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PVA- and PEG-assisted Sol-gel Synthesis of Aluminosilicate Precursors for N-A-S-H Geopolymer Cements

Juan Pablo Gevaudan[1], *Jaqueline D. Wallat*[1], *Bimala Lama*[2], *Wil V. Srubar III*[1†]

[1]Department of Civil, Environmental, and Architectural Engineering, University of Colorado Boulder.

[2]Department of Chemistry, University of Colorado Boulder. [†]Corresponding Author 1111 Engineering Drive, ECOT 441 UCB 428, Boulder, Colorado USA 80309. T +1 303 492 2621,

E: wsrubar@colorado.edu

Abstract

This study investigates critical factors affecting polymer-assisted sol-gel synthesis of synthetic aluminosilicate powders that can be alkali-activated to produce a sodium-stabilized aluminosilicate hydrate (N-A-S-H) geopolymer cement. More specifically, a 2^2 factorial experiment was conducted to elucidate the influence of polymer architecture (*i.e.*, poly(ethylene glycol) (PEG) vs. poly(vinyl alcohol) (PVA)), polymer content (*i.e.*, low vs. high ion-to-polymer-oxide (I/O) atomic ratio), and sol-gel aging pH conditions (*i.e.*, low vs. high) on the atomic structure of resultant synthetic aluminosilicate powders and geopolymer cements. Molecular structure was investigated using solid-state (single pulse and ^1H cross polarization) ^{29}Si and ^{27}Al nuclear magnetic resonance (NMR) and fourier-transform infrared (FT-IR) spectroscopy. The mineralogy of geopolymer cements was assesed with X-ray diffraction and compared to alkali-activated metakaolin-based cements of equivalent stoichiometry. Results demonstrate that polymer architecture (PEG vs. PVA) is a key factor in producing (a) undesirable phase segregation (i.e., γ-alumina) and (b) incomplete dehydroxylation (*i.e.*, vicinal silanol) in synthetic aluminosilicate powders. More specifically, PEG-derived aluminosilicate powders yield partial dissolution and produce geopolymer cements with variable silicate incorporation. Contrastingly, PVA-derived aluminosilicate powders produce geopolymer cements with identical mineralogy to that of metakaolin-based geopolymer cements and exhibit both Brønsted-acid sites near the aluminum nuclei and geminal silanol groups. Sol-gel pH aging conditions reveal the ability to influence the hydroxyl group content, which is an important factor affecting the durability of cementitious materials. Lastly, three plausible mechanisms of metal-complexation are hypothesized to permit incorporation of solubilized metal ions *via* a polymer-assisted sol-gel process.

Keywords: geopolymers, metakaolin, sol-gel synthesis, alkali-activation, nuclear magnetic resonance.

1. Introduction

Polymer-assisted sol-gel synthesis— otherwise known as the organic steric entrapment (OSE) method—was first demonstrated in 1992 as a viable method to produce metal-oxide ceramics. Earlier, in 1931, conventional (*i.e.*, non-polymer-assisted) sol-gel synthesis methods were used to produce ceramics using alkoxysilanes (1,2). The primary aim of sol-gel synthesis is to produce solid ceramics from a solution of liquid metal precursors *via* hydrolysis and subsequent polycondensation into a gel (3). By forming gels in a solution state, sol-gel synthesis methods ensure atomic-level mixing, thereby circumventing challenges associated with solid-state chemistry (*e.g.*, inhomogeneity, phase separation, low yield reactions) (3,4). As a departure from conventional sol-gel synthesis, polymer-assisted sol-gel synthesis was first reported in a study that used polyethylene glycol (PEG) to synthesize nanocrystalline Perovskite materials (5,6). Soon thereafter, polyvinyl alcohol (PVA) was used to produce fine ferrite powders and mixed-metal-oxide materials (7–10). In 1999, polymer-assisted sol-gel synthesis was renamed the OSE method, due to the speculation that weak hydrogen bonding between the polymer and metal oxides was primarily responsible for sterically entrapping and structuring solvated cations in solution (11,12).

OSE has since been used to synthesize metal-oxide precursors to traditional ordinary portland cement (OPC) cementitious binders, as well as alternative cementitious binders such as calcium- and sodium-stabilized aluminosilicate hydrates (i.e., C-N-A-S-H and N-A-S-H) (13–15). Examples of synthesized OPC phases include calcium aluminate, dicalcium silicate, tricalcium silicate, tricalcium aluminate, and tetracalcium aluminate iron oxide (11,16). These synthesized cementitious components were found to be pure, nano- or sub-micron sized and highly reactive. Furthermore, recent renewed interest in this synthesis method has arisen due to the possibility of producing alternative cementitious binders (i.e.

calcium aluminosilicate hydrates and sodium aluminosilicate binders) (13,14,17,18). Production of alternative cementitious binders through OSE presents a unique opportunity to understand the atomic structure and material properties by stoichiometric control of the alternative cement chemistry (19).

Despite advances in polymer-assisted sol-gel synthesis, the effect of processing conditions to produce aluminosilicate precursors that yield structural variants of N-A-S-H cementitious binders is not well understood. Such N-A-S-H cementitious binders, or geopolymer cements, have gained popularity for their controllable chemistry and potential for increased durability, improved fire resistance, and reduced environmental impacts compared to OPC in some applications (20–22). Traditionally, geopolymer materials are composed of N-A-S-H binders, which have a standard composition of $SiO_2/Al_2O_3 = 3.3$, $Na_2O/ Al_2O_3 = 1.1$, and, $H_2O:Na_2O = 11$ (23) with modern N-A-S-H binders having SiO_2/Al_2O_3 between 0.5 and 2.0 given the choice of low calcium precursor used. Multiple studies have been pivotal to understand the atomic structure and properties of N-A-S-H binders as well as dictating the foundation for synthesizing such binders *via* polymer-assisted sol-gel methods using PVA as the polymer cross-linking agent (13,18,19,24–26). However, little scientific understanding on process-structure effects of different N-A-S-H precursor synthesis conditions currently exists.

The aim of this study was to elucidate process-structure relationships of synthetic aluminosilicate powders produced *via* polymer-assisted sol-gel synthesis, as well as process-structure relationships of resultant sodium-stabilized aluminum-silicate-hydrate (N-A-S-H) geopolymer cements. The influence of synthesis processing factors (*i.e.*, polymer architecture, polymer content, and sol-gel aging pH) were explored using a 2^2 factorial design to reveal changes in atomic structure and variations in mineralogy in both synthetic aluminosilicate powders and resultant geopolymer cements. Lastly, the mineralogy of geopolymer cements is compared to that of alkali-activated metakaolin-based cements. **Figure 1** illustrates the scope of work and nomenclature used in this study.

2. Experimental Program

2.1 Materials

Polyvinyl alcohol (PVA) and polyethylene glycol (PEG) polymers of molecular weight 31-50 kDa

(M_w) and 35 kDa (M_n), respectively, were obtained from MilliporeSigma. Aluminum nitrate nonahydrate (99+%, analysis grade, Acros Organics), a 40% by weight colloidal silica suspension (LUDOX TM-40, Millipore), sodium hydroxide (NaOH) (10M, BioUltra grade, MilliporeSigma), and NaOH (reagent grade) were also acquired from MilliporeSigma. Metakaolin (Si:Al = 1.0) was supplied by BASF Chemical Corporation (MetaMax).

2.2 Experimental Methods

2.2.1 2^2 factorial design

The influence of both polymer architecture and sol-gel aging pH was investigated using a 2^2 factorial design of experiments. Additionally, the influence of polymer content was explored in combination with the aforementioned factors. In terms of polymer architecture, both PEG and PVA of similar molecular weights were used to elucidate the role of polymer architecture. Sol-gel aging at two different pH conditions (low pH ~ 1.0, high pH ~ 10) explored pH-dependent metal-polymer interactions. Polymer content was explored by varying the ion-to-polymer-oxide atomic ratios (I/O) in two levels (see supplementary information for calculation of I/O). The "ion" content refers to aluminum metal ions, while the oxide solely refers to the polymer oxide content. The aluminum content of aluminum nitrate nonahydrate salts was determined to be 9.28 wt.% via ICP-OES and used to calculate accurate I/O ratios. As seen in **Table 1**, PVA-derived precursors had I/O ratios of 4.0 (low) and 5.2 (high), while PEG-derived precursors had I/O ratios of 3.7 (low) and 4.4 (high). While similar ratios have been described as metal-to-hydroxide (M/OH) atomic ratios, in the present study, PVA chain hydroxyls are compared to PEG chain ethers and, as a result, a redefinition of this atomic ratio was used to account for the differences in polymer architecture as an I/O ratio, where oxide (O) accounts for ethers or hydroxyls.

2.2.2 Polymer-assisted sol-gel synthesis and characterization of aluminosilicate precursors

Aluminosilicate precursors were synthesized following the polymer-assisted sol-gel procedure developed by (18). As explained earlier, the herein methodology mainly differs from (18) by exploring the effect of polymer content (I/O ratio) as well as sol-gel aging pH condition. PEG and PVA polymeric solutions of 5% (by weight) were produced by incrementally adding the polymer to deionized water over heat (~ 90 ˚C). Once the polymer was completely dissolved, verified by visual inspection, the solutions were left to age for one hour at a temperature of 60 to 70˚C. Synthesis pH during sol-gel aging was controlled at two conditions either low pH (~ 1.0) or high pH (~ 10.0) via order of reactant addition. For example, high-pH samples were synthesized by first adding the colloidal silica suspension reactant and allowing the polymer to interact with the reactant for one hour (sol-gel aging time) at a pH ~10 (sol-gel aging condition). After one hour of sol-polymer interactions at high pH, a 40% (by weight) solution of aluminum nitrate nonahydrate solution was added, which decreases the pH to ~1.0. For low-pH samples, addition of the aluminum nitrate nonahydrate solution was performed first and left to interact with the polymer for one hour before addition of the colloidal silica solution. The sol-gel synthesis conditions remained at a pH of ~1.0. After the sol-gel aging process occurred, all solutions were dried via continuous stirring over heat (70 to 80˚C), during which a viscous and porous xerogel was formed. Samples of the xerogels (*i.e.,* uncalcined synthetic aluminosilicate powders) were collected for subsequent characterization.

2.2.3 Surface area characterization of aluminosilicate precursors

Further following the procedure developed by (18), both PVA and PEG xerogels were calcined at 550˚C and at 900˚C, respectively, with a hold time of one hour (ramp rate of 3˚C/minute). The resultant white material was ground to form a powder and sieved through a No. 100 sieve. Samples of the synthetic aluminosilicate powders were saved for subsequent characterization. The Brunauer–Emmett–Teller (BET) nitrogen adsorption method was used to measure the surface area of the calcined powders. Samples were massed and degassed under vacuum in an inert nitrogen atmosphere at 100°C for at least eight hours. After conducting a blank acquisition, samples were placed into the instrument and nitrogen gas was deposited atop the powder surface by varying the N_2 pressure. For the measurement, eleven data points were collected with relative pressure (P/Po) ranging from 0.05 to 0.30 with a five second equilibration time. From the data, a BET plot was generated using a linear regression with a correlation coefficient of 0.99 for all data generated. The surface area of the resulting powders is reported in **Table 1.** The surface area measurements herein are similar to those reported for in comparable literature (18,27).

2.2.4 Geopolymerization of synthetic and natural precursors

Aluminosilicate powders were alkali-activated via addition of NaOH (10M, BioUltra grade, MilliporeSigma) at a liquid-to-solid weight ratio of 0.75 to form synthetic geopolymers cements, as similarly reported in (19,28). Geopolymers were produced by manual mixing for one minute until a homogenous paste was obtained. Additionally, natural metakaolin-based geopolymer cements were utilized for mineralogical comparison. The mixing procedure consisted of an initial one minute of manual mixing, followed by one minute of mechanical mixing using a Waring PDM112 mixer and one minute of additional manual mixing to ensure that all of the dry components were mixed homogenously.

The natural metakaolin-based geopolymer cements were designed to exhibit equal chemical parameters as the synthetic geopolymer cements. More specifically, NaOH (reagent grade) was dissolved in deionized water to create activating solutions and yield Si:Al and Na:Al ratios of metakaolin-based geopolymer cements of 1.0 and 1.1, respectively. Both natural and synthetic geopolymer cements were cast in cylindrical molds (diameter: 1.26 cm, height: 3 cm) and cured at 35 ± 5˚C and 100% relative humidity for 48 ± 4 hours in a Quincy forced-air laboratory oven. Subsequently, samples were dried at 30˚C overnight (>12 hours) as previously investigated by our research group on calcium-free AAC formulations by (29).

2.2.5 ^{29}Si and ^{27}Al solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR)

Solid-state ^{29}Si and ^{27}Al MAS-NMR spectra were acquired using a Varian INOVA 400 MHz NMR spectrometer (magnetic field 9.39 T; operating frequency of 79.50 MHz for ^{29}Si and 104.27 MHz for ^{27}Al). Samples were packed into 4 mm zirconia rotors sealed at either end with Teflon end plugs, and all spectra were collected with magic-angle spinning (MAS) speed of 10 kHz using a broadband probe equipped with a 4 mm MAS spinning module designed and manufactured by Revolution NMR, LLC (Fort Collins, CO). ^{29}Si chemical shifts were determined using the NMR signal from DSS (2,2-dimethyl-2-silapentanesulfonate) referenced at 1.46 ppm. The spectra were acquired through a Bloch-decay experiment with 1600 scans using a pulse recycle delay of 5 s, a pulse width of 4.5 μs, and an acquisition time of ~20 ms. These experimental parameters are sufficient for the qualitative analysis of the data, as presented herein. Cross-polarization (CP) MAS data were also collected using ^{1}H and ^{29}Si 90° pulse widths of 3.8 and 4.5 μs respectively with recycle delay of 2 s, CP spin-lock time of 3 ms, and 1600 scans. The ^{27}Al chemical shifts were referenced to aluminum nitrate (0.0 ppm) and the Bloch-decay experiment was acquired using a pulse recycle delay of 5 s, a pulse width of 4.5 μs, an acquisition time of ~20 ms, and 256 scans. For cross-polarization (^{1}H–^{27}Al CP) MAS experiments, ^{1}H and ^{13}C 90° pulse widths of 3.8 and 4.5 μs, respectively, were used with a recycle delay of 2 s, CP spin-lock time of 2 ms, and 256 scans. Peak identification and data processing was performed using MestReNova software.

2.2.6 Inductively coupled plasma optical emission spectrometry (ICP-OES)

Chemical characterization was determined with an ICP-OES (ARL 3410+) using an adapted protocol from a widely accepted technique developed by Farrell *et al.* (30). Five mL of a 7:3 mixture of hydrochloric acid and hydrofluoric acid were combined with 2 mL of nitric acid and placed in digestion tubes that were maintained at 95°C in a digestion block (HotBlock by Environmental Express) for approximately two hours. Samples were then cooled and brought to 50 mL with a 1.5% boric acid solution (by mass). The samples were then reheated to 95°C for 15 minutes and cooled for analysis. The samples were diluted 10x with deionized water and analyzed with an ICP-OES, as described above. An analytical blank, along with three standards that were made by accurately diluting certified standards, was used for calibration. Finally, a basaltic internal standard (Valmont Dike, Colorado USA) of known chemical composition was digested and analyzed to ensure accuracy of the results.

2.2.7 Fourier transform infrared spectroscopy (FTIR)

Samples for analysis were ground in a slurry of ethanol using a McCrone micronizing mill with yttrium-stabilized zirconium (American Elements) grinding beads for five minutes to ensure particle sizes < 5μm. Collected slurries were dried overnight at 60°C. Next, 0.02 ± 0.005 grams of each sample were mixed with 2.00 ± 0.050 grams of potassium bromide (KBr) powder (dried at 70°C overnight). Then, the powder mixtures were homogenized in a Spex Grinder mill and pressed into KBr disk pellets for analysis in a Thermo Scientific Nicolet iS10 FTIR Spectrometer. As a result, KBr disks with sample concentrations of 1% (by weight) were produced. Disks were analyzed against a blank background to remove the absorption spectra from the chamber purged with nitrogen.

2.2.8 X-ray diffraction (XRD)

To determine the mineralogy of (1) calcined precursors and (2) both synthetic and natural alkali-activated geopolymer binders, samples were first crushed into a powder with a mortar and pestle. The calcined precursor and synthetic geopolymer binder powders were well packed in XRD sample holders. Metakaolin-based geopolymer binders were prepared for mineral analysis using a modified method based on (31). The former method was modified to employ corundum as an internal standard instead of zincite. All samples were analyzed in a Siemens D500 X-ray diffractometer to acquire X-Ray diffraction patterns for all samples. Samples were analyzed from 5 to 65 degrees 2θ using Cu Kα X-ray radiation, with a step size of 0.02 degrees and a dwell time of two seconds per step. Mineralogy was identified using Jade software (MDI, Version 9) and the International Centre for Diffraction Data (ICDD) 2003 database.

3. Experimental Results and Analysis

3.1 Stoichiometry of Geopolymer Cements

Synthesized geopolymer cements in the herein study have uniform chemical formulations of $Na_{1.22}Si_{1.02}Al\cdot xH_2O$, see **Figure 2**. As a result, the stoichiometry of geopolymer cements yields Si:Al and Na:Al atomic ratios of 1.02 ± 0.07 and 1.22 ± 0.07 respectively, regardless of polymer cross-linking agents (PEG and PVA), synthesis pH conditions (low and high) or I/O ratios (low and high). This chemical composition is similar to the theoretical design composition outlined in section 2.2.4 and bears important differences from "traditional" geopolymer materials, which are reported to have a standard composition of Si:Al = 1.65 and Na:Al = 1 (23). As a result, important morphological differences exist due to their "non-traditional" cement chemistry, as expected from literature(14,27,32). For example, the presence of mineral phases, such as zeolites, is expected at low silicon and high sodium contents when these samples are subjected to hydrothermal curing conditions (33).

3.2 Mineralogy of Aluminosilicate Powders and Geopolymer Cements

Regardless of synthesis pH and I/O ratio, mineralogical differences were only observed in samples produced with different polymers (**Figure 3**). PVA-derived synthetic aluminosilicate powders demonstrate an amorphous curve at 23° 2θ angles and, after alkali activation, the geopolymer cements result in the formation of zeolite-A and sodium carbonate. Contrastingly, PEG-derived synthetic aluminosilicate powders demonstrate the formation of alumina phases, in addition to the aforementioned amorphous curve at 23° 2θ angles. After alkali activation, PEG-derived geopolymer cements result in the formation of sodium carbonate solely and no alumina phases diffraction patterns are observed. Hence evidencing phase segregation, an undesirable product of inhomogeneity during reaction (4), as a result of the presence of ethers (i.e., C-O) in the PEG polymer cross-linker which likely do not coordinate Al^{+3} ions as effectively as hydroxyl groups (i.e., O-H) of PVA polymers. Only synthetic aluminosilicate powders derived from PEG polymer cross-linkers result in the formation of alumina phases, as indicated by XRD (**Figure 3**). Given the high-temperature calcination (i.e., 900 °C) for PEG-derived synthetic aluminosilicate powders, the alumina phase in **Figure 3** likely is that of γ-alumina. This alumina mineral forms due to dehydration between 500 °C and ~900 °C (34), as well as temperatures of up to 1200 °C (35), and has a similar diffraction pattern as η-alumina (36,37).

3.3 FTIR of Synthetic Precursors, Aluminosilicate Powders, and Geopolymer Cements

To probe the molecular structure of all synthesized materials, Fourier-transform infrared spectroscopy (FTIR) was undertaken. For this study, FTIR was collected for each of the samples throughout the reaction (**Figure 4**) and compared to reagent materials (Figure S1-S10 in the supplementary information). In agreement with XRD diffractograms (**Figure 3),** carbonation is evident in the FTIR spectra by a large vibrational peak at 1470 cm^{-1} corresponding to O-C-O stretching of carbonate, which appears mainly for PEG-derived geopolymer cements as indicated by **Figure 4** and **Table 2**.

For PVA-derived uncalcined synthetic aluminosilicate precursors, regardless of pH or I/O, vibrational energy bands are observed with relatively the same peak location and peak intensity (**Figure 4**). Key vibrational bands for PVA-derived products throughout the reaction are listed in **Table 2**. When compared to the uncalcined synthetic aluminosilicate precursor, the synthetic aluminosilicate powders show a (1) decrease of O-H, C-O, and C-H bond vibrational stretching (3500-3000 cm^{-1}, 2925 cm^{-1}, 2850 cm^{-1}, 1730 cm^{-1} and 1645 cm^{-1}); (2) minor changes to the presence of N-O or O-C-O bond asymmetric stretching (1475cm^{-1} and 1380 cm^{-1}); and, (3) presence of Al-O and Si-O-Si bonds (1116 cm^{-1}, 904 cm^{-1}, 932 cm^{-1}, 722-540 cm^{-1}, and 480 cm^{-1}). Upon alkali activation there are a number of key differences in the vibrational energy bands of the resulting materials, (1) the emergence of O-C-O and O-H vibrations due to carbonation and hydration of the cementitious material (1651 cm^{-1}, 1550 cm^{-1}, 1475 cm^{-1}, 1380 cm^{-1}); (2) external linkage of SiO_4 and AlO_4 tetrahedral (560 cm^{-1}); and moreover, (3) aluminosilicate network formation (Si-O-Al) signified by a shift in frequency of peak toward 1000 cm^{-1}, which have traditionally been attributed to geopolymer formation (38,39) or zeolite formation from aluminosilicate precursors (40,41) (**Table 2**). In addition, absorption shoulders at 1116 cm^{-1} and 908 cm^{-1} are also identified in geopolymer cements, which indicate asymmetric Si-O stretching and were also observed in synthetic aluminosilicate powders. Such geopolymer network formation as well as external linkage vibration of Si-O_4 or Al-O_4, typical for zeolites (42), are also verified by XRD results, shown in **Figure 3**.

The analysis of the FTIR from PEG-derived systems indicates that for a given processing condition, the material has similar vibrational energy, regardless of pH and I/O. However, key differences in the extent of geopolymer network formation (Si-O-Al) exist, when compared to PVA-derived products. In the uncalcined state, vibrational energy bands for all samples are observed at relatively the same peak location and peak intensity (**Figure 4**). Key vibrational bands for PEG-derived products throughout the reaction are listed in **Table 3**. Upon calcination at 900ºC, the resulting vibrational energies of the synthetic aluminosilicate powders show (1) a decrease of O-H, C-O, and C-H bond vibrational stretching (3500-3000 cm^{-1}, 2925 cm^{-1}, 2850 cm^{-1}, 2885 cm^{-1}, 1630 cm^{-1}, and 1380cm^{-1}); (2) changes in Si-O-Si asymmetric bond stretching peak (1115cm^{-1}, 1240 cm^{-1}); and moreover, (3) presence of Al-O and Si-O-Si bonds (900 cm^{-1}, 940 cm^{-1}, 840-515 cm^{-1}, 480 cm^{-1}). Upon alkali activation there are a number of key differences of vibrational energy band location and intensity, in particular (1) the emergence of O-C-O and O-H vibrations due to carbonation and hydration of the cementitious material (1450 cm^{-1}, 1380 cm^{-1}); (2) partial reactivity as observed by remaining Si-O-Si vibrations (720 cm^{-1}), which is within the broad distribution of weak resonances seen in the uncalcined synthetic aluminosilicate precursors and synthetic aluminosilicate powders from 840-515 cm^{-1}; and, (3) aluminosilicate network formation (Si-O-Al) signified by a shift toward a new peak centered around 1060 cm^{-1} with shoulders at approximately 1120 cm^{-1} and 900 cm^{-1}. As noted for PVA products, these two shoulder locations are consistent with two main peaks in the synthetic precursors (both uncalcined and calcined). However, in the herein PEG samples the observed Si-O-Al absorption peaks at 1060 cm^{-1} are broad with larger shoulder regions at 1120 cm-1 and 950 cm-1. Thus indicating a variable and lower extent of Si-O-Al polymerization following alkali activation.

3.4 ^{29}Si MAS-NMR and ^{1}H-^{29}Si CP MAS-NMR of Aluminosilicate Powders and Geopolymer Cements

^{29}Si DP MAS-NMR technique (Bloch Decay) was used to study the silicon atomic structure of synthetic aluminosilicate materials. **Figure 5** presents the acquired ^{29}Si spectra for both uncalcined aluminosilicate precursors and synthetic aluminosilicate powders. The collected spectra reveal the predominance of resonances at chemical shifts of -112 ± 0.87 ppm and -111 ± 1.59 ppm assigned to Q^4 Si environments in uncalcined and calcined powders, respectively. As a result, calcination revealed no changes to silicon atomic environments.

After alkali-activation, all geopolymer cements indicate a downfield shift in ^{29}Si signal between -84 and -90 ppm assigned to Q^4 (4Al) atomic environments in the cementitious network. PEG-derived geopolymer cements exhibited an additional resonance at chemical shift of -107 ppm corresponding to remaining Q^4 from unreacted aluminosilicate powder only when synthesized at low I/O ratios, as seen in **Figure 5.** Several other key differences exist between both synthesized geopolymer cements. For example, the average chemical shift in PEG-derived geopolymer cements (-83.67 ppm) was downfield-shifted to a greater extent than that of PVA-derived geopolymer cements (-89.01 ppm). Moreover, when compared to all geopolymer cements, PVA-L samples at low I/O ratio demonstrate a narrow linewidth

(4.78 ppm) and further upfield shift (-89.95 ppm).

^{1}H-^{29}Si CP MAS-NMR experiments were conducted to study the presence of nearby hydrogen atoms to silicon nuclei. In general, PVA-derived and PEG-derived synthetic aluminosilicate precursors as well as aluminosilicate powders demonstrated a ^{29}Si resonance of -105 ±5 ppm in ^{29}Si CP MAS-NMR spectra as expected since cross polarization techniques allows the resonances only from outer surface of the Al-O-Si network which are near protons. Because of the inhomogeneous surface structure and nearby hydroxyl group, the peaks are downshifted in comparison to the bulk structure (-110 ppm vs -105 ppm). This downshift is more prominent in PEG-derived aluminosilicate powders as they exhibit ^{1}H-^{29}Si resonances between -100 ppm and -97 ppm confirming the presence of single hydroxyl containing silica species (Q^3). These differences may be explained by the fact that PEG-derived aluminosilicate powders at high polymer contents (low I/O ratio) do not undergo complete dehydroxylation and, thus, remnant single hydroxyls exist (Q^3) (44). Furthermore, adjacent water molecules may aid in the deshielding of Si atoms as evidenced by ^{29}Si NMR spectra (**Figure 5**). Similar deshielding has been reported by (45) for Halloysite clays as interlayer water hydrogen bonds to the tetrahedral silicate layers and results in a deshielding of the ^{29}Si resonance. Unexpectedly, no ^{1}H-^{29}Si resonance was observed for PVA-L (high I/O) synthetic aluminosilicate precursors, which indicates the absence of near protons to effectively cross-polarize Si.

3.5 ^{27}Al MAS-NMR and ^{1}H-^{27}Al CP MAS-NMR of Aluminosilicate Powders and Geopolymer Cements

^{27}Al MAS-NMR experiments were conducted to study the changes in aluminum atomic structure of synthetic aluminosilicate materials. All ^{27}Al MAS-NMR spectra of uncalcined synthetic aluminosilicate precursors (PEG and PVA derived) show resonances at 0 ppm confirming the presence of aluminum nitrate species (i.e., Al(VI)), which was added to prepare these precursors. Synthetic aluminosilicate powders demonstrated a peak at 8 ppm indicating the presence of similar aluminum species with minimal environment differences (**Figure 3**). However, after alkali-activation, all samples exhibit resonances at both ~60 ppm and ~8 ppm, confirming two different atomic environments for the aluminum one for the unreacted aluminum species Al(VI) and the reacted Al(IV) species, composing the aluminosilicate cementitious network (46,47).

Similarly, ^{1}H-^{29}Al CP-MAS NMR spectra of all uncalcined synthetic aluminosilicate precursors derived from PEG as well as PVA showed resonance near 0 ppm indicating the presence of Al(VI) species. However, no ^{1}H-^{29}Al CP MAS-NMR signal was observed for all calcined synthetic aluminosilicate powders or geopolymer cements, regardless of polymer crosslinker used (**Figure 6**). Hence suggesting that Al(VI) species were incorporated in the network with oxygen but they were very far from the nearby protons of water or hydroxyls. This observation suggests that water molecules were evaporated due to high temperature of calcination process and polymers were volatilized from the Al-Si network in these calcined precursors, as expected from FTIR results. Similar results for geopolymers indicate the presence of Al(IV) species coordinated with SiO_4 in a network with segregated Al(VI) phases as seen in the XRD data (**Figure 3**) with far protons unsuccessful to transfer nuclei polarization.

4. Discussion

4.1 Effect of Polymer Architecture (PEG vs. PVA)

Differences in polymer architecture, more specifically the absence of hydroxyls (i.e., PVA) and presence of ethers (i.e., PEG), result in phase segregation within the xerogel and, as a result, form γ-alumina in the synthetic aluminosilicate powder, as confirmed by XRD (**Figure 3**) and ^{27}Al MAS-NMR (**Figure 6, Table 4**) (48)**.** Moreover, ^{27}Al MAS-NMR of these PEG-derived aluminosilicate powders (**Figure 6**) demonstrates that mainly Al(VI) sites exist, as evidenced by the presence of a resonance peak at ~5-9 ppm (**Table 4**). This finding is seemingly contradictory to the often reported defective spinel structure of γ-alumina (49). However, a decrease in the tetragonal nature of γ-alumina has been observed with increasing temperatures >700ºC and adsorption of gases at high temperatures and may be similar to the ‘γ-alumina, an anhydrous alumina form as verified by the absence of resonance on ^{27}Al-^{1}H MAS-NMR spectra (**Figure 6, Table 4**) (35,50). Moreover, contradictory to recent studies (28,32), the herein study found no evidence of Al(IV) or Al(V) for PVA-L synthetic aluminosilicate powders synthesized at low-I/O ratios (i.e., high polymer contents). This difference is likely due to the redefinition of the I/O ratio, as explained in section 2.2.1, and further detailed in the supplementary information.

Limited silicate incorporation into the gel 1 → gel 2 evolution process (51,52) within PEG-derived geopolymer cements may occur as observed by a higher ^{29}Si NMR deshielding and higher variability of Si polymerization in FTIR results, when compared to PVA-derived samples as indicated in **Table 2, Table 3** and **Table 5**. The gel 1 has been described as an initial Al-rich binder with a high content of Si-O-Al bonds relative to the bulk Si:Al ratio. This initial gel 1 is said to structurally evolve via condensation of silanols and incorporation of silicon metals, hence increasing the effective Si:Al ratio of the binder (53). The ^{29}Si NMR resonances of PEG-derived geopolymer cements are downfield shifted between -80 ppm and -85 ppm, when compared to PVA-derived geopolymer cements as seen in **Table 3**. Deshielding of the ^{29}Si nuclei may be due to next-nearest neighbor (Al) or structural distortions of the gel 2, which are hypothesized to be caused by limited silicate incorporation in the gel 1 precursor (48). Further confirming these results, FTIR results for PEG-derived geopolymer cements demonstrate geopolymer network formation as observed by peak shifts to lower wavenumber corresponding to formation of Si-O-Si and Si-O-Al bonds (1120 cm^{-1} → 1060 cm^{-1}), **Table 3** (54). Contrastingly, PVA-derived geopolymer cements exhibit greater extent of silicate incorporation in the gel 1 → gel 2 evolution process as sharp and intense absorption peaks are observed to be centered around 1000 cm^{-1}.

4.2 Effect of Polymer Content (I/O ratio: Low vs. High)

Decreasing the polymer content (high I/O ratio) reduces Al metal-polymer coordination and results in partial γ-alumina formation for PEG-derived aluminosilicate powders (see **Figure 3**). As a result of the decrease polymer-metal coordination, the aluminosilicate powder produced is considered to be of higher reactivity as evidence by the absence of unreacted Q^4 as presented in **Figure 5**. The geopolymer cements resemble PVA-derived geopolymer cements with Q^4(4Al) atomic sites. Contrastingly, increasing the polymer content (low I/O) produces geopolymer cements with partial reactivity as evidence by the presence of Q^4 and Q^4(4Al) silicon sites. At such high polymer contents, incomplete dihydroxylation is also observed in the aluminosilicate powders by the presence of single silanols (Q^3) or adjacent water (44), see **Table 5**. Similar deshielding has been reported by (45) for Halloysite clays. These results are important as polymer content is evidenced to affect Si-Al atomic coordination. Contrastingly to (19,28,32), no presence of Al(IV) or distorted Al(VI) sites has been observed for similar aluminosilicate powders.

4.3 Effect of Sol-Gel Aging Conditions (pH: Low vs. High)

There are minimal differences in aluminosilicate powders synthetized with low or high pH sol-gel aging conditions indicating that the order of chemical addition bears little effect on the synthesis procedure. For example, PVA-H aluminosilicate powders have slightly higher deshielding of their ^{29}Si nuclei, as seen in **Table 5.** Moreover, when compared to samples synthesized with high PVA polymer contents, samples synthesized with a high pH sol-gel aging condition and low PVA polymer contents have a reduction in the absorption peak intensities associated with Si-O-Si and Si-O-Al bonds at ~1060 cm^{-1} (54).

However, when alkali-activated, synthetic aluminosilicate powders produced with low pH sol-gel aging conditions may improve the extent of geopolymerization and dictate the content of silanol groups in the resultant geopolymer cement. PEG-derived geopolymer cements synthesized with low pH sol-gel aging conditions exhibit higher absorption intensities for Si-O-Si and Si-O-Al bonds, when compared to PEG samples produced in high pH conditions (**Figure 4)**. High absorption intensity may indicate a greater extent of silicate incorporation and content of Q^4(4Al) units in the geopolymer cements, as previously discussed. Additionally, low pH sol-gel aging conditions yield geopolymer cements with no evidence of geminal silanol groups regardless of polymer used during synthesis (56). As seen in **Figure 5** and indicated in **Table 5**, no resonance peak is observed for ^{1}H-^{29}Si cross-polarized signal of both PVA-L and PEG-L synthesized with high polymer contents. This result is likely a consequence of the absence of "near protons" and presence of labile water species (indicated by high intensity -OH vibrational stretching, see **Figure 4, Table 2**, and **Table 3**), which are not near enough for cross-polarization of ^{29}Si nuclei. Moreover, the absence of silanol groups has been described and explained by (57) and it is indicative of well-formed geopolymer binders with the majority of framework sites being Q^4. Lastly, "traditional" chemical compositions of metakaolin-based geopolymer cements have been reported to exhibit residual silanols from unreacted metakaolin particles, as well as geminal and vicinal silanol groups (58).

4.4 Natural Analogue of Synthetic Aluminosilicates: Metakaolin

All synthesized aluminosilicate precursors approximate the chemical composition of calcined clays (i.e., metakaolin) as evidenced by **Figure 2** and (33). Moreover, similarities to metakaolin are evidenced in both the ^{29}Si and ^{27}Al MAS-NMR with a resonances near -110ppm and ~10 ppm corresponding to Q^4 Si units and Al(VI), respectively (**Table 4** and **Table 5**) (48). In addition, the presence of silanol groups in PEG-derived synthetic aluminosilicate powders at low I/O ratios, is similar to reported residual silanol groups in metakaolin (59). Thus, the atomic structure of synthetic aluminosilicate powders may resemble a homogenous mix of Q^4 Si units and Al(VI) units with residual silanol groups in particular cases.

However, the structure of synthetic aluminosilicate precursors differs from that of metakaolin due to the absence of Q^3 sheet-like Si layers, Al(IV), Al(V), or segregated amorphous alumina phases. In general, metakaolin possesses a broad ^{29}Si MAS-NMR resonance peak at -103 ppm with a linewidth of ca. 20 ppm, assigned to Q^3 'sheet-like' layers (60), as well as ^{29}Si resonances corresponding to Q^4(1Al) silicon center (24). Contrastingly, synthesized aluminosilicate powders possess ^{29}Si MAS-NMR resonance peak at −111 ppm, which does not indicate any aluminum bond with silicon. Furthermore, no presence of Al(IV), Al (V), or regions of segregated amorphous alumina are observed in synthesized aluminosilicate powders, as characteristic of the atomic structure of metakaolin (61).

The presence of extra-framework aluminum (EFAl) was reported in 2012 for metakaolin-based geopolymer cements with Si:Al and Na:Al atomic ratios of 1.6 and 1.0, respectively (58). The observed structural stability of these cements was attributed to the presence of these tetrahedrally coordinated aluminum ions (i.e., Al(IV)). More recently, EFAl with an Al(IV) resonance have been observed in geopolymer cements with Si:Al and Na:Al atomic ratios of 1.50 and 1.18, respectively (19). Contrastingly, in the present study, ^{27}Al-^{1}H NMR detected the presence of Al(IV) resonances at 60.5 ±

1.5 ppm for PVA-derived geopolymer cements solely, which is in good agreement with results collected from the literature (**Table 6**). These cross-polarized nuclei resonances have been attributed in other studies to bridging hydroxyl groups (Si–OH$^+$ –Al, Brønsted-acid sites) (58). Presence of these hydroxyl groups, both in Si and Al nuclei, have been shown to hydrogen bond with structural water molecules resulting in the elongation of Al-O bonds (63). An important observation for the stability and durability of these cements.

Similar to studies of alkali-activated metakaolin, PEG-derived geopolymer cements have resonances at -107 ppm (Q^4) from unreacted synthetic aluminosilicate powder (-103 ppm, attributed to Q^3 Si-sheets, in metakaolin) and -85 ppm indicative of Q^4(4Al) aluminosilicate (60) (**Figure 5** and **Table 5)**. Similar resonances have been detected in N-A-S-H binder variants, as seen in **Table 6.** Contrastingly, all PVA-derived geopolymer cements indicate the presence of solely Q^4(4Al) aluminosilicate (**Figure 5** and **Table 5)**, characteristic of N-A-S-H binders of low Si:Al ratios (61), these also resemble the mineralogy of metakaolin-based cements (**Figure 7**). In addition, peaks at 800 cm^{-1} are assigned to Al-O stretching in Al(VI) decrease in intensity or are not visible following alkali-activation, suggesting that the octahedral structure breaks down with geopolymerization (42).

4.5 Mechanisms of the Polymer-Assisted Sol-Gel Synthesis

Data collected suggest three possible mechanisms by which the polymer-assisted sol-gel synthesis permits the incorporation of solubilized aluminum ions (Al^{+3}). As depicted in **Figure 8**, Al^{+3} incorporation may be possible by: (1) complexation with polymer cross-linker, (2) hydrogen bonding with silanol, and (3) competition between these two complexation mechanisms. These will be discussed in the following sections.

4.5.1 Polymer cross-linker complexation of Al^{+3} metal ions

Architecture differences in polymer cross-linker oxide (i.e., ether, hydroxyl) may influence the polymer-metal interactions of Al^{+3} ions by inducing metal complexation or hydrogen bonding. Given that oxygen is a strong electron donor in both PVA and PEG systems, the electron-poor aluminum metal would tend to associate with these atoms to form complexes (64). Evidence for such metal-polymer complexes is observed for PVA-derived uncalcined synthetic aluminosilicate precursors indicated by a shift of a vibrational peak centered around 1750 cm^{-1} in reagent PVA to 1730 cm^{-1} after polymer assisted sol-gel synthesis. The shift of this peak may indicate polymer-metal interactions between residual carbonyl groups on PVA polymer cross-linkers (an artifact from commercial fabrication of PVA from poly(vinyl acetate)) and the aluminum metal (at 1730 cm^{-1}) (**Figure 4**) (65). Changes in vibrational energy toward lower wavenumbers following interactions with metals have previously been attributed to metal-ion complexation with the carbonyl (C-O) moiety in PVA (65,66).

For PEG-derived uncalcined synthetic aluminosilicate precursors, previous literature suggests that Al^{+3} polymer coordination occurs in the C-O-C stretching region between 1110-1105 cm^{-1} (67). For this system, the 1100 cm^{-1} region corresponds to Si-O-Si vibrational stretching and bending frequencies, thus hindering the analysis of metal-polymer coordination for PEG-based systems. For both polymeric systems, it can be speculated that the hydration of components by water during the sol-gel aging would enable hydrogen bonding between water and pendant hydroxyl units, and, as the xerogels develop (i.e., dehydration), metal coordination may be enhanced as with less volume the materials are more likely to interact. For both PEG and PVA systems, following calcination, the vibrational bands at 1730 cm^{-1} as well as broad vibrational bands from 3500-3000 cm^{-1} corresponding to O-H stretching frequency in both PVA and PEG-derived synthetic aluminosilicate powders decrease in intensity. This decrease in intensity may indicate that the polymer, nitrate counter ion, and water were effectively removed following calcination, likely disrupting the Al^{+3} polymer coordination. Such disruptions may explain the absence of Al(IV) and distorted Al(VI) sites in the aluminosilicate powder, contrary to published literature (19,28,32).

4.5.2 Silanol coordination of Al^{+3} metal ions

^{29}Si MAS-NMR (**Figure 5** and **Table 5**) does not reveal bulk aluminum incorporation in the xerogels of the uncalcined synthetic aluminosilicate precursor, however cross-polarization data on these gels suggest the possibility of coordination and sparse hydrogen bonding between silanol and aluminum ions in certain synthesis conditions. However, determination of different Q^4(nAl) sites may be determined based on peak maxima with linewidths of 10 ppm, as described in (33,68), ^{29}Si MAS-NMR spectra collected herein demonstrates the single-phase purity of precursors, due to narrower linewidths than reported in literature and high upfield resonances. As seen in **Table 5,** uncalcined synthetic aluminosilicate precursors demonstrate peak resonances at -111 ppm that are attributed to Q^4 silicon sites. Furthermore, narrow linewidths between 8.3 ppm and 17.4 ppm (**Figure 5**) render the determination of different Q^4(nAl) sites inappropriate, as aforementioned, and no FTIR evidence specifically supports the presence of corresponding Si-O-Al bonds in uncalcined synthetic aluminosilicate precursors, even though vibrational frequency corresponding to Si-O-Si asymmetric stretching is observed (**Figure 4, Table 2** and **Table 3**). However, ^{29}Si CP/MAS NMR signal provides spectra of nuclei spatially close to immobilized hydroxyls, structural water molecules, or other protonated species, typically less than 5 A° (68). As observed in **Table 4**, all uncalcined synthetic aluminosilicate precursors exhibit cross polarization resonances which provide further evidence of Q^4 silicon atomic sites interacting with hydrous species, possibly from the water-shell associated with Al^{+3} cations (i.e., Al(VI))**.** In addition, presence of single silanol groups (Q^3, -100 ppm) remaining in PEG-derived samples aged at high pH values and low I/O suggest the possibility for hydrogen bonding between silica particles and Al^{+3} cations.

FTIR can be used to suggest mechanisms of inter- and intra-molecular coordination, such as hydrogen bonding in the xerogel. For both polymer architectures in the xerogel, the vibrational peak at 1650 cm^{-1} is attributed to H-O-H bending vibrations (69) and is present in the FTIR of silica, aluminum nitrate, and PVA starting materials but at a lesser intensity than in the xerogel. The peak centered at 1650 cm^{-1} in conjunction with the broad stretching vibration of -OH centered at approximately 3400 cm^{-1} are often attributed to hydrogen bonding or water adsorption (70–73). For all xerogel materials, there is an increase in the intensity of these two vibrational frequencies. The increase in intensity may be attributed to hydrogen bonding between hydroxyl units between the polymers, silica, and bound water or to coordination of the silanol to aluminum following xerogel formation (**Figure 8i)** (74,75). The changes in these molecular vibrations do not specifically indicate that silanol is coordinating with aluminum oxide but can suggest this mechanism along with other hydrogen bonding mechanisms.

5. Future Work

In this work, it has been shown that control of the I/O ratio (i.e., polymer content) in polymer-assisted sol-gel synthesis methods is imperative to produce adequate aluminosilicate powders for alkali activation. Contrary to previous publications by (19,28,32), the presence of Al(IV) or distorted Al(VI) was not observed likely due to differences in the polymer content (i.e., I/O ratio). As explained in section 4.5.1, based on previous literature it is known that Al^{+3} metal-polymer coordination occurs in the C-O-C stretching region between 1110-1105 cm^{-1} [70]. Consequently, polymer cross-linker complexation of Al^{+3} metal ions is expected to be the dominant mechanism for producing high-reactivity aluminosilicate powders, hence, explaining the differences of results observed in this study. Thus, further research to probe the mechanisms of polymer-assisted sol-gel is crucial for the replicability and optimization of this synthesis technique.

Mechanisms of polymer-assisted sol-gel are important to leverage the creation of N-A-S-H cements with different atomic structures. Molecular dynamic simulations or further atomic statistical thermodynamic computational modeling is necessary to understand the kinetics and energetic favorability of these synthesis mechanisms. Once these mechanisms are further understood, their application to low-calcium AACs and geopolymer systems may yield important insights into the formation of differing hydroxyl groups, observed herein. In addition, different synthesis pathways for geopolymer cements result in different silanol contents. These results must be verified via a carefully optimized contact time to examine cross-polarization efficiency. An important gap in knowledge is the effect of hydroxyl groups on macro-properties of low-calcium cementitious binders. For example, the role of hydroxyl groups on drying shrinkage properties or water transport has not yet been investigated. Lastly, further exploration of polymer-assisted sol-gel synthesis will enable the study of novel single-phase binders—an important scientific pursuit that is currently in progress by the authors.

6. Conclusion

This study investigated the effects of polymer architecture (i.e., PVA vs. PEG), polymer content (*i.e.,* low vs. high ion-to-polymer-oxide (I/O) atomic ratio), and sol-gel aging pH conditions (i.e., low vs. high) on the atomic structure of resultant synthetic aluminosilicate powders and geopolymer cements. Results have shown that polymer architecture is a primary factor in controlling phase segregation in synthetic aluminosilicate powders and the resulting mineralogy of geopolymer cements. The use of FTIR, XRD, and ^{29}Si and ^{27}Al single pulse and ^{1}H cross-polarized MAS-NMR confirmed the effect of polymer architecture on the metal complexation of Al^{+3} ions, while PEG polymers yielded phase segregation during synthesis and formation of γ-alumina with a predominance of Al(VI) sites. Contrastingly, it is observed that the presence of hydroxyls in PVA may provide higher ion coordination competition, which results in synthetic aluminosilicate powders and geopolymer cements with single atomic environments. Moreover, PEG-derived synthetic aluminosilicate powders are most similar to the atomic environment of metakaolin (i.e., calcined clay).

A decrease of polymer content during synthesis is observed to improve reactivity of the precursor improving the extent of binder formation in these samples. While sol-gel pH aging conditions (affected by order of reactant addition) reveals the ability to influence the content of Brønsted-acid sites (-OH groups) near the aluminum nuclei and geminal silanol groups within geopolymer cements. As a result, the molecular structure and mineralogy of resultant geopolymer cements is affected in the following order of significance: polymer type > polymer content > sol-gel pH aging condition. Finally, metakaolin-based geopolymers resemble the molecular structure and mineralogy of PVA-derived geopolymer cements. Thus, validating the further use of metakaolin as an aluminosilicate precursor to produce highly pure N-A-S-H cementitious binders.

Evidence collected supports three possible mechanisms by which the polymer-assisted sol-gel synthesis permits the incorporation of solubilized aluminum ions (Al^{+3}) and formation of N-A-S-H (sodium-aluminum-silicate-hydrate) geopolymer binders. The proposed mechanisms are hypothesized to be related to: (1) complexation with polymer cross-linker, (2) hydrogen bonding with silanol, and (3) competition between polymer cross-linker coordination and silanol-based poly-condensation. It is expected that Al^{+3} metal-polymer competition dominates the mechanism for the production of high reactivity aluminosilicate powders. However, further understanding on these synthesis mechanisms is imperative to permit the design and synthesis of tailored nanostructures of low-calcium AACs and geopolymer cements.

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8. References

1. Wright JD, Sommerdijk NAJM. Sol-gel materials: chemistry and applications. CRC press; 2014. 1–125 p.
2. King G. Methods for hydrolysis of alkoxysilanes for use in paints, dental cements, treatment of brick, stone and concrete. Paint Test Man. 1931;1:16–20, 52–5.
3. Pierre AC. Introduction to sol-gel processing. Vol. 1. Springer Science & Business Media; 2013.
4. Danks AE, Hall SR, Schnepp Z. The evolution of “sol-gel” chemistry as a technique for materials synthesis. Mater Horiz. 2016;3:91–112.
5. Xi L, Baokun X, Zichen W, Feng C, Muyu Z. Preparation of nanocrystalline materials of perovskite-type La1-xSrxFeO3 (x= 0, 0.1, 0.2, and 0.4) by using gel of poly(ethylene glycol). J Mater Sci Lett. 1992;11:1476–8.
6. Li X, Zhang H, Chi F, Li S, Xu B, Zhao M. Synthesis of nanocrystalline composite oxides La1-xSrxFe1-yCoyO3 with the perovskite structure using polyethylene glycol-gel method. Mater Sci Eng B. 1993;18:209–13.
7. Pramanik P, Pathak A. A new chemical route for the preparation of fine ferrite powders. Bull Mater Sci. 1994;17(6):967–75.
8. Kumar Saha S, Pathak A, Pramanik P. Low-temperature preparation of fine particles of mixed oxide systems. J Mater Sci Lett. 1995;14(1):35–7.
9. Li X, Zhang H, Zhao M. Preparation of nanocrystalline LaFeO3using reverse drop coprecipitation with polyvinyl alcohol as protecting agent. Mater Chem Phys. 1994;37(2):132–5.

10. Sun Y-K, Oh I-H. Preparation of Ultrafine YBa2Cu3O7-x Superconductor Powders by the Poly(vinyl alcohol)-assisted Sol-Gel Method. Ind Eng Chem Res. 1996;(35):4296–300.

11. Gulgun MA, Nguyen MH, Kriven WM. Polymerized organic – inorganic synthesis of mixed oxides. J Am Ceram Soc. 1999;82(3):556–60.

12. Kriven WM, Lee SJ, Gulgun M. Synthesis of oxide powders via polymeric steric entrapment. Ceram Trans. 1999;108:99–110.

13. Walkley B, Provis JL, San Nicolas R, Sani M-A, van Deventer JSJ. Stoichiometrically controlled C–(A)–S–H/N–A–S–H gel blends via alkali-activation of synthetic precursors. Adv Appl Ceram. 2015 Oct 3;114(7):372–7.

14. Walkley B, San Nicolas R, Sani M-A, Bernal SA, van Deventer JSJ, Provis JL. Structural evolution of synthetic alkali-activated CaO-MgO-Na 2 O-Al 2 O 3 -SiO 2 materials is influenced by Mg content. Cem Concr Res. 2017;99(May):155–71.

15. Walkley B, San Nicolas R, Sani M-A, Rees GJ, Hanna J V., van Deventer JSJ, et al. Phase evolution of C-(N)-A-S-H/N-A-S-H gel blends investigated via alkali-activation of synthetic calcium aluminosilicate precursors. Cem Concr Res. 2016 Nov 1;89:120–35.

16. Lee SJ, Kriven WM. Synthesis and hydration study of Portland cement components prepared by the organic steric entrapment method. Mater Struct Constr. 2005;38(275):87–92.

17. Walkley B, San Nicolas R, Bernal S. Effect of MgO incorporation on the structure of synthetic alkali-activated calcium aluminosilicate binders. Conf 27th Bienn Natl Conf Concr Inst Aust. 2015;(August 2015).

18. Walkley B, San Nicolas R, Sani M-A, Gehman JD, van Deventer JSJ, Provis JL. Synthesis of stoichiometrically controlled reactive aluminosilicate and calcium-aluminosilicate powders. Powder Technol. 2016 Sep 1;297:17–33.

19. Walkley B, Rees GJ, San Nicolas R, Van Deventer JSJ, Hanna J V., Provis JL. New Structural Model of Hydrous Sodium Aluminosilicate Gels and the Role of Charge-Balancing Extra-Framework Al. J Phys Chem C. 2018;122(10):5673–85.

20. Vafaei M, Allahverdi A, Dong P, Bassim N. Acid attack on geopolymer cement mortar based on waste-glass powder and calcium aluminate cement at mild concentration. Constr Build Mater. 2018 Dec 30;193:363–72.

21. Palomo A, Blanco-Varela MTT, Granizo MLL, Puertas F, Vazquez T, Grutzeck MWW. Chemical stability of cementitious materials based on metakaolin. Cem Concr Res. 1999;29(7):997–1004.

22. Fernandez-Jimenez A, García-Lodeiro I, Palomo A. Durability of alkali-activated fly ash cementitious materials. J Mater Sci. 2007;42:3055–65.

23. Kriven WM, Bell JL, Gordon M. Microstructure and Microchemistry of Fully-reacted Geopolymers and Geopolymer Matrix Composites. Ceram Trans. 2015;153:227–50.

24. Duxson P, Provis JL, Lukey GC, Separovic F, Deventer JSJ Van. 29Si NMR Study of Structural Ordering in Aluminosilicate Geopolymer Gels. Langmuir. 2005;21:3028–36.

25. Duxson P, Fernández-Jiménez a., Provis JL, Lukey GC, Palomo a., van Deventer JSJ. Geopolymer technology: the current state of the art. J Mater Sci. 2007;42(9):2917–33.

26. Palomo A, Fernández-Jiménez A, Criado M. "Geopolymers": same basic chemistry, different microstructures. Mater Construccion. 2004;54(275):77–91.

27. Singh JP, Bansal NP, Kriven WM, American Ceramic Society. Meeting (106th : 2004 : Indianapolis Ind), Wiley InterScience (Online service), Ceramic-Matrix Composites Symposium (2004 : Indianapolis Ind). Advances in ceramic matrix composites X : proceedings of the 106th Annual Meeting of the American Ceramic Society : Indianapolis, Indiana, USA (2004). American Ceramic Society; 2005. 182 p.

28. Walkley B, San Nicolas R, Sani MA, Gehman JD, Van Deventer JSJ, Provis JL. Phase evolution of Na2O-Al2O3-SiO2-H2O gels in synthetic aluminosilicate binders. Dalton Trans. 2016;45(13):5521–35.

29. Craun Z. The Role of Magnesium in the Acid Degradation of Metakaolin-Based Alkali-Activated Cements. Civ Eng Grad Theses Diss [Internet]. 2018 Jan 1; Available from: https://scholar.colorado.edu/cven_gradetds/352

30. Farrell RF, Matthes SA, Mackie AJ. A simple, low-cost method for the dissolution of metal mineral samples in plastic pressure vessels. US Bur Mines Rep. 1980;(BM-RI-8480):19.

31. Eberl DD. User Guide to RockJock- A program for determining quantitative mineralogy from X-ray diffraction Data. US Geol Surv Open-File Rep. 2003;47.

32. Walkley B, San Nicolas R, Sani MA, Gehman JD, van Deventer JSJ, Provis JL. Synthesis of stoichiometrically controlled reactive aluminosilicate and calcium-aluminosilicate powders. Powder Technol. 2016;297:17–33.

33. Gevaudan JP, Campbell KM, Kane TJ, Shoemaker RK, Srubar WV. Mineralization dynamics of metakaolin-based alkali-activated cements. Cem Concr Res. 2017;94:1–12.

34. Shirai T, Watanabe H, Fuji M, Takahashi M. Structural Properties and Surface Characteristics on Aluminum Oxide Powders. Annu Rep Adv Ceram Res Cent Nagoya Inst Technol. 2009;9:23–31.

35. Paglia G, Buckley CE, Rohl AL, Hart RD, Winter K, Studer AJ, et al. Boehmite Derived γ-Alumina System. 1. Structural Evolution with Temperature, with the Identification and Structural Determination of a New Transition Phase, γ′-Alumina. Chem Mater. 2004;16(2):220–36.

36. Tilley DB, Eggleton RA. The natural occurrence of eta-alumina (n-Al2O3) in bauxite. Clays Clay Mater. 1996;44(5):658–64.

37. Alex TC, Sasi Kumar C, Kailath AJ, Kumar R, Roy SK, Mehrotra SP. Analysis of mechanically induced reactivity of boehmite using kinetics of boehmite to γ-Al2O3transformation. Metall Mater Trans B Process Metall Mater Process Sci. 2011;42(3):592–603.

38. Granizo ML, Alonso S, Blanco□Varela MT, Palomo A. Alkaline activation of metakaolin: effect of calcium hydroxide in the products of reaction. J Am Ceram Soc. 2002;85(1):225–31.

39. Zhang Y, Sun W, Li Z. Infrared spectroscopy study of structural nature of geopolymeric products. J

Wuhan Univ Technol-Mater Sci Ed. 2008;23(4):522–7.

40. Alkan M, Hopa Ç, Yilmaz Z, Güler H. The effect of alkali concentration and solid/liquid ratio on the hydrothermal synthesis of zeolite NaA from natural kaolinite. Microporous Mesoporous Mater. 2005;86(1–3):176–84.

41. Rios CA, Williams CD, Fullen MA. Nucleation and growth history of zeolite LTA synthesized from kaolinite by two different methods. Appl Clay Sci. 2009;42(3–4):446–54.

42. Zhang Z, Wang H, Provis JL, Bullen F, Reid A, Zhu Y. Quantitative kinetic and structural analysis of geopolymers. Part 1. the activation of metakaolin with sodium hydroxide. Thermochim Acta. 2012;539:23–33.

43. Myronyuk IF, Mandzyuk VI, Sachko VM, Gun'ko VM. Structural and morphological features of disperse alumina synthesized using aluminum nitrate nonahydrate. Nanoscale Res Lett. 2016;11(1):153.

44. Maciel GE, Sindorf DW. Silicon-29 Nuclear Magnetic Resonance Study of the Surface of Silica Gel by Cross Polarization and Magic-Angle Spinning. J Am Chem Soc. 1980;102(25):7606–7.

45. Thompson JG. Interpretation of Solid 13C and 29Si Nuclear Magnetic Resonance Spectra of Kaolinite Intercalates. Clays Clay Mater. 1985;33(3):173–80.

46. Stebbins Jonathan F., Lee Sung Keun, Oglesby Jane V. Letters. Al-O-Al oxygen sites in crystalline aluminates and aluminosilicate glasses: High-resolution oxygen-17 NMR results. Am Mineral. 2015;84(5–6):983.

47. Skibsted J, Henderson E, Jakobsen HJ. Characterization of calcium aluminate phases in cements by aluminum-27 MAS NMR spectroscopy. Inorg Chem. 1993 Mar 1;32(6):1013–27.

48. Smith ME, Mackenzie KJD. Multinuclear solid state NMR of inorganic materials. Pergamon Mater Ser. 2002;

49. Lee M-H, Cheng C-F, Heine V, Klinowski J. Distribution of tetrahedral and octahedral A1 sites in gamma alumina. Chem Phys Lett. 1997 Feb 14;265(6):673–6.

50. Rohner MCh, Sharma VK, Richarz W. A magic angle spinning 27Al NMR study of the adsorption of CL2 on γ-alumina. Can J Chem Eng. 1989 Jun 1;67(3):513–5.

51. White CE, Provis JL, Llobet A, Proffen T, van Deventer JSJ. Evolution of Local Structure in Geopolymer Gels: An *In Situ* Neutron Pair Distribution Function Analysis. J Am Ceram Soc. 2011;94(10):3532–9.

52. Fernández-Jiménez A, Palomo A, Sobrados I, Sanz J. The role played by the reactive alumina content in the alkaline activation of fly ashes. Microporous Mesoporous Mater. 2006 Apr 15;91(1):111–9.

53. Provis JL, Palomo A, Shi C. Advances in understanding alkali-activated materials. Cem Concr Res. 2015;78:110–25.

54. Vidal L, Joussein E, Colas M, Cornette J, Sanz J, Sobrados I, et al. Controlling the reactivity of

silicate solutions: a FTIR, Raman and NMR study. Colloids Surf Physicochem Eng Asp. 2016;503:101–9.

55. Klinowski J. Nuclear magnetic resonance studies of zeolites. Prog NMR Spectrosc. 1984;16(C):237–309.

56. Brus J, Kobera L, Urbanová M, Koloušek D, Kotek J. Insights into the structural transformations of aluminosilicate inorganic polymers: A comprehensive solid-state NMR study. J Phys Chem C. 2012;116(27):14627–37.

57. Provis JL, Harrex RM, Bernal SA, Duxson P, van Deventer JSJ. Dilatometry of geopolymers as a means of selecting desirable fly ash sources. J Non-Cryst Solids. 2012 Aug 15;358(16):1930–7.

58. Brus J, Kobera L, Urbanová M, Koloušek D, Kotek J. Insights into the structural transformations of aluminosilicate inorganic polymers: a comprehensive solid-state NMR study. J Phys Chem C. 2012;116(27):14627–37.

59. Rocha J, Klinowski J. Solid-state NMR studies of the structure and reactivity of metakaolinite. Angew Chem Int Ed Engl. 1990;29(5):553–4.

60. Singh PS, Trigg M, Burgar I, Bastow T. Geopolymer formation processes at room temperature studied by 29Si and 27Al MAS-NMR. Mater Sci Eng A. 2005;396(1–2):392–402.

61. Weng L, Sagoe-Crentsil K. Dissolution processes, hydrolysis and condensation reactions during geopolymer synthesis: Part I—Low Si/Al ratio systems. J Mater Sci. 2007 May 9;42(9):2997–3006.

62. Rowles MR, Hanna J V., Pike KJ, Smith ME, O'Connor BH. 29Si, 27Al, 1H and 23Na MAS NMR Study of the Bonding Character in Aluminosilicate Inorganic Polymers. Appl Magn Reson. 2007;32(4):663–89.

63. Hou D, Zhang Y, Yang T, Zhang J, Pei H, Zhang J, et al. Molecular structure, dynamics, and mechanical behavior of sodium aluminosilicate hydrate (NASH) gel at elevated temperature: A molecular dynamics study. Phys Chem Chem Phys. 2018;20(31):20695–711.

64. Chen H, Jiang C, Wu H, Chang F. Hydrogen bonding effect on the poly (ethylene oxide), phenolic resin, and lithium perchlorate–based solid□state electrolyte. J Appl Polym Sci. 2004;91(2):1207–16.

65. Füllbrandt M, Purohit PJ, Schönhals A. Combined FTIR and dielectric investigation of poly (vinyl acetate) adsorbed on silica particles. Macromolecules. 2013;46(11):4626–32.

66. Gan Y, Bai S, Hu S, Zhao X, Li Y. Reaction mechanism of thermally-induced electric conduction of poly (vinyl alcohol)–silver nitrate hybrid films. RSC Adv. 2016;6(61):56728–37.

67. Wieczorek W, Raducha D, Zalewska A, Stevens JR. Effect of salt concentration on the conductivity of PEO-based composite polymeric electrolytes. J Phys Chem B. 1998;102(44):8725–31.

68. Brus J, Abbrent S, Kobera L, Urbanova M, Cuba P. Advances in 27 Al MAS NMR Studies of Geopolymers.

69. Ramasesha K, De Marco L, Mandal A, Tokmakoff A. Water vibrations have strongly mixed intra-

and intermolecular character. Nat Chem. 2013 Sep 22;5:935.

70. Asay DB, Kim SH. Evolution of the adsorbed water layer structure on silicon oxide at room temperature. J Phys Chem B. 2005;109(35):16760–3.

71. Reis EF dos, Campos FS, Lage AP, Leite RC, Heneine LG, Vasconcelos WL, et al. Synthesis and characterization of poly (vinyl alcohol) hydrogels and hybrids for rMPB70 protein adsorption. Mater Res. 2006;9(2):185–91.

72. Sudhamani SR, Prasad MS, Sankar KU. DSC and FTIR studies on gellan and polyvinyl alcohol (PVA) blend films. Food Hydrocoll. 2003;17(3):245–50.

73. Chen T, Wu Z, Wei W, Xie Y, Wang XA, Niu M, et al. Hybrid composites of polyvinyl alcohol (PVA)/Si–Al for improving the properties of ultra-low density fiberboard (ULDF). RSC Adv. 2016;6(25):20706–12.

74. Luo Y, Jiang X, Zhang W, Li X. Effect of aluminium nitrate hydrate on the crystalline, thermal and mechanical properties of poly (vinyl alcohol) film. Polym Polym Compos. 2015;23(8):555.

75. Asay DB, Kim SH. Evolution of the Adsorbed Water Layer Structure on Silicon Oxide at Room Temperature. J Phys Chem B. 2005 Sep 1;109(35):16760–3.

76. Flanigen E, Grose R. Phosphorous Substitution in Zeolite Frameworks. Adv Chem. 1971;101:76–101.

77. Shirasuka K, Yanagida H, Yamaguchi G. The preparation of eta alumina and its structure. Yogyo Kyokai Shi. 1976;84:610–3.

Figure Caption List

Figure 1. Scope of work and nomenclature used for this study.

Figure 2. Chemical composition of all geopolymer cements synthesized from synthetic aluminosilicate precursors. Average values for Si:Al and Na:Al atomic ratios are 1.02 ± 0.07 and 1.22 ± 0.07, respectively.

Figure 3. Mineralogy for (a) synthetic aluminosilicate powders and (b) alkali-activated geopolymer cements. Symbols represent mineral formations as follows – A: γ-alumina (Al_2O_3, PDF#01-074-2206), ZA: Zeolite A ($Al_2O_3SiO_2$, PDF# 00-038-0323), N: Sodium Carbonate (Na_2CO_3, PDF#01-072-0628) (76,77).

Figure 4. Fourier-Transform Infrared Spectroscopy of (a) uncalcined synthetic aluminosilicate precursors (b) synthetic aluminosilicate powders, and (c) geopolymer cements.

Figure 5. ^{29}Si MAS-NMR and ^{1}H-^{29}Si MAS-NMR spectra for uncalcined synthetic aluminosilicate precursors (U), synthetic aluminosilicate powders (A), and geopolymer cements (C).

Figure 6. ^{27}Al MAS-NMR (a-c) and ^{1}H-^{27}Al MAS-NMR spectra for uncalcined synthetic aluminosilicate precursors (U), synthetic aluminosilicate powders (A), and geopolymer cements (C).

Figure 7. Mineralogy of metakaolin-based samples (Si:Al = 1.0, Na:Al = 1.1) with similar curing conditions confirms similar mineralogy as PVA-derived geopolymer cements. ZA: Zeolite A ($Al_2O_3SiO_2$, PDF# 00-038-0323), N: Sodium Carbonate (Na_2CO_3, PDF#01-072-0628), C: Corundum (Al_2O_3, internal standard) (76,77).

Figure 8. Hypothesized mechanisms of polymer-assisted sol-gel synthesis: (i) ionic competition between polymer cross-linker coordination and silanol-based polycondensation; (ii) complexation with polymer cross-linker; (iii) hydrogen bonding with silanol group; and (iv) poor homogenization and phase

segregation, as observed for PEG-derived calcined precursors.

Table List

Table 1. Processing parameters and corresponding surface area (m^2/g) of synthesized aluminosilicate powders with $2SiO_2{\cdot}Al_2O_3$ stoichiometry.

Sample	**Polymer Molecular Weight** (kDa)	**Aging condition** (pH)	**Polymer Content** (I/O ratio)	**BET surface area** (m^2/g)
PVA-L	31-50	~1.0 (Low)	4.0 (Low)	127.3 ± 0.2
	31-50	~1.0 (Low)	5.2 (High)	121.4 ± 0.3
PVA-H	31-50	~10.0 (High)	4.0 (Low)	107.9 ± 0.9
	31-50	~10.0 (High)	5.2 (High)	130.8 ± 0.3
PEG-L	35	~1.0 (Low)	3.7 (Low)	129.6 ± 0.6
	35	~1.0 (Low)	4.4 (High)	132.6 ± 0.7
PEG-H	35	~10.0 (High)	3.7 (Low)	141.9 ± 0.9
	35	~10.0 (High)	4.4 (High)	121.7 ± 0.5

Table 2. Analysis of infrared vibrational bands in PVA derived products, (br) broad, (s) sharp, weak (w), and (sh) shoulder.

(a) Uncalcined Precursor (cm^{-1})	**(b) Calcined Precursor (cm^{-1})**	**(c) Geopolymer Cement (cm^{-1})**	**Assignment**	**Ref**
3500-3000 (br)	Decrease intensity compared to (a)	Increase intensity compared to (b)	O-H vibrational stretching	[41],[42]
2925(w) **2850 (sh)**	Decrease intensity compared to (a)	Decrease intensity compared to (a) (b)	C-H asymmetric and symmetric stretching	[43]
1730(w)(**sh)** **1650**(w)	No peak at 1730 or 1645, new peak at 1670	Peak at 1650 same intensity as (b)	C-O stretching and O-H stretching	[45], [46]
1450(sh) 1380(s)(**br)**	Decrease intensity compared to (a)	Same intensity compared to (b)	N-O stretching or O-C-O asymmetric stretching (CO_3^{2-})	(43),[47] [48]
1193(sh) **1122** (s)(**br)**	Same intensity as (a)	Peak shifts to 1000 (s,b) with 1122 (sh)	Si-O-Si or asymmetric Si-O-Si or Al-O-Si	[49], [50]
900 (s)	Same intensity as (a)	Becomes sh to peak centered around 1000	Al-O, Si-O stretching	[51]
810 (w)(**br)**	Same intensity as (a)	Decrease intensity compared to (b)	Al-O bending mode of AlO_4	[30]
722-540 (w)	Increase intensity compared to (a)	Peak emerges at 560, decrease intensity 722-540	Various Si-O-Si vibrations, with 560 an external linkage of Si-O_4 or Al-O_4	[47],[52]
480 (s,br)	Same intensity as (a)	Decrease intensity compared to (b)	Bending (Si-O-Si and O-Si-O)	[52]

Table 3. Analysis of infrared vibrational bands in PEG derived products, (br) broad, (s) sharp, weak (w), and (sh) shoulder.

(a) Uncalcined Precursor (cm^{-1})	**(b) Calcined Precursor (cm^{-1})**	**(c) Geopolymer Cement (cm^{-1})**	**Assignment**	**Ref**
3500-3000 (br)	Decrease intensity compared to (a)	Increase intensity compared to (b)	O-H vibrational stretching	[46],[59]
2925(w) **2885 (sh)**	Decrease intensity compared to (a)	Decrease intensity compared to (a) (b)	C-H asymmetric and symmetric stretching	[43]
1720(w)(sh) **1630(w)**	Decrease intensity compared to (a)	Same intensity as (b)	C-O stretching and O-H stretching	[45],[46]
1450(sh) **1380(s)(br)**	Decrease intensity compared to (a)	Same intensity as (b)	N-O stretching or O-C-O asymmetric stretching (CO_3^{2-})	[44],[47],[48],[60]
1240(sh) **1115 (s)(br)**	Same intensity as (a)	Peak shifts to 1060 (s,b) with 1122 (sh)	Si-O-Si or asymmetric Si-O-Si or Al-O-Si	[49],[50]
900 (s) **940 (sh)**	Same intensity as (a)	Becomes (sh) to peak centered around 1000	Al-O, Si-O stretching	[51],[53]
810 (w)(br)	Same intensity as (a)	Decrease intensity compared to (b)	Al-O bending mode of AlO_4	[30]
722-540 (w)	Increase intensity compared to (a)	Peak emerges at 720, decrease intensity 722-540	Various Si-O-Si vibrations, with 560 an external linkage of Si-O_4 or Al-O_4	[47],[52],[61]
480 (s,br)	Same intensity as (a)	Decrease intensity compared to (b)	Bending (Si-O-Si and O-Si-O)	[52]

Table 4. Atomic environment assignments of ^{27}Al MAS-NMR and ^{1}H-^{27}Al MAS-NMR spectra for (a) uncalcined precursors, (b) calcined precursors, and (c) geopolymer cements. Assignments are based on (48).

Sample	I/O Ratio	(a) Uncalcined Precursor				(b) Calcined Precursor				(c) Geopolymer Cement			
		^{27}Al δ (ppm)	Al	^{27}Al-^{1}H δ (ppm)	Al	^{27}Al δ (ppm)	Al	^{27}Al-^{1}H δ (ppm)	Al	^{27}Al δ (ppm)	Al	^{27}Al-^{1}H δ (ppm)	Al
PVA-L	Low	0.53	Al(VI)	0.53	Al(VI)	8.53	Al(VI)	-	-	59.29 8.49	Al(IV) Al(VI)	59.68	Al(IV)
	High	0.13	Al(VI)	0.13	Al(VI)	8.09	Al(VI)	-	-	59.17 8.5	Al(IV) Al(VI)	61.54	Al(IV)
PVA-H	Low	0.61	Al(VI)	0.61	Al(VI)	7.62	Al(VI)	-	-	59.67 9.01	Al(IV) Al(VI)	60.2	Al(IV)
	High	1.97	Al(VI)	1.97	Al(VI)	7.39	Al(VI)	-	-	59.04 8.18	Al(IV) Al(VI)	58.97	Al(IV)
PEG-L	Low	0	Al(VI)	0	Al(VI)	6.94	Al(VI)	-	-	60.16 7.14	Al(IV) Al(VI)	-	-
	High	0.15	Al(VI)	0.15	Al(VI)	9.26	Al(VI)	-	-	60.55 6.26	Al(IV) Al(VI)	-	-
PEG-H	Low	0.1	Al(VI)	0.1	Al(VI)	5.35	Al(VI)	-	-	61.68 10.48	Al(IV) Al(VI)	-	-
	High	0.31	Al(VI)	0.31	Al(VI)	9.18	Al(VI)	-	-	59.88 6.95	Al(IV) Al(VI)	-	-

Table 5. Atomic environment assignments of ^{29}Si MAS-NMR and ^{1}H-^{29}Si MAS-NMR spectra for (a) uncalcined precursors, (b) calcined precursors, and (c) geopolymer cements. Assignments are based on (48,55).

Sample	**I/O Ratio**	**(a) Uncalcined Precursor**				**(b) Calcined Precursor**				**(c) Geopolymer Cement**			
		^{29}Si δ (ppm)	Q^n	^{29}Si-^{1}H δ (ppm)	Q^n	^{29}Si δ (ppm)	Q^n	^{29}Si-^{1}H δ (ppm)	Q^n	^{29}Si δ (ppm)	Q^n	^{29}Si-^{1}H δ (ppm)	Q^n
PVA-L	Low	-110.87	Q^4	-106.8	Q^4	-111.38	Q^4	-110.3	Q^4	-89.95	Q^4(4Al)	-	-
	High	-111.91	Q^4	-	-	-111.2	Q^4	-108.02	Q^4	-88.88	Q^4(4Al)	-87.5	Q^2
PVA-H	Low	-112.52	Q^4	-103.6	Q^4	-109.42	Q^4	-106.8	Q^4	-89.34	Q^4(4Al)	-88.33	Q^2
	High	-110.95	Q^4	-111	Q^4	-109.6	Q^4	-110.37	Q^4	-87.86	Q^4(4Al)	-88.14	Q^2
PEG-L	Low	-110.69	Q^4	-111.8	Q^4	-109.09	Q^4	-100	Q^3	-85.06 -108.55	Q^4(4Al) Q^4	-	-
	High	-113.16	Q^4	-102.4	Q^3	-113.28	Q^4	-105.8	Q^4	-80.4	Q^4(4Al)	-83.52	Q^2
PEG-H	Low	-111.82	Q^4	-101.8	Q^3	-109.02	Q^4	-97	Q^3	-83.94 -107.04	Q^4(4Al) Q^4	-84.07	Q^2
	High	-111.2	Q^4	-107.4	Q^4	-112.15	Q^4	-109.3	Q^4	-85.26	Q^4(4Al)	-83.52	Q^2

Table 6. NMR peaks detected by various studies on (C)-N-A-S-H cementitious binder variants.

*Presence of Zeolite A found in samples.

Geopolymer Cement	**^{29}Si NMR (ppm)**	**^{27}Al NMR (ppm)**	**Reference**
$Na_{0.625}Si_{1.00}Al_{0.625}\cdot xH_2O$	-89.0	58.0	(58)
$Ca_{0.800}\,Na_{0.078}Si_{1.00}Al_{\,0.156}\cdot xH_2O$	-75.0, -79.0, -84.0, -86.0, -89.0, -94.0	57.0, 0.0	(15)
$Na_{1.00}Si_{1.08}Al_{1.00}\cdot xH_2O$	-86.5, -89.0*	57.4	(62)
$Na_{1.18}Si_{1.5}Al_{1.00}\cdot xH_2O$	-	61.5, 8.8	(19)
$Na_{\sim 0.015}Si_{1.00}Al_{1.00}\cdot xH_2O$	-87.0, -103.0	78.0	(61)