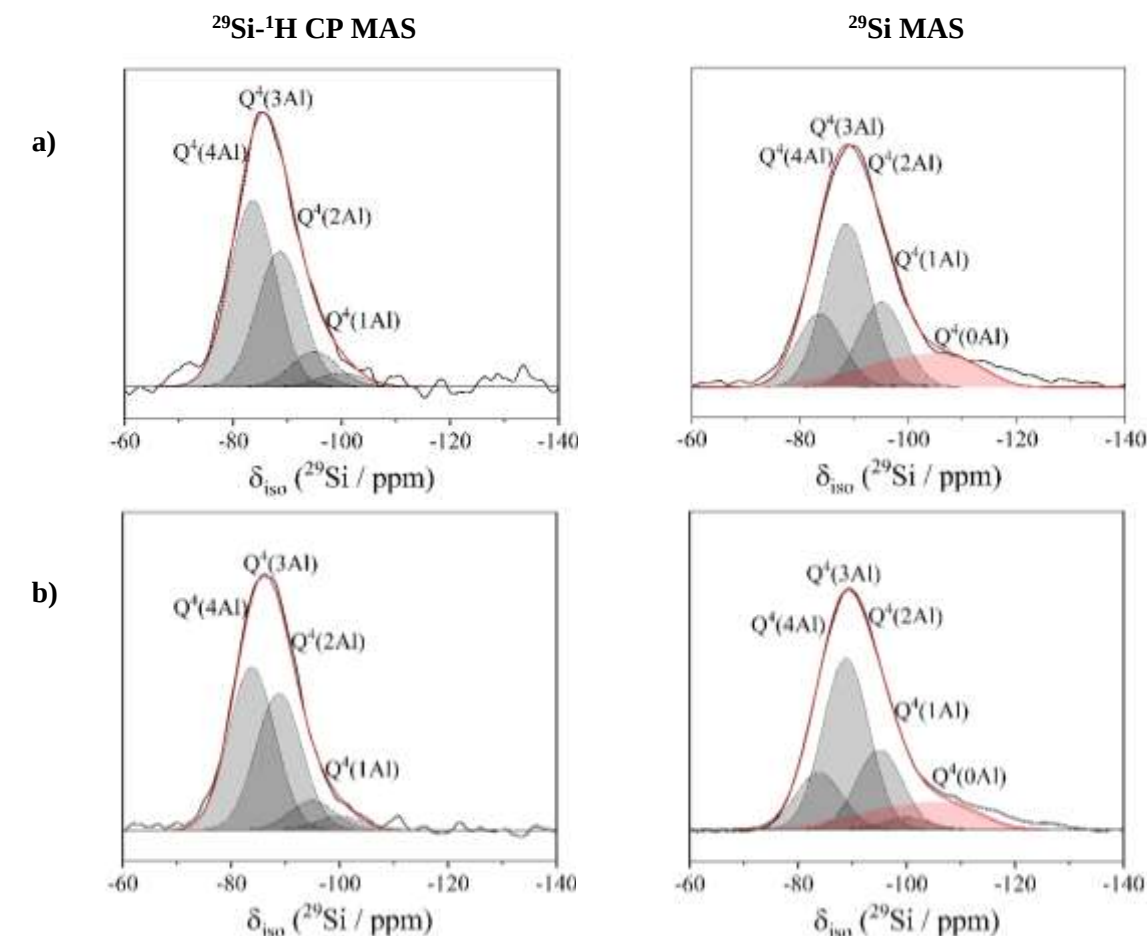


Figure 5-46: ^{29}Si - ^1H CP MAS and ^{29}Si MAS NMR spectra and the associated deconvolutions for the a) CNO_{3_5} sample after 3 days and b) CNO_{3_5} sample after 28 days. The ^{29}Si - ^1H CP MAS NMR data is shown in the left column and the ^{29}Si MAS NMR data is shown in the right column. For each spectrum, the raw data is shown as a solid black line and the model fit is shown as a solid red curve. The deconvolutions that represent each ^{29}Si site within the K-A-S-H gel are depicted as grey curves, whilst the deconvolutions that represent ^{29}Si sites within the unreacted metakaolin are shown in a faded red.

5.2.3.2.3.2 ^{27}Al MAS NMR

The ^{27}Al MAS NMR spectra for the CNO_{3_5} and KGP samples at the 3 and 28 day time points post initial mixing are displayed in Figure 5-47.

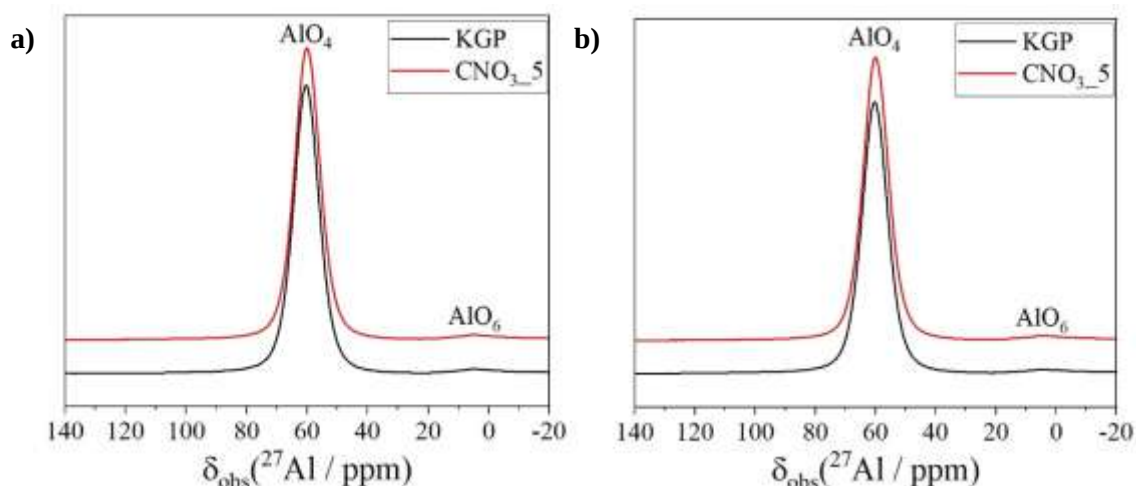


Figure 5-47: ^{27}Al MAS spectra for the CNO_3_5 and KGP samples a) 3 days and b) 28 days after reaction.

The ^{27}Al MAS NMR spectra exhibit two peaks that correspond to the two Al chemical environments present within the geopolymer samples. Firstly, the resonance centred at $\sim \delta_{\text{obs}}=60.3$ ppm and spanning between $\sim \delta_{\text{obs}}=50$ ppm and $\delta_{\text{obs}}=70$ ppm, is recognisable as the tetrahedral Al site (AlO_4^-) found in the K-A-S-H gel phase of the geopolymer [279, 306]. This coordination allows the K-A-S-H gel to bind the positively charged cations present within the sample, as the Al tetrahedra exhibits a net negative charge as Al^{3+} substitutes for Si^{4+} within the network [307]. This negative charge is balanced by cations: K^+ in the KGP sample and, theoretically, a combination of both K^+ and Cs^+ in the CNO_3_5 sample [308].

The small resonance observed at ~ 5 ppm is attributed to the presence of octahedral Al sites (AlO_6) within the samples [274]. The intensity of this peak is negligible when compared to that of the tetrahedral Al peak, and suggests that the majority of the Al within the metakaolin has reacted as the octahedral peaks correspond exclusively to the Al found within the unreacted metakaolin [279]. The ^1H - ^{29}Si CP MAS NMR and ^{29}Si MAS NMR spectra for these samples show that the majority, but not all, of the metakaolin has reacted, which explains the presence of this peak at such low intensities.

5.2.3.2.3.3 ^{39}K MAS NMR

The ^{39}K MAS NMR spectra for the CNO_3_5 and KGP samples at the 3 and 28 day time points post initial mixing are displayed in Figure 5-48.

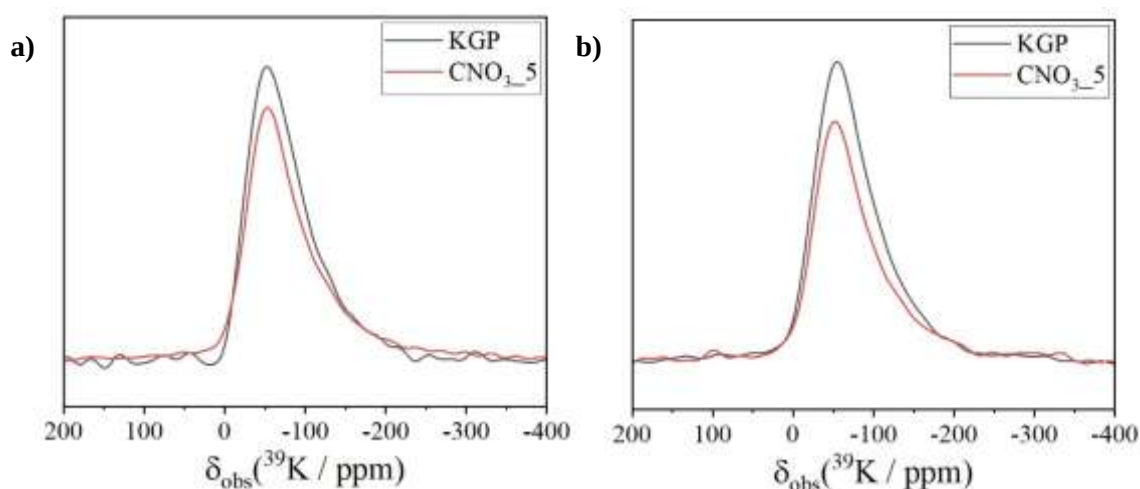


Figure 5-48: ^{39}K MAS NMR spectra for the CNO_3_5 and KGP samples a) 3 days and b) 28 days after reaction.

For both samples and time points, the spectra exhibit one peak centred around $\delta_{\text{obs}} = -53$ ppm. There is very little shift observed after the addition of CsNO_3 to the sample. This is an unexpected result considering the data seen in the XRD section suggesting that there is a significant amount of KNO_3 within the sample at both of the investigated time points. However, the chemical sensitivity of this technique may mean that it is unlikely that small changes such as this will be detected, with this sensitivity being a key reason as to why this technique is not widely performed on solids [349]. Moreover, the breadth of this peak is quite large, which could mean that the peaks for these individual phases are overlapping and cannot be distinguished from one another. Previous work by Moudrakovski and Ripmeester suggests that the peak for niter will fall within the region of the peak shown in Figure 5-48, and so it is likely that this peak is indistinguishable from that of the K in the K-A-S-H gel [350]. The lack of change here most likely indicates the presence of K^+ ions in the charge balancing sites of the K-A-S-H gel, as the spectra for the CNO_3_5 and KGP sample are comparable.

5.2.3.2.3.4 ^{133}Cs Solid-State NMR

Figure 5-49 shows the ^{133}Cs NMR spectra for the CNO_3_5 sample after 28 days of reaction.

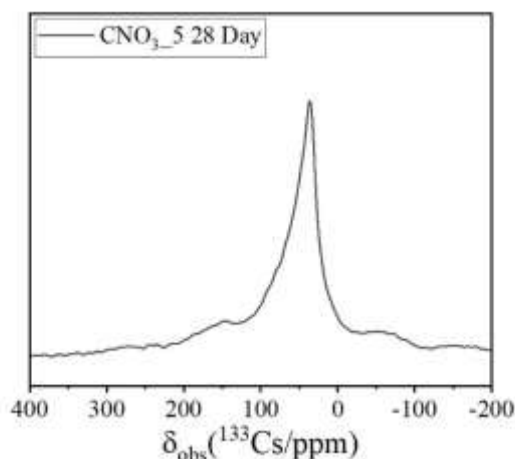


Figure 5-49: ^{133}Cs solid-state NMR spectrum for the CNO_3_5 sample after 28 days of reaction.

The spectrum here appears to show that there is a single clear peak in the spectra that centres around $\delta_{\text{obs}} = 35$ ppm. However, as discussed in Section 4.2.1.2.3.4, the quadrupolar nature of the Cs nucleus should lead to an asymmetrical peak, with a lesser gradient seen as the δ_{obs} decreases to negative values. This is not seen here, instead appearing to have a lesser gradient of descent as the δ_{obs} increases to higher values. This suggests that the peak seen here is the result of two overlapping peaks within the region, but that the instrument power is not strong enough to resolve these peaks. Work by Arbel-Haddad et al. investigated the effect of different wt.% of Cs in metakaolin based geopolymer samples activated by a (Na/Cs)OH activating solution [174]. They showed that the Cs is capable of becoming loaded into zeolitic phases within the geopolymer at similar wt.% as is seen in this work, notably zeolites A and X. Moreover, the peak centres seen in their work align with the peak range that is seen in Figure 5-49. The XRD seen in Section 5.2.3.2.2 shows the presence of a crystalline Cs-A-S-H phase within the CNO_3_5 sample which could correlate to a zeolitic type phase as seen in the work by Arbel-Haddad [174]. However, the use of Na in the activator also promotes that formation of zeolitic phases as opposed to the use of K, which means that it is less likely that these phases are forming in significant quantities in the samples in this work [193]. Therefore, it is possible that the Cs is present in the zeolitic phases, and it is also likely that the Cs^+ is displacing the K^+ ions within the amorphous K-A-S-H gel, which is shown to be in the sample through the use of XRD, FTIR and other NMR techniques used in this work. Furthermore, the solubility of the original CsNO_3 reactant is shown to be relatively low by the order-of-addition experiments, and is also shown to be present within the sample by the XRD, along with traces of Cs_2CO_3 . These phases should also be shown in the NMR, and are likely to be encompassed within the broad peak seen in the spectrum.

5.2.3.3 Conclusions

The isothermal conduction calorimetry data shown here confirms that the introduction of the CsNO_3 salt used in this work acts as a filling material within the geopolymer matrix due to its low solubility within the activating solution. Therefore, the impact of this effect that is seen in the ICC increases with

an increasing mass of the salt, and, likewise, an increasing Cs/Al ratio. The lack of dissolution means that the mechanism of formation is not altered, just slowed. The DRIFTS data shows that the formation of the K-A-S-H gel is very similar between the CNO_3_5 and KGP control samples, and also displays the presence of the solid CsNO_3 that does not dissolve into the solution.

However, the CsNO_3 does impact the resulting structure of the geopolymer, the primary phase of which is shown to be a K-A-S-H gel through the use of FTIR spectroscopy, ^{29}Si MAS NMR and ^{29}Si - ^1H CP MAS NMR. This phase is comprised of Si and Al in tetrahedral coordination, with the Si mainly existing in $\text{Q}^4(4\text{Al})$, $\text{Q}^4(3\text{Al})$ and $\text{Q}^4(2\text{Al})$ environments. The negative Al sites caused by Al^{3+} in tetrahedral coordination are charge balanced by K^+ , and XRD shows that some of the K^+ cations are displaced by the Cs^+ cations and, in some cases, form a crystalline Cs-A-S-H phase. XRD also shows that the crystalline structure of CsNO_3 is observed within the sample, showing that the dissolution of the salt is not complete, as is shown by the order-of-addition experiments. Therefore, it is shown that the geopolymer is capable of both encapsulating the salt within the matrix and chemically incorporating the Cs into the gel. It is shown that the introduction of the CsNO_3 leads to a slight relative increase in the Si/Al ratio, most likely due to the lower extent of reaction of the system compared to the KGP control sample.

^{39}K MAS NMR shows that the CsNO_3 has very little impact on the chemical environments of the K in the structure which is not supporting of the other data seen in the XRD and order-of-addition experiments but the chemical sensitivity of this technique means that small changes may not be apparent.

This work shows that K-silicate activated geopolymers are capable of incorporating wastes containing CsNO_3 at high waste loadings of up to 6.2% by weight. However, in practice, the loadings are likely to be far lower due to activity limits per package on the wasteforms, owing to the radioactivity of the waste in question. Whilst this, and any impact of the radiation and resulting decay products, are not considered in this work, it is important to note that they will likely have a notable effect on the performance of the geopolymer as a wasteform, and further work to determine how great this effect is will be crucial to determine the overall suitability of the wasteform.

However, the findings here display that geopolymer cements are capable of both encapsulating and immobilising CsNO_3 within its structure and proves that these systems show great promise as wasteforms for the long term immobilisation of radioactive waste streams containing ^{137}Cs in the form of CsNO_3 .

5.2.4 Caesium Sulphate

5.2.4.1 Fresh State

5.2.4.1.1 ICC

Figure 5-50 displays the calorimetry curves produced by the formation of the K-geopolymers loaded with Cs_2SO_4 over the first 3 days of reaction.

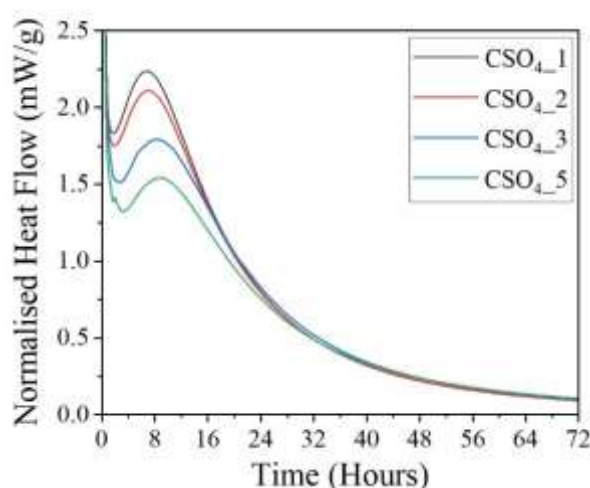


Figure 5-50: The effect on the heat evolution of reaction of loading K-activated metakaolin geopolymers with Cs_2SO_4 over first 24 hours of reaction.

As discussed in Section 4.2.1.1.1, the initial dissolution peak is disregarded in this analysis, and only the visible reaction peak is analysed. In addition, the KGP control sample's heat of evolution, seen in Figure 3-1, is only used to verify the lineshape of the curves for the CSO_4 samples.

Figure 5-50 shows that a greater impact is had on the reaction as the Cs/Al ratio of the samples, altered by the addition of Cs_2SO_4 , increases. The extent of reaction is clearly affected, as the peaks reach a far lower maximum normalised heat flow value for the reaction peaks as the Cs/Al ratio increases. Coupled with this, the time between the end of the dissolution peak, which can be seen in the first 4 hours of the figure, and the beginning of the reaction peak increases with increasing Cs/Al ratio which leads to a retardation of the reaction. It can also be seen that the reaction peaks become broader as the Cs/Al ratio increases, suggesting that the reaction is occurring over an elongated period of time. This points towards the reactants becoming available as the reaction progresses, suggesting slower dissolution of the metakaolin initially. The relationships between the Cs/Al ratio and the time and value of the maximum heat evolution can be seen in Figure 5-51.

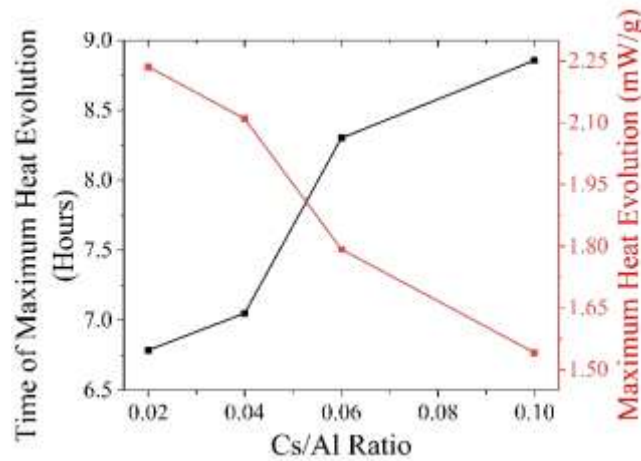


Figure 5-51: The relationship between Cs/Al ratio and the observed time of maximum heat evolution and the value of the maximum heat evolution.

Figure 5-51 shows that the relationships between the Cs/Al ratio and the time and value of the maximum heat evolution respectively are linear. There is no sign that the impact of the Cs_2SO_4 addition is slowing at a Cs/Al ratio of 0.10, suggesting that retardation of the reaction will continue its trend as the Cs/Al ratio increases. Likewise, it is likely that the effect of reducing the Cs/Al ratio below 0.02 will linearly reduce the retardation of the reaction that is seen in Figure 5-50.

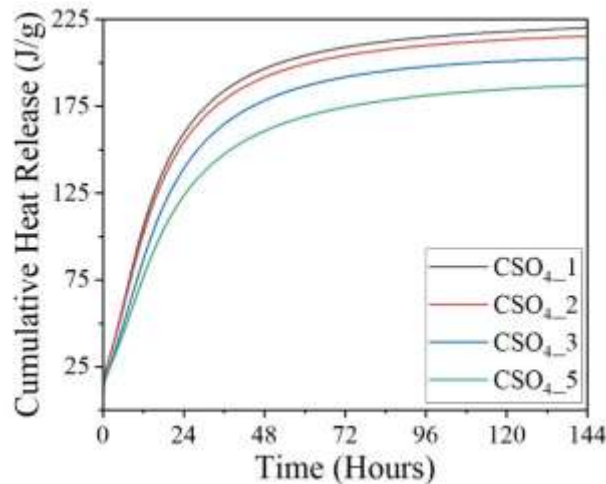


Figure 5-52: The cumulative heat release curves over the first 144 hours of reaction.

Figure 5-52 shows the cumulative heat release of the CSO_4 samples over the first 6 days of reaction. The heat release after 144 hours is equivalent to approximately 2/3 of the total heat release of the system for PC, and this can be assumed to be the same for geopolymer systems [297]. Using this assumption, the total heat release of the geopolymers mixed with Cs_2SO_4 will be no more than 335 J/g even in the case of the CSO_4_1 sample, which shows the greatest cumulative heat release. This is higher than the average heat release of the current nuclear standard, a Portland cement and GGBS blend, which is around 100 J/g, but still meets the guideline value of 180 J/g over the first 24 hours set by the current UK requirements for nuclear wastefoms [298, 299].

5.2.4.1.2 Zeta Potential

The zeta potential values obtained for the surface charge of metakaolin in the presence of Cs_2SO_4 at different pHs is shown in Figure 5-53.

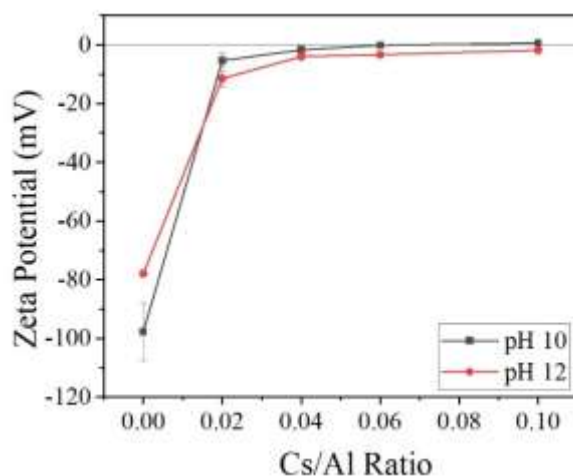


Figure 5-53: Comparing the effect of Cs/Al ratio, altered by the addition of Cs_2SO_4 , on the zeta potential of metakaolin in a KOH solution at pH 10 and 12.

Figure 5-53 shows that the addition of the Cs_2SO_4 leads to a significant increase in the recorded zeta potential for both pH points, from a minimum of $\sim -100\text{mV}$ (Cs/Al ratio of 0, pH of 10) to a maximum of 0.7mV (Cs/Al ratio of 0.1, pH of 10). The Cs^+ ions released by the dissolution of the salt are likely interacting with the negatively charged surface of the metakaolin particles, neutralising the charge and causing the measured zeta potential to rise towards the isoelectric point at 0mV .

At pH 10, the addition of the Cs_2SO_4 in the first instance, at a Cs/Al of 0.02, causes an increase in the zeta potential from -98mV to -5mV , suggesting that even a small increase in the concentration of Cs^+ ions has a major impact on the ability of the metakaolin particles to maintain a stable suspension within the KOH solution. Further addition of Cs^+ ions, indicated by an increasing Cs/Al ratio, does lead to a slight increase in the zeta potential to the point where it passes the isoelectric point, which does agree with the ICC data in Section 5.2.4.1.1, where the retardation of the reaction continues to increase with increasing Cs/Al ratio.

At pH 12, a similar effect is seen to that at pH 10, where the addition of the salt at a Cs/Al ratio of 0.02 causes a significant increase to the zeta potential in comparison to the metakaolin alone, but further addition of the Cs_2SO_4 does not cause as large an increase, especially after a Cs/Al ratio of 0.04. At this higher pH, the relative zeta potentials in comparison to their corresponding values at pH 10, are lower, suggesting that the measured zeta potentials would be more negative at the higher pH seen in the geopolymer systems seen in this work. However, work in the literature suggests that, at very high pH, the recorded zeta potential of metakaolin in KOH solutions increases sharply to more positive values [159]. However, the mechanisms of the Cs^+ ion interaction with the metakaolin particle may make this irrelevant.

The more neutral the zeta potential, the increased likelihood that it will lead to the formation of larger metakaolin particles with a decreased surface area, substantially slowing the dissolution of the metakaolin into the solution [300, 301]. However, the retardation of the reaction seen in the ICC could also be caused by a barrier effect, where the Cs^+ ions form a physical layer around the metakaolin particles which prevents the attack on the surface by the alkaline solution. This mechanism is inspired by the dissolution of glass, as outlined in Frugier et al. [302].

5.2.4.1.3 Order-of-addition Experiments

In order to determine whether the point at which the Cs salt is added to the mix impacts the performance of the geopolymer, order-of-addition experiments were performed as outlined in Section 2.1.1.2.

5.2.4.1.3.1 Order-of-Addition #1

1. The Cs_2SO_4 dissolves within the water leading to a clear solution.
2. The addition of the KOH leads to a release of heat due to the exothermic nature of the KOH dissolution. After this dissolution, the solution is no longer clear, but a cloudy white. The solution is not incredibly viscous, however, it is slightly more so than water. No solid is visible within this solution.
3. The potassium silicate mixes with the solution but does not alter the appearance or apparent properties of the solution.
4. Upon addition with the metakaolin, the layer of activating solution that had not reacted with the Cs_2SO_4 readily reacted with the metakaolin. The less viscous reaction product was partially stuck to the container and so did not completely enter the ampoule. The FTIR of this remaining solid can be seen in Figure 5-54.

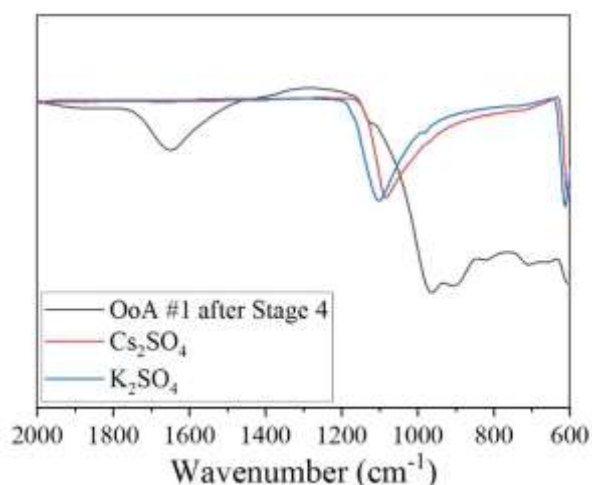


Figure 5-54: The FTIR spectra of the OoA #1 sample after stage 4 compared to pure Cs_2SO_4 and K_2SO_4 .

The solid clearly contains water, shown by the broad peak at $\sim 1500\text{--}1700\text{ cm}^{-1}$. The solid also contains a silicate compound as shown by the peak at $\sim 1000\text{ cm}^{-1}$. The spectra for the solid does not appear to contain any Cs_2SO_4 or K_2SO_4 as shown by Figure 5-54. It is likely that this solid

is potentially a collection of silicate and sulphate phases, although further work is required to prove this that has not been carried out in this thesis.

5.2.4.1.3.2 Order-of-Addition #2

1. The addition of solid KOH to water leads to an exothermic dissolution reaction.
2. The Cs_2SO_4 does not dissolve within the KOH solution. The solution is clear and the Cs salt crystals are clearly visible on the bottom of the container.
3. The potassium silicate mixes with the solution but does not cause the Cs_2SO_4 to dissolve. The solution is no longer clear, instead becoming a cloudy white.
4. Upon addition with the metakaolin, the layer of activating solution that had not reacted with the Cs_2SO_4 readily reacted with the metakaolin. The less viscous reaction product was partially stuck to the container and so did not completely enter the ampoule. The FTIR of this remaining solid can be seen in Figure 5-55.

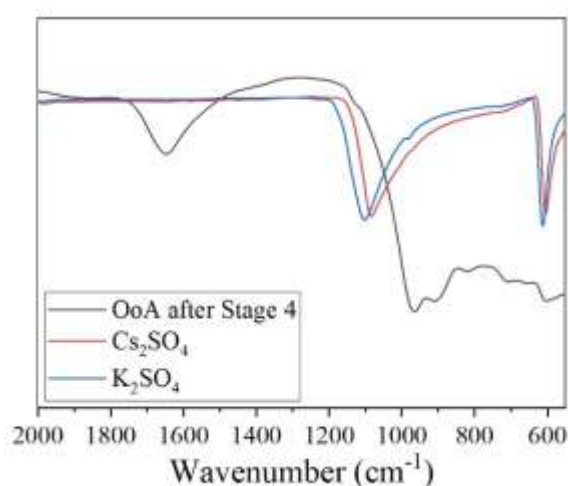


Figure 5-55: The FTIR spectra of the OoA #2 sample after stage 4 compared to pure Cs_2SO_4 and K_2SO_4 .

Much like the solid seen in the order-of-addition #2 experiments, the solid here contains water and a clear silicate compound. Again, this solid does not appear to contain any pure Cs_2SO_4 or K_2SO_4 .

5.2.4.1.3.3 Order-of-Addition #3

1. The addition of solid KOH to water leads to an exothermic dissolution reaction.
2. The addition of the K-silicate stock solution to the KOH solution resulted in a clear liquid mix.
3. The Cs_2SO_4 does not dissolve in the silicate solution, and instead rests at the bottom of the container. The solution is cloudy and it appears that the Cs_2SO_4 reacts with the activating solution to form another solid phase.
4. Upon addition with the metakaolin, the layer of activating solution that had not reacted with the Cs_2SO_4 readily reacted with the metakaolin. The less viscous reaction product easily entered the ampoule and mixed with the metakaolin to form what appeared to be a geopolymer.

5.2.4.1.3.4 Order-of-Addition ICC

Figure 5-56 shows the calorimetry curves generated by the order-of-addition samples containing Cs_2SO_4 over the first 3 days of reaction.

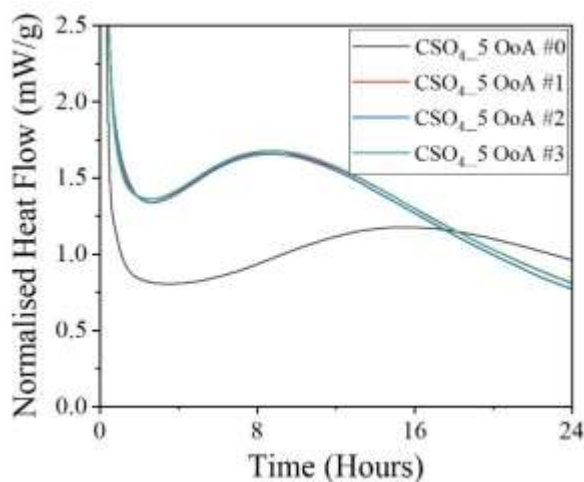


Figure 5-56: The effect on the heat evolution of the reaction of adding Cs_2SO_4 at different stages to K-activated metakaolin geopolymers over the first 3 days of reaction.

There is a clear difference between adding the Cs_2SO_4 to the aqueous phase and adding it to the solid phase, as presented by Figure 5-56. The addition of the salt to the aqueous phase leads to a reaction which forms a secondary solid phase, entrapping the majority of the salt and some of the activating solution. Analysis of this phase has been undertaken, as shown by the FTIR data in Figure 5-54 and Figure 5-55, but it has not been possible to identify the exact composition of the solid. Further work, and analysis, is suggested to identify the phase, although it is likely that it is a silicate that is formed, potentially a Cs-silicate that crystallises out of the solution. Despite this, the rest of the activating solution is free to react in its normal manner with the metakaolin, with the initial dissolution followed by the formation of the K-A-S-H gel. When added to the aqueous phase, as in experiments #1-3, the salt reacts in a similar way, reacting with the solution and forming a secondary solid. Therefore, it is unlikely that any of the Cs makes it into the final mixture that enters the calorimeter, which is supported by the similarity of the curves seen for experiments #1-3. However, this is not true for experiment #0, where the salt is added to the solid phase prior to mixing. In this case, all of the salt is incorporated into the mix, and the reaction between the salt and the activating solution happens in the presence of the metakaolin. Not only does this potentially lead to the consumption of more of the activating solution, it is possible that the metakaolin could become entrapped within the solid, resulting in a lesser mass of available reactants when compared to a system that does not contain Cs_2SO_4 . This explains the difference seen between experiment #0 and experiments #1-3 in Figure 5-56, and can also account for the elongation of reaction and lower extent of reaction in experiment #0.

5.2.4.1.3.5 Order-of-Addition Conclusions

The addition of Cs_2SO_4 at any point prior to the mixing of the geopolymer leads to a less than optimal result. When added to the aqueous phase, the salt reacts with the activating solution and immobilises itself in the solid phase that is formed. This prevents it from being included within the geopolymer gel matrix, with the Cs becoming a charge balancing cation. When added to the solid phase prior to reaction, the exact same thing happens, a reaction between the salt and the activating solution but in the presence of the solid metakaolin. In both cases, the Cs cannot be sufficiently contained within the geopolymer. Therefore, it is recommended that waste streams containing Cs_2SO_4 should be added to a pre-mixed geopolymer, that is to say a geopolymer where the activating solution and metakaolin have already been mixed, but the mix has not been allowed to set yet. This would remove the negative effects of the salts reacting with the activating solution impacting the dissolution of the metakaolin.

5.2.4.1.4 DRIFTS

The DRIFTS spectra for the CSO_4_5 sample in the first 8 hours of reaction can be seen in Figure 5-57.

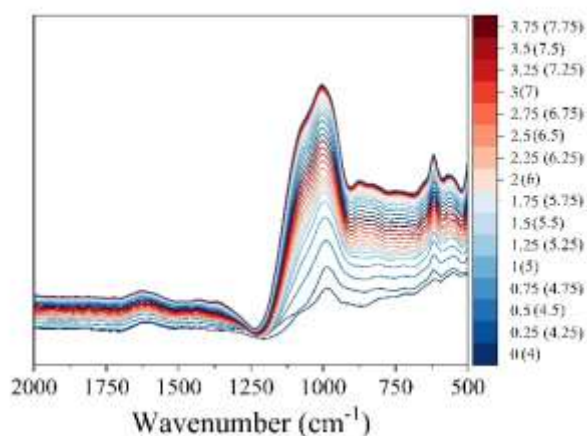


Figure 5-57: DRIFTS spectra for the CSO_4_5 sample in the first 8 hours of reaction. The spectra are displayed in 15 minute intervals, beginning at $t=0$ as marked and progressing through the colour gradient which repeats itself after 4 hours. Times are shown in hours.

The main peak present in the spectra appears immediately after initial mixing. This peak is associated most closely with the formation of a geopolymer, and is the Si-O-T peak centred at $\sim 1000\text{ cm}^{-1}$ [253]. This peak continues throughout the first 8 hours of reaction and is quite broad, with the appearance of a second peak centred closer to 1100 cm^{-1} also forthcoming. This peak can be related to the small peak that is visible in the spectra at $\sim 600\text{ cm}^{-1}$, as both can be attributed to the presence of a sulphate compound within the sample. The FTIR spectra for both Cs_2SO_4 and K_2SO_4 are shown in Figure 5-58.

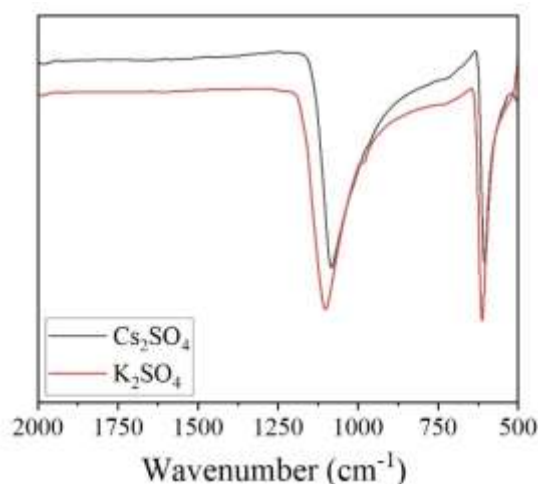


Figure 5-58: The FTIR spectra of Cs_2SO_4 and K_2SO_4 .

It is unclear as to whether the sulphate compound is that of Cs_2SO_4 or K_2SO_4 , or whether it is another sulphate containing compound, as suggested by the order-of-addition experiments in Section 5.2.4.1.3. These peaks are the only major difference between the spectra for the CSO_4_5 and the KGP sample, the spectra of which is shown in Figure 3-3.

The spectra for the CSO_4_5 sample for the remainder of the first day of reaction (8 hours to 24 hours) is displayed in Figure 5-59.

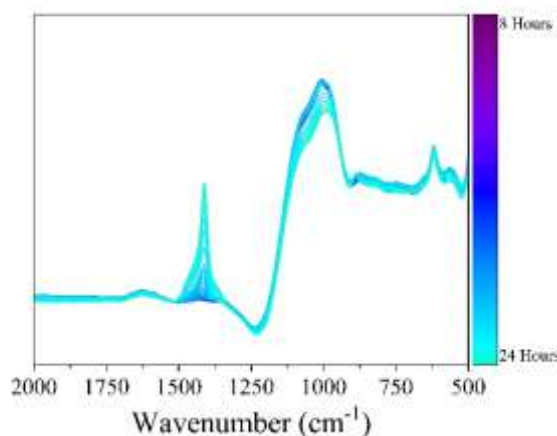


Figure 5-59: DRIFTS spectra for the CSO_4_5 sample from 8 to 24 hours post initial reaction. The spectra are displayed in 15 minute intervals up until the 16-hour mark, at which the time progresses in whole hours, beginning at $t=8$ hours as marked and progressing through the colour gradient. Times are shown in hours.

Throughout the first 24 hours of reaction, the small peak at $\sim 600\text{ cm}^{-1}$ remains present within the spectra. This suggests that the solids that are seen in the order-of-addition experiments, notably experiments #1 and #2, also precipitate into the solution when the salt is added to the metakaolin prior to mixing, as is

done in order-of-addition experiment #0. This solid does not appear to be consumed by further reaction, suggesting that it is chemically stable within the high pH of the system.

In regards to the main Si-O-T peak, the maximum intensity is reached at around 12 hours after mixing. This is significantly later in the reaction than the maximum heat evolution of the sample that is seen in the ICC (Section 5.2.4.1.1), however, the intensity seen in the DRIFTS data does not directly correlate with the extent of reaction. The reduction in intensity is most likely that the shrinkage of the cement is responsible for this drop; as the cement begins to harden, it shrinks, changing the distance between the surface of the sample and the detector [269, 270]. This occurs in this situation as the same sample is used throughout the measurement and, during this time, no changes are made to the apparatus and so the measurement distance does not change. During the geopolymer reaction, the hardening of the surface of the sample may lead to a geometrically flat plane. This surface may become too flat for the efficient use of the diffuse scattering technique [341].

Between 8 and 24 hours after the initial mixing, a further peak appears at $\sim 1400\text{ cm}^{-1}$. The cause of this peak is likely to be the carbonation of the sample due to reaction with the CO_2 in the air [271]. The infrared beam used for the DRIFTS measurement must pass through the surface of the sample to reach the bulk material. Therefore, artefacts from the surface of the sample, notably the point where carbonation would occur, will always be included in the spectra. Due to this, it is most likely that this peak is a reflection of the carbonation of Sr within the sample. This peak is also visible in the spectra for the KGP sample for the 4 to 24 hour period after initial reaction, as seen in Figure 3-4.

5.2.4.2 Hardened State

5.2.4.2.1 FTIR

Figure 5-60 shows the FTIR spectra of the K-geopolymers loaded with Cs_2SO_4 after the first 3 days of reaction.

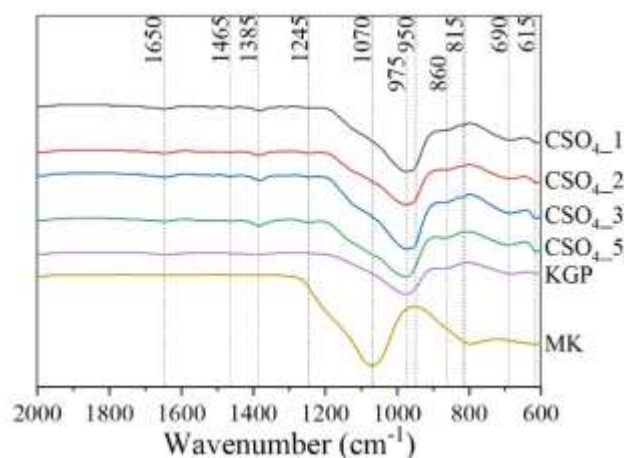


Figure 5-60: The FTIR spectra generated by loading K-activated metakaolin geopolymers with Cs_2SO_4 , the KGP control sample and the unreacted metakaolin after the first 3 days of reaction.

The bond vibrations that are responsible for the resonances seen are discussed in more detail in Section 3.4.2 and summarised in Table 3-4. The peak at $\sim 975\text{ cm}^{-1}$ in all samples in Figure 5-60 is attributed to the asymmetric stretching of Si-O-T bonds within the aluminosilicate framework, where T can be either Si or Al atoms in tetrahedral coordination [253]. A shoulder on this peak at $\sim 1070\text{ cm}^{-1}$ is an indication of the amount of unreacted metakaolin within the sample, as this aligns with the main silicon site peak in the unreacted metakaolin spectra. The intensity of this shoulder appears to increase with increasing Cs/Al ratio, suggesting an increased Cs/Al ratio leads to a lower extent of reaction. This agrees with the trend seen in the ICC (Section 5.2.4.1.1) which suggests there is lesser reaction in the CSO₄_5 peak as opposed to CSO₄_1. The peak at 1385 cm^{-1} has been identified but has not been assigned here. An investigation into this peak has been carried out, due to its presence in the region where bonds associated with the salts of Cs are found. However, it is not caused by the presence of either Cs₂SO₄ or K₂SO₄, as the peaks for these salts are found within the region of $\sim 1100\text{ cm}^{-1}$ as shown by Figure 5-54. The peak at $\sim 1465\text{ cm}^{-1}$ indicates the presence of carbonate groups within the sample. This is due to the carbonation of the samples due to exposure to air [271]. Therefore, the carbonate compound could be a potassium carbonate, a caesium carbonate, or even a mixture of the two.

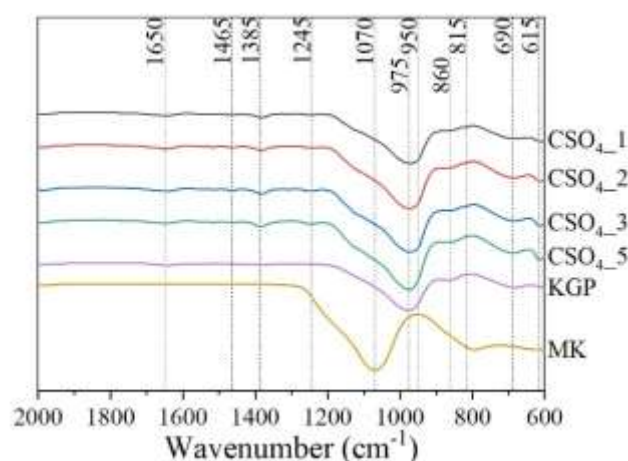


Figure 5-61: The FTIR spectra generated by loading K-activated metakaolin geopolymers with Cs₂SO₄, the KGP control sample and the unreacted metakaolin after the first 28 days of reaction.

The FTIR spectra of the Cs₂SO₄ after the first 28 days of reaction can be seen in Figure 5-61. There is negligible change between this and the spectra after 3 days, suggesting that the main bonds within the gel matrix have been formed by the 3-day mark.

5.2.4.2.2 XRD

The XRD spectra for the geopolymer samples containing Cs₂SO₄ 3 days after initial reaction are shown in Figure 5-62.

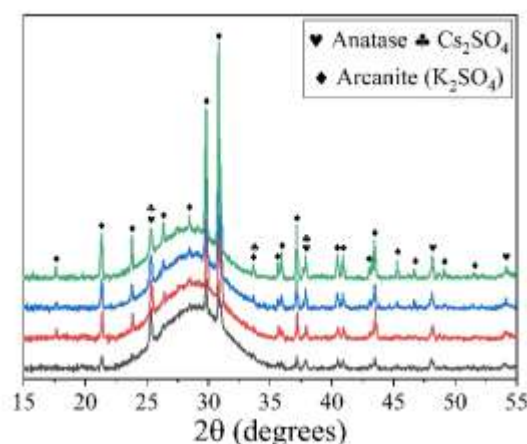


Figure 5-62: The x-ray diffraction spectra generated by loading K-activated metakaolin geopolymers with Cs_2SO_4 after the first 3 days of reaction.

The spectra for all samples show the presence of multiple crystalline phases. Firstly, anatase (TiO_2 , PDF # 01-086-1157) is found in the raw metakaolin reactant and is an inert phase, meaning it will always be present in the final sample, as shown here. The addition of the Cs_2SO_4 salt leads to a reaction with the activating solution, as shown within the order-of-addition experiments in Section 5.2.4.1.3. These observations are supported by the presence of crystalline arcanite (K_2SO_4 , PDF # 00-044-1414), which is formed via the reaction of the Cs salt with the activating solution. The peaks that are attributed to this phase are very intense, suggesting that there is a large concentration of this phase within the sample. Therefore, it is likely that the vast majority of the Cs_2SO_4 salt reacts with the K^+ cations within the activating solution, releasing the Cs^+ cations to be potentially incorporated into the binding phase of the geopolymer. The Cs_2SO_4 (PDF # 00-021-0854) that does not react with the activating solution remains in the initial state, potentially due to the physical barrier between the salt and the activating solution that is caused by the precipitation of the K_2SO_4 . The absence of a carbonate phase here, despite a carbonate phase being present in the DRIFTS data, is likely due to the DRIFTS technique taking into account the carbonation of the pore solution which will not directly relate to a crystalline carbonate phase in the XRD data.

Aside from the crystalline phases, the single broad peak between $\sim 23^\circ 2\theta$ and $34^\circ 2\theta$ which represents the amorphous K-A-S-H gel that is indicative of the formation of a geopolymer gel and appears to be identical in all samples [164].

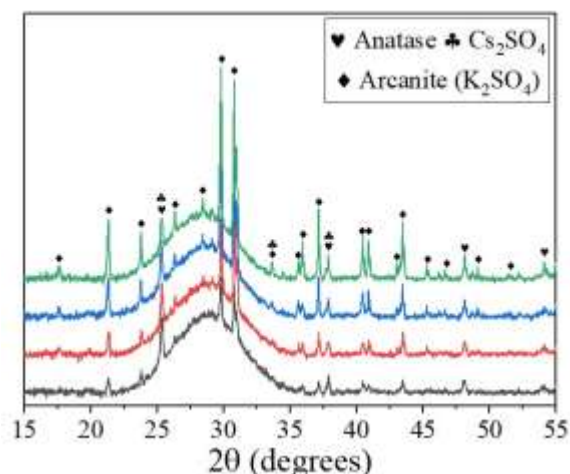


Figure 5-63: The x-ray diffraction spectra generated by loading K-activated metakaolin geopolymers with Cs_2SO_4 after the first 28 days of reaction.

The spectra for the CSO_4 samples after 28 days of reaction, shown in Figure 5-63, exhibit very little change when compared to the spectra after 3 days of reaction. There are no additional crystalline phases present and the relative peak intensities of the crystalline phases initially outlined are similar.

5.2.4.2.3 NMR

5.2.4.2.3.1 ^1H - ^{29}Si CP MAS and ^{29}Si MAS NMR

The ^1H - ^{29}Si CP MAS NMR and ^{29}Si MAS NMR spectra for the CSO_4_5 and KGP samples both 3 and 28 days after the initial reaction are displayed in Figure 5-64.

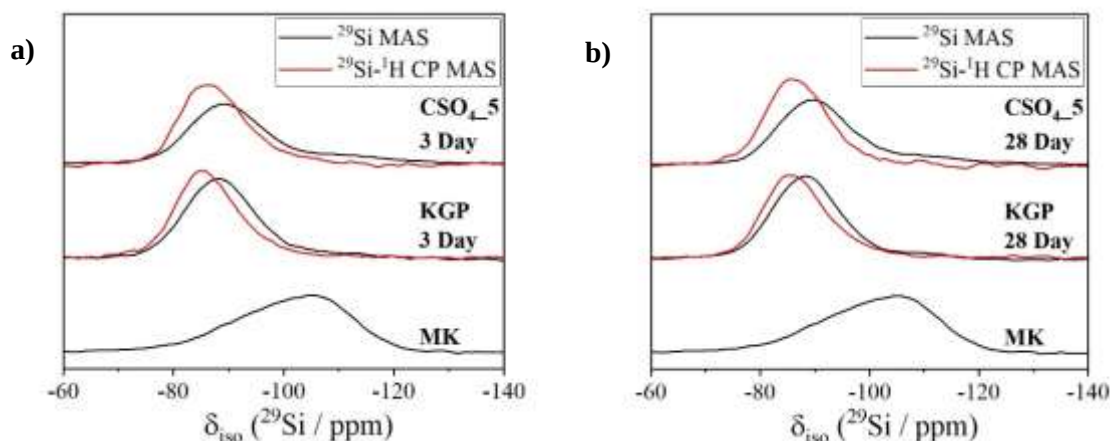


Figure 5-64: ^1H - ^{29}Si CP MAS and ^{29}Si MAS spectra for the CSO_4_5 , KGP samples and the unreacted metakaolin a) 3 days and b) 28 days after reaction.

The rationale for the use of, and differences between the ^1H - ^{29}Si CP MAS NMR and ^{29}Si MAS NMR techniques are discussed in Section 5.2.1.2.3.1. Figure 5-64 shows that the ^1H - ^{29}Si CP MAS NMR spectra, displayed as red curves, constitute a single broad peak between $\delta_{\text{iso}} = -75$ and $\delta_{\text{iso}} = -100$ ppm. The maximum intensity for the KGP sample is observed at a δ_{iso} of -85 ppm, confirming that the geopolymer gels are predominantly comprised of $\text{Q}^4(4\text{Al})$ and $\text{Q}^4(3\text{Al})$ silicon environments as would be expected

from the literature [67, 347]. However, the spectra for the CSO₄_5 samples for both time points are slightly broader than the KGP samples and are centred at lower δ_{iso} values of between -86 ppm and -87 ppm. This suggests that there are a greater number of Q⁴(1Al) and Q⁴(2Al) sites in these samples, showing that the samples are not as highly cross-linked as the KGP samples.

The black curves in Figure 5-64 represent the ²⁹Si MAS NMR spectra for the samples which display all of the Si chemical environments present within the samples, including those for the unreacted metakaolin that remains post reaction. For these spectra, the maximum peak intensity is recorded at a lower δ_{iso} of $\delta_{\text{iso}}=-88$ ppm for the KGP sample and $\delta_{\text{iso}}=-89.5$ ppm for the CSO₄_5 sample.

In both samples, the peak centres clearly shift to the right between the ¹H-²⁹Si CP MAS NMR and ²⁹Si MAS NMR spectra which is expected, as the ²⁹Si MAS NMR spectra show the Si sites that are attributed to the unreacted metakaolin. The extents of reaction for these samples, in terms of percentage, can be seen in Table 5-8.

Table 5-8: The extent of reaction of the CSO₄_5 and KGP samples both 3 and 28 days after initial reaction, calculated using the ²⁹Si MAS NMR spectra.

Sample	Time point	Extent of reaction (%)
KGP	3 Days	82.17
CSO ₄ _5	3 Days	76.70
KGP	28 Days	88.00
CSO ₄ _5	28 Days	78.32

The extents of reactions shown here agree with the ²⁹Si MAS NMR spectra which suggests that there is more unreacted metakaolin in the CSO₄_5 than the KGP sample. The extent of reaction is calculated by subtracting the total percentage of silicon sites present due to the unreacted metakaolin from 100%, which comprises of Si sites from the hydrated gel and the metakaolin, which are calculated using the deconvolutions of the ²⁹Si MAS NMR and the ¹H-²⁹Si CP MAS spectra respectively.

With respect to the deconvolutions seen in Figure 5-65, the ²⁹Si MAS NMR spectra show that the gel structure is dominated by Q⁴(3Al) sites, which agrees with data reported in the literature for potassium activated geopolymers [172]. The spectra observed here are similar to those seen in previous work, suggesting that the K-A-S-H gel is formed by a mixture of Si environments in the form of Q⁴(mAl) sites, where $1 \leq m \leq 4$ [67]. This is supported by Table 5-9, which shows the presence of each Si site as a percentage calculated from the ²⁹Si MAS NMR data.

Table 5-9: Relative integral areas for the Si sites present within the K-A-S-H gel of each sample both 3 and 28 days after initial reaction from the deconvoluted ^{29}Si MAS NMR spectra. The $\text{Q}^4(0\text{Al})$ site attributed to the unreacted metakaolin is disregarded for the quantification of the K-A-S-H gel.

Sample	Time point	Relative Integral Area (%)				Si/Al
		$\text{Q}^4(4\text{Al})$	$\text{Q}^4(3\text{Al})$	$\text{Q}^4(2\text{Al})$	$\text{Q}^4(1\text{Al})$	
KGP	3 Days	25	54	20	1	1.32
CSO_4_5	3 Days	26	49	25	0	1.36
KGP	28 Days	28	44	26	2	1.34
CSO_4_5	28 Days	22	50	27	1	1.37

The deconvolutions here show that, after the first 3 days of reaction, the KGP sample contains a greater percentage of $\text{Q}^4(4\text{Al})$ and $\text{Q}^4(3\text{Al})$ sites than the CSO_4_5 sample. Furthermore, the extent of reaction of the KGP sample after this time is considerably greater than the CSO_4_5 sample. Therefore, the dissolution of the metakaolin in the KGP sample is greater, introducing a larger proportion of the available Al tetrahedra into the aqueous phase of the reaction mixture. This leads to a more successfully cross-linked aluminosilicate structure, resulting in the higher percentage of $\text{Q}^4(4\text{Al})$ and $\text{Q}^4(3\text{Al})$ sites within the structure.

The lower extent of reaction seen in the CSO_4_5 sample can be attributed to the reaction of the Cs_2SO_4 with the activating solution to form the solid that is seen in the order-of-addition experiments in Section 5.2.4.1.3. As previously discussed, the precipitation of this solid is not only trapping some of the activating solution, it is also creating a physical barrier between the solution and the metakaolin, reducing the amount of dissolution. This reduces the available Al in solution to form a highly cross-linked K-A-S-H gel and leads to a greater proportion of $\text{Q}^4(2\text{Al})$ sites. The lower extent of reaction is visualised in Figure 5-65 and Figure 3-6, where the faded red curves display the total number of silicon sites attributed to the unreacted metakaolin. For the CSO_4_5 samples at both time points, the area under the curve is greater, displaying the larger amount of metakaolin present.

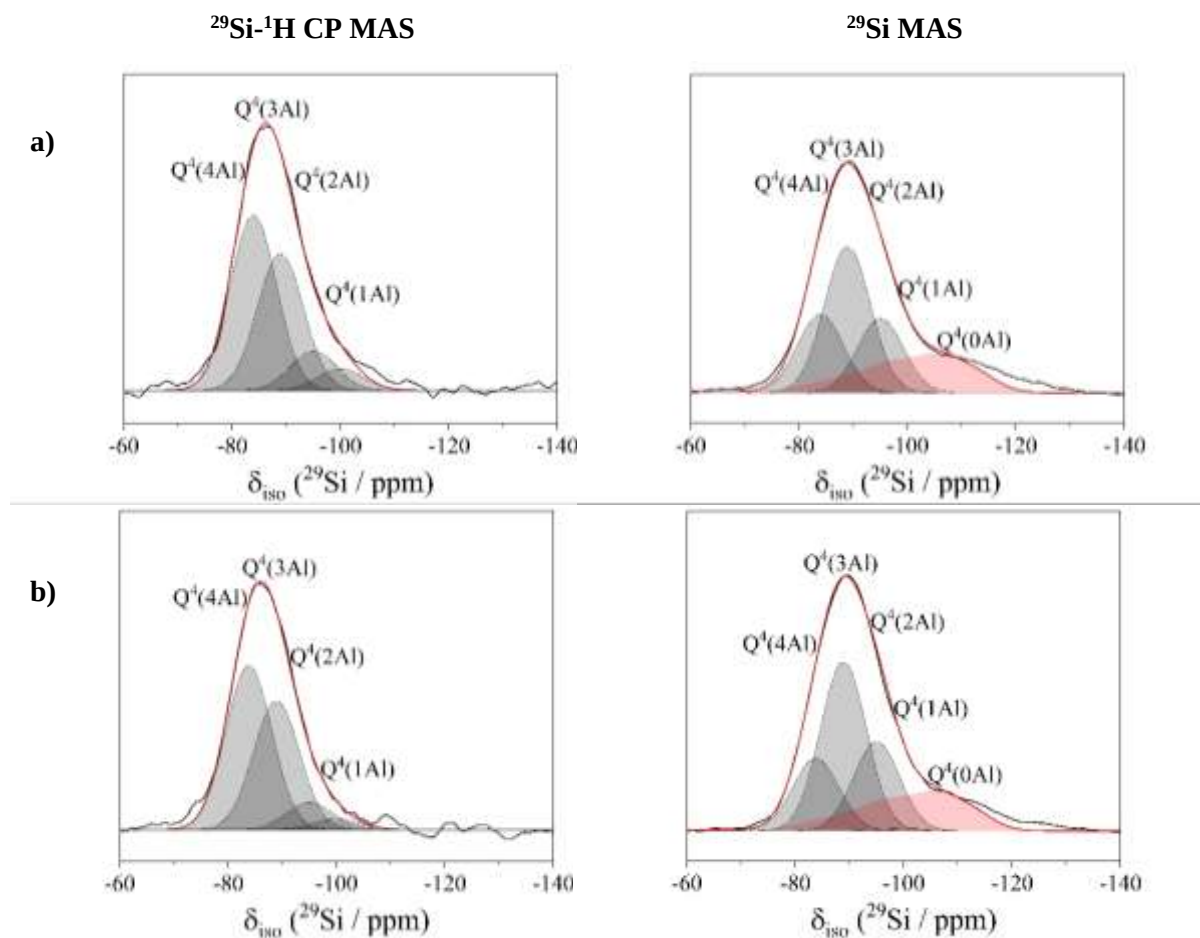


Figure 5-65: ²⁹Si-¹H CP MAS and ²⁹Si MAS NMR spectra and the associated deconvolutions for the a) CSO₄_5 sample after 3 days and b) CSO₄_5 sample after 28 days. The ²⁹Si-¹H CP MAS NMR data is shown in the left column and the ²⁹Si MAS NMR data is shown in the right column. For each spectrum, the raw data is shown as a solid black line and the model fit is shown as a solid red curve. The deconvolutions that represent each ²⁹Si site within the K-A-S-H gel are depicted as grey curves, whilst the deconvolutions that represent ²⁹Si sites within the unreacted metakaolin are shown in a faded red.

5.2.4.2.3.2 ²⁷Al MAS NMR

The ²⁷Al MAS NMR spectra for the CSO₄_5 and KGP samples at the 3 and 28 day time points post initial mixing are displayed in Figure 5-66.

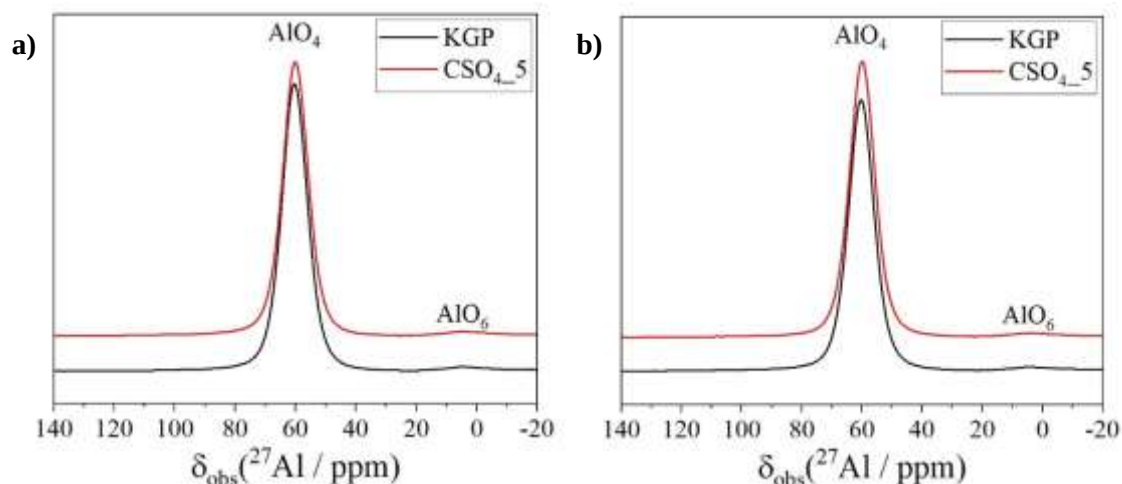


Figure 5-66: ^{27}Al MAS spectra for the CSO_4_5 and KGP samples a) 3 days and b) 28 days after reaction.

For all samples, two peaks are visible within the spectra. Firstly, the intense peak displayed at $\sim \delta_{\text{obs}}=60$ ppm is indicative of the tetrahedral Al site (AlO_4^-) found within the K-A-S-H gel of the geopolymer [279, 306]. It is this site that provides the charge balancing capabilities of the geopolymer, allowing the positive cations within the mix to be chemically bound to the structure. It is this site that allows for the incorporation of the Cs^+ ions into the structure which make geopolymers such a promising candidate for the encapsulation of Cs containing radioactive waste. The preference of Al to exist within the $q^4(4\text{Si})$ coordination is due to the energetic penalty associated with Al-O-Al bonding which explains the absence of any other Al co-ordination within the structure [284, 285].

The other site displayed in the spectra is allocated to the AlO_6 site within the unreacted metakaolin that is present within the samples [274]. The intensity of this peak is far lower than that of the AlO_4^- peak. This is due to the low concentration of unreacted metakaolin in the samples. Moreover, the preferential dissolution of the Al within the metakaolin means that it is likely that the majority of the Al has already dissolved [279].

5.2.4.2.3.3 ^{39}K MAS NMR

The ^{39}K MAS NMR spectra for the CSO_4_5 and KGP samples at the 28-day time point post initial mixing are displayed in Figure 5-67. The ^{39}K MAS NMR spectra for the CSO_4_5 sample after 3 days of reaction was not able to be collected.

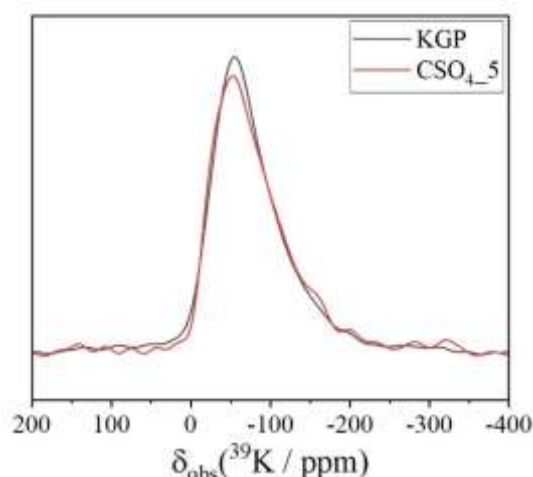


Figure 5-67: ^{39}K MAS NMR spectra for the CSO_4_5 and KGP samples 28 days after reaction.

The ^{39}K MAS NMR spectra here show very little change between the KGP control sample and the CSO_4_5 after 28 days of reaction, suggesting that the K environments within the samples are very similar. However, the XRD data shows that there is a significant presence of K_2SO_4 which is not present in the KGP control sample. However, these environments may not cause a significant shift in the spectra. Moreover, the chemical sensitivity of this technique may mean that it is unlikely that small changes such as this will be detected, with this sensitivity being a key reason as to why this technique is not widely performed on solids [349].

5.2.4.2.3.4 ^{133}Cs Solid-State NMR

Figure 5-68 shows the ^{133}Cs NMR spectra for the CSO_4_5 sample after 28 days of reaction.

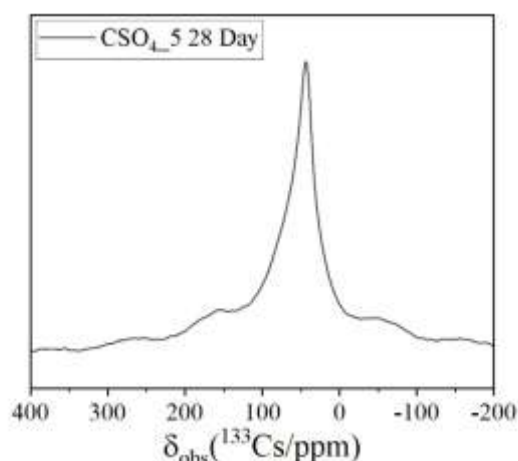


Figure 5-68: ^{133}Cs solid-state NMR spectrum for the CSO_4_5 sample after 28 days of reaction.

The spectrum here appears to show that there is a single clear peak in the spectra that centres around $\delta_{\text{obs}} = 43$ ppm. However, as discussed in Section 4.2.1.2.3.4, the quadrupolar nature of the Cs nucleus should lead to an asymmetrical peak, with a lesser gradient seen as the δ_{obs} decreases to negative values. This is not seen here, instead appearing to have a lesser gradient of descent as the δ_{obs} increases to higher values. This suggests that the peak seen here is the result of two or more overlapping peaks within the

region, but that the instrument power is not strong enough to resolve these peaks. Work by Arbel-Haddad et al. investigated the effect of different wt.% of Cs in metakaolin based geopolymer samples activated by a (Na/Cs)OH activating solution [174]. They showed that the Cs is capable of becoming loaded into zeolitic phases within the geopolymer at similar wt.% as is seen in this work, notably zeolites A and X. Moreover, the peak centres seen in their work align with the peak range that is seen in Figure 5-68. The XRD seen in Section 5.2.3.2.2 shows the presence of a crystalline Cs-A-S-H phase within the CSO₄_5 sample which could correlate to a zeolitic type phase as seen in the work by Arbel-Haddad [174]. However, the use of Na in the activator also promotes that formation of zeolitic phases as opposed to the use of K, which means that it is less likely that these phases are forming in significant quantities here [193]. Therefore, it is possible that the Cs is present in the zeolitic phases, and it is also likely that the Cs⁺ is displacing the K⁺ ions within the amorphous K-A-S-H gel, which is shown to be in the sample through the use of XRD, FTIR and other NMR techniques above. Furthermore, the original Cs₂SO₄ reactant is shown to be present within the sample by the XRD. This phase should also be shown in the NMR, and is most likely encompassed within the broad peak seen in the spectrum.

5.2.4.3 Conclusions

The isothermal conduction calorimetry data shows that the introduction of Cs₂SO₄ into the geopolymer reaction mixture leads to retardation of the reaction. The zeta potential data shows that the salt interacts with the metakaolin when in solution, and, more importantly, the order-of-addition experiments accompanied by the XRD data shows that the Cs₂SO₄ reacts readily with the activating solution. This reaction forms a solid that precipitates out of the solution and encapsulates the reactants, creating a physical barrier between the metakaolin and the activating solution which radically slows the dissolution and consequent polymerisation reaction. The DRIFTS data shows that, although this solid retards the reaction, it does not alter the bonds that are formed.

The primary phase of the formed geopolymer in all cases is shown to be the K-A-S-H gel by the use of FTIR spectroscopy, ²⁹Si MAS NMR and ¹H-²⁹Si CP MAS NMR. The negative Al sites caused by Al³⁺ in tetrahedral coordination are charge balanced by K⁺, although, upon the introduction of Cs⁺ cations, some of the K⁺ is displaced in favour of the Cs⁺. It is shown that the introduction of Cs₂SO₄ to the reaction mix leads to an increase in the Si/Al ratio of the K-A-S-H gel, showing that these gels have a slightly lower charge balancing capacity. ³⁹K MAS NMR shows that, despite the XRD showing the presence of K₂SO₄, a phase that is not found in the KGP control sample, there is not a clear difference between the spectra.

This work shows that K-silicate activated geopolymers are capable of incorporating wastes containing Cs₂SO₄ at high waste loadings of up to 11.3% by weight. However, in practice, the loadings are likely to be far lower due to activity limits per package on the wasteforms, owing to the radioactivity of the waste in question. Whilst this, and any impact of the radiation and resulting decay products, are not

considered in this work, it is important to note that they will likely have a notable effect on the performance of the geopolymer as a wasteform, and further work to determine how great this effect is will be crucial to determine the overall suitability of the wasteform.

The findings of this work show that geopolymer cements are capable of incorporating waste streams containing Cs_2SO_4 into the wasteform. However, the salts should be added to the geopolymer mix after the initial mixing of the metakaolin and the activating solution as to not affect the dissolution of the metakaolin. With this modification, these systems show great promise as wasteforms for the long term immobilisation of radioactive waste streams containing ^{137}Cs in the form of Cs_2SO_4 .

5.2.5 Comparison of Salts

5.2.5.1 Overview

The caesium salts used in this work: CsOH, Cs₂CO₃, CsNO₃, and Cs₂SO₄ react differently when added to the geopolymer reaction mix depending on the anion associated with them. These reactions lead to significant alterations when considering the ability of the Cs to displace the K within the charge balancing sites of the K-A-S-H gel. Most obviously, the solubility of the salts is a key factor as to whether the Cs will be incorporated into the chemical structure of the gel; CsOH and Cs₂CO₃ are readily soluble in the activating solution and so dissociate into the constituent ions within solution. The Cs₂SO₄ is also soluble, however, when dissociating in solution, leads to further, unfavourable reactions between the anion and the activating solution. Finally, the CsNO₃ is mostly insoluble, but the small amount that does dissolve causes further and, in some respects, more favourable reactions. In this section, where appropriate, the effect of adding the salts to the geopolymer mix at an Cs/Al ratio of 0.10 will be compared and discussed.

5.2.5.2 Fresh State

The isothermal calorimetry curves generated by the heat released during the reaction to form the K-A-S-H gel is seen in Figure 5-69.

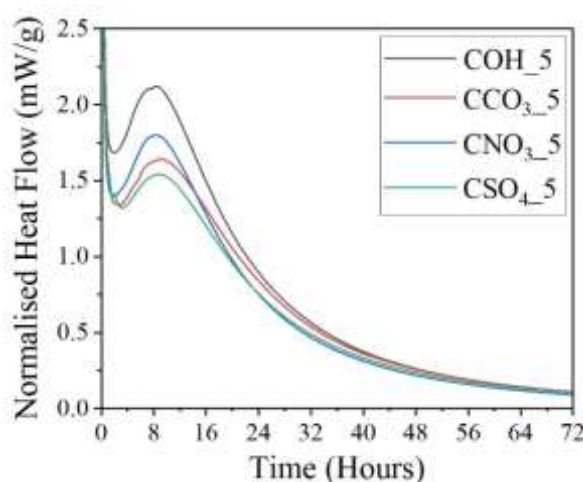


Figure 5-69: The effect on the heat evolution of reaction of loading K-activated metakaolin geopolymers with CsOH, Cs₂CO₃, CsNO₃, and Cs₂SO₄ at an Cs/Al ratio of 0.10 over the first 3 days of reaction.

The solubility of the salt does not appear to have a direct correlation with the change seen in the ICC data. Both soluble salts, the CsOH and Cs₂CO₃ show very different curves, suggesting that the interaction of the ions within solution is different, and, consequently, so are the mechanisms for the change in reaction. The large decrease in the heat evolved between the samples could also be due to the increased wt.% of the Cs₂CO₃ in the CCO₃_5 sample when compared to the CsOH in the COH_5 sample which will reduce the wt.% of geopolymer reactants within the sample. As the heat release is reliant upon the reaction between the metakaolin and activating solution, having a lesser mass of this in the

sample will consequently reduce the total number of polycondensation reactions, and therefore, the amount of heat released. Both of these samples display a change due to this effect.

The CSO₄_5 sample shows the greatest deviation of heat evolved from the COH_5 sample, which is thought to be the most similarly matched sample to the KGP sample, shown in Figure 3-1. The reasoning for not using a direct numerical comparison to the KGP control sample is discussed in Section 5.2.1.1.1. As the main distinguishable difference between these samples is the anion, it can be shown that the SO₄²⁻ anion causes a significant change in the level of reaction of the geopolymer. The Cs⁺ cations are unlikely to be the cause of this change.

Despite the clear differences in the maximum heat evolved for the geopolymers, the time at which this occurs is relatively unaltered between the samples seen in Figure 5-69a). This is also true when compared to the KGP control sample in Figure 5-69b). This suggests that the introduction of the Cs in any of the forms does not significantly retard the reaction; instead, the main impact is the reduction in the level of reaction to form the K-A-S-H gel.

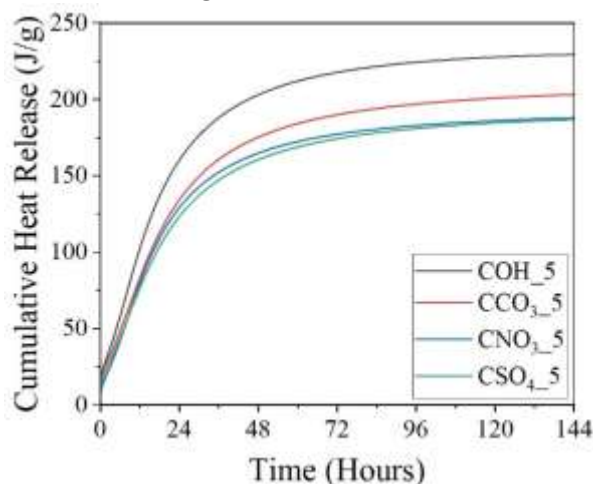


Figure 5-70: The cumulative heat release curves over the first 144 hours of reaction of the geopolymers containing CsOH, Cs₂CO₃, CsNO₃, and Cs₂SO₄.

The cumulative heat curves shown in Figure 5-70 show a similar trend to that seen in the ICC curves after the initial reaction. The heat released by the COH_5 sample far exceeds that of the other samples, and there is a possibility that the introduction of the CsOH does indeed increase the reaction, but it would be expected that this would be mirrored in the extent of reaction seen in the NMR data, which it is not. Furthermore, if a further reaction occurred between the salt and any of the constituents of the geopolymer mix, it would be expected that this reaction product would be seen in the other solid state analysis techniques, but there is no evidence of any unexpected reaction products seen here. The CNO₃_5 and the CSO₄_5 samples both show a very low cumulative heat as opposed to the other samples, which correlates with the lower extent of reaction of these samples due to the reaction of the salt with the activating solution.

The interactions of the Cs^+ cations within the paste can be partially explained by the zeta potential values shown in Figure 5-71.

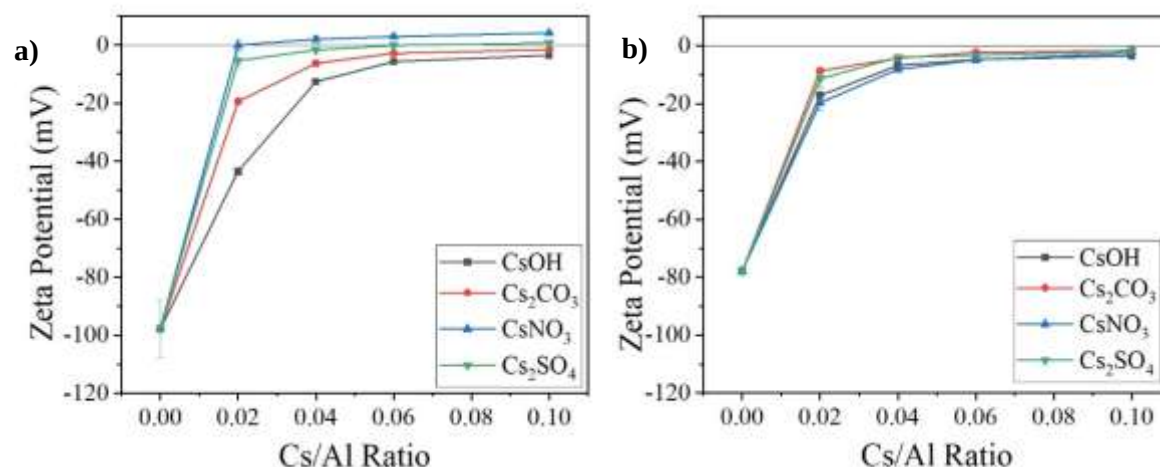


Figure 5-71: Comparing the effect of Cs/Al ratio, altered by the addition of CsOH , Cs_2CO_3 , CsNO_3 , and Cs_2SO_4 , on the zeta potential of metakaolin in a KOH solution at differing pH's: a) pH 10 and b) pH 12.

The zeta potential value for the metakaolin particles in KOH solution is very negative, but the addition of all salts at all Cs/Al ratios and at both pH points leads to the increase of the recorded zeta potential towards 0 mV, the isoelectric point. The zeta potential of the metakaolin particles will be impacted mostly by the introduction of the Cs^+ cations into solution, as the positively charged ions will be attracted to the negatively charged metakaolin particles. The results here show that all of the salts must dissolve, as the zeta potential moves towards 0 mV after the addition of all salts at a Cs/Al ratio of 0.02.

At pH 10, the greatest change is seen by the samples containing the CsNO_3 salt. The recorded zeta potential for this salt increases to above the isoelectric point, showing that the Cs^+ cations have interacted with the metakaolin particles sufficiently to lead to a complete change of charge. The magnitude of this charge results in the electrostatic repulsion between the particles becoming minimal, promoting agglomeration of the particles, which will, ultimately, lead to a larger surface area and slower dissolution.

The CsOH and Cs_2CO_3 are both very soluble in the activating solution of the geopolymer mix, and the zeta potential results here suggest that the high pH of the activating solution promotes this, more notably for the CsOH sample. The similarities between the changes in the zeta potential for each salt suggest that the Cs in all cases has a similar effect, and the effects become more similar with increasing pH, which describes the ICC results seen for the salts. The level of retardation is very similar for all salts, that is the time at which the maximum heat evolution is achieved, and it would be the interaction between the Cs^+ and the metakaolin that would be a leading candidate for the mechanism behind the retardation.

The XRD patterns for the samples with an Cs/Al ratio of 0.10 after 3 days are displayed in Figure 5-72.

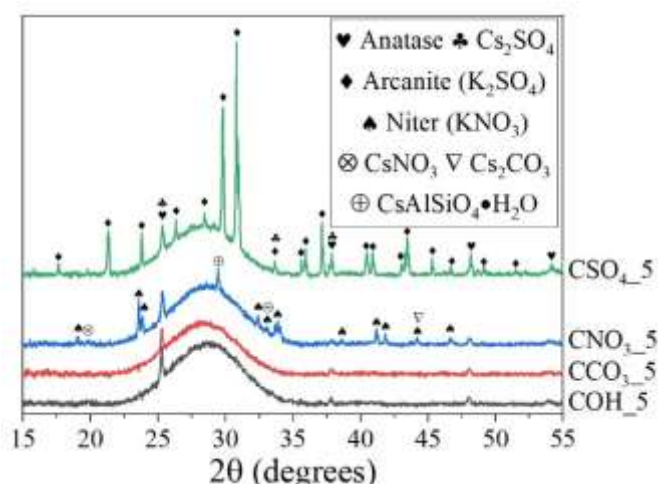


Figure 5-72: The XRD diffraction patterns after 3 days of reaction of the geopolymers containing CsOH, Cs₂CO₃, CsNO₃, and Cs₂SO₄ at a Cs/Al ratio of 0.10. All crystalline phases elucidated by the XRD are shown.

The XRD diffraction patterns for the COH₅ and CCO₃₅ samples are very similar, with the only crystalline phase displayed being that of anatase, an inert phase in the metakaolin precursor. This owes to the high solubility of the salts, and also the lack of reaction of the constituent ions to form further crystalline phases [303].

In the CNO₃₅ and CSO₄₅ samples, the salt has clearly at least partially dissolved and the released ions have further reacted to form crystalline phases within the samples. In the CSO₄₅ samples, the K⁺ cations within the activating solution have reacted with the SO₄²⁻ anions to form K₂SO₄ in large quantities, which is further seen in the order-of-addition experiments for this salt. This reaction is unlike any other seen within this work, as there is no evidence of the rapid solidification of the salt and activating solution mixtures in any of the other order-of-addition experiments.

The CNO₃₅ sample displays an interesting crystalline phase that is not observed in the XRD data for the other samples, that of a caesium aluminium silicate hydrate phase. The observation of this phase is crucial for the argument that geopolymer systems are capable of chemically immobilising the Cs⁺ cations within their structure. There is clear evidence here that the Cs⁺ is capable of displacing the K⁺ within the role of charge balancing cation within the aluminosilicate hydrate gel. If this is capable in this system, then it is likely that this also occurs in the other samples seen in this work, but the phase does not reorder and crystallise, instead remaining amorphous.

From these findings, the impact of each of these mechanisms on the heat of reaction seen in the ICC can be described separately: a) The filler effect does not affect the time of maximum heat evolution, only reducing the value of the maximum heat flow, b) The Cs⁺ adsorbing to the surface of the metakaolin reduces the value of the maximum heat flow in a relationship where these extents are greater

as the solubility of the Cs salt increases, c) The reaction of the Cs salt with the activating solution leads to mainly to a reduction in the maximum recorded heat flow, however, this may also be responsible for some retardation of the reaction. The mechanisms for the alteration of the reaction kinetics discussed here caused by the different Cs salts are shown in Table 5-10.

Table 5-10: A summary of the effects of the Cs salts on the reaction kinetics of the geopolymer and the mechanisms responsible.

Salt	Retards the reaction?	Reduces maximum heat flow?	Mechanism
CsOH	X	✓	Adsorbs to the surface of the metakaolin
Cs ₂ CO ₃	X	✓	Adsorbs to the surface of the metakaolin
CsNO ₃	X	✓	Filler effect + adsorbs to the surface of the metakaolin
Cs ₂ SO ₄	X	✓	Filler effect + reaction with the activating solution + adsorbs to the surface of the metakaolin

5.2.5.3 Hardened State

The FTIR spectra of the samples after 28 days can be seen in Figure 5-73.

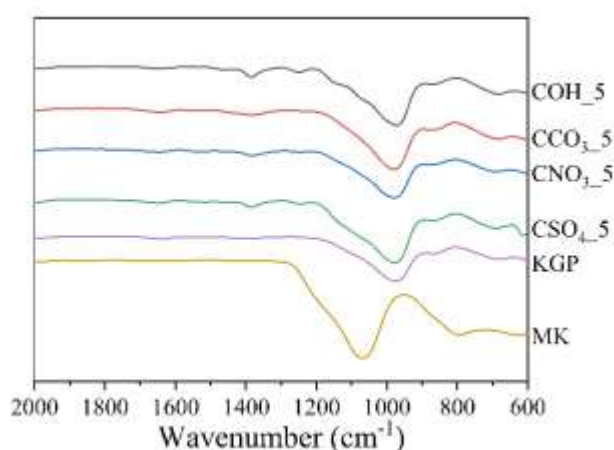


Figure 5-73: The FTIR spectra generated by the COH_5, CCO₃_5, CNO₃_5, CSO₄_5, and KGP samples and the unreacted metakaolin after the first 3 days of reaction.

The spectra for all the samples display similar peaks, with the most obvious being that of the Si-O-T peak signifying the K-A-S-H gel seen at ~1000 cm⁻¹. The difference between the samples I regards to

this peak is the shoulder seen on the higher wavenumber end of these peaks. This shoulder shows greater intensity in the CSO₄_5 and CNO₃_5 samples, which relates to the higher percentage of unreacted metakaolin present in the samples. There are further differences between the samples relating to the original salts that were added that have not fully dissolved, most notably in the CSO₄_5 and CNO₃_5 samples. There are small peaks visible in all of the salt containing samples due to the carbonation of the samples at $\sim 1380\text{ cm}^{-1}$. Overall, the similarity of the FTIR spectra confirms that all samples are of a similar composition, suggesting that the addition of the salts does not have a significant effect on the K-A-S-H gel.

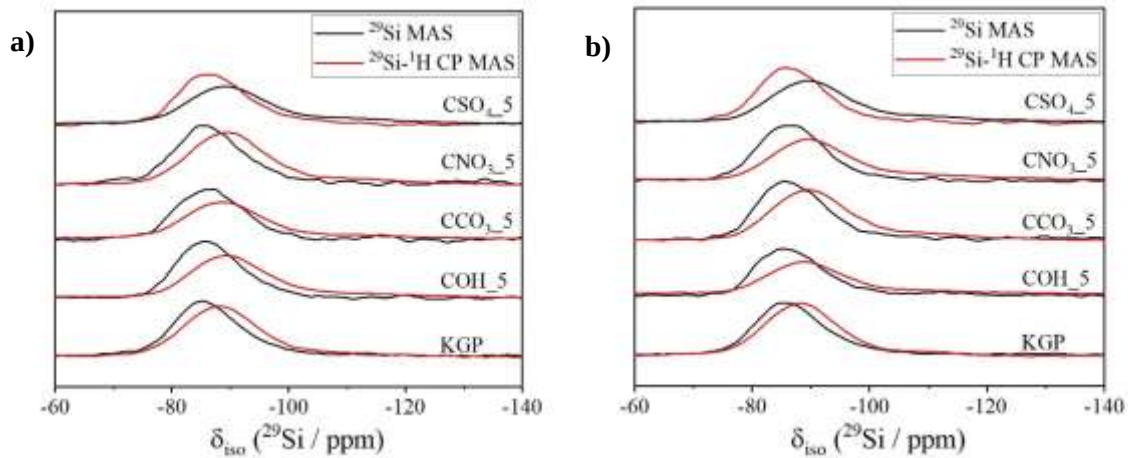


Figure 5-74: ^{29}Si - ^1H CP MAS and ^{29}Si MAS NMR spectra for the COH₅, CCO₃₅, CNO₃₅, CSO₄₅ and KGP samples after the first a) 3 and b) 28 days of reaction.

Comparing the ^{29}Si - ^1H CP MAS and ^{29}Si MAS NMR spectra for all of the samples after 3 and 28-days seen in Figure 5-74, it can be seen that there is very little difference in the local Si chemical environments between the samples. The spectra for all of the samples demonstrate that a geopolymer has been formed, with Q⁴(4Al) and Q⁴(3Al) Si sites dominating. From Figure 5-74, the CSO₄_5 sample, followed closely by the CNO₃_5 sample, contains the most unreacted metakaolin, denoted by the area between the red and black curves between δ_{iso} of 100 and 120 ppm. This directly relates to the extents of reaction of the samples after 3 and 28 days shown in Table 5-11.

Table 5-11: The extent of reaction of each sample both a) 3 and b) 28 days after initial reaction, calculated using the corresponding ^{29}Si MAS NMR spectra.

a)	Sample	Time point	Extent of reaction (%)
	KGP	3 Days	82.17
	COH ₅	3 Days	83.68
	CCO ₃ ₅	3 Days	83.60
	CNO ₃ ₅	3 Days	80.06
	CSO ₄ ₅	3 Days	76.70

	Sample	Time point	Extent of reaction (%)
b)	KGP	28 Days	88.00
	COH_5	28 Days	88.64
	CCO ₃ _5	28 Days	84.01
	CNO ₃ _5	28 Days	83.06
	CSO ₄ _5	28 Days	78.32

The extents of reaction displayed in Table 5-11 show that the samples continue to react between the 3 and 28 day time points, further consuming the metakaolin within the system. The values seen here distinguish a pattern between the salts, showing the salts that have less of an impact on the reaction, namely CsOH and Cs₂CO₃, and those that have more, CsNO₃ and Cs₂SO₄, which agree with findings discussed in the fresh state section above.

5.3 Implications of This Work

In an industrial context, the sample formulations used in the work contain a far greater wt.% of the Cs salts than has been, and would be, used in industrial standards. Therefore, the results seen in this work provide evidence about the behaviour of these salts within a potassium silicate activated, metakaolin based geopolymer system, and this behaviour is likely to be far less significant in samples involving radioactive material. Despite this relatively high Cs salt loading, the K-A-S-H gel of the geopolymer forms as expected, with very little evidence of changes to the Si and Al bonding tetrahedra that are critical to this. However, this work shows that the Cs⁺ is capable of displacing the K⁺ ions that occupy the charge balancing sites of the K-A-S-H gel, providing proof that the geopolymer is capable of chemically binding the Cs into the structure. This finding is critical to developing a use case for these materials as a wasteform for the safe and effective disposal of Cs containing waste streams. The ability for the geopolymer to chemically bind the Cs provides further confidence that the ingress of ground water in a potential GDF will not result in the immediate discharge of the radioactive ¹³⁷Cs back into the environment. Moreover, the work here suggests that higher waste loadings can be achieved in the wasteform than current standards through the use of geopolymers, without negatively impacting the structural integrity of the monolith.

5.4 Future Work

To add to this work, the impact on the addition of the salts on the dissolution peaks in the isothermal conduction calorimetry would be very beneficial. Considering that it is postulated here that the addition of the salts dramatically changes the dissolution of the metakaolin, seeing the change between samples of this peak would allow this to be confirmed directly.

Further to this point, the ICC of the samples should be run at similar times to allow for a direct numerical comparison. However, it is likely more practical to achieve this by altering the technique used for the collection of this data; The data is collected at a reference temperature of 20°C, and so all of the equipment should be pre-heated (or cooled) before use. This should be completed in future work to fully compare the performance of the Cs salt loaded geopolymers and the KGP control sample.

Exploring the effects of the inclusion of Cs salts on the physicommechanical properties of the geopolymer would provide further information on the bulk structural changes seen upon the incorporation of the salts. For example, utilising compression strength testing to check whether the strength of the geopolymer is affected by the addition of the salts. Do the crystalline phases seen, such as the KNO_3 in the CNO_3 samples, disrupt the amorphous K-A-S-H gel and create a mechanically weaker wasteform? Although the strength of the wasteform is not the primary concern for nuclear wasteforms, they must still meet a minimum requirement and so showing that this is possible with the formulations used in this work would add to the use case for geopolymers as a wasteform [298].

An investigation into the effect of adding the salts at much lower weight percentages would also be beneficial to mimic what would be seen if these formulations were realistically used in industry. Likewise, investigating the effect of using much higher waste loadings would give the maximum use case that these systems could reach. This would be useful if, for example, waste sludges of unknown composition were to be incorporated into a geopolymer sample.

The effect of temperature on the geopolymers will be paramount when considering the change in temperature that any wasteform containing radioactive Cs waste will undergo throughout its lifetime in a geological disposal facility [329]. It is projected that temperatures could rise to as high as 80°C in the first 150 years and so the stability of these materials at this temperature will be important.

Finally, the effect of adding multiple salts of Cs into a sample simultaneously will further support the use case for geopolymers encapsulating waste sludges.

6 Chapter 6: Conclusions, Perspectives and Further Work

6.1 Conclusions

This thesis presents a comprehensive analysis of the early stage interactions caused by the inclusion of strontium and caesium salts into a metakaolin based, potassium silicate activated geopolymer cement. The key drivers for this research are the lack of prior research into potassium activated geopolymers for this application, accompanied by the ability for this material to be used to safely dispose of ^{90}Sr and ^{137}Cs , two very mobile radioisotopes which are commonly present in cooling water and sludges from radioactive incidents such as Fukushima Daiichi.

Chapter 3 discussed the potential precursors that can be used for the formation of a geopolymer, both solid and aqueous, before arriving at the conclusion that a metakaolin-based, potassium-activated geopolymer best meets the requirements required for the application of nuclear waste disposal. It is also shown that the reaction of these precursors reliably forms a highly cross-linked geopolymer gel that forms a hardened monolith within the first 24 hours of reaction.

Chapter 4 showed that geopolymer cements are capable of incorporating strontium hydroxide octahydrate ($\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$) strontium carbonate (SrCO_3), strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) and strontium sulphate (SrSO_4) into the material without significant change to the structural make-up of the material.

$\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ is a relatively insoluble salt, and so its inclusion into the geopolymer mix leads to it being stored within the pore structure of the formed K-A-S-H matrix. There is a distinct possibility that some of the dissolved Sr^{2+} ions are incorporated into the structure of the K-A-S-H gel in place of the K^+ ions in charge balancing sites, and this is supported by the ^{87}Sr NMR and the XANES data. During the initial mixing phase of the reaction, the $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ in solution interacts with the metakaolin particles which leads to a slight delay in the reaction which increases with increasing salt content, but does not prevent the setting of the material within the first 24 hours.

The inclusion of SrCO_3 acts in a similar manner, as it is a very insoluble salt of Sr. The inclusion of this salt in the mix has very little effect on both the kinetics and mechanisms of the formation of the K-A-S-H gel. This salt is also likely to reside within the pore structure of the K-A-S-H gel upon its formation.

The results show that adding $\text{Sr}(\text{NO}_3)_2$ into the geopolymer mix dramatically alters the reaction kinetics for the formation of the K-A-S-H gel. The $\text{Sr}(\text{NO}_3)_2$ is very soluble within the activating solution and immediately releases its respective ions into solution. The Sr^{2+} cations interact with the negatively charged surface of the metakaolin particles within solution which is expected to slow the dissolution reaction of these particles. The NO_3^- anions react with the K^+ ions introduced by the activating solution to form KNO_3 which precipitates out of solution, as shown by the order-of-addition reactions. There is little evidence that the remaining Sr^{2+} cations within the structure take the place of the K^+ cations within

the charge balancing role in the K-A-S-H gel, instead appearing to carbonate into the more stable SrCO_3 phase as shown by the XRD and the XANES data.

Much like the $\text{Sr}(\text{NO}_3)_2$ salt, the SrSO_4 salt is soluble within the activating solution. However, it is not so soluble that it completely dissolves, meaning that the reaction mixture contains Sr^{2+} cations, SO_4^{2-} anions and the remaining SrSO_4 salt. The undissolved salt acts in a similar manner to the insoluble salts of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and SrCO_3 , residing within the pore network of the K-A-S-H gel. However, it is also possible for this salt to react with the K^+ cations itself to form a $\text{K}_2\text{Sr}(\text{SO}_4)_2$ phase. The SO_4^{2-} anion interacts with the K^+ cations introduced by the activating solution, much like the NO_3^- anions, to form K_2SO_4 which precipitates out of solution and slows down the reaction process. There is not strong evidence that the Sr^{2+} cations in solution displace the K^+ ions within the charge balancing sites of the K-A-S-H gel, and instead carbonate to form SrCO_3 as shown by the XRD data.

The inclusion of all of the Sr salts into the mix does not prevent the formation of a hardened geopolymer monolith after the first 24 hours of reaction, and the formation of a geopolymer gel is verified by the use of XRD and NMR in all cases.

Chapter 5 revealed that adding various salts of caesium, notably CsOH , Cs_2CO_3 , CsNO_3 and Cs_2SO_4 , to the geopolymer mix at nominal Cs/Al ratios of up to 0.1 does not impact the nanostructure of the resultant material, but that the impact on the reaction kinetics and mechanisms of the formation of this phase are heavily reliant on the anion constituent of the salt.

The inclusion of CsOH within the geopolymer reaction mixture does not appear to alter the reaction kinetics, with the curves for the KGP control and the CsOH containing samples following an identical lineshape as shown by the ICC. The CsOH is very soluble within the activating solution, and so is likely to dissociate into solution to form Cs^+ and OH^- ions. The solution already contains OH^- ions, and so the addition of such a small concentration will not impact the solution, however, the Cs^+ cations are shown by zeta potential measurements to interact with the metakaolin particles in the mix. Despite this, the reaction occurs at a comparable rate to the KGP control, and hardened state analysis shows that resultant structure is also comparable, however, there is evidence showing that the Cs^+ has been immobilised within the K-A-S-H gel in place of the K^+ cations through both the ^{39}K MAS NMR and ^{133}Cs NMR.

Cs_2CO_3 is also a very soluble salt and dissociates into its constituents in solution. It is shown that the maximum rate of reaction decreases with an increasing Cs/Al ratio when this salt is included into the reaction mixture and this is attributed to the interaction between the Cs^+ ions and the negatively charged surface of the metakaolin, slowing the dissolution reaction and minimizing the concentration of reactants within solution. Despite this, the nanostructure of the material does not change when compared to the KGP control, with the main binding phase being shown to be a K-A-S-H gel, although it is suggested that some of the Cs^+ ions in solution displace the K^+ ions from their role as charge balancing

cations by the ^{39}K MAS NMR and ^{133}Cs NMR. This is despite the fact that the geopolymer containing Cs_2CO_3 has a lower charge balancing capacity than the KGP control shown by its higher Si/Al ratio.

The CsNO_3 is a relatively insoluble salt of Cs which does not completely dissolve when added to the high pH activating solution. Therefore, the change in the heat evolution curve elucidated by ICC is attributed to the filler effect of the salt within the mixture. However, interestingly, the XRD of the resultant material after both 3 and 28 days of reaction reveals the presence of a crystalline Cs-A-S-H phase, which has not been seen in any of the other samples in this work. This is direct evidence that the Cs^+ ions are capable of displacing the K^+ ions within the K-A-S-H gel, allowing them to be chemically immobilised within the structure. The fact that the CsNO_3 does not dissolve fully also shows the dual capability of the geopolymer material to both immobilise and encapsulate the Cs within the structure.

When Cs_2SO_4 is included within the reaction mixture, it leads to a reaction between the salt and the activating solution that causes a solid phase to precipitate out of solution, creating a physical barrier between the reactants which, naturally, results in a reduction in both the dissolution and consequent polymerisation reaction. It is not clear what the exact composition of this solid is, although it is expected to be a conglomeration of silicate and sulphate phases. The XRD shows the presence of K_2SO_4 within the sample, which further shows that there is a clear reaction between the salt and the activating solution, and it is likely that the aforementioned solid contains this. There is no clear evidence that the Cs^+ ions are immobilised within the K-A-S-H gel, but the use of XRD and ^{133}Cs NMR shows that the geopolymer matrix is capable of encapsulating the Cs within the structure.

The work presented in this thesis adds to the knowledge base for geopolymer cements, and provides valuable insights into the interactions of the cement and its precursors with common salts of both Sr and Cs. This will aid in the use case for geopolymers to be the material of choice for the safe disposal of waste streams containing these radionuclides, although it is important that these findings are coupled with investigations into the long-term stability of these materials.

6.2 Perspectives

The results of this thesis provide further evidence that geopolymers are ideal candidates for use as an engineered wasteform for the safe containment and disposal of nuclear waste stream containing radioactive strontium and caesium. Although there is still a significant amount of research to be carried out, some of which is alluded to in the following section, the results show that the Sr and Cs can be encapsulated into the alkali aluminosilicate gel structure without significantly damaging the integrity of the material. Furthermore, in some cases, the K-A-S-H gel is shown to be capable of chemically immobilising the Sr and Cs which is a property that is increasingly important within novel nuclear wasteforms. Moreover, the geopolymer samples are shown to be able to contain common anions associated with Sr and Cs. This is incredibly important when considering the potential applications of the geopolymer wasteform within the nuclear industry. The ability of the geopolymer to contain these

anions furthers the use case for radioactive sludges containing various salts of these elements from sites such as Fukushima Daiichi to be disposed of using geopolymers.

The work also shows that these materials are capable of containing relatively high waste loadings, far greater than those currently used in industry. Therefore, this research suggests that geopolymers will be more than capable of incorporating the wastes at the loadings currently used in an industrial setting.

The work here shows that by incorporating certain salts of Sr and Cs, most notably the NO_3 salts of the two elements, it is possible to control the curing time of the material without compromising the structure of the main aluminosilicate gel framework. This is important for maintaining the fluidity of the fresh geopolymer paste for long enough to permeate more complex waste geometries. Moreover, it is also evidence that the waste itself can be used as an additive into the reaction mix which can reduce the need for further research into other chemical additives, such as superplasticisers, which could lead to other negative structural changes.

6.3 *Further Work*

This research is by no means an exhaustive study into the impact of strontium and caesium salts on the early stage formation of geopolymer cements within the first 28 days of reaction. In order to add to the findings outlined here, additional work is required to improve the understanding of the behavior of the loaded geopolymer wasteform over longer periods of time. Potential avenues for this work have been outlined within the individual chapters, but, for clarity, they are collated here:

- An investigation into the change in dissolution of the metakaolin within the activating solution in the presence of the salts used here would be very beneficial. Considering that it is postulated that the addition of the salts dramatically changes the dissolution of the metakaolin, seeing the change between samples of this peak would allow this to be confirmed directly.
- Further to this, controlling the isothermal conduction calorimetry experiment for a greater reduction of error for the recorded heat evolutions will provide further confidence that the cumulative values remain within the regulated limits set for use in the UK nuclear industry.
- An investigation into the effect of adding the salts at much lower weight percentages would also be beneficial to mimic what would be seen if these formulations were realistically used in industry.
- Likewise, investigating the effect of using much higher waste loadings would give the maximum use case that these systems could reach. This would be useful if, for example, waste sludges of unknown composition were to be incorporated into a geopolymer sample.
- Also to this effect, an investigation into adding multiple salts to one geopolymer sample would also determine whether these materials are capable of encapsulating complex wastes containing multiple salts of Sr and Cs, which is very likely considering their high mobility in water.

- Exploring the effects of the inclusion of Sr and Cs salts on the physicochemical properties of the geopolymer would provide further information on the bulk structural changes seen upon the incorporation of the salts. This is a vital piece of work to prove that the geopolymer cement wasteforms meet the minimum required compressive strength as per regulation for use as a nuclear wasteform.
- This work focuses entirely on the early stage kinetics and mechanisms of the geopolymers loaded with Sr and Cs salts but, to justify the use of these materials as encapsulants for radioactive waste, the long term ability of the geopolymers to contain the waste and resist leaching must be considered. Therefore, leaching tests on aged geopolymer samples should be performed and analysed.
- It is projected that temperatures within a GDF could rise to 80°C, and so the stability of these materials at this temperature will be important for use in the application of radioactive waste disposal.
- Investigating the effect of the radioactive decay of the Sr and Cs nuclei within the geopolymer will show whether the material is capable of maintaining its integrity when subjected to radiation. Therefore, investigating the impact of encapsulating radioactive Sr and Cs within the geopolymer system should be carried out, and also whether the products of the decay alter the nanostructure of the material.
- It is likely that the Sr and Cs that are to be incorporated into the geopolymer wasteform will be bound to an ion exchange material if the encapsulation is to happen in a controlled setting, that being where the composition of the waste is well defined. Therefore, further work into the interaction of ion exchange media loaded with the salts used in this work will provide vital information on whether this changes the effects seen in this research.
- Finally, a continuation of the work carried out in this thesis will be beneficial to learn more about the chemical interactions between the salts and the reactants for the geopolymer. The exploration of why a Cs-A-S-H phase is formed in the sample containing CsNO₃ but not any of the other Cs containing samples would provide incredible insight into the reaction conditions required to facilitate the formation of this type of phase.

References

1. Chater, J., *A history of nuclear power*. Focus on Nuclear Power Generation, 2005. **28**.
2. IAEA, *Nuclear Technology Review*. 2024, IAEA.
3. IAEA, *International Status and Prospects for Nuclear Power 2021*, D.G.R.M. Grossi, Editor. 2021, IAEA.
4. Martin, V., *Digest of UK Energy Statistics*, D.f.E.S.a.N. Zero, Editor. 2024.
5. Department for Business, E.I.S., The Rt Hon Greg Hands MP, and The Rt Hon Kwasi Kwarteng MP, *Fund to secure our energy supply and boost cutting-edge nuclear projects opens for business*. 2022.
6. Quadrelli, R. and S. Peterson, *The energy–climate challenge: Recent trends in CO₂ emissions from fuel combustion*. Energy policy, 2007. **35**(11): p. 5938-5952.
7. Brook, B.W., et al., *Why nuclear energy is sustainable and has to be part of the energy mix*. Sustainable Materials and Technologies, 2014. **1**: p. 8-16.
8. Bohr, N. and J.A. Wheeler, *The mechanism of nuclear fission*. Physical Review, 1939. **56**(5): p. 426.
9. Wagemans, C., *The nuclear fission process*. 1991.
10. Suppes, G.J. and T.S. Storvick, *Sustainable Power Technologies and Infrastructure: Energy Sustainability and Prosperity in a Time of Climate Change*. 2015: Academic Press.
11. Meadows, J., *The fission cross sections of uranium-234 and uranium-236 relative to uranium-235*. Nuclear Science and Engineering, 1978. **65**(1): p. 171-174.
12. Baisden, P.A. and G.R. Choppin, *Nuclear waste management and the nuclear fuel cycle*. Radiochemistry and nuclear chemistry, 2007: p. 1-63.
13. Kessler, G., *Sustainable and safe nuclear fission energy: Technology and safety of fast and thermal nuclear reactors*. 2012: Springer Science & Business Media.
14. Fong, P., *Statistical theory of nuclear fission: asymmetric fission*. Physical Review, 1956. **102**(2): p. 434.
15. Sümer Şahin, Y.W., *Fission Energy Production*. Comprehensive Energy Systems, 2018. **3**: p. 590-637.
16. Bruno, J. and R.C. Ewing, *Spent nuclear fuel*. Elements, 2006. **2**(6): p. 343-349.
17. Ewing, R.C., *Long-term storage of spent nuclear fuel*. Nature Materials, 2015. **14**(3): p. 252-257.
18. Arya, S.P., L.N. Grossman, and F.C. Schoenig Jr, *Determining fissile content of nuclear fuel elements*. 1980, Google Patents.
19. McFarlane, H.F. and T. Todd, *Nuclear fuel reprocessing*. 2013, Idaho National Lab.(INL), Idaho Falls, ID (United States).

20. Bunn, M.G., et al., *Interim Storage of Spent Nuclear Fuel: A Safe, Flexible, and Cost-Effective Approach to Spent Fuel Management*. 2001.
21. Rodríguez-Penalonga, L. and B.Y. Moratilla Soria, *A review of the nuclear fuel cycle strategies and the spent nuclear fuel management technologies*. *Energies*, 2017. **10**(8): p. 1235.
22. Taylor, R., *Reprocessing and recycling of spent nuclear fuel*. 2015: Elsevier.
23. Sood, D. and S. Patil, *Chemistry of nuclear fuel reprocessing: current status*. *Journal of Radioanalytical and Nuclear Chemistry*, 1996. **203**(2): p. 547-573.
24. Simpson, M. and J. Law, *Reprocessing of nuclear fuel*. *Nuclear energy*, 2013: p. 153-173.
25. Bunn, M., et al., *The economics of reprocessing versus direct disposal of spent nuclear fuel*. *Nuclear Technology*, 2005. **150**(3): p. 209-230.
26. Forwood, M., G. Mackerron, and W. Walker, *Endless Trouble: Britain's Thermal Oxide Reprocessing Plant (THORP)*. 2019, Report of the International Panel on Fissile Material. [http](http://...)
27. Fettus, G.H. and M.G. McKinzie, *Nuclear Fuel's Dirty Beginnings*. Natural Resources Defense Council, 2012.
28. Authority, N.D., *Radioactive Wastes in the UK: UK Radioactive Waste Inventory Report*. 2017, Nuclear Decommissioning Authority.
29. Authority, N.D., *UK Radioactive Waste Inventory*. 2023, Department for Business, Energy & Industrial Strategy.
30. Jantzen, C.M., 9 - *Development of glass matrices for high level radioactive wastes*, in *Handbook of Advanced Radioactive Waste Conditioning Technologies*, M.I. Ojovan, Editor. 2011, Woodhead Publishing. p. 230-292.
31. Society, T.G., *Geological Disposal of Radioactive Waste*. 2020, The Geological Society, UK.
32. Sharp, J., et al., *Cementitious Systems for Encapsulation of Intermediate Level Waste*. Vol. 3. 2003.
33. Ashworth, A., I. Porter, and B. Thompson. *Regulation and performance assessment for the Drigg low level waste disposal site in the United Kingdom*. in *Planning and operation of low level waste disposal facilities. Proceedings of an international symposium*. 1997.
34. Epstein, J. and D. Harris, *Properties of selected radioisotopes. A bibliography, part 1- Unclassified literature*. 1968.
35. Hirose, K., et al., *Annual deposition of Sr-90, Cs-137 and Pu-239, 240 from the 1961-1980 nuclear explosions: A simple model*. *Journal of the Meteorological Society of Japan. Ser. II*, 1987. **65**(2): p. 259-277.
36. Gustafson, P.F., *Ratio of Cesium-137 and Strontium-90 Radioactivity in Soil*. *Science*, 1959. **130**(3386): p. 1404-1405.
37. Lee, W., et al., *Immobilisation of radioactive waste in glasses, glass composite materials and ceramics*. *Advances in Applied Ceramics*, 2006. **105**(1): p. 3-12.

38. Abdel Rahman, R.O. and M.I. Ojovan, *Toward Sustainable Cementitious Radioactive Waste Forms: Immobilization of Problematic Operational Wastes*. Sustainability, 2021. **13**(21): p. 11992.
39. Whicker, F.W., et al., *Distribution of long-lived radionuclides in an abandoned reactor cooling reservoir*. Ecological Monographs, 1990. **60**(4): p. 471-496.
40. Chen, Z., et al., *Preparation of silica-based titanate adsorbents and application for strontium removal from radioactive contaminated wastewater*. Journal of Radioanalytical and Nuclear Chemistry, 2016. **307**(2): p. 931-940.
41. Wright, S.M., *Predicted Caesium-137 deposition from atmospheric nuclear weapons tests*. 2016, NERC Environmental Information Data Centre.
42. Bunting, R., *Nuclear data sheets for A= 137*. Nuclear Data Sheets, 1975. **15**(3): p. 335-369.
43. Buesseler, K., M. Aoyama, and M. Fukasawa, *Impacts of the Fukushima nuclear power plants on marine radioactivity*. Environmental science & technology, 2011. **45**(23): p. 9931-9935.
44. Hidaka, A. and J. Ishikawa, *Quantities of I-131 and Cs-137 in accumulated water in the basements of reactor buildings in process of core cooling at Fukushima Daiichi nuclear power plants accident and its influence on late phase source terms: Fukushima NPP Accident Related*. Journal of Nuclear Science and technology, 2014. **51**(4): p. 413-424.
45. Marsh, A.I., L.G. Williams, and J.A. Lawrence, *The important role and performance of engineered barriers in a UK geological disposal facility for higher activity radioactive waste*. Progress in Nuclear Energy, 2021. **137**: p. 103736.
46. Department for Business, E.I.S., *Implementing geological disposal – working with communities: long term management of higher activity radioactive waste*, E.I.S. Department for Business, Editor. 2018.
47. Jantzen, C.M., W.E. Lee, and M.I. Ojovan, *Radioactive waste (RAW) conditioning, immobilization, and encapsulation processes and technologies: overview and advances*. Radioactive Waste Management and Contaminated Site Clean-Up, 2013: p. 171-272.
48. Ojovan, M.I. and W.E. Lee, *Glassy wasteforms for nuclear waste immobilization*. Metallurgical and Materials Transactions A, 2011. **42**(4): p. 837-851.
49. Ojovan, M.I., V.A. Petrov, and S.V. Yudintsev, *Glass crystalline materials as advanced nuclear wasteforms*. Sustainability, 2021. **13**(8): p. 4117.
50. El-Alaily, N., et al., *Vitrified municipal waste as a host form for high-level nuclear waste*. Journal of Radioanalytical and Nuclear Chemistry, 2014. **299**(1): p. 65-73.
51. Robbins, R.A. and M.I. Ojovan, *Vitreous materials for nuclear waste immobilisation and IAEA support activities*. MRS Advances, 2016. **1**(63-64): p. 4201-4206.
52. Gasparyan, M., et al., *Local system for purifying process gases from volatile compounds of cesium and iodine at high-temperature stages of spent nuclear fuel reprocessing*. Atomic Energy, 2025: p. 1-7.

53. Radford, J.T., *Assessing the volatility of caesium during the vitrification of intermediate level waste*. 2021, University of Sheffield.
54. Stefanovsky, S.V., et al., *Nuclear waste forms*. Geological Society, London, Special Publications, 2004. **236**(1): p. 37-63.
55. Hyatt, N.C. and M.I. Ojovan, *Materials for nuclear waste immobilization*. 2019, MDPI. p. 3611.
56. Orlova, A.I. and M.I. Ojovan, *Ceramic mineral waste-forms for nuclear waste immobilization*. Materials, 2019. **12**(16): p. 2638.
57. Lee, W.E., et al. *Processing ceramics for radioactive waste immobilisation*. in *Advances in Science and Technology*. 2006. Trans Tech Publ.
58. Vance, E.R., Y. Zhang, and D.J. Gregg, 6.16 - *Ceramic Waste Forms* ☆, in *Comprehensive Nuclear Materials (Second Edition)*, R.J.M. Konings and R.E. Stoller, Editors. 2020, Elsevier: Oxford. p. 445-466.
59. Weber, W.J., et al., *Radiation effects in crystalline ceramics for the immobilization of high-level nuclear waste and plutonium*. Journal of Materials Research, 1998. **13**(6): p. 1434-1484.
60. Cole, M.R., et al., *A disposal-MOX concept for plutonium disposition*. Materials Advances, 2024. **5**(16): p. 6416-6425.
61. Shanks, M., *Plutonium Disposition Strategy*, D.f.E.S.a.N. Zero, Editor. 2025.
62. Ojovan, M.I., W.E. Lee, and S.N. Kalmykov, *An introduction to nuclear waste immobilisation*. 2019: Elsevier.
63. Dezerald, L., et al., *Cement as a waste form for nuclear fission products: the case of ⁹⁰Sr and its daughters*. Environmental Science & Technology, 2015. **49**(22): p. 13676-13683.
64. Bart, F., et al., *Cement-based materials for nuclear waste storage*. 2012: Springer Science & Business Media.
65. Glasser, F., *Application of inorganic cements to the conditioning and immobilisation of radioactive wastes*, in *Handbook of advanced radioactive waste conditioning technologies*. 2011, Elsevier. p. 67-135.
66. Zhou, Q., N. Milestone, and M. Hayes, *An alternative to Portland cement for waste encapsulation—the calcium sulfoaluminate cement system*. Journal of hazardous materials, 2006. **136**(1): p. 120-129.
67. Walkley, B., et al., *Incorporation of strontium and calcium in geopolymer gels*. Journal of hazardous materials, 2020. **382**: p. 121015.
68. Covill, A., et al., *Development of magnesium phosphate cements for encapsulation of radioactive waste*. Advances in Applied Ceramics, 2011. **110**(3): p. 151-156.

69. Coumes, C.C.D., et al., *Calcium sulfoaluminate cement blended with OPC: A potential binder to encapsulate low-level radioactive slurries of complex chemistry*. Cement and Concrete Research, 2009. **39**(9): p. 740-747.
70. Rakhimova, N., *Recent advances in alternative cementitious materials for nuclear waste immobilization: A review*. Sustainability, 2022. **15**(1): p. 689.
71. Corkhill, C. and N. Hyatt, *Nuclear waste management*. 2018: IOP Publishing Bristol:.
72. Van Jaarsveld, J. and J. Van Deventer, *The effect of metal contaminants on the formation and properties of waste-based geopolymers*. Cement and Concrete Research, 1999. **29**(8): p. 1189-1200.
73. S. Curwen and F. Ridley, *Joint BNFL/DOE intermediate level waste research programme*. 1989, British Nuclear Fuels and Department of Energy: Harwell, Oxfordshire, UK.
74. Francis, A., *Joint BNFL / DOE intermediate level waste programme. Product evaluation task force: phase two report for magnox swarf summary*. 1986, British Nuclear Fuels and Department of Energy: Harwell, Oxfordshire, UK.
75. Awal, A.A. and M.W. Hussin, *Effect of palm oil fuel ash in controlling heat of hydration of concrete*. Procedia Engineering, 2011. **14**: p. 2650-2657.
76. Gruyaert, E., N. Robeyst, and B.N. De, *Study of the hydration of Portland cement blended with blast-furnace slag by calorimetry and thermogravimetry*. Journal of thermal analysis and calorimetry, 2010. **102**(3): p. 941-951.
77. Vance, E. and D. Perera, *Geopolymers for nuclear waste immobilisation*, in *Geopolymers*. 2009, Elsevier. p. 401-420.
78. Milestone, N., *Reactions in cement encapsulated nuclear wastes: need for toolbox of different cement types*. Advances in Applied Ceramics, 2006. **105**(1): p. 13-20.
79. Radioactive Waste Management, *Geological disposal: waste package evolution status report*. 2016, RWM-NDA: Didcot, UK.
80. Hewlett, P. and M. Liska, *Lea's chemistry of cement and concrete*. 2019: Butterworth-Heinemann.
81. Hall, C., *On the history of portland cement after 150 years*. Journal of Chemical Education, 1976. **53**(4): p. 222.
82. Poerner, M. and A. Rimpel, *10 - Waste heat recovery*, in *Fundamentals and Applications of Supercritical Carbon Dioxide (sCO₂) Based Power Cycles*, K. Brun, P. Friedman, and R. Dennis, Editors. 2017, Woodhead Publishing. p. 255-267.
83. Taylor, H.F., *Cement chemistry*. Vol. 2. 1997: Thomas Telford London.
84. Minard, H., et al., *Mechanisms and parameters controlling the tricalcium aluminate reactivity in the presence of gypsum*. Cement and Concrete Research, 2007. **37**(10): p. 1418-1426.
85. Newman, J. and B.S. Choo, *Advanced concrete technology 2: concrete properties*. 2003: Elsevier.

86. Oye, B., *Wood ash as raw material for Portland cement*. 2022.
87. Scrivener, K.L. and A. Nonat, *Hydration of cementitious materials, present and future*. Cement and concrete research, 2011. **41**(7): p. 651-665.
88. Bensted, J., *Gypsum in cements*. Structure and performance of cements, 2002. **2**.
89. Berner, U.R., *Modelling porewater chemistry in hydrated Portland cement*. MRS Online Proceedings Library (OPL), 1986. **84**.
90. Scrivener, K., R. Snellings, and B. Lothenbach, *A practical guide to microstructural analysis of cementitious materials*. Vol. 540. 2016: Crc Press Boca Raton, FL, USA:.
91. Scrivener, K.L., P. Juilland, and P.J.M. Monteiro, *Advances in understanding hydration of Portland cement*. Cement and Concrete Research, 2015. **78**: p. 38-56.
92. Bullard, J.W., et al., *Mechanisms of cement hydration*. Cement and Concrete Research, 2011. **41**(12): p. 1208-1223.
93. Madadi, A. and J. Wei, *Characterization of Calcium Silicate Hydrate Gels with Different Calcium to Silica Ratios and Polymer Modifications*. Gels, 2022. **8**(2): p. 75.
94. Nonat, A., *The structure and stoichiometry of CSH*. Cement and concrete research, 2004. **34**(9): p. 1521-1528.
95. Richardson, I.G., *The calcium silicate hydrates*. Cement and concrete research, 2008. **38**(2): p. 137-158.
96. Walkley, B. and J.L. Provis, *Solid-state nuclear magnetic resonance spectroscopy of cements*. Materials Today Advances, 2019. **1**: p. 100007.
97. Hong, S.-Y. and F. Glasser, *Alkali binding in cement pastes: Part I. The CSH phase*. Cement and Concrete Research, 1999. **29**(12): p. 1893-1903.
98. Myers, R.J., et al., *Generalized structural description of calcium–sodium aluminosilicate hydrate gels: the cross-linked substituted tobermorite model*. Langmuir, 2013. **29**(17): p. 5294-5306.
99. Kearney, S., et al., *Chapter 25 - Cement-based stabilization/solidification of radioactive waste, in Low Carbon Stabilization and Solidification of Hazardous Wastes*, D.C.W. Tsang and L. Wang, Editors. 2022, Elsevier. p. 407-431.
100. Aïtcin, P.C., *3 - Portland cement*, in *Science and Technology of Concrete Admixtures*, P.-C. Aïtcin and R.J. Flatt, Editors. 2016, Woodhead Publishing. p. 27-51.
101. Black, L., *17 - Low clinker cement as a sustainable construction material*, in *Sustainability of Construction Materials (Second Edition)*, J.M. Khatib, Editor. 2016, Woodhead Publishing. p. 415-457.
102. Gougar, M.L.D., B.E. Scheetz, and D.M. Roy, *Ettringite and C · S · H Portland cement phases for waste ion immobilization: A review*. Waste Management, 1996. **16**(4): p. 295-303.

103. Schwiete, H.E. and U. Ludwig, *Crystal structures and properties of cement hydration products*. Gultier A, Regourd M. Proceedings of: p. 37-65.
104. Möschner, G., et al., *Solid solution between Al-ettringite and Fe-ettringite ($\text{Ca}_6 [\text{Al} - x\text{Fe}(\text{OH})_6]_2 (\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$)*. Cement and Concrete Research, 2009. **39**(6): p. 482-489.
105. Baquerizo, L.G., et al., *Hydration states of AFm cement phases*. Cement and Concrete Research, 2015. **73**: p. 143-157.
106. Matschei, T., B. Lothenbach, and F.P. Glasser, *The AFm phase in Portland cement*. Cement and Concrete Research, 2007. **37**(2): p. 118-130.
107. Ochs, M., D. Mallants, and L. Wang, *Radionuclide and metal sorption on cement and concrete*. Vol. 2. 2016: Springer.
108. Sakr, K., M. Sayed, and N. Hafez, *Comparison studies between cement and cement-kaolinite properties for incorporation of low-level radioactive wastes*. Cement and concrete research, 1997. **27**(12): p. 1919-1926.
109. Bagosi, S. and L. Csetenyi, *Caesium immobilisation in hydrated calcium-silicate-aluminate systems*. Cement and concrete research, 1998. **28**(12): p. 1753-1759.
110. Evans, N.D.M., *Binding mechanisms of radionuclides to cement*. Cement and Concrete Research, 2008. **38**(4): p. 543-553.
111. Kai, M., L. Zhang, and K. Liew, *Atomistic insights into structure evolution and mechanical property of calcium silicate hydrates influenced by nuclear waste caesium*. Journal of hazardous materials, 2021. **411**: p. 125033.
112. El-Korashy, S.A., *Synthetic crystalline calcium silicate hydrate (I): Cation exchange and caesium selectivity*. Monatshefte für Chemie/Chemical Monthly, 2002. **133**(3): p. 333-343.
113. Bar-Nes, G., et al., *Cesium and Strontium Immobilization in Portland Cement Pastes Blended With Pozzolanic Additives*. Journal of Nuclear Engineering and Radiation Science, 2017. **3**(3).
114. Angus, M.J., et al. *Managing change in the supply of cement powders for radioactive waste encapsulation—twenty years of operational experience*. in *Proceedings of an International Conference, Phoenix*. 2010.
115. Alberici, S., et al., *Fly Ash and Blast Furnace Slag for Cement Manufacturing*, E.I.S. Department for Business, Editor. 2017.
116. Lehne, J. and F. Preston, *Making concrete change: Innovation in low-carbon cement and concrete*. 2018.
117. Whiting, J., *Manufacture of Cement*. 1895: United States.
118. Provis, J.L. and J.S. Van Deventer, *Alkali activated materials: state-of-the-art report, RILEM TC 224-AAM*. Vol. 13. 2013: Springer Science & Business Media.
119. Davidovits, J., *Mineral polymers and methods of making them*. 1982, Google Patents.
120. Malek, R.I., et al., *Slag cement-low-level waste forms at the Savannah River Plant*. 1985, Pennsylvania State Univ., University Park (USA). Materials Research Lab.; Du

121. Provis, J.L., *Alkali-activated materials*. Cement and Concrete Research, 2018. **114**: p. 40-48.
122. Li, Q., et al., *Immobilization of simulated radionuclide $^{133}\text{Cs}^+$ by fly ash-based geopolymer*. Journal of hazardous materials, 2013. **262**: p. 325-331.
123. Provis, J.L. and S.A. Bernal, *Geopolymers and related alkali-activated materials*. Annual Review of Materials Research, 2014. **44**: p. 299-327.
124. Provis, J. and J. Van Deventer, *Geopolymerisation kinetics. 2. Reaction kinetic modelling*. Chemical engineering science, 2007. **62**(9): p. 2318-2329.
125. Sata, V. and P. Chindaprasirt, *19 - Use of construction and demolition waste (CDW) for alkali-activated or geopolymer concrete*, in *Advances in Construction and Demolition Waste Recycling*, F. Pacheco-Torgal, et al., Editors. 2020, Woodhead Publishing. p. 385-403.
126. Rees, C.A., et al., *In situ ATR-FTIR study of the early stages of fly ash geopolymer gel formation*. Langmuir, 2007. **23**(17): p. 9076-9082.
127. Glid, M., et al., *Alkaline activation of metakaolinite-silica mixtures: Role of dissolved silica concentration on the formation of geopolymers*. Ceramics International, 2017. **43**(15): p. 12641-12650.
128. Zhang, Z., et al., *Quantitative kinetic and structural analysis of geopolymers. Part 1. The activation of metakaolin with sodium hydroxide*. Thermochimica acta, 2012. **539**: p. 23-33.
129. Duxson, P., et al., *Geopolymer technology: the current state of the art*. Journal of materials science, 2007. **42**(9): p. 2917-2933.
130. Palomo, A., et al., *Alkaline activation of fly ashes: NMR study of the reaction products*. Journal of the American Ceramic Society, 2004. **87**(6): p. 1141-1145.
131. Duxson, P., et al., *^{29}Si NMR study of structural ordering in aluminosilicate geopolymer gels*. Langmuir, 2005. **21**(7): p. 3028-3036.
132. Davidovits, J. *Properties of geopolymer cements*. in *First international conference on alkaline cements and concretes*. 1994. Kiev State Technical University Kiev, Ukraine.
133. Provis, J.L., G.C. Lukey, and J.S. van Deventer, *Do geopolymers actually contain nanocrystalline zeolites? A reexamination of existing results*. Chemistry of materials, 2005. **17**(12): p. 3075-3085.
134. Bell, J.L., et al., *Atomic structure of a cesium aluminosilicate geopolymer: a pair distribution function study*. Chemistry of Materials, 2008. **20**(14): p. 4768-4776.
135. Criado, M., et al., *An XRD study of the effect of the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio on the alkali activation of fly ash*. Cement and concrete research, 2007. **37**(5): p. 671-679.
136. Fernández-Jiménez, A., A. Palomo, and M. Criado, *Microstructure development of alkali-activated fly ash cement: a descriptive model*. Cement and Concrete Research, 2005. **35**(6): p. 1204-1209.

137. White, C.E., et al., *Evolution of local structure in geopolymer gels: an in situ neutron pair distribution function analysis*. Journal of the American Ceramic Society, 2011. **94**(10): p. 3532-3539.
138. Barney, G.S., *Immobilization of aqueous radioactive cesium wastes by conversion to aluminosilicate minerals*. 1975, Atlantic Richfield Hanford Co.
139. Ofer-Rozovsky, E., et al., *Cesium immobilization in nitrate-bearing metakaolin-based geopolymers*. Journal of Nuclear Materials, 2019. **514**: p. 247-254.
140. Khalil, M. and E. Merz, *Immobilization of intermediate-level wastes in geopolymers*. Journal of Nuclear Materials, 1994. **211**(2): p. 141-148.
141. Bell, J.L., P.E. Driemeyer, and W.M. Kriven, *Formation of ceramics from metakaolin-based geopolymers: Part I—Cs-based geopolymer*. Journal of the American Ceramic Society, 2009. **92**(1): p. 1-8.
142. Kuenzel, C., et al., *Encapsulation of Cs/Sr contaminated clinoptilolite in geopolymers produced from metakaolin*. Journal of Nuclear Materials, 2015. **466**: p. 94-99.
143. Berger, S., F. Frizon, and C. Jousot-Dubien, *Formulation of caesium based and caesium containing geopolymers*. Advances in Applied Ceramics, 2009. **108**(7): p. 412-417.
144. Perera, D.S. *Immobilization of Cs and Sr in geopolymers with Si/Al molar ratio of ~ 2*. in *Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries XI: Proceedings of the 107th Annual Meeting of The American Ceramic Society, Baltimore, Maryland, USA 2005*. 2012. John Wiley & Sons.
145. He, P., et al., *Interplay between storage temperature, medium and leaching kinetics of hazardous wastes in Metakaolin-based geopolymer*. Journal of Hazardous Materials, 2020. **384**: p. 121377.
146. Provis, J.L., P.A. Walls, and J.S. van Deventer, *Geopolymerisation kinetics. 3. Effects of Cs and Sr salts*. Chemical Engineering Science, 2008. **63**(18): p. 4480-4489.
147. McLellan, B.C., et al., *Costs and carbon emissions for geopolymer pastes in comparison to ordinary portland cement*. Journal of cleaner production, 2011. **19**(9-10): p. 1080-1090.
148. Shi, C. and A. Fernández-Jiménez, *Stabilization/solidification of hazardous and radioactive wastes with alkali-activated cements*. Journal of Hazardous Materials, 2006. **137**(3): p. 1656-1663.
149. Hofelich, T., et al., *The Isothermal Heat Conduction Calorimeter: A Versatile Instrument for Studying Processes in Physics, Chemistry, and Biology*. Journal of Chemical Education, 2001. **78**: p. 1080.
150. Swaddle, T.W., J. Salerno, and P.A. Tregloan, *Aqueous aluminates, silicates, and aluminosilicates*. Chemical Society Reviews, 1994. **23**(5): p. 319-325.
151. Hughes, T.L., et al., *Determining cement composition by Fourier transform infrared spectroscopy*. Advanced Cement Based Materials, 1995. **2**(3): p. 91-104.

152. Technologies, P., *EasiDiff Manual*. 2014.
153. Caggiani, M.C., et al., *Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) as a potential on site tool to test geopolymerization reaction*. Talanta, 2022. **250**: p. 123721.
154. Delgado, A.H., R.M. Paroli, and J.J. Beaudoin, *Comparison of IR techniques for the characterization of construction cement minerals and hydrated products*. Applied Spectroscopy, 1996. **50**(8): p. 970-976.
155. Kashani, A., et al., *The interrelationship between surface chemistry and rheology in alkali activated slag paste*. Construction and Building Materials, 2014. **65**: p. 583-591.
156. Bhattacharjee, S., *DLS and zeta potential – What they are and what they are not?* Journal of Controlled Release, 2016. **235**: p. 337-351.
157. Park, S.-J. and M.-K. Seo, *Chapter 1 - Intermolecular Force*, in *Interface Science and Technology*, S.-J. Park and M.-K. Seo, Editors. 2011, Elsevier. p. 1-57.
158. Overbeek, J.T.G., *Quantitative interpretation of the electrophoretic velocity of colloids*. Advances in colloid science, 1950. **3**: p. 797-823.
159. Derkani, M.H., et al., *Mechanisms of dispersion of metakaolin particles via adsorption of sodium naphthalene sulfonate formaldehyde polymer*. Journal of Colloid and Interface Science, 2022. **628**: p. 745-757.
160. Smith, B.C., *Fundamentals of Fourier transform infrared spectroscopy*. 2011: CRC press.
161. Guinebretière, R., *X-ray diffraction by polycrystalline materials*. 2013: John Wiley & Sons.
162. Kearney, S., *Radiolysis and radiation damage effects in cements used in nuclear waste storage and disposal in the UK*. 2020, University of Sheffield.
163. Snellings, R., *X-ray powder diffraction applied to cement*. A practical guide to microstructural analysis of cementitious materials, 2016. **2**: p. 104-176.
164. Duxson, P., G.C. Lukey, and J.S.J. van Deventer, *Evolution of Gel Structure during Thermal Processing of Na-Geopolymer Gels*. Langmuir, 2006. **22**(21): p. 8750-8757.
165. Longhi, M.A., et al., *Metakaolin-based geopolymers: Relation between formulation, physicochemical properties and efflorescence formation*. Composites Part B: Engineering, 2020. **182**: p. 107671.
166. Williams, R.P., R.D. Hart, and A. Van Riessen, *Quantification of the extent of reaction of metakaolin-based geopolymers using X-ray diffraction, scanning electron microscopy, and energy-dispersive spectroscopy*. Journal of the American Ceramic Society, 2011. **94**(8): p. 2663-2670.
167. Arioiz, E., O. Arioiz, and O.M. Kockar, *An experimental study on the mechanical and microstructural properties of geopolymers*. Procedia Engineering, 2012. **42**: p. 100-105.
168. Haddad, M.A., et al., *Formation of zeolites in metakaolin-based geopolymers and their potential application for Cs immobilization*. Journal of Nuclear Materials, 2017. **493**: p. 168-179.

169. Rule, G.S. and T.K. Hitchens, *NMR spectroscopy*. 2006: Springer.
170. Skibsted, J., *High-resolution solid-state nuclear magnetic resonance spectroscopy of portland cement-based systems*. A Practical Guide to Microstructural Analysis of Cementitious Materials; Scrivener, K., Snellings, R., Lothenbach, B., Eds, 2016: p. 213-286.
171. MacKenzie, K.J. and M.E. Smith, *Multinuclear solid-state nuclear magnetic resonance of inorganic materials*. Vol. 6. 2002: Elsevier.
172. Duxson, P., et al., *²⁹Si NMR Study of Structural Ordering in Aluminosilicate Geopolymer Gels*. *Langmuir*, 2005. **21**(7): p. 3028-3036.
173. Duxson, P., et al., *³⁹K NMR of free potassium in geopolymers*. *Industrial & engineering chemistry research*, 2006. **45**(26): p. 9208-9210.
174. Arbel-Haddad, M., et al., *Cesium immobilization in metakaolin-based geopolymers elucidated by ¹³³Cs solid state NMR spectroscopy*. *Journal of Nuclear Materials*, 2022. **562**: p. 153570.
175. Hutchins, G.A., *Electron probe microanalysis*, in *Surface and Colloid Science: Volume 11: Experimental Methods*. 1974, Springer. p. 217-304.
176. Reed, S.J., *Electron probe microanalysis*, in *Microprobe techniques in the earth sciences*. 1995, Springer. p. 49-89.
177. Jensen, O.M., *Chloride ingress in cement paste and mortar measured by Electron Probe Micro Analysis*. 1998.
178. Mori, D., et al., *Applications of electron probe microanalyzer for measurement of Cl concentration profile in concrete*. *Journal of Advanced Concrete Technology*, 2006. **4**(3): p. 369-383.
179. Tajunnisa, Y., et al., *A study on factors affecting geopolymerization of low calcium fly ash*. *GEOMATE Journal*, 2017. **13**(36): p. 100-107.
180. Tajunnisa, Y., et al., *Characterization of low calcium fly ash for geopolymer paste*. *Structural Faults and Repair*, 2016.
181. Penner-Hahn, J.E., *X-ray absorption spectroscopy in coordination chemistry*. *Coordination Chemistry Reviews*, 1999. **190**: p. 1101-1123.
182. Scheidegger, A.M., et al., *The use of (micro)-X-ray absorption spectroscopy in cement research*. *Waste Management*, 2006. **26**(7): p. 699-705.
183. Geddes, D.A., et al., *Alkali-mediated Sr incorporation mechanism and binding capacity of alkali aluminosilicate hydrate in geopolymers*. *Journal of Hazardous Materials*, 2025. **488**: p. 137426.
184. Harris, R.K., et al., *NMR Nomenclature: Nuclear Spin Properties and Conventions for Chemical Shifts: IUPAC Recommendations 2001*. *Solid State Nuclear Magnetic Resonance*, 2002. **22**(4): p. 458-483.

185. Ravel, B. and M. Newville, *ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT*. Journal of synchrotron radiation, 2005. **12**(4): p. 537-541.
186. Rahman, R.O.A., et al., *Cementitious materials for nuclear waste immobilization*. 2014: John Wiley & Sons.
187. Davidovits, J., *Geopolymers and geopolymeric materials*. Journal of thermal analysis, 1989. **35**: p. 429-441.
188. Williams, B.D., et al., *Mineral assemblage transformation of a metakaolin-based waste form after geopolymer encapsulation*. Journal of Nuclear Materials, 2016. **473**: p. 320-332.
189. Davidovits, J., *Geopolymer cement*. A review. Geopolymer Institute, Technical papers, 2013. **21**: p. 1-11.
190. Fernández-Jiménez, A. and A. Palomo, *Nanostructure/microstructure of fly ash geopolymers*, in *Geopolymers*. 2009, Elsevier. p. 89-117.
191. Jain, S., N. Banthia, and T. Troczynski, *Conditioning of simulated cesium radionuclides in NaOH-activated fly ash-based geopolymers*. Journal of Cleaner Production, 2022. **380**: p. 134984.
192. Geddes, D.A., *A study of the suitability of metakaolin-based geopolymers for the immobilisation of problematic intermediate level waste in Department of Materials Science and Engineering*. 2020, The University of Sheffield.
193. González-García, D., et al., *Evolution of a natural pozzolan-based geopolymer alkalinized in the presence of sodium or potassium silicate/hydroxide solution*. Construction and Building Materials, 2022. **321**: p. 126305.
194. Fernández-Jiménez, A., A. Palomo, and M. Criado, *Alkali activated fly ash binders. A comparative study between sodium and potassium activators*. Materiales de Construcción, 2006. **56**(281): p. 51-65.
195. Phillip, E., et al., *On the sustainable utilization of geopolymers for safe management of radioactive waste: A review*. Sustainability, 2023. **15**(2): p. 1117.
196. Munthali, M., et al., *Cs⁺ and Sr²⁺ adsorption selectivity of zeolites in relation to radioactive decontamination*. Journal of Asian ceramic societies, 2015. **3**(3): p. 245-250.
197. Ke, X., et al., *Alkali aluminosilicate geopolymers as binders to encapsulate strontium-selective titanate ion-exchangers*. Dalton Transactions, 2019. **48**(32): p. 12116-12126.
198. Lin, W., H. Chen, and C. Huang, *Performance study of ion exchange resins solidification using metakaolin-based geopolymer binder*. Progress in Nuclear Energy, 2020. **129**: p. 103508.
199. Niu, X., et al., *Adsorption behaviour of simulant radionuclide cations and anions in metakaolin-based geopolymer*. Journal of Hazardous Materials, 2022. **429**: p. 128373.
200. Blissett, R. and N. Rowson, *A review of the multi-component utilisation of coal fly ash*. Fuel, 2012. **97**: p. 1-23.

201. Embong, R., et al., *Strength and microstructural properties of fly ash based geopolymer concrete containing high-calcium and water-absorptive aggregate*. Journal of cleaner production, 2016. **112**: p. 816-822.
202. Liu, M.Y.J., et al., *Microstructural investigations of palm oil fuel ash and fly ash based binders in lightweight aggregate foamed geopolymer concrete*. Construction and Building Materials, 2016. **120**: p. 112-122.
203. Gunasekara, C., D.W. Law, and S. Setunge, *Long term permeation properties of different fly ash geopolymer concretes*. Construction and Building Materials, 2016. **124**: p. 352-362.
204. Khan, M., et al., *Utilisation of steel furnace slag coarse aggregate in a low calcium fly ash geopolymer concrete*. Cement and Concrete Research, 2016. **89**: p. 220-229.
205. Chindaprasirt, P., et al., *Effect of calcium-rich compounds on setting time and strength development of alkali-activated fly ash cured at ambient temperature*. Case Studies in Construction Materials, 2018. **9**: p. e00198.
206. Luhar, I. and S. Luhar, *A comprehensive review on fly ash-based geopolymer*. Journal of Composites Science, 2022. **6**(8): p. 219.
207. Palomo, Á., et al., *Alkaline activation of fly ashes: NMR study of the reaction products*. Journal of the American Ceramic Society, 2004. **87**(6): p. 1141-1145.
208. Vogt, O., et al., *Reactivity and microstructure of metakaolin based geopolymers: Effect of fly Ash and liquid/solid contents*. Materials, 2019. **12**(21): p. 3485.
209. Van Deventer, J., et al., *Reaction mechanisms in the geopolymeric conversion of inorganic waste to useful products*. Journal of hazardous materials, 2007. **139**(3): p. 506-513.
210. Komljenović, M., et al., *Fly ash as the potential raw mixture component for Portland cement clinker synthesis*. Journal of thermal analysis and calorimetry, 2009. **96**(2): p. 363-368.
211. Kamara, S., E. Foday Jr, and W. Wang, *A review on the utilization and environmental concerns of coal fly ash*. Am. J. Chem. Pharm, 2023. **2**(2): p. 53-65.
212. Jindal, B.B., et al., *Geopolymer concrete with metakaolin for sustainability: a comprehensive review on raw material's properties, synthesis, performance, and potential application*. Environmental Science and Pollution Research, 2022: p. 1-26.
213. Criado, M., A. Palomo, and A. Fernández-Jiménez, *Alkali activation of fly ashes. Part 1: Effect of curing conditions on the carbonation of the reaction products*. Fuel, 2005. **84**(16): p. 2048-2054.
214. Fernández-Jiménez, A., et al., *Alkaline activation of metakaolin-fly ash mixtures: Obtain of Zeoceramics and Zeocements*. Microporous and mesoporous materials, 2008. **108**(1-3): p. 41-49.
215. Sanz, J., et al., *Aluminum-27 and Silicon-29 magic-angle spinning nuclear magnetic resonance study of the kaolinite-mullite transformation*. Journal of the American Ceramic Society, 1988. **71**(10): p. C418-C421.

216. Vold, M.J., *Differential thermal analysis*. Analytical chemistry, 1949. **21**(6): p. 683-688.
217. Pławecka, K., et al., *Development of Geopolymers Based on Fly Ashes from Different Combustion Processes*. Polymers, 2022. **14**(10): p. 1954.
218. Tchakouté, H.K., et al., *Influence of the molar concentration of phosphoric acid solution on the properties of metakaolin-phosphate-based geopolymer cements*. Applied Clay Science, 2017. **147**: p. 184-194.
219. Moutinho, S., et al., *Geopolymers and polymers in the conservation of tile facades*. Construction and Building Materials, 2019. **197**: p. 175-184.
220. Rashad, A.M., *Metakaolin as cementitious material: History, scours, production and composition—A comprehensive overview*. Construction and building materials, 2013. **41**: p. 303-318.
221. Zhang, Z., et al., *Activating process of geopolymer source material: Kaolinite*. Journal of Wuhan University of Technology-Mater. Sci. Ed., 2009. **24**: p. 132-136.
222. Duan, P., et al., *Thermal behavior of portland cement and fly ash–metakaolin-based geopolymer cement pastes*. Arabian Journal for Science and Engineering, 2015. **40**: p. 2261-2269.
223. Kakali, G., et al., *Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity*. Applied clay science, 2001. **20**(1-2): p. 73-80.
224. Izzat, A.M., et al., *Microstructural analysis of geopolymer and ordinary Portland cement mortar exposed to sulfuric acid*. Mater. Plast, 2013. **50**(3): p. 171-174.
225. Kou, S.-c., C.-s. Poon, and F. Agrela, *Comparisons of natural and recycled aggregate concretes prepared with the addition of different mineral admixtures*. Cement and Concrete Composites, 2011. **33**(8): p. 788-795.
226. Provis, J.L., P. Duxson, and J.S. van Deventer, *The role of particle technology in developing sustainable construction materials*. Advanced Powder Technology, 2010. **21**(1): p. 2-7.
227. Pouhet, R., *Formulation and durability of metakaolin-based geopolymers*. 2015, Université Paul Sabatier-Toulouse III.
228. Luna-Galiano, Y., et al., *Properties of fly ash and metakaolín based geopolymer panels under fire resistance tests*. Materiales de Construcción, 2015. **65**(319): p. e059-e059.
229. Feng, D., H. Tan, and J. Van Deventer, *Ultrasound enhanced geopolymerisation*. Journal of materials science, 2004. **39**: p. 571-580.
230. Petermann, J.C., A. Saeed, and M.I. Hammons, *Alkali-activated geopolymers: a literature review*. Air Force Research Laboratory Materials and Manufacturing Directorate Airbase Technologies Division, 2010.
231. Bernal, S.A., et al., *Evolution of binder structure in sodium silicate-activated slag-metakaolin blends*. Cement and Concrete Composites, 2011. **33**(1): p. 46-54.

232. Chen, L., et al., *Preparation and properties of alkali activated metakaolin-based geopolymer*. Materials, 2016. **9**(9): p. 767.
233. Granizo, M.L., M.T. Blanco-Varela, and S. Martínez-Ramírez, *Alkali activation of metakaolins: parameters affecting mechanical, structural and microstructural properties*. Journal of materials science, 2007. **42**: p. 2934-2943.
234. Singh, G.B. and K.V. Subramaniam, *Evaluation of sodium content and sodium hydroxide molarity on compressive strength of alkali activated low-calcium fly ash*. Cement and Concrete Composites, 2017. **81**: p. 122-132.
235. Provis, J., *Immobilisation of toxic wastes in geopolymers*, in *Geopolymers*. 2009, Elsevier. p. 421-440.
236. Blackford, M.G., et al., *Transmission electron microscopy and nuclear magnetic resonance studies of geopolymers for radioactive waste immobilization*. Journal of the American ceramic society, 2007. **90**(4): p. 1193-1199.
237. Poulesquen, A., F. Frizon, and D. Lambertin, *Rheological behavior of alkali-activated metakaolin during geopolymerization*, in *Cement-based materials for nuclear waste storage*. 2012, Springer. p. 225-238.
238. Lizcano, M., et al., *Mechanical properties of sodium and potassium activated metakaolin-based geopolymers*. Journal of Materials Science, 2012. **47**: p. 2607-2616.
239. Provis, J.L., et al., *Stabilization of low-modulus sodium silicate solutions by alkali substitution*. Industrial & engineering chemistry research, 2012. **51**(5): p. 2483-2486.
240. Autef, A., et al., *Influence of metakaolin purities on potassium geopolymer formulation: the existence of several networks*. Journal of colloid and interface science, 2013. **408**: p. 43-53.
241. Kim, B., et al., *Development of geopolymer waste form for immobilization of radioactive borate waste*. Journal of Hazardous Materials, 2021. **419**: p. 126402.
242. Singh, B., et al., *Geopolymer concrete: A review of some recent developments*. Construction and building materials, 2015. **85**: p. 78-90.
243. Favier, A., et al., *Flow properties of MK-based geopolymer pastes. A comparative study with standard Portland cement pastes*. Soft Matter, 2014. **10**(8): p. 1134-1141.
244. Favier, A., et al., *Mechanical properties and compositional heterogeneities of fresh geopolymer pastes*. Cement and Concrete Research, 2013. **48**: p. 9-16.
245. Duxson, P., G.C. Lukey, and J.S. van Deventer, *The thermal evolution of metakaolin geopolymers: Part 2–Phase stability and structural development*. Journal of non-crystalline solids, 2007. **353**(22-23): p. 2186-2200.
246. Duxson, P., et al., *Understanding the relationship between geopolymer composition, microstructure and mechanical properties*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2005. **269**(1-3): p. 47-58.

247. Palomo, A., A. Fernández-Jiménez, and M. Criado, *"Geopolymers": same basic chemistry, different microstructures*. *Materiales de Construcción*, 2004. **54**(275): p. 77-91.
248. Institution, B.S., *Cement: Composition, specifications and conformity criteria for common cements*. 2019: British Standards Institution.
249. Davidovits, J., *Geopolymer chemistry and applications*. 2008: Geopolymer Institute.
250. N'Guessan, N.E., et al., *Role of cations on the dissolution mechanism of kaolinite in high alkaline media*. *Applied clay science*, 2021. **205**: p. 106037.
251. Werling, N., et al., *Solubility of precursors and carbonation of waterglass-free geopolymers*. *Clays and Clay Minerals*, 2020. **68**(5): p. 524-531.
252. Angus, M., et al., *The Specification of Cement Powders for Waste Encapsulation Processes at Sellafield site*. 2011.
253. Lee, W. and J. Van Deventer, *Use of infrared spectroscopy to study geopolymerization of heterogeneous amorphous aluminosilicates*. *Langmuir*, 2003. **19**(21): p. 8726-8734.
254. Hajimohammadi, A., J.L. Provis, and J.S. van Deventer, *The effect of silica availability on the mechanism of geopolymerisation*. *Cement and Concrete Research*, 2011. **41**(3): p. 210-216.
255. Wan, Q., et al., *Geopolymerization reaction, microstructure and simulation of metakaolin-based geopolymers at extended Si/Al ratios*. *Cement and Concrete Composites*, 2017. **79**: p. 45-52.
256. Rees, C.A., et al., *Attenuated total reflectance fourier transform infrared analysis of fly ash geopolymer gel aging*. *Langmuir*, 2007. **23**(15): p. 8170-8179.
257. Dhanalakshmi, K., et al., *Exploring the chemistry of metakaolin-based geopolymers*. *Journal of Polymer Research*, 2024. **31**(12): p. 1-11.
258. Farmer, V., *The infrared spectra of minerals: Mineralogical Society*. London, Monograph, 1974. **4**: p. 539.
259. Farmer, V.C., (J. A.) Gadsden. *The infrared spectra of minerals and related inorganic compounds*. London (Butterworths), 1975. 277 pp. Price £15.00. *Mineralogical Magazine*, 1976. **40**(313): p. 540-540.
260. Kljajević, L.M., et al., *Structural and chemical properties of thermally treated geopolymer samples*. *Ceramics International*, 2017. **43**(9): p. 6700-6708.
261. Mozgawa, W., *The relation between structure and vibrational spectra of natural zeolites*. *Journal of Molecular Structure*, 2001. **596**(1-3): p. 129-137.
262. Handke, M., M. Sitarz, and W. Mozgawa, *Model of silicoxygen ring vibrations*. *Journal of molecular structure*, 1998. **450**(1-3): p. 229-238.
263. Rovnaník, P., *Effect of curing temperature on the development of hard structure of metakaolin-based geopolymer*. *Construction and building materials*, 2010. **24**(7): p. 1176-1183.

264. Onutai, S., T. Osugi, and T. Sone, *Alumino-Silicate Structural Formation during Alkali-Activation of Metakaolin: In-Situ and Ex-Situ ATR-FTIR Studies*. Materials (Basel), 2023. **16**(3).
265. Rees, C.A., et al., *The mechanism of geopolymer gel formation investigated through seeded nucleation*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2008. **318**(1-3): p. 97-105.
266. Król, M., et al., *ATR/FT-IR studies of zeolite formation during alkali-activation of metakaolin*. Solid State Sciences, 2019. **94**: p. 114-119.
267. Hajimohammadi, A., J.L. Provis, and J.S. Van Deventer, *Effect of alumina release rate on the mechanism of geopolymer gel formation*. Chemistry of Materials, 2010. **22**(18): p. 5199-5208.
268. Walkley, B., et al., *Phase evolution of Na₂O–Al₂O₃–SiO₂–H₂O gels in synthetic aluminosilicate binders*. Dalton Transactions, 2016. **45**(13): p. 5521-5535.
269. Kuenzel, C., et al., *Ambient temperature drying shrinkage and cracking in metakaolin-based geopolymers*. Journal of the American Ceramic Society, 2012. **95**(10): p. 3270-3277.
270. Trincal, V., et al., *Shrinkage mitigation of metakaolin-based geopolymer activated by sodium silicate solution*. Cement and Concrete Research, 2022. **162**: p. 106993.
271. Pouhet, R. and M. Cyr, *Studies of natural and accelerated carbonation in metakaolin-based geopolymer*. Advances in Science and Technology, 2014. **92**: p. 38-43.
272. Kobera, L., et al., *Structural stability of aluminosilicate inorganic polymers: influence of the preparation procedure*. Ceramics-Silikáty, 2011. **55**(4): p. 343-354.
273. Kolodziejski, W. and J. Klinowski, *Kinetics of cross-polarization in solid-state NMR: a guide for chemists*. Chem Rev, 2002. **102**(3): p. 613-28.
274. Singh, P.S., T. Bastow, and M. Trigg, *Structural studies of geopolymers by ²⁹Si and ²⁷Al MAS-NMR*. Journal of materials science, 2005. **40**: p. 3951-3961.
275. Scanferla, P., et al., *Polycondensation reaction effect on the thermal behavior of metakaolin-based potassium geopolymers*. Journal of Sol-Gel Science and Technology, 2023: p. 1-14.
276. Engelhardt, G., et al., *²⁹Si-NMR-Untersuchungen zur Verteilung der Silicium- und Aluminiumatome im Aluminosilikatgitter von Zeolithen mit Faujasit-Struktur*. Zeitschrift für anorganische und allgemeine Chemie, 1981. **482**(11): p. 49-64.
277. Larin, A.V., *The Loewenstein rule: the increase in electron kinetic energy as the reason for instability of Al–O–Al linkage in aluminosilicate zeolites*. Physics and Chemistry of Minerals, 2013. **40**: p. 771-780.
278. Walkley, B., et al., *New Structural Model of Hydrous Sodium Aluminosilicate Gels and the Role of Charge-Balancing Extra-Framework Al*. The Journal of Physical Chemistry C, 2018. **122**(10): p. 5673-5685.
279. Duxson, P., et al., *Effect of Alkali Cations on Aluminum Incorporation in Geopolymeric Gels*. Industrial & Engineering Chemistry Research, 2005. **44**(4): p. 832-839.

280. Kobera, L., et al., *Biaxial Q-shearing of ^{27}Al 3QMAS NMR spectra: Insight into the structural disorder of framework aluminosilicates*. Solid State Nuclear Magnetic Resonance, 2014. **57**: p. 29-38.
281. Kim, B. and S. Lee, *Review on characteristics of metakaolin-based geopolymer and fast setting*. Journal of the Korean Ceramic Society, 2020. **57**: p. 368-377.
282. Gharzouni, A., et al., *A MAS-NMR analysis of ^{29}Si , ^{27}Al and ^1H on the temperature's impact on geopolymer grouts derived from argillite and metakaolin*. Journal of Non-Crystalline Solids, 2024. **642**: p. 123163.
283. Prasanphan, S., et al., *^{29}Si and ^{27}Al NMR study of the structural transformation of calcined kaolin residue-based geopolymer using low alkali activator content for sustainable construction materials*. Journal of Building Engineering, 2023. **70**: p. 106332.
284. Provis, J.L., et al., *Statistical Thermodynamic Model for Si/Al Ordering in Amorphous Aluminosilicates*. Chemistry of Materials, 2005. **17**(11): p. 2976-2986.
285. Lecomte, I., et al., *(Micro)-structural comparison between geopolymers, alkali-activated slag cement and Portland cement*. Journal of the European Ceramic Society, 2006. **26**(16): p. 3789-3797.
286. MackenzieKJD, S., *Multinuclear solid state NMR of inorganic materials (6)*. 2002, Pergamon: Elsevier.
287. Geddes, D., et al. *Metakaolin-based geopolymers for nuclear waste encapsulation*. in *Calcined Clays for Sustainable Concrete: Proceedings of the 2nd International Conference on Calcined Clays for Sustainable Concrete*. 2018. Springer.
288. Gasperi, J.d., et al., *Effect of Activator Type and Concentration, Water-to-Solid Ratio, and Time on the Flowability of Metakaolin-Based Geopolymer Pastes*. Journal of Materials in Civil Engineering, 2022. **34**(9): p. 04022205.
289. Vance, K., et al., *Observations on the rheological response of alkali activated fly ash suspensions: the role of activator type and concentration*. Rheologica Acta, 2014. **53**: p. 843-855.
290. Silva, P.D., K. Sagoe-Crenstil, and V. Sirivivatnanon, *Kinetics of geopolymerization: Role of Al_2O_3 and SiO_2* . Cement and Concrete Research, 2007. **37**(4): p. 512-518.
291. Provis, J.L. and C.A. Rees, *7 - Geopolymer synthesis kinetics*, in *Geopolymers*, J.L. Provis and J.S.J. van Deventer, Editors. 2009, Woodhead Publishing. p. 118-136.
292. Yao, X., et al., *Geopolymerization process of alkali–metakaolinite characterized by isothermal calorimetry*. Thermochimica Acta, 2009. **493**(1-2): p. 49-54.
293. Reuter, H., S. Kamaha, and O. Zerzouf, *Hydrogen bonds in the crystal structure of strontium hydroxide octahydrate $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$* . Zeitschrift für Naturforschung B, 2007. **62**(2): p. 215-219.

294. Avet, F., et al., *Report of RILEM TC 267-TRM phase 2: optimization and testing of the robustness of the R3 reactivity tests for supplementary cementitious materials*. Materials and Structures, 2022. **55**(3): p. 92.
295. Li, X., et al., *Reactivity tests for supplementary cementitious materials: RILEM TC 267-TRM phase 1*. Materials and Structures, 2018. **51**(6): p. 151.
296. Berodier, E. and K. Scrivener, *Evolution of pore structure in blended systems*. Cement and Concrete Research, 2015. **73**: p. 25-35.
297. Glasser, F., & Atkins, M. , *Cements in Radioactive Waste Disposal*. . MRS Bulletin, 1994. **19**(12): p. 33-38.
298. Wilding, C.R., *The performance of cement based systems*. Cement and Concrete Research, 1992. **22**(2): p. 299-310.
299. Isaacs, M., et al., *Processing and product characteristics of a blended cement grout incorporating polycarboxylate ether superplasticiser*. Advances in Cement Research, 2018. **30**(4): p. 148-158.
300. Li, H., et al., *Salt coagulation or flocculation? In situ zeta potential study on ion correlation and slime coating with the presence of clay: A case of coal slurry aggregation*. Environmental Research, 2020. **189**: p. 109875.
301. Korayem, A.H., et al., *A review of dispersion of nanoparticles in cementitious matrices: Nanoparticle geometry perspective*. Construction and Building Materials, 2017. **153**: p. 346-357.
302. Frugier, P., et al., *SON68 nuclear glass dissolution kinetics: Current state of knowledge and basis of the new GRAAL model*. Journal of Nuclear Materials, 2008. **380**(1): p. 8-21.
303. Lide, D.R., *CRC handbook of chemistry and physics*. Vol. 85. 2004: CRC press.
304. Glasser, L.S.D., R.P. Gunawardane, and R.A. Howie, *The crystal structure of sodium strontium silicate, Na₄SrSi₃O₉*. Zeitschrift für Kristallographie - Crystalline Materials, 1991. **197**(1-4): p. 59-66.
305. Gunawardane, R. and F. Glasser, *Crystal chemistry and synthesis of ternary silicates and germanates containing alkali (Na⁺, K⁺) and alkaline earth (Ca²⁺, Sr²⁺, Ba²⁺) cations*. Zeitschrift für anorganische und allgemeine Chemie, 1975. **411**(2): p. 163-172.
306. Davidovits, J., *Geopolymers: inorganic polymeric new materials*. Journal of Thermal Analysis and calorimetry, 1991. **37**(8): p. 1633-1656.
307. Stebbins, J.F., et al., *Quantification of five- and six-coordinated aluminum ions in aluminosilicate and fluoride-containing glasses by high-field, high-resolution ²⁷Al NMR*. Journal of Non-Crystalline Solids, 2000. **275**(1): p. 1-6.
308. Kuenzel, C., et al., *Encapsulation of Cs/Sr contaminated clinoptilolite in geopolymers produced from metakaolin*. Journal of Nuclear Materials, 2015. **466**: p. 94-99.

309. Ropp, R.C., *Chapter 3 - Group 16 (O, S, Se, Te) Alkaline Earth Compounds*, in *Encyclopedia of the Alkaline Earth Compounds*, R.C. Ropp, Editor. 2013, Elsevier: Amsterdam. p. 105-197.
310. Smith, H., *The crystal structure of strontium hydroxide octahydrate, Sr (OH) 2.8 H₂O*. Acta Crystallographica, 1953. **6**(7): p. 604-609.
311. Reuter, H., S. Kamaha, and O. Zerzouf, *Hydrogen Bonds in the Crystal Structure of Strontium Hydroxide Octahydrate Sr(OH)₂ · 8H₂O*. 2007. **62**(2): p. 215-219.
312. Arbel Haddad, M., et al., *Formation of zeolites in metakaolin-based geopolymers and their potential application for Cs immobilization*. Journal of Nuclear Materials, 2017. **493**: p. 168-179.
313. Zhang, B., K.J. MacKenzie, and I.W. Brown, *Crystalline phase formation in metakaolinite geopolymers activated with NaOH and sodium silicate*. Journal of materials science, 2009. **44**: p. 4668-4676.
314. Perrotta, A. and J. Smith, *The crystal structure of brewsterite,(Sr, Ba, Ca)(Al₂Si₆O₁₆). 5H₂O*. Acta Crystallographica, 1964. **17**(7): p. 857-862.
315. Artioli, G., J.V. Smith, and Å. Kvik, *Multiple hydrogen positions in the zeolite brewsterite,(Sr_{0.95}, Ba_{0.05}) Al₂Si₆O₁₆. 5H₂O*. Acta Crystallographica Section C: Crystal Structure Communications, 1985. **41**(4): p. 492-497.
316. Trueman, C.N., et al., *Geochemistry | Inorganic* ☆, in *Encyclopedia of Analytical Science (Third Edition)*, P. Worsfold, et al., Editors. 2019, Academic Press: Oxford. p. 271-282.
317. Longhi, M.A., et al., *Metakaolin-based geopolymers: Relation between formulation, physicochemical properties and efflorescence formation*. Composites Part B: Engineering, 2020. **182**: p. 107671.
318. Joseph, K., et al., *Iron phosphate glasses: Bulk properties and atomic scale structure*. Journal of Nuclear Materials, 2017. **494**: p. 342-353.
319. Wilke, M., et al., *Oxidation state and coordination of Fe in minerals: An Fe K-XANES spectroscopic study*. American Mineralogist, 2001. **86**(5-6): p. 714-730.
320. Farges, F., et al., *The effect of redox state on the local structural environment of iron in silicate glasses: a combined XAFS spectroscopy, molecular dynamics, and bond valence study*. Journal of Non-Crystalline Solids, 2004. **344**(3): p. 176-188.
321. Longhi, M.A., et al., *Metakaolin-based geopolymers: Efflorescence and its effect on microstructure and mechanical properties*. Ceramics International, 2022. **48**(2): p. 2212-2229.
322. Kuenzel, C., *Metakaolin based geopolymers to encapsulate nuclear waste*. 2013, Imperial College London.
323. Walkley, B., et al., *New structural model of hydrous sodium aluminosilicate gels and the role of charge-balancing extra-framework Al*. The Journal of Physical Chemistry C, 2018. **122**(10): p. 5673-5685.

324. von der Handt, A., et al., *Recent Advances in the Analysis of Nitrogen by EPMA*. Microscopy and Microanalysis, 2019. **25**(S2): p. 2320-2321.
325. Mosenfelder, J.L., et al., *Nitrogen incorporation in silicates and metals: Results from SIMS, EPMA, FTIR, and laser-extraction mass spectrometry*. American Mineralogist: Journal of Earth and Planetary Materials, 2019. **104**(1): p. 31-46.
326. Kemp, S.J., et al., *Kalistrontite, its occurrence, structure, genesis, and significance for the evolution of potash deposits in North Yorkshire, UK*. American Mineralogist: Journal of Earth and Planetary Materials, 2018. **103**(7): p. 1136-1150.
327. Kemp, S., et al., *An improved approach to characterize potash-bearing evaporite deposits, evidenced in North Yorkshire, United Kingdom*. Economic Geology, 2016. **111**(3): p. 719-742.
328. Yusuf, M.O., *Bond Characterization in Cementitious Material Binders Using Fourier-Transform Infrared Spectroscopy*. Applied Sciences, 2023. **13**(5): p. 3353.
329. Prentice, D.P., et al., *Thermodynamic modelling of BFS-PC cements under temperature conditions relevant to the geological disposal of nuclear wastes*. Cement and Concrete Research, 2019. **119**: p. 21-35.
330. IAEA. *Nuclear Power Stations Under Construction*. 2025 [cited 2025 25/02/2025]; Available from: <https://pris.iaea.org/pris/worldstatistics/underconstructionreactorsbycountry.aspx>.
331. Yim, M.-S., *Nuclear waste management*. 2022: Springer.
332. Tokuyama, H. and S. Igarashi, *Seasonal variation in the environmental background level of cosmic-ray-produced ²²Na at Fukui City, Japan*. Journal of environmental radioactivity, 1998. **38**(2): p. 147-161.
333. Li, J., L. Chen, and J. Wang, *Solidification of radioactive wastes by cement-based materials*. Progress in Nuclear Energy, 2021. **141**: p. 103957.
334. Merz, E., D. Dyckerhoff, and R. Odoj, *Characterization of Radioactive Wastes Incorporated in a Cement Matrix*. 1987.
335. Nuclear Decommissioning Authority, Radioactive Waste Management, and Sellafield Limited, *Case study - Forward planning to ensure cement supplies*. . 2019.
336. Liu, J., et al., *Solidification performance and mechanism of typical radioactive nuclear waste by geopolymers and geopolymer ceramics: A review*. Progress in Nuclear Energy, 2024. **169**: p. 105106.
337. Topark-Ngarm, P., P. Chindaprasirt, and V. Sata, *Setting time, strength, and bond of high-calcium fly ash geopolymer concrete*. Journal of materials in civil engineering, 2015. **27**(7): p. 04014198.
338. Aldawsari, S., et al., *Setting time, microstructure, and durability properties of low calcium fly ash/slag geopolymer: a review*. Materials, 2022. **15**(3): p. 876.

339. Longhi, M.A., et al., *New selective dissolution process to quantify reaction extent and product stability in metakaolin-based geopolymers*. Composites Part B: Engineering, 2019. **176**: p. 107172.
340. N'Cho, W., et al., *Effect of mixing metakaolins: Methodological approach to estimate metakaolin reactivity*. Ceramics International, 2023. **49**(12): p. 20334-20342.
341. Ylmén, R., et al., *Early hydration and setting of Portland cement monitored by IR, SEM and Vicat techniques*. Cement and Concrete Research, 2009. **39**(5): p. 433-439.
342. Kasprzhitskii, A., et al., *Mechanism of Cs Immobilization within a Sodalite Framework: The Role of Alkaline Cations and the Si/Al Ratio*. International Journal of Molecular Sciences, 2023. **24**(23): p. 17023.
343. Provis, J.L. and J.S. Van Deventer, *Geopolymerisation kinetics. 1. In situ energy-dispersive X-ray diffractometry*. Chemical engineering science, 2007. **62**(9): p. 2309-2317.
344. ASTM, *ASTM C1308, Standard Test Method for Accelerated Leach Test for Measuring Contaminant Releases From Solidified Waste*. 2021.
345. Double, D., A. Hellowell, and S. Perry, *The hydration of Portland cement*. Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences, 1978. **359**(1699): p. 435-451.
346. He, P., et al., *Effects of Si/Al ratio on the structure and properties of metakaolin based geopolymer*. Ceramics International, 2016. **42**(13): p. 14416-14422.
347. Rowles, M., et al., *29 Si, 27 Al, 1 H and 23 Na MAS NMR study of the bonding character in aluminosilicate inorganic polymers*. Applied Magnetic Resonance, 2007. **32**: p. 663-689.
348. Trivedi, M.K., et al., *Spectroscopic characterization of disodium hydrogen orthophosphate and sodium nitrate after biofield treatment*. Journal of Chromatography & Separation Techniques, 2015. **6**(5).
349. Barbosa, V.F. and K.J. MacKenzie, *Synthesis and thermal behaviour of potassium sialate geopolymers*. Materials Letters, 2003. **57**(9-10): p. 1477-1482.
350. Moudrakovski, I.L. and J.A. Ripmeester, *39K NMR of Solid Potassium Salts at 21 T: Effect of Quadrupolar and Chemical Shift Tensors*. The Journal of Physical Chemistry B, 2007. **111**(3): p. 491-495.

Appendix

Appendix 1: Fitting Residue from KGP Deconvolutions

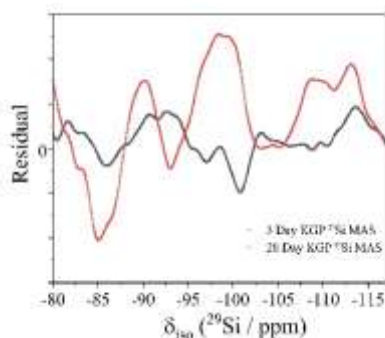


Figure A- 1: Fitting residuals for the 3 and 28 days KGP Control sample ^{29}Si MAS deconvolutions seen in Figure 3-6.

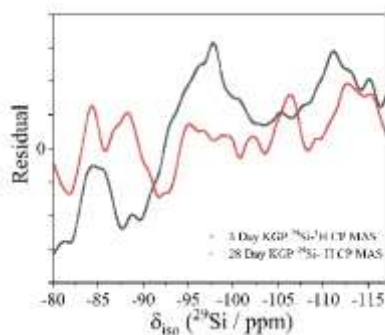


Figure A- 2: Fitting residuals for the 3 and 28 days KGP Control sample ^{29}Si - ^1H CP MAS deconvolutions seen in Figure 3-6.