Investigation of Activation Kinetics in Geopolymer Paste using Quasielastic Neutron Scattering

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Abstract

Quasielastic neutron scattering (QENS) has been used to investigate the binding process of water molecules in pastes of calcium geopolymer prepared with low and high calcium fly ash contents, and at two different NaOH molarities, 10 and 14 M. The *in-situ* measurements were carried at ambient and elevated curing temperatures (60°C). By carefully monitoring the time evolution of the elastic peak intensity, we infer a gelation process, followed by polymerization and a hardening in the high calcium geopolymer paste at 60°C, in agreement with previously proposed geopolymerization model. This behavior was neither observed at ambient temperature in both low and high calcium geopolymer cement paste, within the precision of the neutron instrument. Our study clearly shows that a minimal amount of heat is necessary to form gelation and polymerization during the activation process. The activation of geopolymer paste with high NaOH molarity involves more chemically bound water molecules than that at lower activator concentration. This work shows that the QENS technique can be effectively used to characterize the alkali-activation kinetics in certain geopolymer pastes, and that temperature and molarity of the activator play a vital role in controlling the gel mechanism.

Key Words: Fly Ash; Quasielastic Neutron Scattering (QENS); Geopolymer; Characterization; Gelation; Dissolution

Introduction

Geopolymer concrete or alkali activated binder is an emerging technology, which has exhibited a wide range of advantages such as high corrosion and temperature resistance, reduced CO₂ emission construction material, a minimum energy-consuming binder and also negligible carbon foot print [1, 2]. Duxson *et al.* [3-5] introduced the geopolymer reaction process, starting with the dissolution, specific equilibrium, gelation, reorganization and finally leading to polymerization and hardening. The current study investigates the geopolymerization process of fly ash based alkali-activated paste using quasielastic neutron scattering (QENS), a powerful probe for studying dynamical processes in hydrogenous compounds [6].

Fig 1. Conceptual geopolymerization model from Duxson *et al.* (2007). Developed from the concepts from reference [3, 7]

The geopolymer mechanism introduced in the Figure 1 exhibits a transitional change from a solid alumino silicate source such as fly ash, metakaolin and clay into alkali activated alumino silicate. In the initial stage the solid particles from the source material comes in contact with the alkali solution. This

causes an amorphous component of these particles to dissolve, releasing aluminate and silicates [8]. Dissolution occurs rapidly in amorphous alumina silicates such as fly ash or metakaolin at high pH leading to a supersaturated alumina silicate solution [9]. Upon dissolution, initiation of a complex mixture of aluminosilicate species develops with the ongoing gel rearrangement and crystallization process. In high alkaline solution this leads to gelation during which water that was initially adsorbed during the dissolution stage is released. Details regarding each phase evolution could be found in references [1, 3, 10, 11]. This mechanism is validated and well-studied for geopolymers formed with low calcium fly ashes or metakaolin [11]. The understanding of the reaction pathways involving high calcium based precursors is not complete, since the initial model was based fundamentally on the formation of Si-O-(Si,Al) bonds [12]. The current study focuses on analyzing this mechanism based on high calcium geopolymers and formation of geopolymeric gels during this dynamic process. Neutron scattering is one of the preferred techniques which can be used to study the dissolution phase of the mechanism [13]. The current work is one of the preliminary studies conducted using *in-situ* QENS studies on fly ash based geopolymer pastes.

In the past, several studies have used QENS to understand the metamorphosis of multiphase mechanisms which evolve during the hydration process incorporating alumino silicate source such as fly ash or ground granulated blast furnace slag into Ordinary Portland Cement (OPC) [14-22]. Most studies in the past have dealt with hydration process of OPC incorporating admixtures using QENS technique, while the current study is the first kind where QENS technique is used for examining the alkali activation process in geopolymers. QENS helps in tracking the motion of hydrogen and states of water in the mixture revealing the time-evolution mechanism during the hydration process. During the hydration process the bonding states of water can be distinguished as free, constrained and chemically bound water [14]. Because the neutron signal is largely dominated by hydrogen, the observed immobile molecules are mostly representative of the chemically bound water[23].

The bulk water present in cement matrix is associated to free water, the restricted water is attributed to constrained water where the mobility of water is limited, since it is present inside the gel pores. Chemically bound water is related to the structural water present inside the calcium silicate hydrates which is a hydration product of OPC based system. Details regarding the calculation of the free and constrained water could be found elsewhere [13, 14, 24]. Understanding the alkali activation process has been a great challenge for cement chemists and material scientists [11]. QENS assists in determining the chemically bound water, a parameter that is , in studying the microstructural evolution during the hydration, and that can be related to the nucleation and growth of synthetic gels such as calcium-silicate-hydrate(C-S-H), calcium aluminosilicate hydrate (C-A-S-H) and sodium aluminosilicate hydrate (N-A-S-H) [25, 26].

C-S-H is the binding agent in Portland cements; while potassium-alumino-silicate-hydrate (K-A-S-H) or N-A-S-H gel is considered as a predominant glue in geopolymers depending on the type of activator (potassium hydroxide or sodium hydroxide) used during the alkali activation process[4, 12, 27]. C-A-S-H gels are formed upon alkali activation of Blast Furnace Slag (BFS) and the formation of the structure is governed by the type of activator used for alkali activation. Sodium hydroxide activated BFS exhibits ordered and layered structures of C-A-S-H gel than silicate activated binders [28, 29]. A density functional theory (DFT) based atomistic model of N-A-S-H gel was examined at elevated temperatures[30]. As seen in C-S-H gels, the Si:Al and Ca:Mg ratio plays a vital role in governing the initial activation process and therefore the chemistry of the precursor materials (fly ash or Metakaolin) and activators need to be selected carefully before the geopolymerization process. Although, several studies have been published on N-A-S-H gels, but the role of water during activation and geopolymerization process is an active area of research. The current study provides an insight into the activation kinetics and the movement of water during the course of alkali activation. The current study reports the first application of QENS to study alkali activated materials using low and high calcium

content fly ashes. This technique was used to study the diffusional water dynamics and water bonding during initial period (~10 hours) of the activation process.

Recent studies conducted by Suraneni *et al.* 2014 [31] show that set times of geopolymer cements can significantly vary as compared to Portland cements. The variation in setting times is influenced by calcium oxide content, LOI and particle size distribution of the precursor material (fly ash) [32]. Although, measurement of setting time via Vicat needle test as per ASTM C191 has been used for measuring setting times of Portland cements, it does not provide an insight into the chemical reactions taking place during hydration [33]. A relatively new technique known as Ultrasonic Wave Reflection (UWR) could compliment the setting behavior obtained via QENS technique [34]. In UWR, a buffer material is used where an acoustic impedance is detected and the intensity of the buffer/sample is observed as a function of time. However, using UWR the shear waves can propagate in solids and not fluids, thus the water dynamics of cement paste cannot be accurately measured using UWR technique. QENS, can successfully track the motion of water during hydration providing an insight into the rotational and translation motion of the free water during the course of hydration.

Experimental Procedure

Geopolymer paste was prepared using high and low calcium fly ash and was alkali activated by sodium silicate and sodium hydroxide solution, just before the neutron measurements. The chemical composition of the fly ashes is shown in Table 1. Chemical analysis of the fly ash samples was performed via X-ray fluorescence (XRF) following ASTM standard D 4326 using a Thermo Scientific ARL Quant'x Energy-Dispersive XRF Spectrometer [35]. DH and MO were designated as low (CaO= 5%) and high (CaO= 12.93%) calcium fly ashes respectively. An activator/binder ratio of 0.6 was maintained throughout the experiment. The activator solution consisting of sodium hydroxide: sodium silicate was maintained 1:1, while the fly ash was the binder. A 10 and 14 M sodium hydroxide and

sodium silicate manufactured by P Q corporation (45% by weight and SiO_2 to Na_2O ratio of 2:1) was used in the preparation of the geopolymer paste. The geopolymer paste was prepared by addition of the sodium silicate to the fly ash and mixing it for 1 minute. The mixture was then alkali activated by adding the sodium hydroxide. The mixture was uniformly stirred for 1 minute and a thin paste was applied on the glass slide, as shown in Figure 2. The geopolymer paste was sandwiched between two quartz slides. An aluminum foil was wrapped inside the sample holder and the geopolymer paste was placed inside the specimen holder. The specimen was then placed in the high resolution backscattering spectrometer (BASIS) at the spallation neutron source (SNS) at the Oak Ridge National Laboratory (ORNL).

Fig 2. Preparation of Geopolymer paste and specimen setup a) Fly ash and activators, b) specimen holder and parts included for the setup. c) Geopolymer paste applied on the glass slide, d) Geopolymer paste sandwiched between two glass slides and inserted inside the specimen holder, e) BASIS Sample Environment (Close-Cycle Refrigerator (CCR)) f) Specimen holder attached to the stick and ready to be inserted in CCR.

Table 1. Chemical composition of fly ashes obtained via XRF analysis

Component (mass % as oxide)

Fly ash ID	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	SO ₃	Na ₂ O	TiO ₂	MnO ₂	K ₂ O	Mc	LOI	Type of Ash
DH	58.52	20.61	5.00	9.43	1.86	0.49	0.52	1.09	0.16	1.89	0.14	0.17	LCFA
MO	55.61	19.87	12.93	4.52	2.49	0.49	0.67	1.72	0.03	0.86	0.02	0.22	HCFA

Mc: Moisture content, LOI: Loss on ignition at 1000°C

HCFA: High calcium fly ash

LCFA: Low calcium fly ash

BASIS is an inverse geometry time-of-flight backscattering neutron spectrometer, in which high quality Si (111) crystal analyzers are used to Bragg-select the final energy of the neutron ~ 2.08 meV ($6.27\text{\AA}$) after it scatters from the sample. For the present data analysis, a clean dynamic range from -100 to 100 μeV (free from spurious instrumental background) with a corresponding energy resolution of about 3.5 μeV (Full-Width-Half-Maximum) was used. At the time of our experiment, the proton accelerator was stabilized around 850 kW, which is about 60% of the future power upgrade of 1.4 MW. Nevertheless the resulting neutron flux on the instrument was high enough to yield decent statistics over the time allocated for this experiment. A flat cell geometry configuration was used for inserting samples at 135° with respect to incident neutron beam such that low angle detectors banks were in transmission mode. There is a total of 112 ^3He detectors on the spectrometer, which monitor the scattering as a function of time and angular position. The resulting Q-range covered in the present experiment was from 0.3 to $1.55\text{ \AA}^{-1}$, binned as single spectra to improve statistics. For more details regarding the instrument, the reader is referred to Mamontov and Herwig [6]. The data reduction and modeling of the data was performed using the NIST DAVE software package[36].

Quasielastic neutron scattering technique is effective in tracking the immobile molecules, which are dominated by the chemically bound water, and the constrained water during the hydration process. Immobile molecules refers to hydrogen containing molecules considered stationary on the assessable timescale of this instrument. QENS spectra, $S(Q,E)$ represents the incoherent

scattering from hydrogen (S) as a function of energy change (ω) and scattering vector (Q). The scattering from a thin hollow vanadium cylinder was measured for normalization purposes over the same Q-range. The scattering from a thin hollow vanadium (100% incoherent) cylinder was used to correct for fluctuations in the detector efficiency with changing Q. The amounts of hydrogen in chemically bound, constrained and free water were determined at each time step (1 hour long runs) using a **delta function (representing the immobile H atoms) and two Lorentzian functions, which characterize respectively the dynamics of the confined or constrained water molecules, and the free unrestricted bulk-like water component [13, 24, 37].** We denote by Γ_1 the **half-width at half-maximum (HWHM) of the slowly diffusing constrained water component and by Γ_2 the HWHM of the free water. To account for instrument resolution effect at BASIS,** we measured a flat vanadium plate (which scatters incoherently) oriented in the same configuration as the sample holders. Although **the instrumental resolution function was found to be narrower than the relevant signal, we use it to perform full numerical convolution for accuracy and precision.** This measured resolution $R(E)$ is directly convoluted with the following scattering model $S(E)$, which includes contributions from water that is **chemically** bound (or static on the instrument window), water that diffuses slowly due to the spatial confinement, and water that moves freely around [38],

$$S(E) = C[\delta(E = 0)] + P \left(\frac{\Gamma_1}{\pi(E^2 + \Gamma_1^2)} \right) + F \left(\frac{\Gamma_2}{\pi(E^2 + \Gamma_2^2)} \right) \quad (1)$$

The intensities related to elastic scattering ($\sim$ chemically bound), slow diffusion ($\sim$ constrained water), and fast diffusion (highly mobile or free water) are denoted as C, P, and F, respectively. Γ_1 is the HWHM associated with the spatially constrained water and Γ_2 that of the free water. Both Γ_1 and Γ_2 are free adjustable fitting parameters in our fits. A sloping background term $B(E)=aE+b$, although not included in the convolution, accounts for the baseline intensity, and improves the quality of the fits. A representative fitted QENS spectrum (1 hour long collection of high calcium content sample) for alkali activation reaction is shown in Figure 3.

Fig 3. One hour-long neutron spectrum observed at BASIS for 14 M NaOH high calcium geopolymer paste (black circles) at 60° C, summed over a wide range of Q (as indicated in the legend). The best full model fit (blue line) and the corresponding fit components representing respectively the freely diffusing bulk-like water (dashed red line), the slowly diffusing or constrained water (solid green line) and the chemically bound water (dashed black line) are also shown.

Using the three-component model described above, we calculate the bound water index (BWI) using [13],

$$BWI = \left(\frac{C+P}{C+F+P} \right) \quad (2)$$

which corresponds to the states of bond water or the relative amount of bound water molecules, including those slowly moving molecules. Conversely, we can calculate the free water index (FWI) using,

$$FWI = 1 - BWI = \frac{F}{C + F + P} \quad (3)$$

Results and Discussion

The quasielastic neutron spectra of geopolymer paste prepared with the low calcium fly ash (DH) is shown in Figure 4. This data shows the effect of neutron scattering intensity at various temperatures and at initial (approximately 5 minutes was taken to prepare the sample, load and open the shutter for neutron beam exposure), while the later time was measured 10 hours later. “Initial time” indicates as soon as the paste was alkali activated and the exact temperature was stabilized. Figure 4 indicates a significant change between the initial QENS line shape at 20 and 60°C and their corresponding line shape after 10 hours. Application of heat caused significant broadening of the QENS wings that can be attributed to the movement of water molecules, both constrained and free water. However, as the geopolymer paste starts to react, the elastic component (energy transfer $E=0$) starts to increase over time, and the broad QENS signal ($E \neq 0$) decreases. We observed similar behavior at other temperatures, therefore capturing the kinetics of the paste reactions. The activation kinetics indicate the transition from liquid to solid state with the nucleation to polymerization finally leading to the hardened cement paste [1, 39].

Fig 4. Time evolution quasielastic neutron response of Geopolymer paste prepared with low calcium fly ash (DH) at 20°C and 60°C. Spectra shown are 10 minutes long. ‘Initial’ and ‘later’ refer respectively to the time when the specimen was prepared and 10 hours later.

In-situ geopolymer pastes were maintained at 60°C and 20°C, while the measurements were taken at a time step of 10 and 3 minutes for 60°C and 20°C, respectively as shown in Figure 5. To increase the statistical quality of these short runs for use in the data analysis, we binned ~6 successive short ~10 minutes counts spectra into 1 hour-long spectrum. The HWHM Γ_1 in these summed QENS spectra for high calcium content Geopolymer paste at 20°C remains unchanged from its value at ~3.7 μeV in the first ½ hour of the data collection up to 12 hours later. In contrast, the same Γ_1 at 60°C is observably broader and appears to change slightly from $(6.5 \pm 0.25) \mu\text{eV}$ in the first ½ hour down to $(5 \pm 0.25) \mu\text{eV}$ in the 8-9th hour after which it stays more or less constant (~5 μeV) for the duration of the experiment (See Figure 9). This apparent change may be associated with the decrease in the parameter P with time, which complicates the extraction of Γ_1 at longer time. These observations indicate that the temperature plays a vital role in controlling the setting and hardening of geopolymer pastes. In addition, this shows that the free water in the pore solution is significantly reduced and the temperature has expedited the formation of bound hydrogen. Heat thus plays a crucial role in controlling the geopolymer mechanism and expedites the re-organization and hardening process of geopolymer cements [7], in agreement with previous studies [40].

Fig 5. Quasielastic neutron spectra of geopolymer paste at 60°C and 20°C prepared with low Calcium Fly Ash (Geopolymer paste-DH). The spectra shown were collected over fairly short period of times, respectively 10 minutes (left panel), and 3 minutes long (right panel), to track the time evolution of the elastic intensity.

Geopolymer prepared with high calcium fly ash (MO) and alkali activated with 14M NaOH solution is shown in Figure 6. The energy resolved QENS spectra shows the variation of neutron scattering intensity with time. This figure indicates the time slice just after mixing until some 15 hours later. It can be clearly seen that the QENS broadening decreases with increasing time, while the elastic component increases.

Fig 6. Neutron Scattering Intensity with increment with time for Geopolymer paste prepared with High Calcium Fly ash and 14 M sodium hydroxide solution. These spectra represent snapshots of the scattering intensity in time, collected for about 10 minutes at each timestep.

The time dependence of the maximum elastic intensity of geopolymer paste prepared with high calcium fly ash and alkali activated using 14 M NaOH, which was cured at 60°C and ambient temperature is shown in Figure 7. As soon as the fly ash is alkali activated and kept at 60°C the dissolution phase is initiated and elastic intensity increases till ~ 150th min. The gelation phase can be associated with the drop in elastic intensity, which occurs at around 210th minutes followed by reorganization which then leads to polymerization and hardening [7, 10]. Reorganization and hardening are an ongoing process and depends on factors such as particle size distribution of the fly ash, loss of ignition, calcium oxide content and crystalline to amorphous ratio. The geopolymer paste prepared with high calcium fly ash (MO) and ambient cure did not exhibit any significant increase in elastic intensity as shown in Figure 7. This may

be due to limitations of the machine (Backscattering spectrometer, BASIS) or the reaction mechanism may be too rapid for BASIS. Further research is required and use of other instruments (having broader dynamic range) such as the Cold Neutron Chopper Spectrometer (CNCS) is necessary to capture faster reactions, during the initial activation process. Unfortunately due to neutron kinematics and engineering constraint, there is no single neutron instrument that is capable of probing all (Q,E) space in a single shot. BASIS is only optimized to investigate slow dynamical process at molecular length scale (0.3 to 3 nm). Other instruments are required to access dynamics outside this range.

Fig 7. Elastic Intensity normalized to the intensity initial of geopolymers prepared with high calcium Geopolymer paste with 14 M NaOH concentration.

The variation with time of the observed elastic intensity for geopolymer paste prepared with 10 M NaOH solution is shown in Figure 8. Geopolymer paste was prepared with high calcium fly ash (MO) when subject to 60°C exhibited an almost similar trend as shown by geopolymer paste at 14 M NaOH. In our opinion, this process was initiated by dissolution phase followed by gelation at 190 minutes. We attribute the slight drop in elastic intensity to the initiation of gelation. Studies have shown that when fly ash is activated with sodium hydroxide a lag period is observed before the re-organization process [39]. This behavior indicates the time taken to form stable nuclei before the initiation of the growth, which is characterized by an increase in intensity with time. The indication of the lag period is attributed to initial preferential dissolution of alumina from the fly ash that initiates a siliceous layer on the fly ash. Adsorption of aqueous Al species on the surface causes the surface to passivate by inhibiting the approach of hydroxyl ions which slows the dissolution process [41]. Over a time period the retarded dissolution process slowly releases sufficient silica to react with aqueous alumina to stop the inhibition. This process accelerates the dissolution of fly ash leading to a formation of gel network. The gelation process was followed by the re-organization leading to polymerization and hardening of the paste. A significant change in the elastic intensity was observed during the re-organization phase for geopolymer paste prepared with 14 M NaOH solution as compared with 10 M NaOH solution (see Figure 7). This strong variation could be attributed to leaching mechanism when higher molarity of alkali activated solution is used in preparation of geopolymer paste. Independent studies based on other techniques such as small angle neutron/X-ray scattering techniques are required for better understandings the leaching mechanism.

The gelation and polymerization trend was not clearly visible in the low calcium geopolymer paste (DH), while the high calcium geopolymer paste (MO) when subjected to 60°C exhibited the gelation and polymerization stage. One possible reason could be the reaction in low calcium geopolymer paste occurs much rapidly than the BASIS instrument can record. Further studies using cold neutron chopper spectrometer (CNS) or high flux backscattering spectrometer (HFBS) may be necessary to capture alkali-activation reactions using low calcium geopolymer pastes. This study shows that high calcium

geopolymers pastes requires heat to form the gel and to re-organize during the polymerization stage,
 which was not possible at ambient temperature.

Fig 8. Elastic Intensity of Geopolymer paste prepared with High calcium fly ash with 10 M NaOH concentration.

Free-Water-Index (FWI) for high calcium fly ash geopolymer prepared with 10M and 14 M NaOH was calculated using Equation 3, and displayed in the top panel of Figure 9. An alternative FWI in which only the truly free water (F) is considered is also shown for comparison. In both cases, FWI clearly decreases with time, indicating that free water is being utilized during the geopolymer reaction to form either chemically bound water or spatially constrained water. Gelation can be observed in the range of 0-8 hours, as a continuous drop of the FWI, indicating steady reduction in free water with time. The change in

slope after ~8 hours shows a drastic change in the free water reduction rate. This is consistent with Figures 7 and 8 where a gradient shift in elastic intensity was observed with increasing time. A steady decrease in FWI indicates an increase in gelation, which we associate with reorganization and polymerization driven hardening of the geopolymer cement paste. Geopolymer paste prepared with 14M NaOH solution exhibited a slightly higher decrease in intensity as compared to the pastes prepared with 10M NaOH concentration over the time period probed. This indicates that the higher the molarity of activator (NaOH) the greater the free water is being utilized in the reaction, for the formation of chemically bound water. At same temperature conditions, molarity of the activator plays a crucial role in governing and expediting the hardening mechanism of geopolymer cement pastes.

Fig 9. Top panel: Free water index for high calcium Fly ash geopolymer paste prepared with 10 and 14M NaOH solution and cured at 60°C, depending on whether the constrained water (open symbols) is included or not (solid symbols). **Bottom Panel:** Corresponding width parameter HWHM as a function of time for the 10M NaOH (black circles) and 14M NaOH (red circles) geopolymer pastes. The decay rates shown are derived from fits (solid lines) to the exponential decay function indicated, and correspond to

the times the constrained water (Γ_1) would remain observable on the BASIS instrument, based on the observed trend.

The bottom panel of Figure 9 shows the time dependence of the fitted width Γ_1 for our two compounds at 60° C. It is interesting to note that the 10 M NaOH high Ca fly ash exhibits Γ_1 values that are somewhat larger than those of the 14 M compound. Assuming an exponentially decay rate for Γ_1 , we get a time constant of respectively ~107 and 60 hours for the 10 M and 14 M samples, respectively, confirming that hardening will occur much faster in the 14 M. These derived values correspond roughly to the times the constrained water (Γ_1) would remain observable on BASIS (from the time the sample is prepared), or the time by which all of the discernible constrained water molecules (or P parameter) would transfer to the chemically bound side (C parameter). Additionally, the fitted Γ_2 characterizing the free water, are found to be largely independent of time, staying approximately at ~50 μeV in the 10 M sample compared to ~35 μeV in the 14 M at 60° C at all time investigated here. Based on this observation, we can conclude that the free water component appears to be much more mobile in the 10 M than in the 14 M compound at the same temperature. For this reason, a neutron instrument with coarser resolution would be more suitable for tracking water behavior in the 10 M compound.

The current study cannot predict new reaction mechanism as the structure of the gel formed needs to be recognized and examined. Additional characterization is required to study the structure of these gels using small angle neutron/X-Ray scattering. It is attributed to the possible formation of the sodium aluminosilicate hydrate (N-A-S-H) gels, while separate study is required to analyze the behavior of N-A-S-H gels using QENS technique. Although, the reaction mechanisms of geopolymeric gels are different compared to Portland cements, in case of geopolymer gel depending on the type of activation, we observe Sodium Aluminosilicate Hydrate (N-A-S-H) or Calcium, Sodium aluminosilicate hydrate (C-N)-A-S-H gels [42]. This work focuses on tracking the free water during geopolymerization and, suggest that some amount of heat is necessary for initiating the onset of gelation. However, that the movement of water inside the geopolymeric gel is difficult to

quantify with QENS because the amount of water diffusing is continuously evolving with time, and data can not be collected in the steady state with sufficient statistics to get the required Q information. Future work is thus required to confirm the diffusion coefficients using for example NMR relaxometry.

This study focus on the early age behavior during the activation process which leads to these gels by bonding of the hydrogen atoms which then precipitates form the geopolymeric gel. Chemically bound and constrained form of water is shown in Figure 10 as a percentage of bound water states. High calcium fly ash was activated with 10 and 14 M sodium hydroxide solution cured at 60°C. This BWI quickly reaches ~50% within the first hour in both samples (with a slightly higher value with the 10 M sample). The remainder 50% water takes several hours to bind to the cementitious gel structure. The BWI increases steadily to about 60% after 4-5 hours. Beyond this point, the amount of chemically bound water molecules increases faster in the 14 M sample than in the 10 M one, likely due to the higher gelation rate in the 14 M. Following an additional 5 hours, both curves start to flatten to a constant value. The percentage of constrained water changes little with time, starting at 18-20% at time zero and ending at 13-14% 19 hours later for both samples. This decrease is in part responsible for the increase in the amount of chemically bound water molecules.

Fig 10. Estimated water bonding states of the 10M and 14 M geopolymer pastes with 0.6 activator/binder ratio and cured at 60°C. The solid symbols refer to the chemically bound water (~C parameter) and the open symbols are the spatially constrained water in the paste (~P parameter).

The constrained water for the geopolymer pastes activated with 10 and 14 M was less than the chemically bound water. This can be associated to initiation of gelation and growth that can increase chemically bound water [14, 43, 44]. These results are in conjunction of the work conducted by Rees *et. al* [39, 45, 46]. These results show that an initial lag period between 2-3 hours s followed by evolution of gelation for high calcium geopolymer paste (MO) activated with 14 M concentration. An increase in network formation was associated with an increase in NaOH solution, as compared to fly ash activated using 10 M concentration. This behavior can be attributed to the increased alkalinity due to high molar concentration accompanied by strong ion-paring that allows greater number of hydrogen atoms to be fixed. The

increased molarity only contributes to a certain point and after that it is followed by a reduction in the gel network accompanied by the reorganization process which is dependent on heat curing.

Conclusions

High and low calcium fly ash based geopolymer pastes were studied using *in-situ* QENS technique. During the alkali activation process the transition from liquid to solid state was observed via nucleation of the gels leading to reorganization and polymerization when subject to 60°C. This reaction mechanism was not observed on geopolymer pastes at ambient temperature. Geopolymer pastes prepared with 14 M concentration showed higher chemically bond water as compared to pastes prepared with 10 M concentration. Molarity of NaOH and curing temperature together play a vital role in the formation of initial geopolymer gels and polymerization at the later stage of the reaction. This study shows that the high calcium geopolymers are more suitable for gelation and the activation process is temperature dependent.

During the initial activation period the chemically bound and constrained water increases, upon initiation of nucleation and growth period the constrained water remained approximately constant. The initial increase in constrained water could be attributed to the decrease in total surface area and starts to retard as the conversion to gel pores are formed due the decrease in the volume of the surface area. Overall quasielastic neutron scattering is an effective technique for studying the early age dynamic characteristics of certain geopolymeric gels.

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426 *List of Notations*

(C,N)-A-S-H	: (Calcium, Sodium)-Alumino-Silicate-Hydrate
BASIS	: Neutron Backscattering Spectrometer
BFS	: Blast Furnace Slag
BWI	: Bound Water Index
C	: Chemically Bound Water
C-A-S-H	: Calcium-Alumino-Silicate-Hydrate
CCR	: Close Cycle Refrigerator
CNS	: Cold Neutron Chopper Spectrometer
C-S-H	: Calcium-Silicate-Hydrate
DAVE	: Data Analysis and Visualization Environment
DFT	: Density Functional Theory
DH	: Dolet Hills, Low calcium Fly Ash
E	: Energy Transfer
F	: Amount of Free Water
FWHM	: Full-Width-Half-Maximum
FWI	: Free Water Index
HCFA	: High Calcium Fly Ash
HFBS	: High Flux Neutron Backscattering Spectrometer
HWHM	: Half-width at Half-maximum
LCFA	: Low Calcium Fly Ash
LOI	: Loss of Ignition
M _c	: Moisture Content
MO	: Monticello, High Calcium Fly Ash
N-A-S-H	: Sodium-Alumino-Silicate-Hydrate
NMR	: Nuclear Magnetic Resonance
OPC	: Ordinary Portland Cement
ORNL	: Oak Ridge National Laboratory
P	: Constrained Water
QENS	: Quasielastic Neutron Scattering
S(Q,E)	: Neutron Scattering Intensity as function of Energy change (E) and Scattering wavevector (Q)
SNS	: Spallation Neutron Source
UWR	: Ultrasonic Wave Reflection
XRF	: X-ray Fluorescence
Γ_1	: Lorentzian Half-width-at-Half-Maximum of the Slowly Diffusing Constrained Water Component
Γ_2	: Lorentzian Half-Width at Half-Maximum of the Free Water

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