

GEOPOLYMER SYNTHESIS FROM DEMOLISHED CONCRETE WASTES

Arvind Pathak¹ and Vinay Kumar Jha²

¹Department of Chemistry, Tri-Chandra Multiple Campus
Tribhuvan University, Kathmandu, Nepal

²Central Department of Chemistry, Tribhuvan University, Kirtipur, Kathmandu, Nepal
E-mail: ¹apathak2070@gmail.com, ²vinayj2@yahoo.com

Abstract: After the earthquake on April 25, 2015 and its aftershocks a total of 4,784 public and 531,266 private buildings were either destroyed or damaged. It generated large wastes that imposed economic burden and contributed to environmental pollution. The alumino-silicate found in such wastes can be used as raw material for the synthesis of geopolymers. Geopolymers have been synthesized from construction waste such as coal fly ash (CFA) and brick dust (BD) using alkali and alkali-silicate as activators. Geopolymerization can transform a wide range of waste alumino-silicate materials into building materials with excellent chemical and physical properties such as fire, acid and earthquake resistance. A maximum compressive strength of 2.21 MPa was obtained with concrete powder treated with 6 M NaOH solution and a maximum compressive strength of 45.4 MPa was obtained with 1.0 mass ratio of Na₂SiO₃ to construction wastes cured for 28 days at 40 °C. The compressive strength of geopolymers initially increases and then decreases with alkali concentration and varies inversely with the particle size.

Keywords: activator, compressive strength, construction waste, geopolymerization

Introduction

The term “geopolymers” was coined by Davidovits in 1972 to refer to the three-dimensional (3D) aluminosilicate that was formed at low temperature and short time by naturally occurring alumino-silicate (Davidovits & Orlinski, 1988). These polymers exhibit properties similar to many non-metallic materials including formability comparable to epoxies, high temperature stability and chemical resistance comparable to ceramic oxides and compressive strengths superior to concrete (Hos *et al.*, 2002).

Geopolymers are formed by activating aluminosilicates with alkaline or alkaline-silicate solutions at ambient or higher temperature. Geopolymerisation can be approximately partitioned into two periods: (I) dissolution-hydrolysis, (II) hydrolysis-polycondensation. However, these two steps occur simultaneously once the solid material mixed with liquid activator (Hongling *et al.*, 2005). The exact separation of these two steps from the point of view of thermodynamics (Zuhua *et al.*, 2009). When

alkaline silicate solutions were employed with higher concentration than used for zeolite synthesis, a hard amorphous product was formed by a condensation-like reaction during thermal setting (Hos *et al.*, 2002; Davidovits, 1991). The resulting inorganic polymeric material can be considered to be the amorphous equivalent of geological feldspars, but synthesized in a manner similar to thermosetting organic polymers. These materials have also been termed “geopolymers”, in recognition of being inorganic polymer analogues to conventional organic polymers (Hos *et al.*, 2002).

Over the last two decades, geopolymers, which are also known as mineral polymers or inorganic polymer glasses, have received much attention as a promising new form of inorganic polymer material that could be used as a substitute for conventional or ordinary Portland cement, plastics, and many other mineral-based products (Davidovits, 1991; Rahier *et al.*, 1996; Duxson *et al.*, 2007).

In alumino-silicate structures, silicon is always 4- coordinated, while aluminum ions can be 4- or 6- coordinated. It is possible that the co-ordination number of aluminum in the starting materials will have an effect on its eventual bonding in the matrix. A highly reactive intermediate gel phase is believed to form by the copolymerization of individual alumino- and silicate species. Little is known about the behavior of this gel phase and the extent to which the nature of the starting materials and the actual concentrations in solution are affecting the formation and setting of this gel phase (Xu & Deventer, 2000). The compressive strength of the coal fly ash based geopolymer has been reported to be 41.7 MPa (Pathak & Jha, 2012). Also, in other work, compressive strength of brick dust based geopolymer has been reported to be 11.43 MPa (Pathak *et al.*, 2014).

Recently in Nepal after Gorkha earthquake on April 25, 2015 and its aftershocks a total of 4,784 public and 531,266 private buildings were either destroyed or damaged. Such a large deposit of wastes imposes an economic burden and contributes to environmental pollution (ekantipur, 2015). By the use of geopolymerization technique, these wastes can be utilized to make valuable building material. The potential uses of geopolymers include: an alternate to cement, adhesives, aggregates, coating, composites, fibers and textiles, fluid containment, insulation, marine structures, refractories, soil stabilization, waste encapsulation *etc.* Environmental and economic benefits of using geopolymer materials are due to utilization of wastes from energy manufacture, 80% of which are not utilized and have to be land filled (Bakharev, 2005).

The main objective of the present work is to find out amicable solutions for the utilization of concrete waste as raw materials for the synthesis of cement-like products at ambient temperature.

Experimental methods

Sample preparation

The demolished concrete mixture used in this study was obtained from one demolished part of Central Library, Tribhuvan University, Kirtipur, Kathmandu. It was ground manually by using *Khal*, mortar and pestle to obtain a fine powder form. The powder was further modified through wet-milling by using iron balls (2 mm diameter) and distilled water in a plastic bottle and placed in a self-assembled machine to rotate at room temperature. The solid sample was separated from solution by filtration, washed with distilled water several times and then dried in an oven (N6c, Philip Harris, England) at 80°C overnight.

Preparation of concrete powder based geopolymer

To prepare concrete powder based geopolymer, several parameters such as NaOH concentration, particle size, amount of sodium silicate and curing time were taken into account.

- a) **Variation of NaOH concentration:** In the first case, the dried concrete powder sample was blended manually for 2 min with 2-8 M NaOH solution separately using mortar and pestle. The blended mixtures were separately placed in cuboidal plastic moulds (length × breadth × height: 2.5 cm × 2.5 cm × 1.5 cm), air bubbles were removed, sealed with thin plastic films and allowed to cure for 7 days in an oven at 40°C.
- b) **Variation of particle size:** In the second case, the dried concrete powder of particle size $\leq 53 \mu\text{m}$ – $\leq 120 \mu\text{m}$ was blended manually using mortar and pestle with 6 M NaOH solution. The blended mixtures were separately placed in cuboidal plastic moulds, sealed with thin plastic films and allowed to cure for 7 days in an oven at 40°C.
- c) **Variation of amount of sodium silicate:** In the third case, concrete powder was blended manually using mortar and pestle with a varying mass ratio of Na_2SiO_3

to construction waste between 0.50-2.00 while the concentration of NaOH solution was fixed to 6 M. The blended mixtures were separately placed in cuboidal plastic moulds, sealed with thin plastic films and dried in an oven at 40°C for 28 days.

- d) **Variation of curing time:** In the fourth case, a mixture of Na₂SiO₃ and concrete powder have mass ratio of 1.0 was blended manually with the 6 M NaOH solution using mortar and pestle. The blended mixtures were separately placed in cuboidal plastic moulds, sealed with thin plastic films and allowed to cure for 3-28 days in an oven at 40°C.

After curing, all the samples were de-moulded and cut into finite sizes. The area of the sample was measured prior to the strength measurement. From this step, variation of the compressive strength with curing time was performed and hence the appropriate curing time for optimum compressive strength was achieved.

The compressive strength of the prepared geopolymer was measured using SLF Load frame machine at Central Material Testing Laboratory, Institute of Engineering, Pulchowk Campus, Tribhuvan University. The raw sample and fragments from the crushing tests of few characteristic samples were powdered and examined by X-ray diffraction (Bruker, D8 Advance Diffractometer, Germany) at Central Department of Geology, Tribhuvan University, Kirtipur, Kathmandu. Morphological characterization of the fractured samples was carried out by scanning electron microscope (SEM 840, JEOL, Japan with a Kevex EDX attachment). Fourier transform infrared spectroscopy (Nicolet 5700 spectrometer, Thermo Electron Corporation, USA) was used for structural characterization of geopolymers. Samples for FTIR analysis were prepared by mixing the concrete powder with KBr.

Results and discussion

Chemical composition of waste

The chemical composition of the concrete powder is given in Table 1.

Table 1. *Chemical Composition (Mass %) of Milled Concrete Powder*

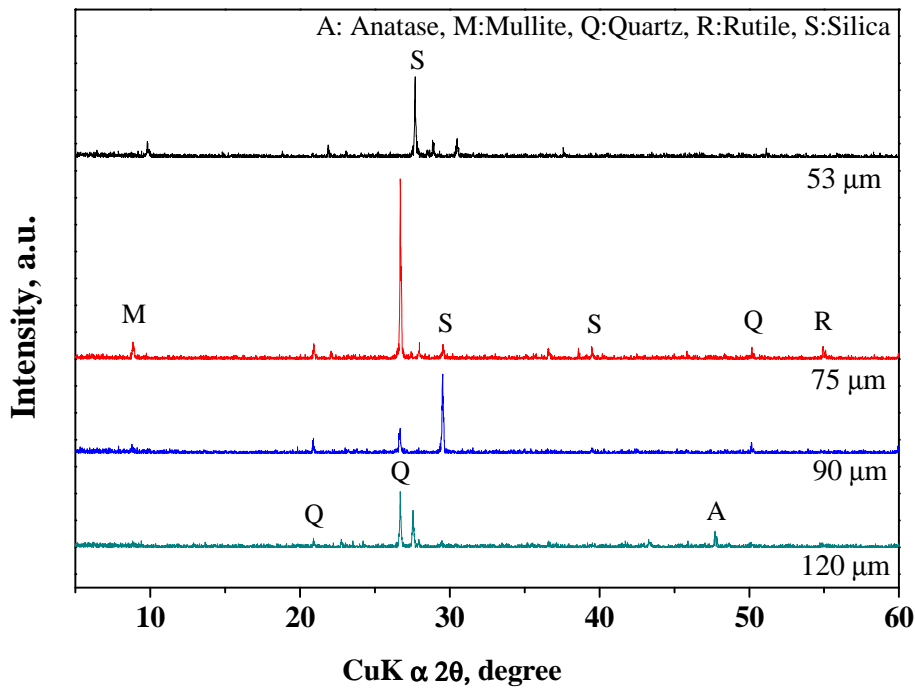
Radicals	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	K ₂ O	LOI*
Mass %	58.22	14.28	2.00	0.69	0.21	5.11	8.76

*Loss on ignition

Characterization of waste

The raw concrete powder was grounded and sieved, and different size portions of the powder were separated. The XRD patterns of raw concrete powder of various particle sizes (≤ 53 - ≤ 120 μm) were obtained and are shown in Figure 1.

Figure 1. XRD Patterns of Raw Concrete Powder of Different Particle Size 53-120 μm



The XRD patterns of the raw material of various sizes have shown the presence of mainly mullite, quartz, anatase, rutile, calcium carbonate and silica. The quartz peak ($2\theta = 26.69^\circ$) was sharpened in going from particle size 120 to 75 μm . The calcium carbonate peak ($2\theta = 29.53^\circ$) was sharpened in going from particle size 120 to 90 μm and then diminished by further decreasing the size of the particle. Several other peaks were diminished with decreasing particle size while a new peak at $2\theta = 27.68^\circ$ was appeared which was characterized as SiO_2 .

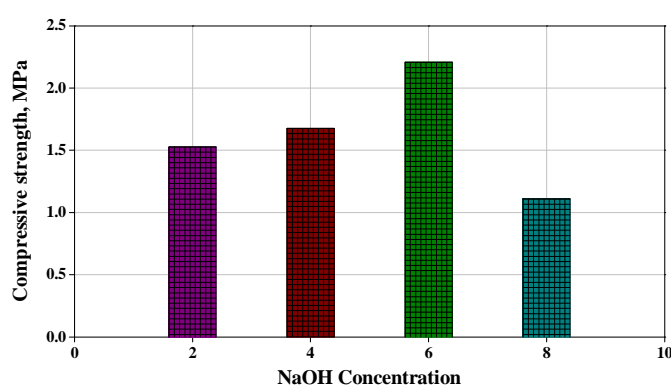
The diminishing of several XRD peaks and increase of the amorphous nature of the sample with reducing particle size attributed to the fact that the mechanical grinding increases the collision frequency which in turn leads to a faster diffusion process (Lü *et al.*, 1998).

Geopolymer products and their compressive strengths

Compressive Strength with NaOH Concentration Variation

For the synthesis of geopolymer from concrete waste, NaOH concentration varied from 2 to 8 M. The compressive strength was found to initially increase then decrease with increasing NaOH concentration (Figure 2).

Figure 2. *Variation of Compressive Strength of Geopolymer as a Function of NaOH Concentration*

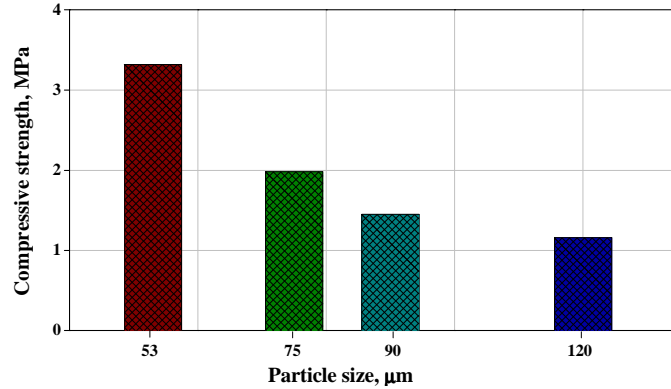


The increase in the compressive strength with increasing NaOH concentration was due to the fact that a higher amount of OH⁻ ions facilitate the dissolution of silicate and aluminate species and thus promotes polymerization (Komnitsas & Zaharaki, 2007). But under very high alkaline condition the connectivity of silicon anion may be reduced which causes aluminosilicate gel to precipitate at an early stage resulting in poor polymerization, i.e., NaOH molecule is incorporated between two geopolymer precursors which break the silicon anion connectivity thus preventing polymerization (Singh *et al.*, 2005). Further, the excess NaOH forms potassium carbonate by atmospheric carbonation (Barbosa *et al.*, 2000).

Variation of Compressive Strength with Particle Size

After the selection of NaOH concentration, the particle size of the raw material varied. The compressive strength of the geopolymeric products treated with 6 M NaOH solution with particle size variation (≤ 53 , ≤ 75 , ≤ 90 and ≤ 120 μm) were obtained (Figure 3).

Figure 3. Change of Compressive Strength with the Variation in Particle Size of Geopolymeric Products

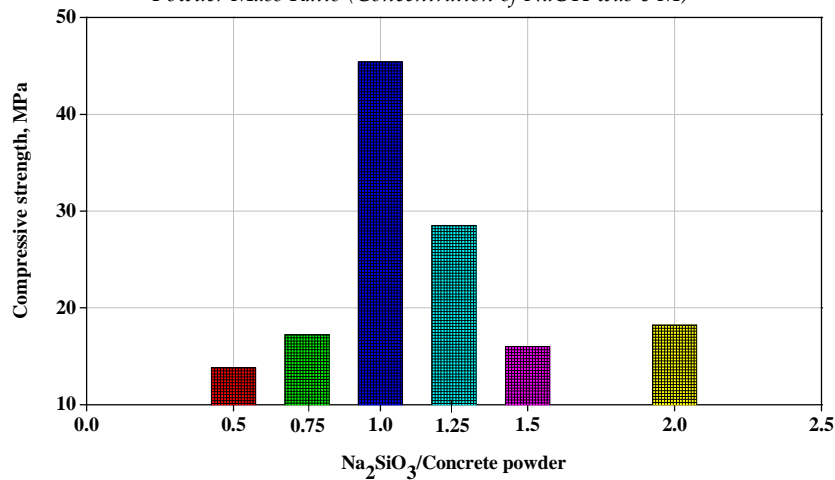


The compressive strength of geopolymer products were found to increase with decreasing particle size. It was already shown in the XRD patterns of the raw material with variation of particle that with decrease of particle size, the amorphous nature of the sample increased. This is a clear indication that an amorphous nature in the starting material is more preferable for geopolymers with better compressive strength. This can be attributed to the enhanced dissolution of alumino-silicate particulates from amorphous material and thereby accelerated condensation of the monomer in the presence of higher NaOH concentration. Furthermore, the process of geopolymerization involves dissolution, polymerization, condensation and hardening steps which are more favorable if the starting material is amorphous in nature.

Na₂SiO₃ to Concrete Powder Mass Ratio and Compressive Strength

The compressive strength of geopolymer products with variation of the mass ratio of Na₂SiO₃/concrete powder is shown in Figure 4.

Figure 4. The Compressive Strengths of Geopolymer Products with the Variation of Na₂SiO₃/Concrete Powder Mass Ratio (Concentration of NaOH was 6 M)



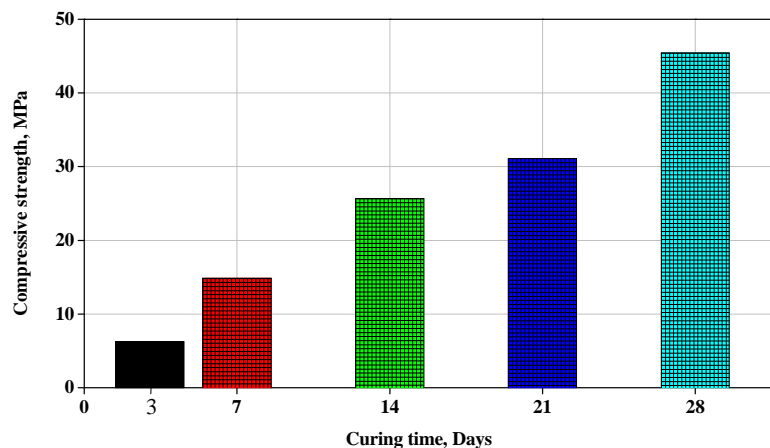
The compressive strength of geopolymers was found to increase initially and then decrease with an increase in mass ratio of Na_2SiO_3 /concrete powder with 6 M NaOH.

The amount of added sodium silicate plays a significant role on the final crushing strength of the geopolymer products. Sodium silicate solution contains self-polymerizing species (monomer, dimer and larger oligomer containing Si-O-Si chain) which influence soluble alumino-silicate units to polymerize (McCormick *et al.*, 1989; Wang *et al.*, 2005). The crushing strength was found to initially increase then decrease with increasing concrete powder to Na_2SiO_3 mass ratio. This is expected to be due to excess silicate which hinders water evaporation and structure formation (Chang & Chiu, 2003). A 1:1 mass ratio of concrete powder to Na_2SiO_3 was found suitable in terms of the crushing strength of the geopolymer product. Further increase of silicates concentration decreases the rate of geopolymerization reaction and the solidification of the paste takes prior to geopolymerization (Provis & Deventer, 2007a, b).

Compressive strength and curing time

Adequate curing is necessary to achieve advanced mechanical and durability performances. The presence of water and its removal by evaporation play a major role in obtaining crack-free geopolymers. Curing for long periods of time at relatively high temperatures has shown to weaken the structure as a small amount of water needs to be retained for the polymer to be crack-free and its structural integrity (Perera *et al.*, 2007). The curing time of the geopolymer products varied from 3 to 28 days at a temperature of 40°C. The samples were removed from the oven after the required time period and cut into the desired size. These samples were polished in 400 to 1500 waterproof papers. The compressive strength of each sample was measured. The compressive strength was found to increase with increasing curing time which is shown in Figure 5.

Figure 5. *Change of Compressive Strength of Geopolymer Product with Curing Time (Concentration of NaOH was 6 M and Na_2SiO_3 /Concrete Powder = 1)*

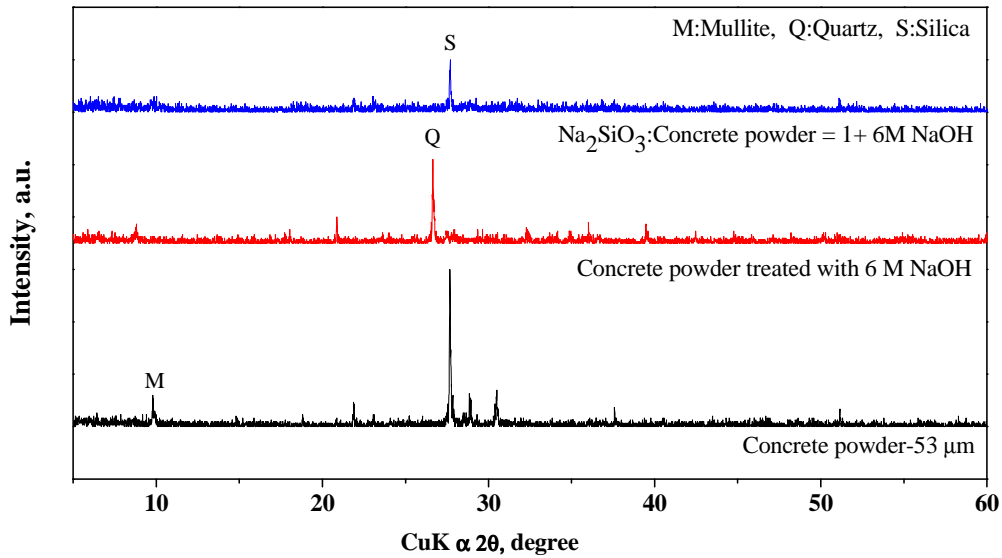


This is because at low temperature, condensation of geopolymer precursors and evaporation of the water molecules take place simultaneously preventing the formation of voids and cracks inside the material thus increasing the compressive strength (Perera *et al.*, 2007). This suggests that curing for longer time period at low temperature is preferable for the synthesis of geopolymers having higher compressive strength.

Characterization of geopolymer products

The XRD patterns of starting raw material ($\leq 53 \mu\text{m}$), starting material treated with 6 M NaOH solution and mixture of equal masses of starting raw material, raw material treated with 6 M NaOH and Na_2SiO_3 : raw material = 1 with 6 M NaOH are shown in Figure 6.

Figure 6. The XRD Patterns of Starting Raw Material and Its Geopolymeric Products

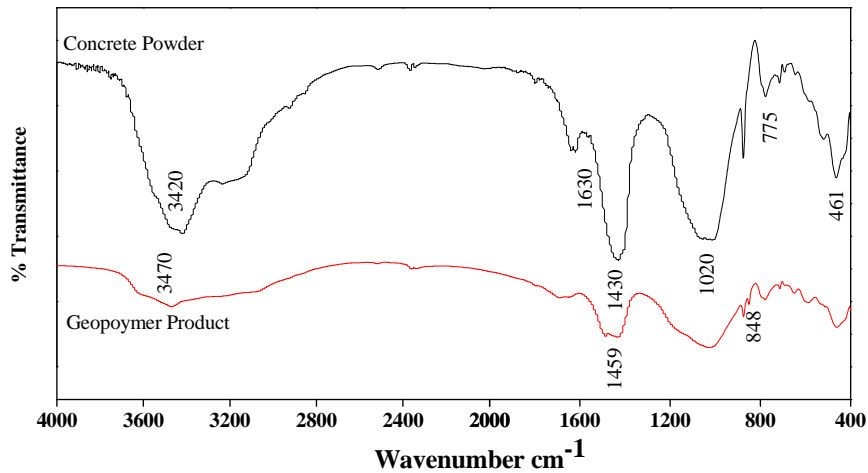


The diminishing XRD peaks of the raw material after the application of NaOH and sodium silicate is due to the dissolution of aluminosilicate and the formation of geopolymeric products. The sodium hydroxide and sodium silicate act as binders during the process of geopolymerization.

FTIR analysis of geopolymer products

The FTIR spectra of concrete powder and its geopolymer product are shown in Figure 7.

Figure 7. FTIR Spectra of Concrete Powder and Its Geopolymer Product

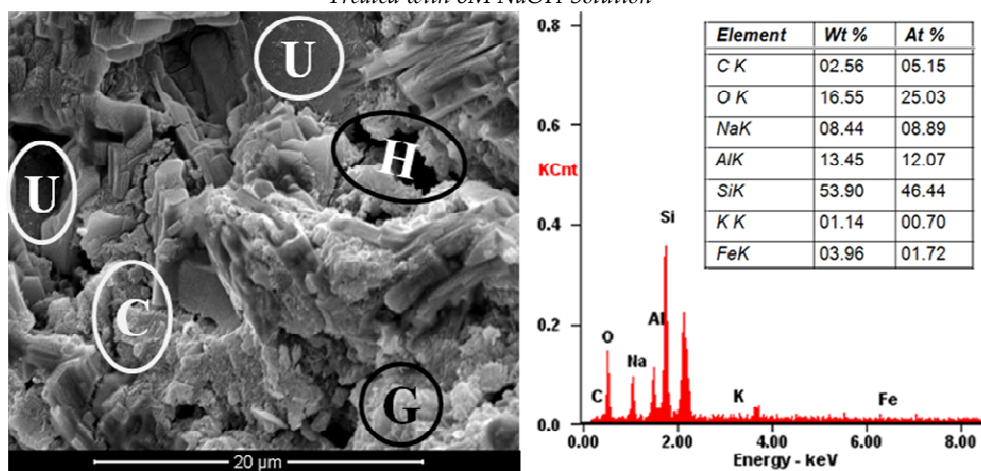


The band at 461 cm^{-1} was due to the presence of Al-O/Si-O. The band at 775 cm^{-1} may be due to the octahedral Al-O stretching mode getting widened, and a new band appeared at 848 cm^{-1} . The Si-O stretching band around 1020 cm^{-1} shifts to lower wavenumber which may be due to the substitution of trivalent ions into a tetrahedral position in a silicate network (Kumar & Kumar, 2011). The large band centered at 1459 cm^{-1} may be due to the presence of Na_2CO_3 or carbonation (Yousuf *et al.*, 1993).

SEM-EDX analysis of geopolymer products

The SEM-EDX of geopolymer synthesized from concrete powder: $\text{Na}_2\text{SiO}_3 = 1$ treated 6M NaOH solution is shown in Figure 8.

Figure 8. SEM-EDX Images of Geopolymer Product Synthesized from Concrete Powder: $\text{Na}_2\text{SiO}_3 = 1$ Treated with 6M NaOH Solution



SEM-EDX analysis showed that the morphology of the obtained geopolymer product having a slightly lower Si/Al ratio of 4.01 was of a tabular gel type, shown as G. This is probably due to the nucleation of the aluminosilicate matrix. In comparison, a higher portion remained unreactive, indicated by U. Also, the morphology shows the product is compact with some crack developed, indicated by C, and some void, shown by the dark spot (H). The average molar ratio by weight of seven different selected point analysis of the geopolymer product was found as: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 6.85$, $\text{SiO}_2/\text{Na}_2\text{O} = 1.59$, $\text{SiO}_2/\text{M}_2\text{O} = 1.46$, $\text{Si}/\text{Na} = 2.00$, $\text{Si}/\text{M} = 1.66$, $\text{Al}/\text{Na} = 0.33$.

Conclusions

The geopolymers were synthesized from concrete powder by varying concentration of NaOH, amount of Na_2SiO_3 and curing time. The compressive strength was found to initially increase then decrease with increasing NaOH concentration. A maximum compressive strength of 2.208 MPa was obtained with concrete powder treated with 6 M NaOH solution. With variation in amount of sodium silicate, the compressive strength increased initially and then decreased with a higher concentration of sodium silicate. A maximum compressive strength of 45.4 MPa was obtained with 1.0 mass ratio of Na_2SiO_3 to concrete powder. It was due to the compact nature of binding and geopolymerization reaction characterized by FTIR and SEM-EDX analysis.

The compressive strength was found to increase with increasing curing time suggesting that curing for longer period of time at low temperature is preferable for the synthesis of geopolymers having higher compressive strength.

Acknowledgements

The authors are thankful to Nepal Academy of Science and Technology (NAST) for offering the support on geopolymer synthesis. We would like to acknowledge Mr. Siddhartha Shanker, Head of Central Material Testing Laboratory, Institute of Engineering Pulchowk Campus, Tribhuvan University, Pulchowk, Lalitpur for helping to measure the compressive strength of the synthesized geopolymer and Prof. Dr. Lalu Prasad Paudel, Head of the Central Department of Geology, Tribhuvan University, Kirtipur, Kathmandu for his valuable help in X-Ray diffraction measurement of samples. Thanks to Dr. Santanu Bhattacharjee, Dr. Swapan Kumar Das and Dr. S. K. Tiwari, CSIR-NML Jamshedpur for chemical analysis, SEM-EDX and FTIR measurements.

References

- Bakharev, T. (2005). Durability of geopolymer materials in sodium and magnesium sulfate solutions. *Cement and Concrete Research*, 35 (6), pp. 1233-1246.

- Barbosa, V.F.F., MacKenzie, K.J.D. & Thaumaturgo, C. (2000). Synthesis and characterisation of materials based on inorganic polymers of alumina and silica: Sodium polysialate polymers. *International Journal of Inorganic Materials*, 2, pp. 309-317.
- Cheng, T.W. & Chiu, J.P. (2003). Fire-resistant geopolymer produced by granulated blast furnace slag. *Minerals Engineering*, 16 (3), pp. 205-210.
- Davidovits, J. (1991). Geopolymers: Inorganic polymeric new materials. *Journal of Thermal Analysis*, 37 (8), pp. 1633-1656.
- Davidovits, J. & Orlinski, J. (1988). Soft mineralurgy and geopolymers. In J. Davidovits and J. Joseph (Eds.), *Proceedings of the 1st International Conference on Geopolymer '88* (pp. 19-23). Compiègne: France.
- Duxson, P., Fernández-Jiménez, A., Provis, J.L., Lukey, G.C., Palomo, A. & van Deventer, J.S.J. (2007). Geopolymer technology: The current state of the art. *Journal of Materials Science*, 42, pp. 2917-2933.
- Hongling, W., Haihong, L. & Fengyuan, Y. (2005). Synthesis and mechanical properties of metakaolinite-based geopolymer. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 268, pp. 1-6.
- Hos J.P., McCormick, P.G. & Byrne, L.T. (2002). Investigation of a synthetic aluminosilicate inorganic polymer. *Journal of Materials Science*, 37, pp. 2311-2316. <http://www.ekantipur.com/2015/06/02/capital/over-4000-unsafe-buildings-demolished/405996.html>. (Accessed on 5 June 2015)
- Komnitsas, K.A. & Zaharaki, D. (2007). Geopolymerisation: A review and prospects for the minerals industry. *Minerals Engineering*, 20 (14), pp. 1261-1277.
- Kumar, S. & Kumar, R. (2011). Mechanical activation of fly ash: Effect on reaction, structure and properties of resulting geopolymer. *Ceramics International*, 37, pp. 533-541.
- Lu, L., Lai, M.O. & Ng, C.W. (1998). Enhanced mechanical properties of an Al based metal matrix composite prepared using mechanical alloying. *Materials Science and Engineering: A*, 252 (2), pp. 203-211.
- McCormick, A.V., Bell, A.T. & Radke, C.J. (1989). Multinuclear NMR investigation of the formation of aluminosilicate anions. *Journal of Physical Chemistry*, 93, pp. 1741-1744.
- Pathak, A. & Jha, V.K. (2012). Synthesis of geopolymer from inorganic construction waste. *Journal of Nepal Chemical Society*, 30, pp. 45-51.
- Pathak, A., Kumar, S. & Jha, V.K. (2014). Development of building material from geopolymerization of construction and demolition waste (CDW). *Transactions of Indian Ceramic Society*, 73 (2), pp. 133-137.
- Perera, D.S., Uchida, O., Vance E.R. & Finnie, K.S. (2007). Influence of curing schedule on the integrity of geopolymers. *Journal of Materials Science*, 42, pp. 3099-3106.

- Provis, J.L. & Van Deventer, J.S.J. (2007a). Geopolymerisation kinetics. 1. *In situ* energy-dispersive X-ray diffractometry. *Chemical Engineering Science*, 62 (9), pp. 2309-2317.
- Provis, J.L. & van Deventer, J.S.J. (2007b). Direct measurement of the kinetics of geopolymerisation by *in-situ* energy dispersive X-ray diffractometry. *Journal of Materials Science*, 42 (9), pp. 2974-2981.
- Rahier, H., Van, M.B., Biesemans, M., Wastiels, J. & Wu, X. (1996). Low-temperature synthesized aluminosilicate glasses: Part I. Low-temperature stoichiometry and structure of a model compound. *Journal of Material Science*, 31, pp. 71-79.
- Singh, P.S., Bastow, T. & Trigg, M. (2005). Structural studies of geopolymers by ^{29}Si and ^{27}Al MAS-NMR. *Journal of Materials Science*, 40, pp. 3951-3961.
- Wang, H., Li, H. & Yan, F. (2005). Synthesis and mechanical properties of metakaolinite based geopolymer. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 268, pp. 1-6.
- Xu, H. & van Deventer, J.S.J. (2000). The geopolymerisation of alumino-silicate minerals. *International Journal of Mineral Processing*, 59, pp. 247-266.
- Yousuf, M., Mollah, A., Hess, T.R., Tsai, Y.N. & Cocke, D.L. (1993). An FTIR and XPS investigations of the effects of carbonation on the solidification/stabilization of cement based systems-portland type V with zinc. *Cement and Concrete Research*, 23, pp. 773-784.
- Zuhua, Z., Xiao, Y., Huajun, Z. & Yue, C. (2009). Role of water in the synthesis of calcined kaolin-based geopolymer. *Applied Clay Science*, 43 (2), pp. 218-223.