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A Laboratory Scale Synthesis of Geopolymer from Locally Available Coal Fly Ash from Brick Industry

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Abstract

In this work, geopolymers have been synthesized from coal fly ash (CFA) using KOH and Na_2SiO_3 as activators. Some parameters such as alkali concentration, amount of Na_2SiO_3 and curing time have been varied in order to improve the quality of geopolymeric product. The geopolymerization process was carried out using 3-8 M KOH solutions, Na_2SiO_3 to CFA mass ratio of 0.25-2.00 and curing time variation from 6-28 days. The curing temperature was fixed at 40°C in all the cases. During the variation of KOH concentration, the maximum compressive strength of 6.62 MPa was obtained with CFA treated with 7 M KOH solution. Similarly, with the variation of the mass ratio of Na_2SiO_3 to CFA, the maximum compressive strength of 28.1 MPa was obtained with Na_2SiO_3 to CFA mass ratio of 1.75. Furthermore, the compressive strength was found to be increased with increasing curing time and 41.9 MPa was achieved with 28 days of curing time.

Keywords: *Geopolymer, Coal fly ash, Curing time, Geopolymerization, Compressive strength.*

Introduction

Due to rapid urbanization, there is high rate of new building constructions. For this, a large amount of bricks are required and in order to fulfill the demand of large amount of bricks and a huge amount of coal has been used as fuel for brick production. As a result, there is a large production of coal fly ash (CFA) as a byproduct. CFA is one of the residues generated in the combustion of coal. It typically comprises fine and powdery particles that are predominantly spherical, solid or hollow and mostly amorphous (glassy) materials. The chemical properties of CFA are greatly influenced by the chemical content of the coal burned.

Most of the CFA is used in construction related applications such as cement and concrete manufacturing, production of lightweight aggregates and as additives for ceramics. Bulk CFA is also used in road and rail-road bases, pavement and in filling mining excavations[1]. New potential utilization of CFA are as additives for the capture of industrial and water treatment waste, sources of valuable metals, sorbents for flue gas desulphurization, fire-proofing materials, filter materials for the production of various products, synthesis of zeolites and geopolymers *etc*[2-10].

The industrial production of cement has two major drawbacks. The first one is the increase in environmental pollution and global warming as the manufacture of Portland cement produces large amounts of CO_2 and the second one is the high energy consumption during the manufacture of cement as it involves very high temperature (about 1600ºC). Thus we are facing three severe problems; one associated with the huge amount of CFA waste, the second one is the atmospheric pollution and third one is the high consumption of energy. Hence, if it is possible to prepare geopolymers of reasonable compressive strength with CFA waste at ambient temperature, it can become a suitable alternative for minimizing the waste as well as for reducing the atmospheric pollution and energy consumption.

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The term "geopolymer" was coined by Davidovits in 1972 to the three-dimensional (3D) alumino-silicate that is formed at low temperature and short time by naturally occurring alumino-silicate[11]. The potential uses of geopolymers include: alternate for cement, adhesives, aggregates, coating, composites, fibers and textiles, fluid containment, insulation, marine structures, refractories, soil stabilization, waste encapsulation etc.

The geopolymer synthesized from metakaolin was cured at 65ºC for 10 hrs. The maximum compressive strength of the sample was observed to be 35 MPa at 35 days[12]. A report on the effect of alkali and Si/Al ratio on the development of mechanical properties of metakaolin- based geopolymer showed that the minimal change in the compressive strength of specimens was generally observed in specimens of different types of alkali in between 7 and 28 days of ageing. However, mixed alkali specimens with high Al/Si ratio exhibited significant increase in strength and pure alkali specimens displayed decreased strength[13]. The blast furnace slag-metakaolin based geopolymers had shown that geopolymer containing 50 % slag and synthesized at steam curing (80ºC for 8 hrs) exhibits high compressive strength of 75.2 MPa[14]. The geopolymers synthesized from coal combustion fly ashes having glass content higher than 90 % achieved the compressive strength about 60 MPa. Such geopolymers were synthesized using 12 M NaOH and by curing at 80ºC for 48 hrs[15].

The influence of calcium compounds on the mechanical properties of fly ash geopolymer was studied and found that the calcium compounds improved the mechanical strength of samples cured at ambient temperature while on increasing the curing temperature at 70ºC the compressive strength of samples were decreased[16].

Geopolymer mortars of compressive strength 24-58 MPa were synthesized from lignite bottom ash with mean particle size of 15.7 µm using liquid alkaline/ash ratio of 0.429-0.709, the sodium silicate to NaOH ratio of 0.67-1.5 and 7.5- 12.5 M[17]. Geopolymers from mechanochemically treated clinoptilolite were synthesized using NaOH and sodium silicate solutions which showed increasing compressive strength up to around 25 MPa with increasing curing time[18].

The main objective of the present work is to find out amicable solutions for the utilization of CFA as raw materials for the synthesis of cement-like product at very low temperature in comparison to the ordinary cement production temperature.

Experimental Methods

Sample Preparation

The CFA used in this study was obtained from Uma-Maheshwor Brick Factory of Kirtipur, Kathmandu. The CFA was ground manually by using mortar and pestle to obtain in fine powder form. The powder was further modified wet-milling by 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 80°C for overnight.

Preparation of CFA Based Geopolymer

To prepare CFA based geopolymer, several parameters such as KOH concentration, amount of sodium silicate and curing time were taken into account.

Variation of KOH concentration

In first case, the dried CFA powder sample was blended manually for 2 minutes with 3-8 M KOH solution separately using mortar and pestle. The blended mixtures were separately placed in cuboidal plastic moulds (length × breadth × height: 2.6 cm × 2.6 cm ×1.0 cm), air bubbles were removed, sealed with thin plastic films and allowed to cure for 4 days in oven at 40°C.

Variation of amount of sodium silicate

In second case, CFA was blended manually using mortar and pestle with the varying amount of Na_2SiO_3 while the concentration of KOH solution was fixed to 7 M. The blended mixtures were separately placed in cuboidal plastic moulds, sealed with thin plastic films and allowed to cure for 4 days in oven at 40°C.

Variation of curing time

In third case, Na_2SiO_3 to CFA mass ratio of 1.75 was blended manually with the 7 M KOH 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 6-28 days in oven at 40°C.

After curing, all the samples were demoulded and cut into finite sizes. The area of each piece of 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.

The compressive strength of the samples was measured using MARUTO testing machine (s56A, Japan) available at National Academy of Science and Technology (NAST), Khumaltar, 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, Germany).

Results and Discussion

Characterization of Waste

The XRD pattern of CFA, CFA treated with 7 M KOH solution and Na_2SiO_3/CFA mass ratio of 1.75 treated with 7 M KOH solution are shown in Fig. 1. CFA contains mostly amorphous glassy material and consists of a peak centered on ~ 26 º of 2θ angle. The presence of the sharp peaks was due to the presence of trace quartz and/or mullite phase [Fig. 1 (a)]. This quartz or mullite phase crystalline was found diminished with KOH treatment [Fig. 1 (b)] while the peaks for nucleation of zeolite X began to appear with alkali treatment. These zeolite X phases were also found diminished with sodium silicate treatment of the raw CFA (Fig. 1 (c)).

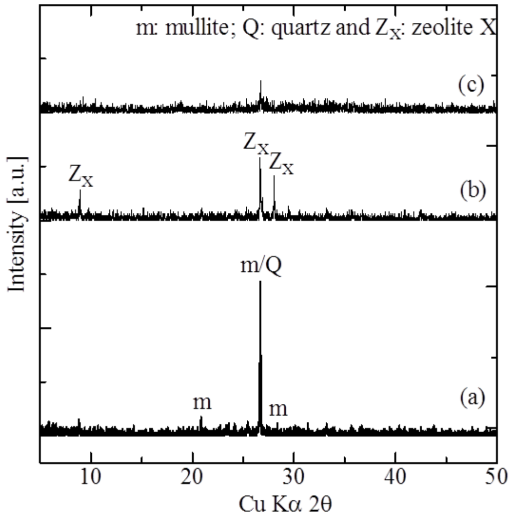
The diminishing of quartz/mullite phase due to the reaction of alkali solution was due to the dissolution of alumino-silicate phase in alkaline medium. This dissolved alumino-silicate in alkaline phase is the suitable condition for the nucleation of zeolite phase which can be seen in the XRD pattern. But as the treatment was done at the temperature of 40ºC, this temperature was not appropriate for the progress and formation of zeolite over its nucleation seed and hence upon the addition of sodium silicate activator the zeolite phases were diminished.

Compressive Strength with KOH Concentration Variation

As shown in Fig. 2, the compressive strength was found to increase initially and then decrease with increasing KOH concentration. The increase in the compressive strength with increasing KOH concentration was due to the fact that higher amount of OH- ions facilitate the dissolution of silicate and aluminate species and thus promotes polymerization[19]. But under very high alkaline condition the connectivity of silicon anion may be reduced which causes aluminosilicate gel to precipitate at early stage resulting in poor polymerization i.e. KOH molecule is incorporated between two geopolymer precursors which break the silicon anion connectivity thus preventing polymerization[20]. Further, the excess KOH forms potassium carbonate by atmospheric carbon[21].

Na2SiO3 to CFA Mass Ratio and Compressive Strength

The variation of the compressive strength of geopolymer products with the variation of the mass ratio of Na_2SiO_3/CFA is shown in Fig. 3. The compressive strength of geopolymer was found increasing initially and then decreased with the increasing mass ratio of Na_2SiO_3/CFA (7 M KOH). This behavior of changing compressive strength is because at higher concentration of silicates stronger ion pair formation is expected which results in formation of chain oligomer as well as Al-O-Si complex[22]. But further increase of silica decreases the rate of geopolymerization reaction and the solidification of the paste takes prior to geopolymerization[23-24].



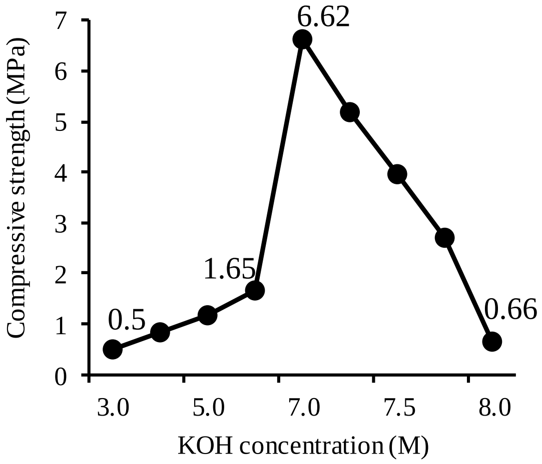


***Fig. 1 (left):** XRD patterns of (a) raw coal fly ash (CFA), (b) CFA treated with 7 M KOH solution and (c) Na2SiO3/CFA mass ratio of 1.8 treated with 7 M KOH solution.* ***Fig. (right)2:** Variation of compressive strength of product as a function of KOH concentration.*

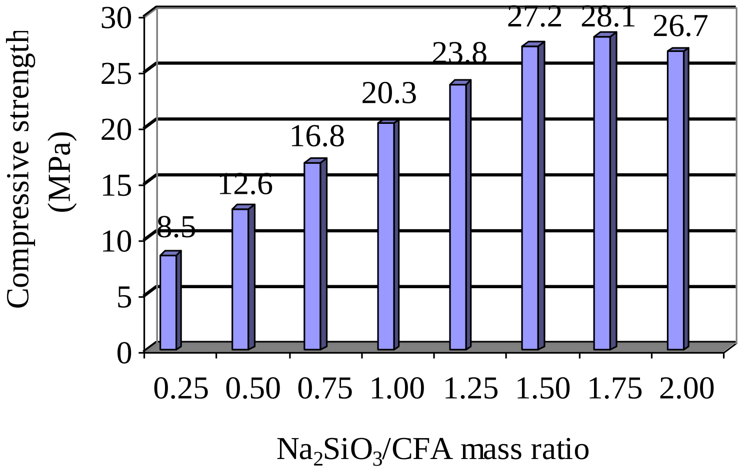


***Fig.3:** Variation of compressive strength of product as a function of Na_2SiO_3/CFA mass ratio.*

Compressive Strength with Curing Time Variation

The compressive strength was found increasing with increasing curing time and is shown in Fig. 4: 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[25]. This suggests that curing for longer time period at low temperature is preferable for the synthesis of geopolymer of higher compressive strength.

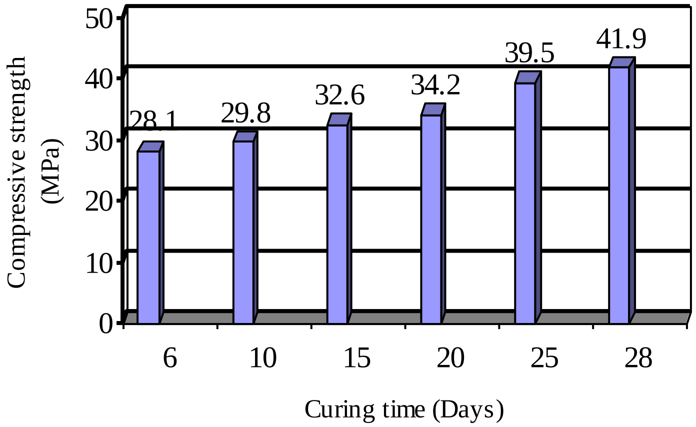


Fig. 4: *Change of compressive strength of geopolymer product with curing time (concentration of KOH was 7 M).*

Conclusions

The geopolymers were synthesized from CFA by varying concentration of KOH, amount of Na_2SiO_3 and curing time. The compressive strength was found initially increasing and then decreasing with increasing KOH concentration. The maximum compressive strength of 6.62 MPa was obtained with CFA treated with 7 M KOH solution.

With the variation of amount of sodium silicate, the compressive strength increased initially and then decreased with higher concentration of sodium silicate. The maximum compressive strength of 28.1 MPa was obtained with 1.75 mass ratio of Na_2SiO_3 to CFA.

The compressive strength was found increasing with increasing curing time suggesting that curing for longer period of time at low temperature is preferable for the synthesis of geopolymer of higher compressive strength. The compressive strength was found increasing up to 41.9 MPa with the curing time of 28 days.

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