Study on the Disposition of Water in Fly Ash-Based Geopolymers Using ATR–IR

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ABSTRACT

This paper addresses the question of whether the main product of low calcium fly ash-based geopolymer is a hydrate, namely, sodium aluminosilicate hydrate (N-A-S-H). The answer to this question is important for understanding geopolymer characteristics. One of these is its fire resistance. In this study, fly ash-based geopolymers were synthesized using the combination of Na_2CO_3 and $\text{Ca}(\text{OH})_2$. Samples were cured at ambient temperature for 7 days, then placed in the oven at 105°C for 24 h, and then calcined at 1050°C for 48 h. IR was used to examine the produced geopolymers at each stage so as to further knowledge on the following issues: the possibility of co-existence of calcium aluminosilicate hydrate (C-A-S-H) and N-A-S-H, the roles of cations as compensator and network modifier as well as the role of water. The results obtained suggest that the primary geopolymerization products, which are potentially good fire-resistant, are unlikely to contain hydrates. Even if there were hydrates, their amount must be very small such that the escaping of water does not compromise the structure's integrity.

1. INTRODUCTION

Geopolymer is an “environmentally green” material, which has been claimed to excel Portland cement in many aspects, a material that could potentially be the future “cement.” It was proposed by Davidovits in the late 1970s, referring to the amorphous to semi-crystalline three-dimensional silico-aluminate materials activated in a highly alkaline environment (Davidovits, 2008). As the understanding of geopolymers increases, the chemistry behind geopolymerization process gradually unravels. One aspect that has recently been researched is to determine whether geopolymer is a hydrate. Davidovits (2008) has used the term polysialate to describe all geopolymers that have at least one M-(Si–O–Al), that is, M-sialate unit (sialate is an abbreviation for alkali silicon-oxo-aluminate and M stands for metal ions). This term is represented by the empirical formula: $\text{M}_n(-(\text{SiO}_2)_z-\text{AlO}_2)_n \cdot w\text{H}_2\text{O}$, in which the water molecule is not considered as an integral part of the geopolymer matrix. To avoid confusion about different terminologies of water throughout this research, the water in geopolymers discussed, will be classified in three categories: free water, physically adsorbed water, and structural water. Free water is the water that is absorbed and held in macro-pores and is beyond the range of the surface forces of the solid phase. The transition temperature, enthalpy, and peaks obtained in DSC curves for the free water are equal to those of pure water as in the case of free water defined in cement chemistry (Nakamura,

Hatakeyama, & Hatakeyama, 1981; Neville, 2011). The term structural water as used in this research refers to the part of water molecules, which is rigidly bound mainly by hydrogen bonding and constitutes an integral part of the geopolymer matrix in the form of molecular water. Thus, structural water, if any exists in geopolymers, should be rigidly bound and different from adsorbed water. It should constitute an integral part of a geopolymer and the loss of which would causes the decomposition of its structure. From this perspective, it is analogous to the “H” in C-S-H, which constitutes an integral part of what is known as C-S-H gel. It is therefore appropriate to note here that the term “gel” has also been used to describe the amorphous and polymeric property of geopolymers.

Contrary to Davidovits' perception about geopolymer not being a hydrate, some researchers since 2005 (Fernández-Jiménez, Palomo, Sobrados, & Sanz, 2006; Fernández-Jiménez, A., Garcia-Lodeiro, I., & Palomo, A. 2007; Palomo, Fernández-Jiménez, Kovalchuk, Ordoñez, & Naranjo, 2007), have claimed that Na geopolymer is sodium aluminosilicate hydrate (N-A-S-H). The term is “*an acronym for sodium aluminosilicate gel forming as the main reaction product in alkali activated fly ash materials,*” and “*terminological analogy to C-S-H gel*” as well as “*descriptive analogy to actual gel composition (sodium aluminosilicate hydrate, N-A-S-H)*” (Fernández-Jiménez & Palomo, 2009). This term,

together with K-A-S-H (potassium aluminosilicate hydrate) or similar gels, was introduced by Fernández-Jiménez and Palomo (2005a). Prior to this, the understanding of geopolymeric product was not based on it being defined as a hydrate, it was considered as an “aluminosilicate” (Alonso & Palomo, 2001a, 2001b). Nevertheless, in those research papers (Shi, Fernández-Jiménez, & Palomo, 2011) that considered the main product of geopolymer as a hydrate, the role and deposition of the water, especially the structural water, were not addressed.

In 2009, Fernández-Jiménez and Palomo (2009) claimed that the concept “N-A-S-H” was first introduced in an early paper (Fernández-Jiménez & Palomo, 2005b) they published in 2005. However, in that very paper (Fernández-Jiménez, Palomo, & Criado, 2005c), the term N-A-S-H has appeared only once in the conclusion section without explanation of what exactly it stood for. In the rest of the paper (Fernández-Jiménez, Palomo, & Criado, 2005), the geopolymer product was referred to as “aluminosilicate gel.” Also, the role of water was not addressed except for the brief mention of the appearance of stretching and deformation modes of water, which appear in the FTIR spectra at 3500 and 1600 cm^{-1} , respectively. However, these two vibration modes are not exclusive to structural water; free water also exhibits such vibration modes at these two frequencies. This was not clearly discussed in the aforementioned paper. Nevertheless, the concept “N-A-S-H” was widely accepted in the description of geopolymers (White, Provis, Proffen, & Van Deventer, 2011, 2010). In 2010, Fernández-Jiménez, Pastor, Martín, and Palomo (2010) further explained that part of the water in geopolymers can be considered as zeolite water¹, and the Na^+ is in a “hydrated” state filling the gaps of the geopolymer matrix. They based this explanation on the observation that the evaporation of this water does not compromise the stability of the geopolymers when exposed to high temperatures. However, the water in zeolites comprises zeolite water as well as structural water, wherein the loss of structural water leads to the destruction of the zeolite’s structure (Castaldi & Santona, 2005). Furthermore, Fernández-Jiménez, Palomo, Pastor, and Martín (2008) attribute the large amounts of weight lost at 100°C, which was observed in TGA, to the loss of adsorbed and some combined water in the N-A-S-H gel, which resembles weight loss of C-S-H in Portland cement cases. Nevertheless, although nanosized crystalline formation and zeolites have been found as secondary products

in geopolymers (Bakharev, 2006; Oh, Moon, Mancio, Clark, & Monteiro, 2011), their quantities are not substantial. Duxson (2006) and Fernández-Jiménez et al. (2007) concluded that the majority of the water in geopolymers is in the form of free water, with the remaining “*likely to be present as tightly bound water or hydroxyl groups on the surface of the gel.*”

Davidovits (2012), however, has clearly pointed out that a geopolymer is not a hydrate and the term N-A-S-H is not correct to define a Na geopolymer. Moreover, he called for an effort to be made to stop giving “*bad*” definition to geopolymers with non-proven facts. It is thus evident that the key argument relies on whether there is structural water in the geopolymeric product. It is known that, the main product of most Portland cement, C-S-H (calcium silicate hydrate) crumbles at 600°C, which leads to most of the Portland cement’s failure and spalling (Neville, 2011). The authors agree with Duxson, Lukey, and van Deventer (2007) that it serves no scientific purpose to argue whether the other names for geopolymers, such as low-temperature aluminosilicate glass and inorganic polymer concrete, are correct. However, it is important to know whether N-A-S-H or sodium aluminosilicate gel stands for a hydrate. This is important because this knowledge would actually inform whether geopolymers have predominant structural water and the nature of this water, which is vital for explaining its good fire-resistance property compared to Portland cement concrete.

Therefore, the main focus in this research is to explore whether the geopolymer product is a hydrate (N-A-S-H or C-A-S-H). Fly ash-based geopolymers activated by Na_2CO_3 and $\text{Ca}(\text{OH})_2$, treated under various temperatures, were synthesised, and IR was used as the main technique to investigate the role of water/hydroxyls in geopolymers.

2. EXPERIMENTAL PROGRAMME

2.1 Synthesis of geopolymers

F-fly ash was used as the raw material for producing geopolymers, and the combination of Na_2CO_3 and $\text{Ca}(\text{OH})_2$ was used as the activator. These are less conventional activators, and their use results in producing NaOH and CaCO_3 . The main components of F-fly ash used in this research are SiO_2 and Al_2O_3 whose contents were 63.46 and 26.71%, respectively (De Weerd et al., 2011). The basic mix comprised $\text{Ca}(\text{OH})_2$, Na_2CO_3 , and fly ash, with a mass ratio of 1:0.24:5. The solids to water ratio was 1.66.

An environmental room (denoted as ER) was used for maintaining uniform curing conditions of 23°C and 58% relative humidity. The mixture was stirred for 15 min using an electrical mixer, and the paste was cast in polyethylene vials with dimensions: 55 mm in

¹ “Zeolite water” is also another term frequently used by researchers. It mainly comprises of weakly bound water (free water) and metal-bound water, in which the metal-bound water co-ordinates with adsorbed metal ions, and hence, zeolite water is mainly adsorbed water and a change in the conditions of the zeolite can lead to its desorption (White et al., 2010).

length and 16 mm in diameter. Each of the vials had an air-tight cover. All the vials were sealed in a plastic bag and placed in the environmental room for 7 days (this stage is denoted as 7-ER). At the age of 7 days, the samples were stripped out of the plastic vials and placed in an oven at 105°C for 24 h (this stage is denoted as G-105) for further curing. Finally, they were placed in a muffle furnace at 1050°C for 48 h (this stage is denoted as G-1050) for calcination. The micro-structure investigation includes the necessity to stop the reaction at each stage where the certain samples reach their final intended terminal (as detailed below), crushing specimens into powdery form, and then taking samples using the quartering method. Later, the samples were investigated using ATR-IR.

2.2 Reaction-stopping procedures

A commonly used method for stopping further reactions of a geopolymer sample in a particular stage is to immerse the sample in a solvent exchanging agent for a specific period of time and then dry it at 40–60°C. In this research, two methods for stopping reactions of samples 7-ER from proceeding further were adopted. In method 1, immediately after 7 days' curing (denoted as 7-ER), a sample is placed directly in a desiccator connected to a constantly operating vacuum pump until the sample is sent for infrared spectroscopy (IR) examination. In method 2, selected samples were immersed in 95% ethanol for 1 h, the solution was then filtered, and the residue was placed in an oven at 40°C until its weight became constant (denoted as 7-ER-E). Samples 7-ER and 7-ER-E were then placed in the oven at 100°C for 30 min (denoted as 7-ERD and 7-ER-ED, respectively). Infrared spectroscopy was applied on samples treated by both methods and thus allowed examining differences in microstructure that may have occurred as a result of applying either method.

2.3 Attenuated total reflectance-infrared spectroscopy (ATR-IR) test conditions

IR has been widely used for identification of compounds and microstructure analysis in both cement reactant products and geopolymers, especially with respect to functional groups of oxygen-hydrogen and Si-O-T (Si and Al). The common XRD technique including quantification, however, is limited to analysing the microstructure of crystalline phases and quantifying the amorphous phase. Therefore, ATR-IR technique is used in this research to further investigate the produced disordered amorphous product. ATR-IR tests were conducted using PerkinElmer Spectrum 100 FTIR equipped with the universal ATR accessory of a diamond/Zn Se crystal. Spectra were measured from 4000 to 650 cm^{-1} with a 4- cm^{-1} resolution, single bounce, and total of 32 scans.

3. RESULTS AND DISCUSSION

The results obtained using XRD in previous research (Fang & Kayali, 2013) showed that the majority of the synthesized geopolymers are mainly amorphous, especially the sodium contained complex. The residual calcium, on the other hand, exists in the form of calcite, portlandite, and gypsum. After 48 h of calcination at 1050°C, the amorphous Na complex reappeared as albite and labradorite. The common XRD technique including quantification, however, is limited to analysing the microstructure of crystalline phases and quantifying the amorphous phase. Therefore, ATR-IR technique is used to further investigate the produced disordered gel.

The IR technique has been successfully adopted to identify compounds and structures including both amorphous and crystalline phases of Portland cement since 1960s (Fernandez-Carrasco et al., 2012). It has also been widely used for studying geopolymers in an effort to investigate the formation of N-A-S-H and C-A-S-H, which, in some cases, were considered to be the geopolymerization products (Garcia-Lodeiro, Palomo, Fernández-Jiménez, & Macphee, 2011). In general, stretching and bending are the two forms of molecular vibrations present in IR spectra. The former involves changes in the bond length, stretch in-phase (symmetrical stretching) or out-phase (asymmetric stretching), and the latter involves changes in the bond angle (Fernandez-Carrasco et al., 2012).

In the following subsections 3.1 and 3.2, IR was employed to first examine the development of geopolymers' main backbone structure, whether a matured Si-O-T (T = Si or Al)-based network has been formed. Then, IR was used to further explore the changes of oxygen-hydrogen bond at different stages. In addition, the comparison between geopolymers and main cement hydration products is discussed in the light of IR analysis. The data analysis and discussion are meant to be thorough and open to further discussion, follow-up research, and potential repeatability.

3.1 Si-O-T (T = Si or Al) evolution at various stages of geopolymerization

The IR spectra of geopolymers at various stages are shown in Figure 1. The principal absorption band at 1050.9 cm^{-1} in the fly ash is a combination of the vibrations of asymmetric Si-O-Si stretching of amorphous silica and Si-O-Al networks relating to amorphous aluminosilicate (Padmaja, Anilkumar, Mukundan, Aruldas, & Warriar, 2001). A strong peak in this region (950–1250 cm^{-1}) is typical of the glassy phase in fly ash (Lee & Van Deventer, 2003), which is the main provider of Si and Al sources for the later formation of geopolymers. The peaks at 793.5 and

690 cm^{-1} are associated with four coordinated Al–O stretching vibrations and Si–O symmetrically stretching vibrations, respectively, attributed to mullite in the fly ash. The peak which appears at 776 cm^{-1} , on the other hand, is frequently found in natural quartz (Davidovits, 2008; Murray & Gualtieri, 1989). After 7 days of curing, the spectrum of fly ash has completely changed showing several different bands, indicating that the addition of activators have changed the structure of fly ash and formed a new product. The first noticeable change is its broad peak at 1050.9 cm^{-1} , which has disappeared and shifted to 950 cm^{-1} as a relatively sharp peak in 7-ER and to 954.5 cm^{-1} in G-105. The shifting of the band at this interval is attributed to Si–O–T asymmetric stretching vibrations. Its position and intensity changes carry vital information on the geopolymer development, especially the incorporation of Al, an observation which has also been reported by several researchers (Padmaja, Anilkumar, Mukundan, Aruldas, & Warriar, 2001; Rees, Provis, Lukey, & van Deventer, 2007).

As the bond length of Al–O is longer than that of Si–O, a smaller bonding force is initially required when more Al substitutes for Si^{4+} in the networks, leading to a reduction in the T–O–T bond angle and, correspondingly, the Si–O–T bond shifts to a lower frequency. As Al participation slows down, a higher degree of silica participation continues under hydrothermal conditions, resulting in more cross-linkages and an increment in the T–O–T bond angle and hence, a back shift to a higher frequency in the IR spectra was observed. This phenomenon (shifting to a lower frequency and

then to a slightly higher frequency) demonstrates a higher degree of geopolymerization, which is an important characteristic contributing to the increase in mechanical strength (Criado, M., Fernández-Jiménez, A., & Palomo, A. 2010; Fernández-Jiménez, Pastor, Martín, & Palomo, 2010). This vibration band, which has its maximum absorbance point depicted in the region 900–1200 cm^{-1} , varies with different Si to Al ratios and Ca content in the geopolymers. It was found that this band appears at a lower frequency at around 950–960 cm^{-1} in a pure synthetic aluminosilicate gel system with a high Ca content (CaO to SiO_2 ratio of 3.2 and SiO_2 to Al_2O_3 ratio of 2), in which its main precipitation is C–A–S–H, including C–S–H, whereas in those synthetic gels with low Ca contents (CaO to SiO_2 ratio of 0.24 and SiO_2 to Al_2O_3 ratio of 3), the aforementioned band has been observed in the higher frequency of 1020–1065 cm^{-1} , in which the main precipitation is from N–A–S–H (García-Lodeiro, Palomo, Fernández-Jiménez, & Macphée, 2011).

According to this observation, the amorphous gel in 7-ER and G-105 is more likely to be calcium aluminosilicate gel instead of sodium aluminosilicate gel and instead of C–S–H. However, this observation of the ternary system is based on pure synthetic gels using sol–gel method, and it may not represent the actual geopolymeric product. As a matter of fact, it was reported that in successful Na geopolymers with proven rigidity in water, 950–995 cm^{-1} is the shift range of the Si–O–T band. In addition, this range is largely dependent on the silica content in the activators (Rees, Provis, Lukey, & van Deventer, 2007).

Figure 1. IR spectra of geopolymers at various stages.

In fact, the possibility of finding C-S-H in the geopolymers synthesized in this research is little. This is supported by the fact that G-1050 maintained its structural integrity instead of spalling and that igneous-rock minerals were formed after extremely high temperatures. This bears similarities with most of Na geopolymers upon heating. Although the existence of C-S-H has been found together with geopolymer gel in the metakaolin and blast furnace slag systems (Yip, Lukey, Provis, & van Deventer, 2008; Yip, Lukey, & Van Deventer, 2005), those geopolymers were not subjected to extreme temperatures. Furthermore, if C-S-H is present in G-105, the structural water would also have a strong O-H stretching band at 3360 cm^{-1} and a deformation band at 1641.6 cm^{-1} . Yet both of these bands were nearly absent. So questions such as: is there any evidence suggesting the existence of N-A-S-H, and what are the peaks related to water and hydroxyl groups do arise. These questions will be discussed at length in the subsection below.

3.2 OH environments at various stages of geopolymerization

The IR spectra of the geopolymers at various stages are given in Figure 2. Peaks at 3357 cm^{-1} in 7-ER spectrum and 3360 cm^{-1} in 7-ER-E spectrum are related to the O-H stretching band in water. This vibration band is observed as a very strong peak in the spectrum of distilled water at 3315 cm^{-1} , the intensity and range of which is much stronger and wider than those in 7-ER and 7-ER-E. Peaks at 1641 cm^{-1} in 7-ER spectrum and 1642 cm^{-1} in 7-ER-E spectrum are associated with the O-H deformation band, which gives a sharp medium-range peak at 1637 cm^{-1} in the spectrum of water. The shoulder at 1042 cm^{-1} in

7-ER-E is the C-C-O stretching band due to ethanol residue. In addition, compared with the IR spectrum of 7-ER-E, the intensity of those bands related to water seems to be stronger in 7-ER. Other than that, the IR spectra of 7-ER and 7-ER-E are similar. In terms of IR, ethanol-quenched sample seems to be drier than the sample placed in the oven, but leaves ethanol residue inside the sample.

Besides the aforementioned two regions, structural water has an additional infrared active region in the wavelength range $600\text{--}300\text{ cm}^{-1}$, which is out of range for this mid-IR equipment (George, 2001). Therefore, it is not completely certain whether the OH vibration band of water detected in the 7-ER samples is composed entirely of free moisture or contains a certain amount of structural water. However, the signals at 3357 and 1642 cm^{-1} in G-105 are not clearly resolved and are almost absent. This suggests that even if water is trapped within the lattice of geopolymers, it can only be a small amount, which may interact with the metal ions (Al^{3+} and Na^+).

The peaks at 3669 cm^{-1} in 7-ER-E and 3668 cm^{-1} in 7-ER are ascribed to terminal OH species in which hydrogen bonding could be partially involved, while the peak at 3521 cm^{-1} in G-105 is the stretching mode of intermolecular hydrogen-bonded OH groups (George, 2001). This information suggests that there is a certain amount of terminal OH species forming H-O- dimmers or polymer. Hydroxyl species, which originate from alkalies and water, are more likely to attach to the surface of produced gel as terminal OH species and in covalent bond with Al atoms.

It is known that cement products, such as C-S-H, tobermorite, and jennite, have several peaks present in

Figure 2. IR spectra of 7-ER, 7-ER-E, and water.

the OH stretching region ($2800\text{--}3750\text{ cm}^{-1}$) in the mid-IR spectra. This reveals important information on the OH environments and hydrogen bonding, especially in relation with Ca and Si ions. On a closer look at Figure 2, there seems to be some small shoulder peaks around $3500\text{--}3700\text{ cm}^{-1}$ region in 7-ER and 7-ER-E sample, and are less obvious in G-105 sample. Despite the ambiguity about the existence of structural water in geopolymers, it is more likely that the sodium ions tend to interact with the water residing in the pores (Rowles, Hanna, Pike, Smith, & O'Connor, 2007). Therefore, if 7-ER and 7-ER-E are heated for a short period of time, e.g., heated at 100°C for 30 min, changes of OH stretching vibrations relating to sodium or calcium ions in the pore solution or even in the C-A-S-H, if it exists, can be observed. In addition, these changes can be differentiated from bands attributable to a developed framework in G-105, which is made from heating 7-ER sample at 105°C for 24 h.

The small shoulders, which are centered at 3675 and 3669 cm^{-1} have the strongest intensities in 7-ER. The intensity decreases in the order of 7-ER-E and 7-ERD, and is nearly absent in G-105 and 7-ER-ED. This means that both heat and ethanol affect the appearance of the regions and intensity of these OH stretching vibrations, and, evidently heat has greater ability of eliminating these OH groups because these two peaks are still evident in 7-ER-E but much weaker in 7-ERD. Further, the fact that Al ... O-H stretching has also been observed in the same region (Kubicki, Sykes, & Rossman, 1993) suggests that these vibrations are probably contributed to hydrogen bond of Al-OH and sodium ions that are in the pore solution. These two peaks are unlikely to be Ca-OH correlated [the OH groups in $\text{Ca}(\text{OH})_2$ are not considered to be hydrogen bonded], as cement product, such as tobermorite, calcium aluminosilicate, and jennite, seem to have OH stretching band in a lower region ($3624\text{--}3100\text{ cm}^{-1}$) (Yu, Kirkpatrick, Poe, McMillan, & Cong, 1999). In addition, jennite has several distinctive narrow OH bands in this region with well-defined hydrogen bond distance (around $3.10\text{--}2.83\text{ \AA}$). It also has a broad band centered at 3140 cm^{-1} due to the interlayer and surface adsorbed water (Yu, Kirkpatrick, Poe, McMillan, & Cong, 1999).

On the other hand, the similar intensity decreasing order observed at 3623 and 3520 cm^{-1} is more likely to be Ca-OH correlated as it is also observed in jennite (Yu et al., 1999). It has a smaller O-H ... O distance ($3.137\text{ \AA}$) than that in sodium-correlated OH stretching, attributed to the substitutions of cation that is bonded to an OH group, which can cause a shift in the frequency by a magnitude of 100 cm^{-1} in aluminosilicates (Kubicki, Sykes, & Rossman, 1993). The aforementioned regions are probably a result of the hydrogen bonds in the structures, such as

$\text{Na}^+(\text{OH})_2\text{ Al-O-Si}$, in geopolymers' pore solution, as they are very weak and nearly absent in samples that are dried using heat, such as 7-ERD, 7-ER-ED, and G-105. When the geopolymers have sufficient pore solution or accessible hydroxyl groups, some Na and Ca cations in the cavities tend to associate with Al anions as a charge compensator and get to be surface bound to the matrix, in the form of $\text{M}^{n+}\text{-Al-(OH)}_3$ (M^{n+} stands for cations with n number of positive charges) (Bouyer, Geneste, Ispas, Kob, & Ganster, 2010; Rowles, Hanna, Pike, Smith, & O'Connor, 2007). On the other hand, some of these cations tend to associate with the non-bridging oxygen of the framework's siliceous part and form $\text{Si-O}^- \dots \text{M}^{n+}$, in which they act as the network modifier and become incorporated in the matrix. In this situation, the monovalent cations fully meet the requirement, which is balancing the negative monovalent charge² of Al, while divalent ions, such as Ca^{2+} , meet it only partially. This could also explain the fact that Ca-containing minerals appeared in 7-ER and G-105, but were absent in any Na-containing minerals. This is because in terms of the ability of getting incorporated in the geopolymer matrix, Ca cations are weaker competitors than Na cations (Fang & Kayali, 2013). When the pore solution is reduced, such as in the case of G-105, the cations that are surface bound tend to associate with the siliceous part of the framework. Also, the small absorption band at 3643 cm^{-1} in G-105, which is nearly absent in the other samples, suggests its association with Si-OH and is indicative of a more developed network.

When heat is applied to geopolymers during curing stages, moderate temperatures are adopted ($40\text{--}80^\circ\text{C}$), and part of the adsorbed water is still retained; thus, some researchers have characterized the structure of a geopolymer as N-A-S-H (Yu et al., 1999). However, when the temperature exceeds a certain threshold, the water that appears to be incorporated in the structure escapes and leaves little structural water in the matrix. This may explain the phenomenon that sample G-1050 maintains its shape when the temperature reaches 1500°C instead of spalling such as most ordinary hardened Portland cement paste. The threshold of the temperature needs to be further investigated using TGA-DSC, which will be explored in further research.

² The statement that Al bears a negative charge is used in a particular structure – sialate (silicon-oxo-aluminate). A sialate consists of SiO_4 and AlO_4 linked alternately by sharing all oxygen atoms. In order to satisfy the octet rule, in this particular structure unit, Si can be either an electron donator or a receiver while oxygen an electron receiver, and thus, Al is an electron donator in acidic medium and receptor in alkaline medium (Davidovits, 2008). Therefore, the notion of "negative Al" or "negatively charged Al" is often used in the geopolymer terminology.

4. CONCLUSIONS

1. This research has explored the role of water and micro-structure of class F fly ash-based geopolymers activated by Na_2CO_3 and $\text{Ca}(\text{OH})_2$. The main backbone structure, the Si–O–T bond, shifted to a higher frequency and later shifted back to a lower frequency in the region $950\text{--}960\text{ cm}^{-1}$, in the mid-IR spectra. This indicated that two different stages are involved in the geopolymerization process: initially, more Al substitutes for Si^{4+} in the networks and, later, as Al participation slows down, a higher degree of silica participation continues under hydrothermal conditions, resulting in more cross-linkages. The position of this principal band and other obtained data further suggests that the produced geopolymers do not comprise C–S–H and probably not C–A–S–H.
2. The OH stretching vibrations, which are not related to free water, exhibit changes in the region $3520\text{--}3675\text{ cm}^{-1}$. This provides information on the state of cations in geopolymers. The fact that these bands are sensitive to heat (105°C) and exhibit differences between ethanol-quenched and desiccator vacuum-pumped samples suggests the association of sodium and calcium cations with terminal hydroxyl groups or water that most likely reside in the pores. This indicates that some amounts of the water are adsorbed water and surface bound. Furthermore, some of the metal cations are not able to be incorporated in the three dimensional matrix to coordinate with Al.
3. The evidence obtained from IR is not adequate to prove the existence of structural water, and the assumption that the main product of Na-geopolymer is N–A–S–H is not favoured. Even if there is structural water, it must be a small amount and is not easy to be detected, as the produced geopolymers still maintained its structural integrity and even gained strength after firing at 1050°C . If there is structural water in the matrix, the amount must be very small so that its evaporation pathway in the pores would not compromise its mechanical strength.

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