Evolution of geopolymer binders: a review

M F Nuruddin1, A B Malkawi1,2, A Fauzi1,3, B S Mohammed1, H M Almattarneh2

1Civil and Environmental Engineering Department, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia
2Civil Engineering Department, Najran University, 11001 Najran, Saudi Arabia
3Civil Engineering Department, Politeknik Negeri Lhokseumawe, 24301 Lhokseumawe, Aceh, Indonesia
E-mail: fadhilnuruddin@petronas.com.my

Abstract. This study aimed to present the current state of research about the terminology, chemical reactions, mechanisms, and microstructure modelling of geopolymer binders. Modelling the structure of the geopolymerization products is essential for controlling the product properties. The currently available models have shown some limitations in determining the rate of geopolymerization and setting time of the gel. There is a need for deeper knowledge regarding the physicochemical analysis of geopolymer binders. Most of the available models have used pure material like metakaolin; however, the less pure materials are expected to have different mechanisms. The FTIR and MAS-NMR analysis are considered as effective tools in providing information on the molecular deviations during geopolymerization. However, XRD analysis is not effective because most of the changes take place in amorphous phases. Also, the role of the iron oxides and some of the other impurities still not clear where none of the previous method of investigation can be used to detect the molecular changes of the iron compounds. This issue is very relevant hence the iron oxides are existed in substantial amounts in most of the waste materials that are suitable to be used as geopolymer source materials.

1. Introduction
The concrete industry is critical to the world economy with a share of 3.97US$ trillion of the global economy [1]. This industry, mainly based on the cement as a binding material with a worldwide production of 3.57 trillion tons [2]. Thus, concrete is next to water of the most used commodity worldwide. The huge consumption of concrete and cement have significant effects on the global environment; this is because of the enormous amount of energy needed for the quarrying and calcination of clinker, which is basically generated by fuel combustion. The cement industry is considered to be responsible for 5-8% of the global CO2 emissions [3]. The global warming issues and the increasing demand in addition to the sustainability issues, create an urgent need to search for new materials.

Geopolymer binders are green materials that have the potential to replace cement in the construction industry. Geopolymer binders are based on the utilization of waste materials such as fly ash (FA), granulated blast furnace slag (GBFS), rice husk ash and red mud. In fact, any material that mainly consists of aluminosilicate can be used as a base material for geopolymer binder production.
The use of such binder can reduce the carbon dioxide emissions by 80-90% compared to ordinary Portland cement (OPC) cement [4]. Geopolymer binders, display a wide range of properties that are superior to the cement and can be used to produce concrete with superior properties in term of strength and durability [5].

Implementation of geopolymers in the construction industry is still limited, currently, it is used by a few concrete companies mostly in Australia such as WAGNERS and Zeobond. The main hurdles facing the widespread of this material may include; the shortage of the information regarding its long-term behavior, in addition to the absence of the standards that control the use of such new technology. The markets will remain unwilling to take such a risk until the regulations of the carbon tax become actually implemented.

2. Geopolymer binders

Geopolymer binders are inorganic materials that can develop binding characteristics formed by the alkali activation of an aluminosilicate precursor. This binder buildup of a three-dimensional network, in which the aluminate and silicate species are covalently bonded by co-sharing of oxygen atoms. Elevated temperature sometimes is required to activate the aluminosilicate precursor particles; however, from a terminological point of view, this material should be hardened at the ambient temperature so we can call it geopolymer cement, else, it should be called geopolymer binders [6].

Geopolymer cement considered as a good alternative to OPC in the construction applications, pavement infrastructure applications, and offshore applications [7]. Geopolymer cement production requires mainly two components; the first is the source material, which can be any material that mainly composed of the alumina and silicate species. The second is the alkali-activating solution, which may be composed of any alkali silicate, hydroxide, carbonate, sulfate and thereof mixture. Sodium silicate or potassium silicate solutions are the most used solutions [8]. It is worth mentioned that the alkali solution should be user-friendly, and can be easily used in the field and mass applications. Using of strong alkali solution is unacceptable for geopolymer cement, and this can be user-hostile, and requires a special preparation for using in site and for the mass applications.

It should be differentiated between alkali-activated materials (AAM) and geopolymers. Many researchers got confused between them. Geopolymers are not alkali activated materials nor geopolymerization is the same as the alkali activation [9]. Geopolymer cement is based on the use of friendly alkali solution, which is usually sodium, or potassium silicates dissolved in water and can be produced at ambient temperatures. However, alkali-activated materials usually use strong activators and requires heat curing. Geopolymerization process should produce a stable durable product; however, alkali activation usually produces unstable products, where the alkali remains free and out of the structure, and can be easily leached out.

2.1. Geopolymer formation mechanism

Geopolymer binder has different formation mechanism compared to the known OPC reactions. The reaction processes in geopolymer binders are known as the geopolymerization reactions which mainly involve three processes; the first process is the dissolution processes where the alkali solution dissolves the aluminosilicate precursors to liberate the aluminum and silicon species in the mixture. These dissolved species, hydrolyze and deprotonated to produce the aluminate and silicate monomers \([\text{Al(OH)}_3^-]\) and \([\text{Si(OH)}_4^-]\), respectively. The second process is the condensation processes, where the aluminate and the silicate monomers adjoining together by co-sharing of the oxygen atoms to produce oligomers and form larger networks. During this process, the water that was consumed during the hydrolysis processes expelled out of the structure. The last stage occurs when the mixture become oversaturated with the aluminosilicate gel (which is initially rich with Al bonds). More silicates are dissolved to the mixture, where the rearrangement processes occur and more silicates are introduced to the aluminosilicate gel. This increases the connectivity of the network and the geopolymer gel starts to harden [10, 11]. These processes are described in Figure 1(a). Geopolymerization processes are controlled by several factors that mainly specify the dissolution rate. The main factors that affect this
rate include; the amount of reactive phase in the source material, source material particle size, the alkalinity of the mixture, curing temperature, and the amount of the liquefied silicate that may be provided by the alkali solution [12, 13].

Fernández-Jiménez et al. [14] gave more details in their model for the FA geopolymerization. This model has assumed that most of the FA particles are composed of hollow spheres that have a crust housed additional smaller FA particles inside of it. They assumed that the alkali solution starts to dissolve the FA particle at one point, where the particle crust eroded forming a hole and then the solution enter inside the particle and the reactions start in the both directions from outside and inside also the inner particles start to react. The reaction products start filling the space and deposed on the surface of the unreacted FA particles, which prevents further reactions and the processes slowdown and become controlled by the diffusion process.

Provis [11] has proposed a detailed model for the geopolymerization of metakaolin (MK) and FA. This model includes more details regarding the silicate oligomers, which might be incorporated into the alkali solution. These oligomers, have been divided into two phases; amorphous phase and nanocrystalline phases, depending on the Si/Al ratio. Also, another reaction pathway was introduced for the direct formation of the aluminosilicate gel in addition to the zeolite phase. This sequence of geopolymerization reactions is shown in Figure 1(b).

2.2. Geopolymer chemical structure

The chemical structure of geopolymers is mainly described as a phase of aluminosilicate gel, which composed of covalently bonded aluminate and silicate 3D-tetrahedral units that sharing oxygen atoms. The negative charge of the aluminate groups is balanced by joining the alkali cations [15].

According to Davidovits [4], geopolymers has been described by the structural formula Mnz-(SiO2)x-Al2O3y·wH2O where M represents any alkali cations, z is 1, 2, 3, w is the number of water molecules, and n represents the degree of polycondensation. Based on the Si/Al ratio, three different types of monomeric -Si-O-Al- structure are believed to define geopolymers [16]. The basic monomer unit is the poly-sialate unit, where Si/Al=1 [-Si–O–Al–O]. When the Si/Al=2 it is called poly(sialate-siloxo) which contains two Si atoms [-Si–O–Al–O–Si–O–], and when the Si/Al=3 it contains three Si atoms [-Si–O–Al–O–Si–O–Si–O–].

Many attempts were tried to draw the 3D geopolymer structure schematic diagrams. This type of efforts will probably be apprehensive with difficulty, because of the disordered nature of the geopolymer along with the difficulty involving perfectly representing a 3D framework in 2D representation. Figure 2(a) shows Davidovits’s model [4] for geopolymer structure based on MK as a source material using the poly(sialate-siloxo) monomers as a base unit. This model has assumed a bulk
polymer, which was similar to the organic polymers. However, this model did not account for the presence of water. Barbosa et al., [17] have proposed a new model. They have assumed that the geopolymers are similar to vitreous bodies like aluminosilicate glass. Both geopolymers and aluminosilicate glasses have similar 3D structure organization, nonetheless, aluminosilicate glasses structures do not contain any water and it exists without pores. A representative model of the proposed structure is shown in Figure 2(b).

![Figure 2](image_url)

**Figure. 2. Geopolymer structure (a) Davitovits’s model [4], (b) Barbosa et al.’s, model [17].**

### 3. Geopolymers microstructure

Geopolymer microstructure is mainly composed of three phases that include; the geopolymer aluminosilicates gel phase, which is considered as the main phase of geopolymers, the unreacted particles and incompletely reacted particles phase, and the pore water phase [4, 11]. Figure 3 (A-D) shows the scanning electron microscopy (SEM) for FA based geopolymer. These micrographs show that the main composition of the FA based geopolymer is the aluminosilicate gel (points 4 and 5) also, we can see big amounts of unreacted and incompletely reacted rounded FA particles (points 2 and 3, respectively). The fly ash morphology seems to consist of spherical particles of different size in the range from 10 to 200 micrometer, most of these spheres are solid and also hollow spheres are existed (point 3 in Figure3a). This figure also shows the creation of new crystalline phase, which is similar to the zeolite crystals and this phase may be considered as the last stage of the geopolymerization processes. However, some of these crystals initially existed as a composition of the source materials, which may originally contain quartz and hematite as a crystalline phase; these crystals are represented by the points 6, 7, and 8 in Figure 3(B&D).

Figure 3(C) shows some of the FA particles that are incompletely covered by the reaction products, which indicates the incomplete or weaker geopolymerization processes. This figure also presents the variation in the FA reactivity, which suggests the variability in the properties of the FA particles or the partial or inadequate exposure of the FA particles to the geopolymerization reactions. Hence, it will be difficult to predict the degree of geopolymerization in the case of using the FA as a geopolymer source material.

Comparing to MK-based geopolymer, the MK-based geopolymer displays a more homogenous microstructure with less amount of the unreacted or incompletely reacted phase. This may refer to the higher reactivity of the MK material. In contrary, FA-based geopolymer displays a less homogenous microstructure, where a large amount of the unreacted particles are present. These particles are joining together by the reaction products [18]. Figure 3(E) and Figure 3(F) display the microstructure of MK and FA-based geopolymers, respectively. It should be stressed that the reaction degree is mainly reliant on the morphology of the source materials. The MK particles composed of alumina and silica in the form of layered sheets. Compared to the FA particles which are spherical in shape, the dissolution reaction of the MK particles will peel off the surface layers; while, for the rounded FA
particles the dissolution reaction products will deposit on the outer surface. This will expose additional layers of the MK particles to the reactions and the reaction will continue; however, for the FA particles the precipitated products will encapsulate the surface of the particles and prevent further dissolution where the reaction will become diffusion controlled and this will slow down the reaction rates and more particles will remain unreacted or partially reacted.

Figure 3: SEM micrographs of FA and MK-based geopolymers [11].

4. Geopolymer scientific means of investigation

The high resolution nuclear magnetic resonance (NMR) is considered as one of the powerful tools that may provide useful structural data. The NMR analysis of the geopolymer products ensures the Si(IV) and Al (IV) occurrence in geopolymers. The $^{27}$Al MAS NMR analysis of MK-based geopolymers shows the presence of Al (IV) (around 60 ppm), the Al(VI) and Al(V) phases that was originally available in the MK particles has converted to the Al(IV) sites and the alkali cations has become connected to balance the charge. However, the Al(VI) (around 0 ppm) has detected in small amounts which indicate the presence of unreacted metakaolin particles but not the formation of new Al(VI) as a reaction product. The $^{29}$Si MAS NMR analysis of MK shows a broad resonance in the range 80-100 ppm and this depends on the Si/Al ratio, however, this resonance mainly associated with the presence of Si(IV) and the presence of silicate in amorphous structure. Nonetheless, the use of the deconvolution method has allowed relating the featureless silicate resonance to the Q$^4$(mAl) centers that contain the aluminosilicate framework [19, 20]. Similar results were reported in [21] for the $^{29}$Si MAS NMR of the FA-based geopolymers which showed main shifts of -97 ppm and -89 ppm that was related to the Si(IV)(2-3Al) and Al(IV)(4Si), respectively. The shift of -107 ppm which related to Si(IV)(0Al) that form the main shift for the unreacted FA powder was less represented in the FA-based geopolymer, which indicates the penetration of the Al into the Si(IV) skeleton.

Comparing the MAS NMR of the $^{27}$Al and $^{29}$Si spectra for MK powder and MK-based geopolymer with the $^{27}$Al and $^{29}$Si spectra for fly ash and fly ash based geopolymer that are shown in Figure 4, we can see that the main difference between the unreacted materials is that the fly ash contains higher amount of the Al(IV) however, after reaction this wide peak become sharper and have higher structural order. For the $^{29}$Si spectra both metakaolin and fly ash geopolymers showed a broad resonance in the range 80-100 ppm, however, the sharper peaks were noted for the fly ash geopolymers which may be related to the presence of the crystalline originally provided by the unreacted materials like quartz [10, 23].
Powder X-ray diffraction (XRD) analysis depends on the diffraction angle which gives an indication about the interlayer spacing of the crystal structure. Since the similarity of diffraction patterns indicates the similarity of the crystal structure. Many researchers reported that the main structure of geopolymers is described to be amorphous phase and their X-ray diffractograms have main hunched around 27-29° 2θ and this description looks to be true in spite of the type of the source material, curing conditions, and alkali activation solution type [23, 24].

Comparing the XRD diffractograms for geopolymer binder produced based on low calcium fly ash with that for the original fly ash materials, it can be seen that the geopolymerization processes have insignificant effects on the crystalline phase originally available in the fly ash (quartz, mullite, magnetite, etc.). However, the peaks observed in the geopolymer binder diffractograms seems to sharpen and slightly shifted to higher values over the original fly ash; also, the proportion of the amorphous phases have been increased [14, 25]. For shorter curing duration (4 hours) and in geopolymer binder cured at ambient temperature, the detection of the newly crystalline phase may refer to the formation of Thermonatrite (Na2CO3.H2O) crystals [25]. However, this phase has disappeared when the samples cured for a longer duration (24 hours). This may attribute to the lower reaction rate which caused a higher concentration of remaining sodium hydroxide solution. The remaining sodium hydroxide will react with the carbon dioxide from the atmosphere which has resulted in forming of these new crystals.

A typical XRD micrograph is shown in Figure 5, this figure display the XRD patterns for unreacted fly ash and for geopolymer at different temperature, this figure displays several low and broad diffraction bands which indicate the presence of amorphous phases that may be combinations of the newly formed geopolymer gel and the remaining unreacted fly ash amorphous oxides.

Figure 5: X-ray analysis of FA and FA-based geopolymer cured at different temperature [26].
The Fourier transform infrared spectroscopy (FTIR) analysis also provides a good evaluation of the geopolymerization processes and the reaction products formation. The infrared spectrum of the FA powder shows main bands in the range 1080-1090 cm\(^{-1}\) which related to the Si-O and Al-O bonds vibration. This range shifts to lower values after the geopolymerization reactions usually in the range at 900-1000 cm\(^{-1}\) [21, 27]. This shift is related to the penetration of Al in the network of the Si-O-Si. The higher shift indicates the higher penetration into the Si(IV) network. Other bands may include bands in the range 450-470 cm\(^{-1}\) corresponds to the Si-O bonds vibration and the band 797 cm\(^{-1}\) corresponds to the Al-O bonds vibration. After geopolymerization reactions, it was noted that the band at 797 cm\(^{-1}\) was almost disappeared; this may be related to the consumption of the Al(IV). From the other hand, some of the new bands were reported in the range 3440-3450 cm\(^{-1}\) corresponds to the formation of H-O bonds, 1650 cm\(^{-1}\) corresponds to the formation of H-OH bonds, and in the range of 1450-1500 cm\(^{-1}\) corresponds to the formation of C-O bond as reaction products. The H-O and H-OH bonds may indicate the formation of water and the C-O bonds may indicate the formation of alkali carbonates as a result of the reaction with the carbon dioxide from the atmosphere [28, 29]. A typical FTIR spectrum is shown in Figure 6.

Figure 6: X-ray analysis of FA and FA-based geopolymer cured at different temperature [30].

5. Conclusions
Geopolymer cement is considered as a green building material, which can replace OPC in the concrete industry. Use of geopolymer binders can produce concretes with a wide range of properties. Until now, the geopolymerization model and mechanism are still not clearly understood. More research is needed to understand and control the properties of the produced geopolymers. Geopolymers and AAMs are different; geopolymerization reactions are known to produce a stable chemical structure, where the alkali cations are rigidly joined and not vulnerable to leaching. The geopolymer gel is composed of nanoparticles separated by nanopores, which produce a very tiny microporosity matrix that promotes the superior properties of geopolymers. The rounded shape of the FA particles plays an important role in increasing the mixture workability without additional amount of water, which reduce the product permeability. Also, the unreacted FA particles play the role of micro-aggregates, which increase the amounts of aggregates in the mixture and give higher stability. The \(^{29}\)Si and \(^{27}\)Al NMR spectroscopy is considered as an effective technique for rendering the data about the structural skeleton of geopolymer binders. Geopolymers are mainly structures of Al(IV)(4Si), Si(IV)(3Al), and Si(IV)(2-3Al) coordination. The Si(IV)(0Al) coordination that originally exist in the aluminosilicate precursor has a less representation after geopolymerization reactions, which confirms the penetration of the Al into the Si(IV) skeleton. The FTIR analysis shows the presence of water in the form of free water and it exists within the gel structure.
References

[1] United Nations: 2015 UN national accounts main aggregates database, http://unstats.un.org/unsd/snaama/dnllist.asp.

[2] U.S. Geological Survey: Mineral commodity summaries 2015: U.S. geological survey, pp. 196, http://dx.doi.org/10.3133/70140094.

[3] E. Benhelal, G. Zahedi, E. Shamsaei & A. Bahadori, 2013 Journal of cleaner production, vol. 51, pp. 142-161.

[4] J. Davidovits, 2011 Geopolymer chemistry and applications. Saint-Quentin, France.

[5] J. Davidovits, 2013 Technical paper#8, Geopolymer Institute, pp. 1-7.

[6] H. K. Tchakoute, C. H. Rüscher, J. N. Y. Djobo, B. B. D. Kenne & D. Njopwouo, 2015 Applied clay science journal, vol. 107, pp. 188-194.

[7] J. Davidovits, M. Izquierdo, X. Querol, D. Antennuci, H. Nugteren, V. Butselaar-Ortlieb, Y. Luna, 2014 Technical paper #22. Geopolymer Institute, pp. 1-11.

[8] D. Hardjito, C. C. Cheak & C. H. L. Ing, 2008 Modern applied science, vol. 2(4), pp. 3.

[9] J. Davidovits, 2014 geopolymer camp 2014, Saint Quentin, France.

[10] P. Duxson, A. Fernández-Jiménez, J. L. Provis, G. C. Lukey, A. Palomo & J. S. J. van Deventer, 2007 Journal of materials and science., vol. 42(9), pp. 917-933.

[11] J. L. Provis, 2006 Modelling the formation of geopolymers. (PhD), University of Melbourne.

[12] A. A. Adam & X. X. X Horianto, 2014 Procedia engineering, vol. 95, pp. 410-414.

[13] J. L. Provis, P. Duxson, E. Kavalerova, P. V. Krivenko, Z. Pan, F. Puertas & J. S. J. van Deventer, 2014 Alkali activated materials, vol. 13, pp. 11-57.

[14] A. Fernández-Jiménez, A. Palomo & M. Criado, 2005 Cement and concrete research, vol. 35, pp. 1204-1209.

[15] M. Kanuchova, L. Kozakova, M. Drabova, M. Sisol, A. Estokova, J. Kanuch & J. Skvarla, 2015 Environmental progress & sustainable energy, vol. 34(3), pp. 841-849.

[16] F. Škvára, 2007 International conference alkali activated materials--research, production and utilization, Česká rozvojová agentura, Praha.

[17] V. F. Barbosa, K. J. MacKenzie & C. Thaumaturgo, 2000 International journal of inorganic materials, vol. 2(4), pp. 309-317.

[18] Sindhunata, 2006 A conceptual model of geopolymerisation. (PhD), University of Melbourne.

[19] A. Favier, G. Habert, N. Roussel & J. B. d'Espinose de Lacaillerie, 2015 Cement and concrete research, vol. 75, pp. 104-109.

[20] M. Frias, S. Martínez-Ramírez, T. Blasco, M. F. Rodriguez & D. Viehland, 2013 Journal of the american ceramic society, vol. 96(7), pp. 2306-2310.

[21] F. Škvára, L. Kopecký, J. Nemecek & Z. Bittnar, 2006 Ceramics-Silikaty, vol. 50, pp. 208-215.

[22] P. S. Singh, T. Bastow & M. Trigg, 2005 Journal of materials science, vol. 40(15), pp. 3951-3961, 2005.

[23] S. A. Bernal, J. L. Provis, V. Rose, R. M. de Gutiérrez & J. Biernacki, 2013 Journal of the american ceramic society, vol. 96(6), pp. 1951-1957.

[24] T. Yang, X. Yao & Z. Zhang, 2014 Construction and building materials, vol. 69, pp. 109-115.

[25] J. Xie & O. Kayali, 2014 Construction and building materials, vol. 67, pp. 20-28.

[26] F. Winnefeld, A. Leemann, M. Lucuk, P. Svoboda & M. Neuroth, 2010 Construction and building materials, vol. 24(6), pp. 1086-1093.

[27] C. A. Casárez, S. P. Arredondo, J. M. Gómez, J. L. Alamaral, R. Corral, M. d. Chinchillas, et al., 2014 International journal of advances in computer science and its applications, vol. 4, pp. 221-226.

[28] I. Cătăinescu, M. Georgescu & A. Melinescu, 2012 U.P.B. Sci. Bull., Vol. 74(1), pp. 3-14.

[29] A. Allahverdi & E. N. Kani, 2009 International journal of civil engineering., vol. 7, pp. 154-160.

[30] M. M. Al Bakri, K. Hussin, M. Bhnussain, K. N. Ismail, Z. Yahya, & R. A. Razak, 2012 International journal of molecular sciences, vol. 13, pp. 7186-98.