

Comparative Study of the Geopolymers Synthesized from Various Types of Construction Wastes

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Abstract

Demolition of old houses and construction of new buildings are in peak in urban sectors which generate a huge amount of construction wastes. These wastes are rich source of alumino-silicate. Geopolymerization can transform a wide range of alumino-silicate materials into building materials with excellent physicochemical properties. Thus, geopolymers have been synthesized from construction wastes such as sand-cement-mixture (SCM), concrete mixture (CM), brick dust (BD), etc using alkali and alkali-silicate as activators. Parameters like alkali concentration (for dissolution of alumino-silicate), ratio of alkali-silicate to construction wastes and curing time were varied to improve the quality of geopolymeric products. The maximum compressive strengths of geopolymeric products obtained from BD, SCM and CM were 60.0, 47.0 and 45.5 MPa respectively.

Key words: alkali-activator, compressive-strength

Introduction

The cement industry is our nation's one of the highest payer of Central Excise and Major contributor to GDP. With infrastructure development growing and the housing sector booming, the demand for cement is also bound to increase. However, the cement industry is extremely energy intensive. The manufacturing of Portland cement is the most energy intensive process (at 1.3 kWh/kg of cement) (Rajamane *et al.* 2009).

Producing one ton of cement requires about 2 tons of raw materials (shale and limestone) and releases 0.87 ton of CO₂, about 3 kg of Nitrogen Oxide (NO_x), an air contaminant that contributes to ground level smog and 0.4 kg of PM10 (particulate matter of size 10 μm), an air borne particulate matter that is harmful to the respiratory tract when inhaled. The global release of CO₂ from all sources is estimated at 23 billion tons a year and the Portland cement production accounts for about 7% of total CO₂ emissions. The cement industry has been making significant progress in reducing CO₂ emissions through improvements in process technology and enhancements in process efficiency, but further improvements are limited because CO₂

production is inherent to the basic process of calcinations of limestone. Mining of limestone has impact on land-use patterns, local water regimes and ambient air quality and thus remains as one of the principal reasons for the high environmental impact of the industry. Dust emissions during cement manufacturing have long been accepted as one of the main issues facing the industry. The industry handles millions of tons of dry material. Even if 0.1 % of this is lost to the atmosphere, it can cause havoc environmentally. Fugitive emissions are therefore a huge problem, compounded by the fact that there is neither an economic incentive nor regulatory pressure to prevent emissions (Rajamane *et al.* 2009).

The name geopolymer was first applied to the synthetic aluminosilicate materials by a French materials scientist Joseph Davidovits in 1970 (Buchwald *et al.* 2007), although similar materials had been developed in the former soviet Union since 1950, originally under the name "soil cements" (Dombrowski *et al.* 2007 and Granizo *et al.* 2002). Davidovits has proposed that the famous Egyptian pyramids are composed of geopolymers cast in their final positions in the

structure rather than being blocks of solid limestone hauled into position. He also considered that Roman cement and the small artifacts of the Tiahuanaco civilization, previously thought to be stone, were made using the knowledge of geopolymer techniques (van Jaarsveld *et al.* 1999 and Yip *et al.* 2008).

Unlike ordinary Portland/pozzolanic cements, geopolymers do not form calcium-silicate-hydrates (CSHs) for matrix formation and strength, but utilize the polycondensation of silica and alumina precursors to attain structural strength. Two main constituents of geopolymers are: source materials and alkaline liquids. The source materials on aluminosilicate should be rich in silicon (Si) and aluminium (Al). They could be by-product materials such as fly ash, silica fume, slag, rice-husk ash, red mud, construction waste, etc. Geopolymers are also unique in comparison to other aluminosilicate materials (*e.g.* aluminosilicate gels, glasses, and zeolites). The concentration of solids in geopolymerisation is higher than in aluminosilicate gel or zeolite synthesis.

The geopolymeric systems have gained the scientific interest during the last two decades. This is attributed to the large variety of solid aluminosilicate raw materials that can be used for the synthesis of geopolymers. Among the potential solid aluminosilicate raw materials, industrial minerals, such as kaoline, feldspars, bentonite, perlite, *etc.* (Cioffi *et al.* 2003, Xu and van Deventer. 2000 and Wang *et al.* 2005), as well as solid industrial byproducts, such as fired-coal fly ash, alumina red mud, tailings from bentonite and perlite exploitation, metallurgical slag, building demolition materials, *etc.* (Swanepoel and Strydom 2002, Wu and Sun 2007, Parias *et al.* 2007, van Jaarsveld *et al.* 2002 and Chang and Chiu 2003), are the most important raw materials. The latter class of potential raw materials is extremely attractive, mainly for environmental reasons. Indeed, the European Union has identified the harmful effects caused by industrial wastes and promotes in the Member States the establishment of a legal framework to protect the human health and the environment against these effects. Through that framework, the European Union among the others encourages the recovery and re-use of waste in order to conserve natural resources. The geopolymerization technology has the potential to utilize the solid industrial aluminosilicate wastes as raw materials for the production of alternative

construction materials with excellent mechanical properties and unique thermal properties.

A brick is a block, or a single unit of a ceramic material which are typically produced in common or standard sizes in bulk quantities. They have been regarded as one of the longest lasting and strongest building materials used throughout history. In our continents the preparation of brick normally starts with the raw clay, preferably in a mix with 25-30% sand to reduce shrinkage. The clay is first ground and mixed with water to the desired consistency. The clay is then pressed into steel moulds with a hydraulic press. The shaped clay is then fired at 900-1000°C to achieve strength (<http://en.wikipedia.org/wiki/Brick>).

Much of the drive behind research carried out in academic institutions involves the development of geopolymers as a potential large-scale replacement for concrete produced from Portland cement (<http://en.wikipedia.org/wiki/Geopolymers>). This is due to geopolymers' lower carbon dioxide production emissions, greater chemical and thermal resistance and better mechanical properties at both ambient and extreme conditions. On the other side, industry has implemented geopolymer binders in advanced high-tech composites and ceramics for heat- and fire-resistant applications, up to 1200 °C.

The main objective of the present work is to show the possibility of the utilization of construction wastes as raw materials for the synthesis of geopolymer with higher compressive strength capacity at ambient temperature. In this process, various types of construction wastes were utilized and further there was neither the emission of CO₂ nor burning of extra fuel required and thus can be said environment and eco-friendly process of cement-like material.

Methodology

Sample preparation

The shapeless demolished old bricks were obtained from a Brick Factory of Kirtipur, Kathmandu. The sand-cement-mixture (SCM) and concrete-mixture (CM) were obtained from demolished part of Tribhuvan University Central Library, Kirtipur, Kathmandu.

The brick-dust (BD), SCM and CM were ground manually by using *Khal*, mortar and pestle separately to obtain in fine powder form. Each powder was further modified by wet-milling using iron balls (2 mm diameter) and distilled water in a plastic bottle and placed for rotating in self-assembled machine at room temperature. The solid sample was separated from solution by filtration and washed with distilled water for several times and then dried in oven (N6c, Philip Harris, England) at 120 °C for overnight in order to remove water and other volatile matters.

Preparation of construction waste based geopolymers

To prepare BD, SCM and CM based geopolymers, 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 first case, the dried BD, SCM and CM powder samples were separately blended manually for 2 minutes with 2-8 M NaOH solution separately using mortar and pestle. The blended mixtures were separately placed in cuboidal plastic moulds sealed with thin plastic films and allowed to cure for 7 days in oven at 40 °C.
- b) **Variation of particle size:** In second case, the dried BD, SCM and CM powder samples of particle size $d > 53 \mu\text{m}$ to $d > 120 \mu\text{m}$ were separately 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 oven at 40 °C.
- c) **Variation of amount of sodium silicate:** In third case, BD, SCM and CM powder samples were separately blended manually using mortar and pestle with the 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 oven at 40 °C for 28 days.
- d) **Variation of curing time:** In fourth case, Na_2SiO_3 to BD, SCM and CM powder samples mass ratio of 1.0 were separately 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 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, the variation of the compressive strength with curing time was performed and hence the appropriate curing time for optimum compressive strength was achieved.

Instrumental analysis

The compressive strength of the prepared geopolymer was measured using SLF 9 Load frame machine at Central Material Testing Laboratory, Institute of Engineering Pulchowk Campus, Tribhuvan University, Pulchowk, Lalitpur.

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) available at Central Department of Geology, Tribhuvan University, Kirtipur, Kathmandu.

Results and Discussion

Characterization of wastes

Sand is a naturally occurring granular material composed of finely divided rock and mineral particles. The composition of sand is variable, depending on the local rock sources and conditions. The most common constituent of sand, in inland continental settings and non-tropical coastal settings, is silica (SiO_2), usually in the form of quartz, which, because of its chemical inertness and considerable hardness, is the most common mineral resistant to weathering (<http://en.wikipedia.org/wiki/Sand>). Concrete is a composite construction material composed primarily of aggregate, cement, and water. The aggregate is generally coarse gravel or crushed rocks such as limestone or granite, along with a fine aggregate such as sand.

So the most predominating phase in all these three types of construction wastes is silica or quartz. The X-ray diffraction (XRD) patterns of BD, SCM and CM are shown in Fig. 1. The quartz peaks at $2\theta = 26.6^\circ$ and 20.8° were less sharp in case of BD as it was fired at temperature about 1000 °C. In this temperature range most of the chemically bonded hydroxyl ions in clay are removed and it converts to meta-stable phase (Bellotto *et al.* 1995).

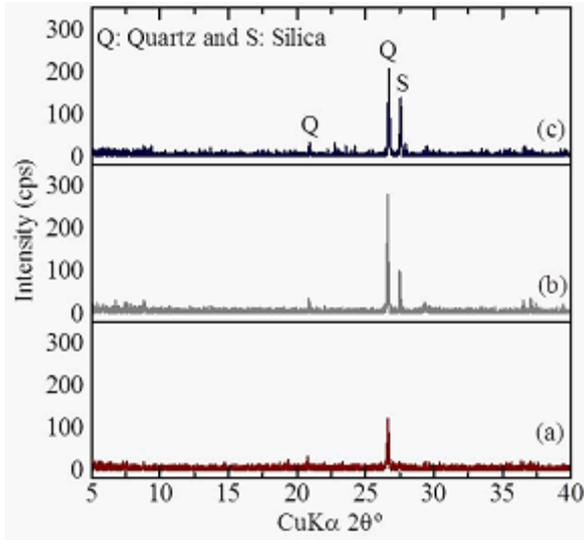


Fig. 1. XRD patterns of (a) brick-dust (BD), (b) sand-cement-mixture (SCM) and (c) concrete-mixture (CM) construction wastes.

Geopolymer products and their compressive Strengths

Variation of NaOH concentration

In order for the selection of appropriate concentration of alkali for the synthesis of geopolymer from above mentioned three types of construction wastes the alkali concentration was varied from 2 to 8 M. The change in compressive strength of products obtained from construction wastes as a function of alkali concentration is shown in Fig. 2.

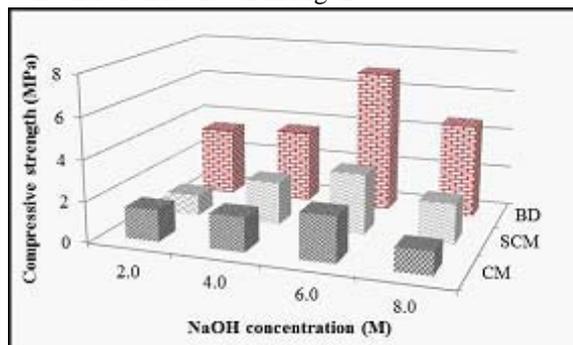


Fig. 2. Variation of alkali concentration and change in compressive strength of products obtained from construction wastes (BD-brick-dust, SCM-sand-cement-mixture and CM- concrete-mixture).

The compressive strength was found initially increased attaining the highest with 6 M NaOH concentration in all the three types of construction wastes. The

increase in the compressive strength with increasing alkali concentration was due to the fact that higher amount of OH⁻ ions facilitate the dissolution of silicate and aluminate species and thus promote polymerization (Komnitsas and Zaharaki 2007). Among the three types of construction wastes the highest compressive strength was obtained with BD sample. The reason behind this was the rate of dissolution of aluminosilicate in alkaline medium was faster. Furthermore, the faster rate of dissolution of aluminosilicate in case of BD was attributed to its amorphous and reactive nature. The XRD patterns of NaOH treated samples are shown in Fig. 3. The characteristic XRD peaks of BD treated with NaOH were found more diminished in comparison to SCM and CM samples.

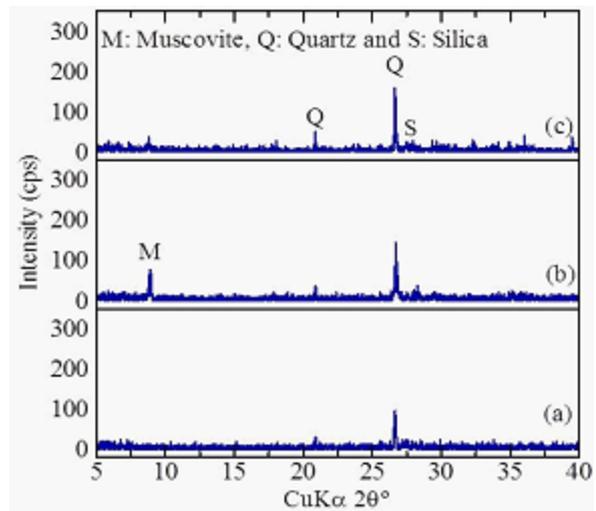


Fig. 3. XRD patterns of (a) brick-dust (BD), (b) sand-cement-mixture (SCM) and (c) concrete-mixture CM construction wastes treated with 6 M NaOH solution.

Variation of Na₂SiO₃ to construction waste mass ratio

The compressive strength of geopolymer products with the variation of the mass ratio of Na₂SiO₃: construction waste while the sodium hydroxide concentration was set constant (6 M) is shown in Fig. 4. The compressive strength of geopolymer obtained from CM waste was found increasing and attained the highest strength (33.5 MPa) with 1:1 mass ratio of Na₂SiO₃: CM whereas in cases of BD and SCM the highest compressive strengths were 43.9 and 42.6 MPa respectively with 1.5:1 mass ratio of Na₂SiO₃: BD and SCM.

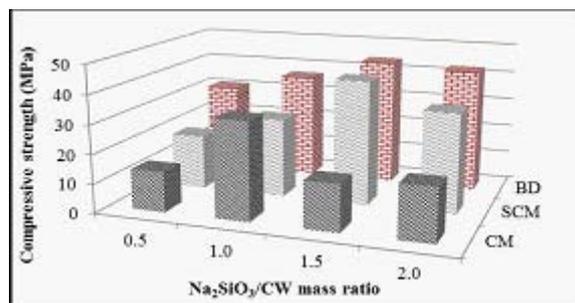


Fig. 4. Variation of the mass ratio of Na₂SiO₃/construction wastes (CW) and change in compressive strength of products

The sodium silicate which acts as binder in process of geopolymer formation plays a vital role on gaining the compressive strength of the products. Sodium silicate solution contains self-polymerizing species (monomer, dimer and larger oligomer containing Si—O—Si chain) which influence soluble aluminosilicate units to polymerize (Hos *et al.* 2002; Wang *et al.* 2005). But the excess amount of sodium silicate has adverse impact over the strength of the geopolymeric product. The reason behind decrease of strength is excess silicate hinders water evaporation and structure formation (Chang & Chiu 2003). Further increase of silicates concentration decreases the rate of geopolymerization reaction and the solidification of the paste takes prior to geopolymerization (Provis and van Deventer 2007a and 2007b).

Variation of curing time

The curing time of the geopolymer products varied from 7 to 28 days at the 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 300 to 1200 water-papers. The compressive strength of each sample was measured. The compressive strength was found increasing with increasing curing time which is shown in **Fig. 5**. The compressive strengths of CM, SCM and BD based geopolymer products after 28 days of curing time at 40 °C temperature were 45.4, 47.0 and 60.0 MPa respectively.

The curing of the geopolymer products is necessary to achieve advanced mechanical and durability performances. The presence of water and its removal by evaporation play major role in order for obtaining crack-free geopolymer. The curing for long time period at relatively high temperature has shown to weaken

the structure as some small amount of water need to be retained for crack-free and structural integrity (Perera *et al.* 2007). In geopolymers, the curing temperature and the curing time play significant roles not only as accelerators of chemical reaction, but also determine the extent of that reaction (Davidovits 1994, 1999). 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 geopolymer of higher compressive strength.

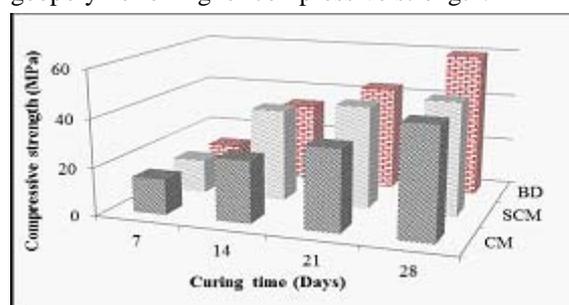


Fig. 5. Change in compressive strength of the geopolymer products obtained from various types of construction wastes with the variation of curing time (BD-brick-dust, SCM-sand-cement-mixture and CM- concrete-mixture).

The compressive strength of the geopolymer products obtained from all the three types of construction wastes such as sand-cement-mixture, concrete-mixture and brick-dust is comparable with the ordinary Portland cement. The compressive strength was found the highest in case of the geopolymer product obtained from brick-dust, followed by sand-cement-mixture and concrete-mixture. Following conclusions can be made from this study: This concrete does not require water for curing, and utilizes waste-product materials. Therefore, it is more eco-friendly and sustainable. Construction waste materials rich in Silicon (Si) and Aluminum (Al), such as sand-cement-mixture, concrete-mixture, old brick-dust and other similar materials, are added to react with highly alkaline liquid (typically a combination of sodium silicate and sodium hydroxide solution) to produce binders for the geopolymer products. Synthesis of geopolymer products from construction wastes not only reduces landfilling but also consumes the waste material resulting in the reduction of its environmental impact.

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References

- Buchwald, A., H. Hilbig, and C. Kaps. 2007. Alkali-activated metakaolin-slag blends - performance and structure in dependence on their composition. *Journal of Materials Science* **42**: 3024–3032.
- Bellotto, M., A. Gualtieri, A. Artioli and S.M. Clark. 1995. Kinetic study of the kaolinite-mullite reaction sequence. *Physics and Chemistry of Minerals* **22**: 207–217.
- Chang, T.W. and J.P. Chiu. 2003. Fire-resistant geopolymer produced by granulated blast furnace slag. *Minerals Engineering* **16**: 205-210.
- Cioffi, R., L. Maffucci and L. Santoro. 2003. Optimization of geopolymer synthesis by calcination and polycondensation of a kaolinitic residue. *Resources, Conservation and Recycling* **40**: 27-38.
- Davidovits, J. 1994. Properties of geopolymer cements. *First International Conference on Alkaline Cements and Concretes; 1994; Kiev, Ukraine, 1994*: SRIBM, Kiev State Technical University: pp. 131-149.
- Davidovits, J. 1999. Chemistry of geopolymeric systems, terminology. *Geopolymer '99 International Conference, France (June 30 to July 2, 1999)*: pp. 9-40.
- Dombrowski, K., A. Buchwald and M. Weil. 2007. The influence of calcium content on the structure and thermal performance of fly ash based geopolymers. *Journal of Materials Science* **42**: 3033–3043.
- Granizo, M.L., S. Alonso, M.T. Blanco-Varela and A. Palomo. 2002. Alkaline activation of metakaolin: effect of calcium hydroxide in the products of reaction. *Journal of American Ceramic Society* **85**: 225–231.
- Hos, J.P., P.G. McCormick and L.T. Byrne. 2002. Investigation of a synthetic aluminosilicate inorganic polymer. *Journal of Materials Science* **37**: 2311-2316. <http://en.wikipedia.org/wiki/Brick>-Retrieved October 21, 2012.
- <http://en.wikipedia.org/wiki/Geopolymers>-Retrieved October 3, 2012.
- <http://en.wikipedia.org/wiki/Sand>-Retrieved October 21, 2012.
- Komnitsas, K. and D. Zaharaki. 2007. Geopolymerisation: A review and prospects for mineral industry. *Mineral Engineering* **20**: 1261-1277.
- Panias, D., I. Giannopoulou and T. Perraki. 2007. Effect of synthesis parameters on the mechanical properties of fly ash-based geopolymers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **301**: 246-254.
- Perera, D.S., O. Uchida, E.R. Vance and K.S. Finnie. 2007. Influence of curing schedule on the integrity of geopolymers. *Journal of Materials Science* **42**: 3099–3106.
- Provis, J.L. and J.S.J. Van Deventer. 2007a: Direct measurement of the kinetics of geopolymerisation by in-situ energy dispersive X-ray diffractometry. *Journal of Materials Science* **42**: 2974–2981.
- Provis, J.L. and J.S.J. Van Deventer. 2007b: Geopolymerisation kinetics. 1. In situ energy-dispersive X-ray diffractometry. *Chemical Engineering Science* **62**: 2309-2317.
- Rajamane, N.P., N. Lakshmanan and M.C. Nataraja. 2009. Geopolymer concrete - A new eco-friendly material of construction. *The Masterbuilder (India's Premier Construction Magazine)* **11**: 200-206.
- Swanepoel J.C. and C.A. Strydom. 2002. Utilisation of fly ash in a geopolymeric material. *Applied Geochemistry* **17**: 1143-1148.
- van Jaarsveld, J.G.S., J.S.J. van Deventer and A. Schwartzman. 1999. The potential use of geopolymeric materials to immobilise toxic metals: part II. Material and leaching characteristics, *Mineral Engineering* **12**: 75–91.
- van Jaarsveld, J.G.S., J.S.J. van Deventer and G.C. Lukey. 2002. The effect of composition and temperature on the properties of fly ash- and kaolinite-based geopolymers. *Chemical Engineering Journal* **89**: 63-73.
- Wang, H., H. Li and F. Yan. 2005. Synthesis and mechanical properties of metakaolinite-based geopolymer. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **268**: 1-6.
- Wu, H.C. and P. Sun. 2007. New building materials from fly ash-based lightweight inorganic polymer. *Construction and Building Materials* **21**: 211-217.
- Xu, H. and J.S.J. van Deventer. 2000. The geopolymerisation of alumino-silicate minerals. *International Journal of Mineral Processing* **59**: 247-266.
- Yip, C.K., G.C. Lukey, J.L. Provis and J.S.J. van Deventer. 2008. Effect of calcium silicate sources on geopolymerization. *Cement and Concrete Research* **38**: 554-564.